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ARGENTOMETRISCHE TITRATIONEN MIT REDOXINDICATION—II

BESTIMMUNG VON AMMONIAK, AMMONIUM-IONEN UND STICKSTOFFHALTIGEN ORGANISCHEN SUBSTANZEN

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Zusammenfassung—Es wurde ein Verfahren zur massanalytischen Ammoniakbestimmung ausgearbeitet. Das Ammoniak wird mit Natriumtetraphenylborat gefällt, und dessen acetonhaltige Lösung in Anwesenheit von Variaminblau als Redoxindicator mit Silbernitratmasslösung titriert. Die Titration lässt sich auch auf indirektem Wege, durch Messung der überschüssigen Tetraphenylborationen durchführen.

Die Methode wurde auch auf die Stickstoffbestimmung in organischen Stoffen ausgebreitet, indem nach der Kjeldahlschen Zerstörung der Stickstoff direkt im Zerstörungsrückstand bestimmt wurde.

Das Natriumtetraphenylborat wurde zuerst von Wittig und Mitarbeitern[1] als analytisches Reagens angewandt. Raff und Brotz[2] arbeiteten die gewichtsanalytische Bestimmung der Kalium- während Kohler[3] die der Ammoniumionen aus. Die argentometrische Titration des in Aceton gelösten Kaliumtetraphenylboratniederschlages wurde von Rüdorff und Zannier,[4] weiterhin von Hahn[5] ausgearbeitet, u.zw. in Anwesenheit von Eosin bzw. Kaliumchromat als Indicator. Das Verfahren mit Eosin ist als eine Differentialtitration zu betrachten, da Eosin nur nach Zugabe von bekannter Menge an Kaliumbromid als Indicator funktioniert. Kaliumchromat ist indessen in acetonhaltiger Lösung ein nicht genügend empfindlicher Indicator. In einer früheren Mitteilung[6] berichteten wir über die argentometrische Titration von Kaliumtetraphenylborat in Anwesenheit von Variaminblau, als Indicator. Diesen Indicator fanden wir auch bei der Bestimmung der Ammoniumionen als gut geeignet. Wir breiteten die Methode auch auf die Stickstoffbestimmung von stickstoffhaltigen und mit Kjeldahl Verfahren zerstörbaren organischen Verbindungen aus.

Die Fällung der Ammoniumionen mit Lithium- oder Natriumtetraphenylborat (Kalignost) lässt sich entweder in neutraler oder in saurer Lösung vornehmen. Das pH der Lösung ist zwischen 1 und 6,5 einzustellen.

EXPERIMENTELLER TEIL

Lösungen

0,05 *n Silbernitratlösung*. 8,4944 g des handelsüblichen, anal. reinen Silbernitratpräparats werden in Wasser auf 1 Liter gelöst.

Acetonhaltige 0,05 *n Silbernitratlösung*. Eine 0,1 n Silbernitratlösung wird mit Aceton genau auf doppeltes Volumen verdünnt.

0,1 *m Natriumtetraphenylborat-Fällungsreagens*. 3 g des handelsüblichen Natriumtetraphenylborats (Kalignost) werden in 100 ml Wasser gelöst. Um die etwas trübe Lösung zu klären wird sie mit 0,5 g Aluminiumoxyd versetzt, 5 Minuten lang umgeschüttelt und sodann durch ein dichtes Filtrierpapier filtriert. Der erste Einzelteil des Filtrats wird auf das Filtrier-papier zurückgeschüttet

Die Lösung ist höchstens 3 Tage lang brauchbar. 0,6 ml Fällungsreagens entspricht 1 mg NH_4^+.

Waschflüssigkeit. Der Ammoniumtetraphenylboratniederschlag wird nach der weiter unten folgenden Arbeitsvorschrift (*a*) bereitet. Dem mit Wasser gründlich ausgewaschenen Niederschlag werden 0,1–0,2 g Mengen entnommen und in 1 Liter Wasser 25 min lang geschüttelt. Um die Lösung zu klären werden 2–3 g anal. reines Aluminiumoxyd zugefügt. Die Lösung wird sodann wieder 5 Minuten lang umgeschüttelt und schliesslich durch dichtes Filtrierpapier filtriert.

1 %*-iger Variaminblauacetatindicator.* 0,2 g des handelsüblichen Variaminblau B-präparats werden unter gründlichem Verreiben in einem Mörser in 20 ml Wasser gelöst. Die Lösung wird in einen 100 ml Scheidetrichter gebracht, mit einer Messerspitze Ascorbinsäure reduziert und mit Hilfe von 5 ml 1 n Natriumhydroxydlösung wird die schwerlösliche Variaminblau Base gefällt. Die niederschlaghaltige Flüssigkeit wird mit 20 ml Benzol zusammengeschüttelt und die Benzolschicht in einen anderen Scheidtrichter' abgelassen. Da vermischt man dieselbe mit 20 ml 20 %-iger Essigsäurelösung und die Variaminblau Base wird damit wieder—nun aber schon als essigsaures Salz—in die wässrige Phase gebracht. Als Indicator wird diese abgesonderte essigsaure Lösung gebraucht. Aus dieser Indicator-lösung wenden wir zu einer Titration 2–3 Tropfen an.

(*a*) *Arbeitsverfahren in Abwesenheit von Schwermetallionen*

Die etwa 5–50 mg (am günstigsten 20–50 mg) Ammoniumionen enthaltende beinahe neutrale Lösung wird mit Wasser dermassen verdünnt, dass auf 1 mg NH_4^+ etwa 8 ml des Lösungsvolumens entfallen. Sodann wird die Lösung pro 50 ml Lösungsvolumen mit je 1 ml 0,1 n Essigsäurelösung versetzt (pH = 3–5), und unter beständigem Rühren werden die Ammoniumionen mit 0,1 m Natriumtetraphenylboratlösung kalt gefällt. Vom Fällungsreagens wird ein etwa 50 %-iger Überschuss angewandt, d.h. auf jedes mg NH_4^+ wird insgesamt 1 ml Fällungsreagens gerechnet. Die niederschlaghaltige Flüssigkeit wird sodann wenigstens auf 5 min beiseitegestellt und nachher durch feinporösiges Filterpapier filtriert. Der Niederschlag wird mit etwa 50 ml Waschflüssigkeit in 4–6 Teilen dekantiert und samt Filterpapier in das Becherglas zurückgebracht. Sodann werden je nach der Menge des Niederschlages 6–60 ml Aceton zugefügt und löst darin unter Umrühren mit einem Glasstäbchen den Niederschlag auf. Nach Zugabe von 1 ml 2 n Essigsäurelösung und 2–3 Tropfen Variaminblauacetatindicator titriert man die Lösung unter beständigem Umrühren mit einer 0,05 n Silbernitratmasslösung bis zum Erscheinen der violetten Farbe. Die Anwesenheit des Filterpapiers stört die Titration nicht. Gegen Ende der Titration soll man nach Zugabe jeden einzelnen Tropfens der Masslösung ungefähr 15–30 sec die niederschlaghaltige Flüssigkeit kräftig umrühren. 1 ml 0,05 n Silbernitratmasslösung entspricht 0,8515 mg NH_3, 0,9020 mg NH_4^+ bzw. 0,7004 mg N.

Bemerkungen. Zur Überprüfung der Methode wurde aus p.a. Ammoniumchlorid durch genaue Einwaage eine Stammlösung bereitet deren Einzelteile nach obiger Arbeitsvorschrift titriert wurden. Die Ergebnisse weichen vom Sollwert bei der Bestimmung von 13 mg Ammoniumchlorid um −0,97 %, und bei der Bestimmung von 133 mg Ammoniumchlorid um +0,01 % ab. Bei der Bestimmung von 27 mg Ammoniumchlorid aus 6 Paralleltitrationen wurde die Standarddeviation und die Abweichung vom Sollwert festgestellt. Die Abweichung vom Sollwert betrug −0,17 % und die Standarddeviation ±0,11 %.

Arbeitsverfahren in Anwesenheit von Schwermetallionen

J. H. Cluley[7] beseitigte die störende Wirkung der fremden Metallionen bei der Bestimmung von Kaliumionen mit Tetraphenylborat durch Fällung entweder in stark saurem Medium (pH ~ 2) oder in Anwesenheit von Natriumäthylendiamintetraacetat Na_2-EDTA in einer beinahe neutraler Lösung (pH ~6,5). Laut unserer Versuche lässt sich unter diesen Versuchsumständen die störende Wirkung der Fremdionen auch bei der Ammoniumbestimmung beseitigen. K, Rb, Cs, Ag, Hg(I), Hg(II) und Th(IV) wirken aber auch in diesem Falle störend ein. In Anwesenheit dieser Ionen muss man das Ammoniak aus alkalischer Lösung abdestillieren bzw. man soll die weiter unten angegebene indirekte Bestimmungsmethode (d) anwenden.

(*b*) *Fällung in stark saurer Lösung.* Die etwa 5–50 mg Ammoniumionen enthaltende, beinahe neutrale Lösung wird mit Wasser derart verdünnt, dass auf 1 mg NH_4^+ 8 ml des Lösungsvolumens entfallen, und sodann mit soviel 0,1 n Salzsäure versetzt, dass deren Menge ein Zehntel des Lösungsvolumens betrage. Das pH der Lösung stellt sich derart auf etwa 2 ein. Im weiteren führt man Fällung, Filtration, Auswaschen und Titration wie im Abschnitt (a) bereits beschrieben, aus.

(*c*) *Fällung in Anwesenheit von* Na_2-EDTA. Die etwa 5–50 mg Ammoniumionen und höchstens

100 mg Schwermetallionen enthaltende Lösung wird mit 1 g Na_2-EDTA versetzt und nach dessen Auflösung in Anwesenheit von 2 Tropfen 0,04%-iger Chlorphenolrotindicatorlösung mit 1 n Natriumhydroxydlösung bis zum Farbumschlag von Gelb nach Rot (pH = 6,5) neutralisiert. Die Lösung wird sodann mit destilliertem Wasser derart verdünnt, dass auf jedes mg NH_4^+ 8 ml des Lösungsvolumens entfalle. Fällung, Filtration, Auswaschen und Titration führt man wie im Abschnitt (a) bereits beschrieben, aus.

Die Ergebnisse beweisen, dass die Bestimmung lässt sich in Anwesenheit von Mg, Ca, Ba, Zn, Pb, Al, Fe(III), Cu, Co, Mn(II), Ni, Cr(III), Ti(IV), As(III) und Sb(III) mit gutem Erfolg durchführen.

TABELLE I

Methoden	Carbamid Einwaage, *g*	Theoretischer N-gehalt, *mg*	Verbrauch an		N gefunden *mg*	Abweichung vom Sollwert	
			0,1 n HCl, *ml*	0,05 n $AgNO_3$, *ml*		*mg*	%
Verfahren nach Kjeldahl	0,2200	102,63	14,69 14,63 14,67		102,67	+0,04	+0,04
Direkte Ammoniumbestimmung im Zerstörungsrückstand	0,1775	82,80		23,61 23,64 23,62	82,71	−0,09	−0,10
Indirekte Ammoniakbestimmung im Zerstörungsrückstand	0,2500	116,62		33,18 33,21 33,15	116,19	−0,43	−0,36

(*d*) *Bestimmung neben K-, Rb- und Cs-Ionen.* Das Ammoniak wird von den begleitenden Schweralkalimetallionen durch Destillation in alkalischem Medium getrennt. Als Absorptionsflüssigkeit dient entweder überschüssige Salzsäure-, Schwefelsäure- oder 40 ml gesättigte Borsäurelösung. Das im Recipienten aufgefangene Ammoniak wird gemäss Arbeitsverfahren (a) bestimmt. Die Fällung lässt sich aus der borsauren Lösung direkt, ohne Einstellung des pH durchführen.

Bestimmung von Ammoniumionen durch Rücktitration

Die Bestimmung der Ammoniumionen lässt sich auch durch Titration des im Überschuss angewandten Natriumtetraphenylborats ausführen. In diesem Falle muss man das Fällungsreagens in bekannter Menge und von bekanntem Wirkungswert anwenden. Der Niederschlag muss durch Filtrieren entfernt werden, weil die Titration in Anwesenheit von Kaliumtetraphenylborat nicht durchgeführt werden kann, da sich das Silbertetraphenylborat schlechter löst als das Kaliumtetraphenylborat, was einen Überverbrauch an Masslösung bewirkt. Das Natriumtetraphenylborat enthaltende Filtrat muss auch mit Aceton mindestens von gleichem Volumen versetzt werden, denn sonst fällt der Variaminblauindicator als Variamintetraphenylboratniederschlag aus.

Titerbestimmung der 0,1 *m Natriumtetraphenylboratlösung.* 10,00 ml des 0,1 m Natriumtetraphenylborat-Fällungsreagens werden mit 1 ml 2 n Essigsäure, 11 ml Aceton und 2–3 Tropfen Variaminblauacetat versetzt. Die Lösung wird sodann mit 50 Volumenprozent enthaltender, 0,05 n Silbernitratlösung titriert. (Eine 0,1 n Silbernitratlösung von bekanntem Wirkungswert wird mit Aceton genau aufs Doppelte verdünnt). Gegen Ende der Titration wird nach jedem Tropfen der zugefügten Masslösung 15–20 sec gewartet. Der Endpunkt der Titration wird durch Erscheinen der violetten Farbe des oxydierten Variaminblaus bekanntgegeben.

Die Titration lässt sich auch mit wässriger 0,05 n Silbernitratmasslösung durchführen, in diesem Falle muss man aber die zu titrierende Lösung mit soviel Aceton versetzen, dass deren Acetongehalt beim Endpunkt der Titration mehr als 50 Volumenprozent beträge. Die zu titrierende Lösung darf natürlich keine Chloridionen enthalten.

(e) *Arbeitsvorschrift für das indirekte Verfahren.* Die zu bestimmende etwa 5 mg Ammoniumionen enthaltende Ammoniumsulfat- oder Ammoniumnitratprobe wird in einen 100 ml Messkolben eingewogen, mit 10 ml 0,1 n Essigsäurelösung versetzt und mit Wasser auf etwa 40 ml verdünnt. Unter beständigem Umschütteln des Kolbens werden 50,00 ml 0,1 m Natriumtetraphenylboratlösung in den Kolben pipettiert, welchen man sodann mit Wasser bis zur Marke auffüllt. Nach Zusammenschütteln lässt man die niederschlaghaltige Flüssigkeit etwa 5 min stehen und filtriert durch trockenes Filtrierpapier in einen trockenen Kolben. Das erste Detail des Filtrats wird weggeworfen. Aus dem weiteren Filtratteilen werden 25,00 ml auspipettiert, mit 1 ml 2 n Essigsäurelösung und 25 ml Aceton versetzt und in Anwesenheit von 2–3 Tropfen Variaminblauacetat als Indicator mit 50% Aceton bereiteter 0,05 n Silbernitratlösung titriert. Das Vierfache des Masslösungsverbrauches substrahiert man vom Volumen der mit dem eingewogenen 50,00 ml 0,1 m Natriumtetraphenylborat äquivalenten 0,05 n Silbernitratmasslösung. Aus dieser Differenz ergibt sich die den Ammoniumionen entsprechende Menge der 0,05 n Silbernitratlösung. Die Titration lässt sich auch bei diesem Verfahren mit wässriger 0,05 n Silbernitratlösung ausführen, in diesem Falle muss man aber die zu titrierende Lösung mit soviel Aceton versetzen, dass der Acetongehalt der Lösung im Endpunkt der Titration mindestens 50 Volumenprozent betrage.

Tabelle II

Untersuchte Substanz	Theoretischer N-gehalt,	Verbrauch an 0,05 n $AgNO_3$-lsg	Mittelwert N gefunden,		Abweichung vom Sollwert,	
	mg	*ml*	*ml*	*mg*	*mg*	%
Carbamid	16,55	23,64 23,66 23,64	23,64	16,55	±0,0	±0,0
Carbamid	23,34	33,14 33,18 33,14	33,16	23,23	−0,11	−0,47
Sojamehl	13,16	18,56 18,68 18,70	18,64	13,05	−0,11	−0,83
Eiweiss (getrocknet)	5,05	7,20 7,16 7,22	7,18	5,02	−0,03	−0,60

Unsere mit obiger Methode erhaltenen Ergebnisse zeigen eine +0,84%-ige Abweichung vom Sollwert bei der Bestimmung von 32 mg Ammoniumsulphat und eine −0,24%-ige bei der Bestimmung von 130 mg Ammoniumsulphat. Die Genauigkeit der Methode und ihre Standarddeviation wurde aus 6 Paralleltitrationen von 130 mg Ammoniumsulphat bestimmt. Die Abweichung vom Sollwert ergab sich zu −0,19%, während die Standarddeviation ±0,19% betrug. Die Resultate der Rücktitration weichen vom Sollwert besser ab als die der direkten Titration.

Sämtliche oben beschriebene argentometrische Ammoniumbestimmungsverfahren sind günstiger als das übliche Destillationsverfahren, da bei der Durchführung derselben keine Destillationsapparatur benötigt wird und die aus der Destillationsmethode hervorgehenden sämtlichen Fehler dabei beseitigt werden. Ein weiterer Vorteil der neuen Verfahren besteht darin, dass die Bestimmung sich auf eine sehr spezifische Reaktion gründet, auf die genaue Einstellung des pH nicht empfindlich ist und schliesslich sehr genaue Ergebnisse liefert.

ARGENTOMETRISCHE TITRATION VON STICKSTOFFHALTIGEN ORGANISCHEN STOFFEN

Die rasche Bestimmungsmöglichkeit der Ammoniumionen legte den Gedanken nahe den Stickstoffgehalt von organischen Substanzen nach der Kjeldahlschen Zerstörung direkt im Zerstörungsrückstand ohne Destillation zu bestimmen. Es liegen nach der Zerstörung zwei Möglichkeiten zur Bestimmung des entstehenden Ammoniaks vor. Der ersten Methode gemäss wird das Ammoniak auf oben beschriebene Art—Verfahren (*a*)(*d*)—nach Fällung, Filtration, Auswaschen und Auflösung in Aceton mit Silbernitratmasslösung titriert. Nach der anderen Methode—Verfahren (*e*)—wird die das zu bestimmende Ammoniak enthaltende Lösung quantitativ in einen Messkolben gebracht, wo man das Ammoniak mit bekannter Menge Natriumtetraphenylborat fällt. Nach Auffüllen des Kolbens und Abfiltrieren eines aliquoten Teils wird der Natriumtetraphenylboratüberschuss titriert. Daraus wird so dann der Stickstoffgehalt bestimmt.

Um die Methode zu kontrollieren bestimmten wir den Stickstoffgehalt von Carbamid sowohl mit Hilfe des Kjeldahlverfahrens mit acidimetrischer Endpunktsanzeige als auch mit unseren argentometrischen direkten und indirekten Verfahren. Laut Angaben der Tabelle II sind die Ergebnisse von befriedigender Genauigkeit. Über die Genauigkeit von einigen Stickstoffbestimmungen in organischen Stoffen gibt Tabelle II Aufklärung.

Summary—The authors have developed a new method for the titrimetric determination of ammonia. Ammonia is precipitated by means of potassium tetraphenylboron and its solution in acetone is titrated with standard silver nitrate solution in the presence of Variamin Blue acetate as indicator. The titration can also be carried out indirectly by measuring the excess of tetraphenylboron.

This method can also be used to determine nitrogen in organic compounds after a Kjeldahl digestion.

Résumé—Les auteurs ont proposé une nouvelle méthode pour le dosage titrimétrique de l'ammoniaque. Celui-ci est précipité par le tetraphénylborure de potassium et sa solution dans l'acétone est titrée par une solution de nitrate d'argent étalon en présence de bleu d'acétate de variamine. Le titrage peut aussi être conduit indirectement en mesurant l'excès du tetraphenylborure.

Cette méthode peut aussi être utilisée pour déterminer l'azote dans des produits organiques après une minéralisation au kjeldahl.

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ARGENTOMETRIC TITRATIONS BY MEANS OF REDOX INDICATION—III

DETERMINATION OF NITRATE IONS AND NITRO COMPOUNDS

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Summary—A new method for the determination of nitrate has been worked out. (*a*) Nitrate ions can be reduced to ammonia in acidic medium by means of *ferrum reductum* in the presence of nickel sulphate. Ammonia can be precipitated in acidic medium as ammonium tetraphenylboron. After filtering and washing, the precipitate can be dissolved in acetone and the solution can be titrated with silver nitrate with Variamin Blue acetate as indicator. (*b*) Nitrate ions can be reduced in alkaline medium with Devarda's alloy, the ammonia being distilled and titrated as described above. This method has been applied to the determination of nitrates accompanied by organic material, and of nitrozo, azo and diazo compounds.

THE most precise methods for the determination of nitrate are based on the reduction of nitrate ions to ammonia. These methods all have the same principle, namely ammonia formed by reduction is distilled from a neutral or alkaline medium, and the separated ammonia is titrated by alkalimetric methods or with sodium hypobromite.[1–4] Z. Szabó and his co-workers[5,6] carry out the reduction in the presence of silver ions with iron^{II} hydroxide as a reducing agent, and either titrate the iron^{III} ions formed, or back-titrate the remaining iron^{II} by redox methods after the separation of ammonia.

Work published up to the present does not offer a specific and satisfactorily precise method for the determination of ammonia formed by reduction from the nitrate ions. Excellent results which we obtained by titration of ammonium ions with sodium tetraphenylboron (Kalignost)[7] suggested the use of this precise and reasonably specific method for the determination of ammonia formed by the reduction of nitrate ions.

REDUCTION OF NITRATE IONS IN ACID MEDIUM BY MEANS OF METALS

Among methods using metals as reducing agents, the best known is that of Ulsch[1] who reduces the nitrate ions with "*ferrum reductum*". Although Martin also suggests the use of metallic zinc for the reduction,[8] the present authors, like Ulsch, were unable to obtain satisfactorily precise results with this method. To investigate the efficiency of the reduction parallel experiments were carried out with various common metals having different standard potentials. To a known amount of sodium nitrate was added an equivalent amount of the well-powdered metal, and the amount of ammonia formed by the reduction was measured. Under the conditions mentioned, metallic iron was found to be the best reducing agent. Using a 5–10 fold excess of the metal over the stoichiometric amount, in the case of iron the reduction is complete, but with the other metals smaller amounts of ammonia than calculated were always obtained. The amount of iron can be considerably reduced by the addition to the solution of nickel or cobalt sulphate as a catalyst.

Reagents

1. $0{\cdot}1N$ *Silver nitrate standard solution* was prepared by weighing and dissolving 16·9888 g p.a. silver nitrate per litre. $0{\cdot}01N$ and $0{\cdot}05N$ solutions were made by appropriate dilution of the former.
2. $0{\cdot}1M$ *Sodium tetraphenylboron* (*Kalignost*): a 3·5% solution was prepared in water, clarified with 0·5 g aluminium oxide for each 100 ml, and filtered through a thick filter. About 0·6 ml of this solution is equivalent to 1 mg NH_3. The solution is stable for some days.
3. *Wash solution:* a small amount of ammonium tetraphenylboron was precipitated, and washed thoroughly with distilled water. 0·1–0·2 g of the precipitate was suspended in 1 litre of distilled water, shaken for 25 minutes, clarified with aluminium oxide and filtered through a thick filter. The clear filtrate was used as a wash solution.
4. *Indicator solution: Variamin Blue acetate,* 1% *solution:* 0·2 g of commercial Varamin Blue dye (which is a hydrochloric acid salt of the base) was dissolved in 20 ml water and reduced by 0·5 g ascorbic acid. The solution was then rendered alkaline with 5 ml *N* sodium hydroxide and the precipitated free base was dissolved by shaking the solution with 20 ml benzene. The organic layer was separated, and shaken with 20 ml 20% acetic acid solution. The Varamin Blue acetate which formed was to be found in the acetic acid phase; the latter was used as an indicator. The indicator solution prepared by this way is stable for 3–4 weeks.
5. $0{\cdot}2M$ *Disodium ethylendiamine tetra-acetate solution* (Na_2-EDTA) was prepared by dissolving 74·4 g Na_2-EDTA in water and dilution to 1 litre.
6. $0{\cdot}2M$ *Sodium acetate solution:* 27·2 g sodium acetate was dissolved in water and diluted to 1 litre.

Procedure

The sample, which contained 1–120 mg of nitrate, was weighed in a 100-ml Kjeldahl flask; 0·5 g finely powdered "ferrum reductum," 0·3 g nickel sulphate and 15 ml $2N$ sulphuric acid were added. Into the neck of the flask a test tube with a ball blown in the middle part and containing water for cooling was placed. The mixture was gently heated with a micro-burner, and after 10 minutes the flame was regulated, so that the mixture was just boiling. Reduction was complete after 1 hour treatment and the iron was dissolved completely. After cooling the mixture was washed into a beaker; 10–15 ml of $0{\cdot}2M$ sodium acetate solution and 60 ml $0{\cdot}2M$ Na_2-EDTA solution were added. To this solution $0{\cdot}1M$ sodium tetraphenylboron was added dropwise at room temperature until the reagent was in 50% excess. Precipitation was complete in 5 minutes. The precipitate was collected on a thick filter paper 7 cm in diameter, and was washed 5–6 times with small portions of wash-solution. The filter paper containing the precipitate was returned to the beaker, and was thoroughly stirred with acetone, using a glass rod. The acetone dissolved the precipitate. To the mixture (containing filter-paper-shreds) 1–2 ml $2N$ acetic acid and 1–2 drops of 1% Variamin Blue acetate indicator were added, and it was then titrated while shaking, against $0{\cdot}1N$ or $0{\cdot}01N$ silver nitrate solutions until a blue colour appeared. Near the end-point it was advisable to titrate slowly and to mix the solution well after each drop of the standard solution was added. The shreds of filter paper did not interfere. At the end-point the solution must contain at least 50% of acetone.

The method was controlled by analysing samples of nitrite-free sodium nitrate solution prepared from nitric acid, which was controlled acidimetrically. According to Table I, results are very accurate even in micro quantities. The accuracy and standard deviation were established by 11 parallel titrations in $0{\cdot}01N$ solution. Results show that the method is very accurate, with a standard deviation of $\pm 0{\cdot}25\%$. In $0{\cdot}1N$ solution, when greater amounts of nitrate were determined, the accuracy was even better.

The method can be combined with the distillation of ammonia. Distillation is recommended especially when potassium, thallium, thorium or mercury salts are present, or if other heavy metal salts are present in large quantities. After reduction the solution must be washed into a distillation apparatus, and rendered alkaline with sodium hydroxide. Ammonia can be then distilled. About 40 ml of saturated boric acid solution (4·9 g H_3BO_3 dissolved in 100 ml water) or an excess of sulphuric acid is placed in the collector flask. After neutralisation of the strong acid (boric acid must not be neutralized) ammonium tetraphenylboron can be precipitated. In this case Na_2-EDTA should not be added since precipitation of ammonia with sodium tetraphenylboron is highly specific.

TABLE I.—ACCURACY OF THE TITRATION AS A FUNCTION OF THE AMOUNT OF NITRATE

0·01*N* HNO_3 taken, *ml*	0·01*N* $AgNO_3$ consumed, *ml*	Average, *ml*	Difference	
			ml	%
9·94	9·76 9·84 9·81	9·80	−0·14	−1·4
14·88	14·88 14·80 14·83	14·84	−0·04	−0·26
24·85	24·76 24·78 24·81	24·78	−0·07	−0·28

0·1*N* HNO_3 taken, *ml*	0·1*N* $AgNO_3$ consumed, *ml*	Average, *ml*	Difference	
			ml	%
4·97	4·97 4·95 4·95	4·96	−0·01	−0·2
9·94	9·89 9·92 9·95	9·92	−0·02	−0·20
19·88	19·84 19·92 19·87	19·88	±0·0	±0·0

The method is free from errors which occur normally when ammonia is titrated by alkalimetric methods. Traces of sodium hydroxide picked up by the vapour, dissolved alkali from the condenser or carbon dioxide dissolved from the air have no effect on the accuracy. Experience has shown that errors caused by traces of alkali picked up are only found if potassium hydroxide is used for liberating the ammonia. Another advantage of the method lies in the fact that only one standard solution is required. It is especially advantageous that the determination can be carried out even after an alkalimetric titration (see later).

DETERMINATION OF NITRATE IONS AFTER REDUCTION IN ALKALINE MEDIA

For the reduction of nitrate ions in alkaline media Devarda's alloy (50% Cu, 5% Zn and 45% Al) is usually recommended.[2] The method is simple and rapid, but a positive error occurs in almost all cases due to alkali picked up mechanically by the evolved hydrogen. The extent of the error depends largely on the construction of apparatus used; it can be reduced using an apparatus equipped with a trap,[9] but cannot be completely eliminated. The Schulek-Vastagh apparatus[10] is one of the best of this sort, but even using this an error of +3·8% in the determination of 30 mg sodium nitrate, due to the drops of alkali picked up by hydrogen, was found. Comparable experiments using a simple distillation apparatus (Fig. 1) which consisted of a 250-ml flask, a simple ball-condenser and a dropping funnel gave as much as +15% error. The error is a function of the quantity of Devarda's alloy used and of the velocity of hydrogen gas evolution. In addition there is frequently an error due to the alkali silicates dissolved from the condenser. Therefore even in the best constructed distillation apparatus a considerable positive error arises in the Devarda method, if the determination is finished by an alkalimetric titration of ammonia.

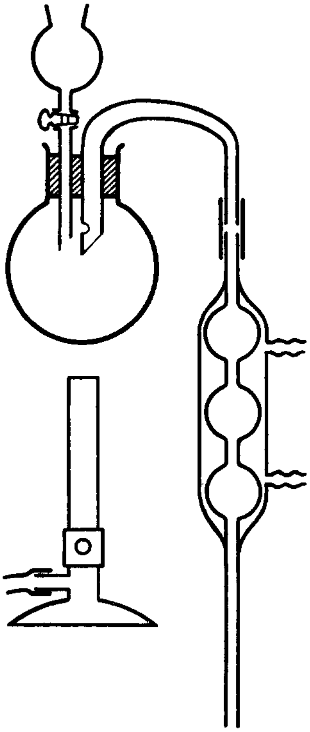

FIG. 1.

These errors can be eliminated if the ammonia is determined by precipitation of ammonia in form of ammonium tetraphenylboron instead of by an acid-base titration. The precipitate can be also weighed; but, especially when small amounts of ammonia are to be determined, it is more convenient to titrate it argentometrically. Since the determination is not sensitive to intrusive traces of alkali the simple apparatus of Fig. 1 may be used for the distillation. The use of potassium hydroxide must of course be avoided. The reduction and distillation time can be shortened to about 10 minutes, so that the total time required (which is lengthened by precipitation and filtration) is no greater than in the Devarda method. Na_2-EDTA should be used in the precipitation to complex the traces of the Devarda's alloy which occasionally pass through the apparatus. It is suggested that 0·1*N* sulphuric acid should be used in the collector flask; its amount need not be known but it must always be in excess. For accurate work addition of methyl orange or methyl red to the sulphuric acid is not recommended since the end-point of the argentometric titration cannot readily be seen.

Experience has shown that using this simple distillation apparatus the determination can be carried out without error when 2–5-fold amounts of potassium, thallium, mercury or other heavy metal salts are present besides nitrate, since only negligible traces of these are carried over.

Procedure

The sample to be determined is weighed in the flask of the apparatus shown in Fig. 1. The sample which should contain 6–150 mg of nitrate is dissolved in 50 ml water and 2 g of well-powdered Devarda's alloy are added. The apparatus is assembled immediately, the collector flask containing 50 ml of 0·1*N* sulphuric acid; 50 ml of 30% sodium hydroxide solution are added through the dropping funnel. The solution must be heated, first gently, but later more strongly, till 50 ml of liquid is distilled over. During this time the ammonia is distilled completely. When necessary, the acidity of the collector solution is checked using a small piece of litmus paper. On completing the distillation the cooler is lifted out of the collector flask and washed with water.

To the solution collected in the flask, 50 ml of 0·2*M* sodium acetate and 50 ml of 0·2*M* Na_2-EDTA solution are added the (pH of the solution is about 2–4), and after cooling 0·1*M* sodium tetraphenylboron reagent is added dropwise until the latter is in slight excess. The mixture is allowed to stand for 15 minutes, and after this time the precipitate is collected on a thick filter paper (7 cm in diameter), and washed 5–6 times with the wash solution. The paper with the precipitate is returned to the flask in which the precipitation was carried out. The precipitate is dissolved in 15 ml of acetone by shaking, and 1–2 ml of 2*M* acetic acid and 1–2 drops of 1% Variamin Blue acetate indicator are added; the solution is then titrated with 0·1*N* or 0·01*N* silver nitrate solution until an intense blue colour appears. Near the end-point the silver nitrate is added dropwise and the mixture is mixed thoroughly after adding each drop. The solution should contain at least 50% of acetone at the end-point.

Sulphuric acid can be replaced by boric acid; 40 ml of saturated solution must be used and it is then unnecessary to use sodium acetate in the precipitation. Addition of Na_2-EDTA solution is of course necessary.

Comparative experiments were carried out using this alkaline reduction with (i) an acid-base, (ii) a tetraphenylboron-argentometric finish. The results are shown in Table II. Reduction and distillation were carried out in the Schulek-Vastagh apparatus in series I, and in the simple apparatus shown in Fig. 1 in series II. These results show that the tetraphenylboron method is accurate even when the simpler apparatus is used; on the other hand results obtained with acid-base titrations are inaccurate and deviations are high.

DETERMINATION OF NITRATE IONS AFTER A SULPHURIC ACID–SALICYLIC ACID DESTRUCTION

It is often necessary to determine nitrate ions in the presence of organic materials. In such case it is usual to form nitro compounds of aromatic substances which readily accept the nitro group. Such substances are, for example, salicylic acid or

TABLE II.—COMPARISON OF DISTILLATION APPARATUS

Dist. apparatus	0·1N NaNO$_3$,	0·1N HCl consumed after distillation,	Average,	Difference,		0·1N AgNO$_3$ consumed after distillation,	Average,	Difference,	
	ml	*ml*	*ml*	*ml*	%	*ml*	*ml*	*ml*	%
I	5·00	5·17 5·20 5·21	5·19	+0·19	+3·8	4·96 5·00 4·98	4·98	−0·02	−0·4
	20·00	20·34 20·20 20·28	20·27	+0·27	+1·35	20·01 20·02 20·02	20·02	+0·02	+0·1
II	5·00	5·75 5·60 5·82	5·72	+0·72	+14·4	4·95 4·99 5·03	4·99	−0·01	−0·2
	20·00	20·94 20·85 20·79	20·86	+0·86	+4·3	20·02 20·04 20·02	20·03	+0·03	+0·15

phenol. These nitro-compounds are easy to reduce in a concentrated sulphuric acid medium. After the reduction, organic material can be destructed by boiling with concentrated sulphuric acid.

Procedure

The organic material containing 10–120 mg nitrate is weighed on a cigarette paper strip, and added to a 250-ml Kjeldahl flask; 5–6 ml concentrated sulphuric acid containing 70 mg salicylic acid per ml are introduced. In the neck of the flask is placed a test-tube condenser. The mixture is heated carefully until dissolution is complete; the nitration of the salicylic acid is then also complete. 2–3 g of crystallized sodium thiosulphate are added and thoroughly mixed; finely divided elementary sulphur which precipitates reduces the nitro-group to the amino-group. After heating for 10–20 minutes the test-tube is removed from the neck of the flask, and, after addition of 0·05 g elementary selenium or 1 g copper sulphate as catalyst, destruction can be achieved by heating. If method (*a*) is used for the determination of the ammonia formed, selenium must be used as a catalyst. If the organic material is not destroyed easily, 2–3 g anhydrous solium sulphate must be added to the solution. After the destruction is complete (and the solution becomes clear) heating must be continued for about 20 minutes. Ammonia can be determined in this mixture by two different ways, (*a*) without distillation and (*b*) with distillation.

Method (*a*). The cold solution is diluted carefully (under cooling) with water up to 100 ml, 2 g sodium acetate are added and the solution is neutralized with 30% sodium hydroxide until thymol blue indicator changes from red to yellow. The pH of the solution is in this case between 2 and 4. After cooling, ammonium tetraphenylboron is precipitated with 0·1M sodium tetraphenylboron. The precipitate is filtered and washed, and is dissolved in acetone. After addition of 1–2 ml of 2N acetic acid the solution is titrated with 0·1N silver nitrate solution using Variamin Blue acetate indicator.

Method (*b*). The cold solution is diluted with water carefully to 100 ml, and is washed into the flask of a distillation apparatus. It is rendered alkaline with an adequate amount of 30% sodium hydroxide solution. The ammonia liberated is distilled into an excess of 0·1N sulphuric acid or 40 ml of saturated boric acid solution. The determination of ammonia can be carried out as described above.

According to results obtained in the determination of a sodium nitrate sample containing organic material, using both methods (*a*) and (*b*) the determination can be carried out with an average error of 0·3–0·7%.

Table III.—Analysis of chemical fertilizer "Pétisó"

Determination of ammonia-nitrogen content

Weight of the sample, mg	0·05*N* $AgNO_3$ consumed, *ml*	Nitrogen, %	0·1*N* HCl consumed, *ml*	Nitrogen, %	Difference from distillation method, *ml*	
					ml	%
140·15	19·45 19·40 19·37	9·70	9·74 9·71 9·76	9·74	−0·04	−0·4

Determination of total nitrogen content

Weight of the sample, mg	0·05*N* $AgNO_3$ consumed, *ml*	Nitrogen, %	0·1*N* HCl consumed, *ml*	Nitrogen, %	Difference from distillation method, *ml*	
					ml	%
140·15	39·20 38·92 39·06	19·53	19·50 19·45 19·40 19·46	19·46	+0·07	+0·3

DETERMINATION OF ORGANIC AZO, DIAZO AND NITRO COMPOUNDS

The nitrogen content of organic compounds cannot always be determined by the Kjeldahl method. If the nitrogen atom in the organic compound is not bound to carbon and hydrogen atoms, but there is a nitrogen–nitrogen or a nitrogen–oxygen bond, reliable results are obtained only when a reduction is first carried out. Sodium thiosulphate in a concentrated sulphuric acid medium gives good results for the reduction.

Procedure

The organic material containing 10–100 mg nitrogen is weighed on a cigarette paper strip, and added to a 250-ml Kjeldahl flask; 5 ml of concentrated sulphuric acid and 2 g of crystalline sodium thiosulphate are added. The mixture should stand for 12 hours. When the reduction is complete, organic material is destroyed and ammonia can be determined by either (*a*) or (*b*) as described above. Results obtained with this method are satisfactory for azobenzene, picric acid and dinitronaphthalene, and have an average error of 0·1–0·5%. Determinations on nitrobenzene and hydrazine sulphate were unsatisfactory.

PRACTICAL USES OF THE METHOD

The method has been used with satisfactory results for the determination of ammonium nitrogen and total nitrogen content of chemical fertilizers.

Procedure

7·005 g of the fertilizer was weighed into a 1-litre volumetric flask and water was added. The contents of the flask were shaken thoroughly and after sedimentation the mixture was filtered through a dry filter. The first part of the filtrate was discarded. 20·00 Ml of the filtrate were pipetted into a beaker and ammonia was precipitated with a slight excess of sodium tetraphenylboron (about 12–15 ml). After 15 minutes the precipitate was filtered and washed with a saturated solution of ammonium tetraphenylboron (it was found to be sufficient to wash it 5 times). The filter paper containing the precipitate was returned to the beaker in which the precipitation was made; the precipitate was dissolved in 15 ml acetone, 1–2 ml of 0·1*N* acetic acid and 1–2 drops of Variamin Blue acetate were added and the solution was titrated with 0·05*N* silver nitrate solution. The solution should contain at least 50% of acetone at the end-point.

To determine the total nitrogen content of the sample 20·00 ml of the filtrate were placed in a 100-ml Kjeldahl flask, and 0·5 g of *ferrum reductum*, 0·3 g of nickel sulphate and 15 ml of 2*N* sulphuric acid were added. The mixture was heated for 1 hour, when reduction was complete. After addition of 10 ml 2*N* sodium acetate the ammonium tetraphenylboron was precipitated by a slight excess (about 25–30 ml) of 0·1*M* sodium tetraphenylboron. The precipitate was filtered, washed, replaced in the Kjeldahl flask, and dissolved in 15 ml acetone. After addition of 1–2 ml of 0·1*N* acetic acid and 1–2 drops of Variamin Blue acetate indicator the solution was titrated to the appearance of the blue colour. The results obtained are shown in Table III.

Zusammenfassung—Eine neue Methode zur Bestimmung von Nitration wurde entwickelt. (*a*) Nitrat wird in saurem Medium durch Eisen(II)—sulfate in Gegenwart von Nickelsulfate zu Ammoniak reduziert. Ammoniak kann aus saurem Medium mit Tetraphenylbor gefällt werden. Nach Filtrieren und waschen wird der Niederschlag in Azeton gelöst und das Tetraphenylbor mit Silbernitrat titriert, wobei Variamin Blau-acetat als Indikator dient. (*b*) Nitrat wird in alkalischer Lösung nach Dewarda reduziert, das Ammoniak abdestilliert und nach der obigen Methode bestimmt. Die neue Methode wurde zur Bestimmung von Nitrat in Gegenwart von organischen Substanzen verwendet, sowie zur Bestimmung von Nitroso-, Azo und Diazoverbindungen.

Résumé—On propose une nouvelle méthode pour le dosage du nitrate: (*a*) Les ions nitrate peuvent être réduits en ammoniaque par réduction en milieu acide par l'ion ferreux en présence de sulfate de nickel. L'ammoniaque peut être précipité en milieu acide à l'état de tetraphénylborure d'ammonium. Après filtration et lavage, le précipité peut être dissous dans l'acétone et la solution peut être titrée par le nitrate d'argent en utilisant l'acétate de bleu de variamine comme indicateur. (*b*) Les ions nitrate peuvent être réduits en milieu alcalin par la méthode de Devarda, l'ammoniaque étant alors distillé et titré comme précédemment. Cette nouvelle méthode a été appliquée au dosage de nitrates en présence de matières organiques et au dosage de composés nitrosés, azoiques et diazoiques.

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A DIRECT-READING CURRENT INTEGRATOR FOR COULOMETRIC ANALYSIS

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Summary—A direct reading current integrator for coulometric analysis has been developed. This employes a bevel gear differential and a standardization device incorporated to add stability to the instrument as a whole. The advantages over existing coulometers and integrators include a high power output, a stable curve through the origin, the integration of small currents, no dead zone, and a cancellation of the background current by a zero adjustor. Under good conditions about 0·3% deviation may be achieved. The determination of copper by controlled potential shows that this instrument is applicable to coulometric analysis.

COULOMETRIC analysis with controlled potential and with constant current techniques requires the accurate measurement of the quantity of electricity passed through the electrolysis cell. In the constant current technique, this may be measured by counting the current and the time, by using chemical coulometers (*i.e.* the silver, titration, hydrogen-oxygen, or hydrogen-nitrogen coulometers),[1] or by using electromechanical integrators, such as the low-inertia integrating motor.[2] In the controlled potential technique, this also may be measured by using any chemical coulometer or any integrator (*i.e.* Lingane-Jones' ball and disc integrator,[3] Meites' electromechanical integrator,[4] or others[5]), or by integrating the current-time curve.[6] Although very precise, chemical coulometers are inconvenient and require much manipulation.

At present there are various types of integration methods, one of which is the commutator motor type. The principle of this type is based on the fact that the rotor revolution speed n at any one moment is proportional to the input current i:

$$n \propto i$$

or, when converted to an equation:

$$n = \mathrm{K}i$$

Upon integration from t_1 to t_2, the following equation is derived:

$$\int_{t_1}^{t_2} n \, dt = \mathrm{K} \int_{t_1}^{t_2} i \, dt$$

The quantity of electricity Q corresponds to $\mathrm{K}\int_{t_1}^{t_2} i \, dt$, and also, $\int_{t_1}^{t_2} n \, dt$ equals the total number of revolutions. Therefore, the quantity of electricity corresponds to the sum total of revolutions.

The integrator using a low-inertia integrating motor is based on this principle. In this motor, as in all mechanical devices, mechanical friction is always present. It influences the dead zone (starting voltage is always required) and also makes it difficult to integrate increasing current from small current in the neighbourhood of zero. These influence the stability and the linearity of the rotating speed versus the input current. Thus when the integrator is designed to decrease this friction, the over-all output power is cut down, resulting in difficulty when using a large-scale counter. An integrator so designed is sensitive to external conditions such as temperature, so that it is difficult to keep the linearity constant. To eliminate such disadvantages, the present author has used a bevel gear differential and various motors and has obtained good results.

This paper describes a current integrator which is readily adaptable to both the constant current and the controlled potential techniques. The bevel gear differential is the main mechanism, and is driven by a d.c. integrating motor. When this integrator is used with the constant current apparatus, the timer is eliminated and a simple current source is usable, *i.e.* a battery and a high resistor; with the controlled potential apparatus, chemical coulometers are unnecessary. Further advantages for both techniques are that this device possesses a high power output which can be adapted to drive other mechanisms, such as recorders and/or large-scale mechanical counters; it draws a characteristic curve which is linear and passes through the origin; it makes direct reading possible; it eliminates the dead zone; it permits small current integration in the neighbourhood of zero per cent of rated current, *i.e.* rated current of the lowest range—1 mA. Table I shows the relation of count/coulomb versus input current at a rated current of 50 mA. The range below 2% of rated current has not been measured; however, measurement of the observed current between 2% and zero is possible, although with a rather large deviation. Using the constant current technique with this integrator, about 0·3% coefficient of variation may be obtained by selecting the input sensitivity range which provides a suitable current between 50 to 100% of rated current. Using the controlled potential technique, about 0·39% coefficient of variation may be obtained by selecting the input sensitivity range which provides an initial electrolysis current near the rated current. Table I indicates that at lower per cents of rated current, the deviation is large; however, this has little effect on the practical determination, for there is a possibility of obtaining a coefficient of variation about 0·39% (Table II).

TABLE I.—CALIBRATION FACTORS
(count/coulomb)

I(mA)	1	3	5	10	20	30	40	50
$\bar{x}$	388·8	383·0	383·4	382·6	381·7	382·9	381·6	381·6
Std. dev.	16·97	4·74	1·89	1·51	0·89	1·32	0·93	0·77
C.V. (%)	4·36	1·24	0·49	0·39	0·23	0·34	0·24	0·20

I : input current
$\bar{x}$: mean count/coulomb of 10 measurements
Std. dev.: standard deviation
C.V. : $\frac{\text{Std. dev.}}{\bar{x}}$ = coefficient of variation

TABLE II.—ESTIMATED DEVIATION FOR CONTROLLED POTENTIAL COULOMETRIC ANALYSIS

Q_i	C.V.	Dev. = $Q_t \times$ C.V.
Q × [(50 – 40)/50]	0·002	0·0004 · Q
Q × [(40 – 30)/50]	0·0024	0·00048 · Q
Q × [(30 – 20)/50]	0·0034	0·00068 · Q
Q × [(20 – 10)/50]	0·0023	0·00046 · Q
Q × [(10 – 5)/50]	0·0039	0·00039 · Q
Q × [(5 – 3)/50]	0·0049	0·000196 · Q
Q × [(3 – 1)/50]	0·0124	0·000496 · Q
Q × [(1 – 0)/50]	0·0436	0·000872 · Q
		/+
Q	total C.V.	0·003974 · Q

therefore, the deviation for the total quantity of electricity is 0·39%.

Q: total quantity of electricity.

Q_t*: quantity of electricity which is assumed to be measured with coefficient of variation at each input current value.

C.V.: coefficient of variation from Table I.

Dev.: deviation at each Q_t.

* With controlled potential technique

$$i_t = i_0 \, 10^{-Kt} \tag{1}$$[1]

$$Q = \int_0^t i_t \, dt \tag{2}$$

from equations (1) and (2)

$$Q \doteqdot \frac{i_0 - i_t}{2{\cdot}303K} \tag{3}$$[10]

therefore, i_t and Q are proportional.

APPARATUS

This integrator (Fig. 1) consists essentially of the following units: 1. an integrating motor driving unit: a d.c. motor and d.c. motor control unit; 2. an error detection and correction unit: a 2-phase servo motor, a.c. amplifier, and d.c. tachogenerator; 3. a d.c. supply source; 4. a bevel gear differential; 5. a synchronous motor; 6. a counter.

Bevel gear differential[7]

The differential gear (Fig. 2) is composed of 1. a vertical shaft Y–Y′ and a horizontal shaft X–X′ which are fixed; 2. bevel gears which are free on the two shafts. A constant input gear speed is supplied by a synchronous motor; a variable input gear speed, dependent on the measuring current, is provided by a d.c. integrating motor.

When the two gears A and A′ revolve reversely and at the same speed, the gears B and B′ on the horizontal shaft also revolve equally. The fixed shafts are stationary and register a zero reading. When gear A revolves faster than gear A′, the revolutions of the gears B and B′ alone are not capable of equalizing this increased speed of gear A. To accommodate this increase, the X–X′ shaft rotates about the Y–Y′ shaft in the same direction as the faster gear A is revolving. The X–X′ shaft rotates about the Y–Y′ shaft according to the equation

$$S_{Y-Y'} = \frac{S_A - S_{A'}}{2}$$

where S_A is the speed of the integrating motor, $S_{A'}$ is the speed of the synchronous motor (always constant), and $S_{Y-Y'}$ is the rotation speed of the Y–Y′ shaft. This speed of the Y–Y′ shaft is proportional to the measuring current, because the quantity of electricity corresponds to the total number of revolutions.

Brass bevel gears with 24 teeth and a diameter of 18·5 mm are used for the differential gear. The input gears from the synchronous motor and the integrating motor are of the same type.

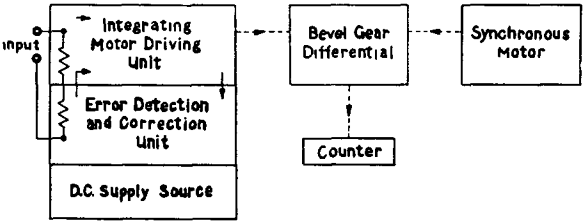

Fig. 1.

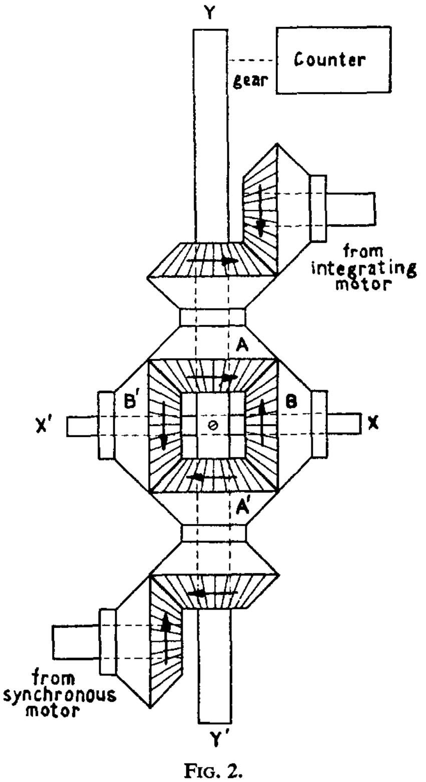

Fig. 2.

Integrating motor driving unit

The d.c. motor of the driving unit is a micromotor with a tachogenerator which are built in one body and have a common shaft. The micromotor, Model CLE 3R-60 of Nihon Micromotors Co., has characteristics (rated values) of 7·5 V input voltage, 92 mA maximum current, and 0·75 watt. This motor follows the 12 cycle square wave input current (*i.e.* the direction of rotation changes 24 times per second).

The plate current of a 6Y6 vacuum tube controls this micromotor (Fig. 3). The observed current is added to the input grid resistor. The 4 kilo-ohm input resistor gives a rated current of 1 mA, and if necessary the rated current may be adjusted by replacing the input resistor or by using a shunt resistor. This induced grid voltage of 6Y6 varies, in turn proportionally altering the plate current.

Therefore, this plate current affects the d.c. integrating motor speed. If necessary the cathode resistor R_3 (ordinary variable resistor) of the 6Y6 tube controls the motor speed. When the amplified error voltage drives the 2-phase servo motor, a worm gear train transfers the rotation to the above-mentioned variable resistor R_3.

Error detection and correction unit

As stated above, the proportional relation of the observed current and the integrating d.c. motor speed is not always constant. To keep this relation constant, this integrator requires an error detection and correction unit. For such a correction, a standard is necessary. The linear and relatively stable characteristic curve of output voltage versus tachogenerator speed provides this standard.

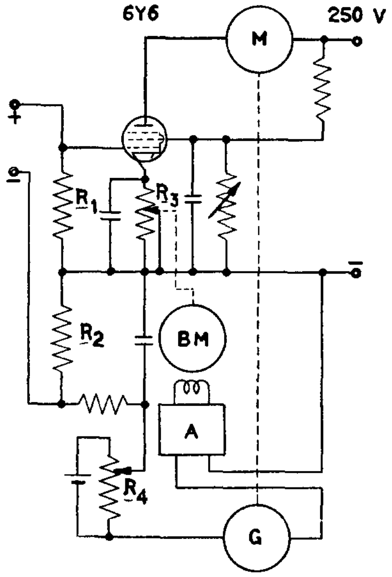

Fig. 3.

The observed current moves the d.c. motor. The voltage of the generator is proportional to the d.c. motor speed (generator and motor being on one shaft). The observed current also induces the voltage of the input standard resistor (R_2 in Fig. 3). If a difference occurs between the generated voltage and the induced voltage, this voltage difference is amplified by the a.c. amplifier and drives the 2-phase servo motor. This motor in turn controls the d.c. motor speed by the cathode of the 6Y6 tube until the generator voltage equals the input standard resistor R_2 voltage. Therefore the proportional relation of the d.c. motor speed and the observed current becomes constant.

When the observed current is zero, the cathode resistance and screen grid voltage adjust the initial d.c. motor speed to equal the synchronous motor speed (differential gear shafts are stationary). The voltage of the generator, proportional to the d.c. motor speed, is cancelled by voltage from a dry cell and a variable resistor R_4. When the dry cell voltage is changed, a difference occurs between the generator voltage and the altered dry cell voltage. This difference is amplified in the error detection unit, and in turn changes the d.c. motor speed. The zero adjustment of the counter is controlled by this variable resistor R_4. The dry cell voltage is always superimposed on the observed current voltage.

The a.c. amplifier of the error detection unit consists of an a.c. converter and two 12AX7 and one 6AU7 vacuum tube. The detected error voltage is converted to 60-cycle alternating current, is amplified to about 100 dB by the tubes 12AX7 and 6AU7, and is used to drive the 2-phase servo motor.

The tachogenerator, Model CLE 3R-60, has a speed of 30 to 48 r.p.m. (gear ratio 1 : 60) and an output of 6 mV per 1 r.p.m. This tachogenerator was used because the characteristic curve is linear in the range that was used.

d.c. supply source

A rectifier tube 80BK and an ordinary radio-use power transformer are used for the d.c. supply source. The output d.c. voltage is 250 volts; the rated current is 65 mA.

Synchronous motor

A 5 watt, 30 r.p.m. synchronous motor is used.

Counter

A needle-type, 5-unit counter (meter type) is used, because the driving power of digital-type counters is not constant (more power required every 10 units). The driving power of this needle-type counter is supplied by the output and is always constant.

To summarize: The observed current drives the d.c. integrating motor, which in turn drives one input of the differential gear. At the same time the synchronous motor drives the other input of the differential gear. The difference between the speed of the two motors is indicated by the counter. The count equals the total number of revolutions, which in turn equals the quantity of electricity. The stability is kept constant by the d.c. tachogenerator of the error detection unit.

Although this is a complicated mechanism, this apparatus is easily assembled in an ordinary laboratory, since all the gears rotate in only one direction. This enables the use of mechanical parts which need not be of highest quality; the total character of the apparatus, however, is not affected.

The typical calibration factors, obtained over several days, are shown in Table I. The input current used was rated at 50 mA (input resistor about 100 ohms). The standard quantity of electricity was calculated from the constant current and time. The count per coulomb was calculated from the standard number of coulombs and from the count at the various current values. With the constant current technique, the smallest deviation is obtained in the range of 50 to 100% of the rated current. With the controlled potential technique, the initial deviation is small—about 0·2%, since the initial electrolysis current is adjusted (at the input section) to the neighbourhood of 100% of the rated current; but as the electrolysis current decreases to the lower 10% of the rated current, the deviation becomes larger—about 4%. However, the total deviation is small—about 0·39% (Table II), when the entire range from 0 to 100% of the rated current is taken into consideration. These results only show the range from 2 to 100% of rated current; however, it is possible to measure the input current in the neighbourhood of zero, although with some loss in accuracy.

EXPERIMENTAL

The determination of copper was carried out to test the applicability of this integrator to controlled potential coulometric analysis. Copper sulphate solutions containing from 0·5 to 5·0 mg copper and 0·5*N* hydrochloric acid were used. The cathode was a copper-gauze cylinder. The method of determination, described by Yamashita and the present author in a previous publication,[8] has been modified slightly in this experiment.

Cell

The cell used is shown in Fig. 4. The cathode chamber has a volume of 200 ml; the anode chamber 80 ml; and the middle chamber 30 ml. Between these chambers are sintered-glass discs of 20-mm diameter.

Electrodes

The cathode is a 25-mesh copper-gauze cylinder with a diameter of 30 mm and a height of 30 mm. The anode is a 1-mm platinum spiral wire. The saturated calomel electrode is one of the commercial portable type.

Reagents

99·99% copper was used for the standard sample. Copper sulphate solutions were made from the standard sample with concentrations of 0·462 mg per 10 ml, $0{\cdot}924_5$ mg per 10 ml, $2{\cdot}311_5$ mg per 5 ml, and 4·623 mg per 10 ml. The electrolyte was 0·5*N* hydrochloric acid (reagent grade).

Automatic potential control

This unit employs a modified Lingane-Jones' potentiostat[9] which is on the market in Japan.

Procedure

The cathode chamber is filled with 100 ml of hydrochloric acid, the anode chamber with 60 ml, and the middle chamber with 25 ml (the middle chamber acid level is higher than others). The electrodes are set up and connected as shown in Fig. 4. The cathode potential of the potentiostat is adjusted to −0·34 V versus S.C.E. A magnetic stirrer continually agitates the cathode chamber. A rapid stream of nitrogen gas, initially passed through pyrogallol solution for removal of oxygen, is used throughout the determination. Nitrogen gas is bubbled through the cathode chamber for 15 min before pre-electrolyzing. Pre-electrolyzing is continued till the background current becomes very nearly constant. Even at this point there is a slight trace of dissolved copper and other unreducible impurities. Although this trace is constantly present, it has no effect on the results. When the background current becomes nearly constant, the counter reading is set at zero by adjusting the variable resistor R_4 (zero adjustor) to change the d.c. motor speed to equal the synchronous motor speed. A known volume of the sample is then pipetted into the cell, and the electrolysis is continued until the counter comes to a stop. At this point the background current has again become nearly constant. This counter reading is the net quantity of electricity consumed for the electrolysis of copper to be determined: *i.e.* the total quantity of electricity passed through the cell minus the quantity of electricity required by the background current. The number of coulombs is calculated from this counter reading and a factor (count/coulomb). The copper content can be calculated from this number of coulombs.

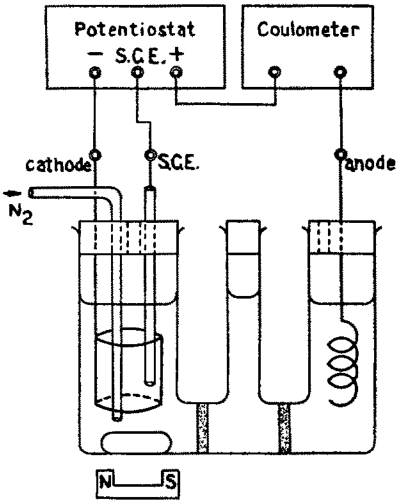

FIG. 4.

RESULTS

A cross-section of results obtained in the determination of various quantities of copper is shown in Table III. The electrolyses required about 10–15 minutes after each sample was introduced. The coefficient of variation of the 0·462-mg sample is larger than the coefficient of variation of the other samples. The initial concentration of the 0·462-mg sample is of the order of $10^{-4}M$, so that this difference in coefficients of variation may be large; consideration shows, however, that the standard deviation of the 0·462-mg sample has about the same value as that obtained from the other samples. The differences between the theoretical concentrations and the means of the measured concentrations are all negative values. This seems to be due to systematic error; the cause has not been ascertained. Error may possibly be introduced into the calibration factor by the fluctuation of constant current source and by error in time and current measurement. The use of a silver coulometer to obtain the calibration factor might yield better accuracy.

TABLE III.—COULOMETRIC DETERMINATION OF COPPER

Taken, *mg*	Equiv. to, *coul*	Found, *coul*	Mean, *coul*	Std. dev., *coul*	Std. dev., *mg*	C.V., %	Diff., *mg*
0·462	1·404	1·303 1·329 1·337 1·379 1·426 1·457	1·372	0·055	0·018	4	−0·011
0·925	2·807	2·658 2·697 2·681 2·653 2·692	2·676	0·019	0·006	0·7	−0·043
2·312	7·019	7·029 7·052 6·932 6·971 7·089	7·015	0·056	0·018	0·8	−0·001
4·623	14·039	13·995 13·930 13·896 14·039 14·039 14·112	14·002	0·072	0·024	0·5	−0·012

Acknowledgements—I wish to thank Professor T. Takahashi, Institute of Industrial Science, University of Tokyo, for his valuable suggestions and criticisms during the work. I also wish to thank Professor S. Hirano, Faculty of Engineering, University of Tokyo, for his very helpful advice on many matters; also Mr. M. Katori, Chief Director of the Government Industrial Research Institute, Nagoya, for his very keen interest in this work.

Zusammenfassung—Ein direkt anzeigender Stromintegrator für coulometrische Analysen wurde entwickelt. Das Instrument enthält ein konische Differential-Verzahnung und eine Standardisierungsvorrichtung was zur Stabilisierung der gesamten Anordnung beiträgt. Der Vorteil gegenüber bestehenden Instrumenten liegt u.a. in folgendem: hohe Energieleistung, stabile Kurve durch den Ursprung, Integration auch kleiner Ströme, Fehlen einer "Leerzone" und Vorhandensein eines Nullpunktkompensators. Bei guten Bedingungen werden Abweichungen von nur 0,3% erhalten. Die Bestimmung von Kupfer zeigte die Anwendbarkeit des Instrumentes in coulometrischen Analysen.

Résumé—L'auteur propose un intégrateur de courant à lecture directe pour l'analyse coulométrique. Celui-ci utilise un engrenage conique différentiel et un dispositif d'étalonnage incorporé pour augmenter la stabilité de l'instrument.

Les avantages sur les coulomètres et intégrateurs existants sont: une grande puissance de sortie, une courbe stable jusqu'à l'origine, l'intégration de petits courants, l'absence de zone morte, et l'élimination du courant résiduel par un réglage de zéro. Dans de bonnes conditions on peut atteindre un écart de 0,3%. Le dosage du cuivre à potentiel contrôlé montre que cet appareil est utilisable en analyse coulométrique.

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CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—II

THE IODOMETRIC DETERMINATION OF SELENOCYANIDE*

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Summary—The interference of certain anions in the iodometric determination of selenocyanide has been examined. Sulphate, chloride and perchlorate do not interfere, whilst in the presence of bromide, selenocyanide can only be partially oxidised by bromine to selenite, so that high results are obtained. The interference of bromide can be eliminated by sodium tungstate, or by determining the bromocyanogen formed, after distillation.

IN a preceding communication,[1] a method was presented for the micro determination of elementary and loosely bound selenium. Other micromethods for the determination of selenium and selenium compounds were also discussed in detail.

As we desired to apply this method in a rather broad field to the analysis of selenium and its compounds, the possibilities of determination in the presence of various anions were first subjected to a thorough examination.

It was found that selenium can be determined with an adequate accuracy even in the presence of large amounts of chloride, sulphate and perchlorate, although in the case of extremely high concentrations of sulphate a stronger acidification of the solution is necessary. Bromide ions interfere in relatively low concentrations.

In practice, the presence of bromide ions must always be taken into account. The interpretation of its interference and the possibilities of its elimination will therefore be discussed here in detail.

On brominating selenocyanide under prescribed experimental conditions (concentration, pH, temperature),[1] a reaction characterised by the following overall equation takes place:

$$SeCN^- + 4Br_2 + 4H_2O = BrCN + SeO_4^{2-} + 7Br^- + 8H^+ \tag{1}$$

It must be emphasized, however, that in the course of bromination several processes which reach equilibrium with each other must be considered.

The amount of excess bromine added was found to play an essential role in the determination. When only as much bromine-water is added to the solution as is required to obtain a slightly yellow colour, after binding the bromine with phenol, selenite can still be detected in the solution, in addition to bromocyanogen and selenate. This proves that, of the reactions combined into the overall equation (1), the oxidation of selenite leads mainly to the equilibrium:

$$H_2SeO_3 + Br_2 + H_2O \rightleftharpoons HSeO_4^- + 3H^+ + 2Br^- \tag{2}$$

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* Paper I of this series: *Z. analyt. Chem.* 1953, **139**, 20.

According to the measurements of Sherril and Izard,[2] the equilibrium constant of this reaction is of the order of 0·88. Thus, the reaction in the forward direction can only be complete at a low concentration of hydrogen and bromide ions. By increasing in favour of the quantity of bromide ions, reaction (2) shifts the formation of selenite.*

In an acid medium selenite oxidizes iodide to iodine with liberation of elementary selenium; in a bicarbonate medium selenite is not oxidised to selenate by iodine.[3]

This simple interpretation of the interfering effect of bromide suggested the necessity for a modification of the method when higher concentrations of bromide ion are present. The interference may be eliminated either by reducing the concentration of selenate (effectively of selenite) or by removing the bromocyanogen. When the solution contains bromide ions, selenate cannot be precipitated by barium ion, due to the solubility of barium selenate in acid media. In contrast, good results were obtained even at much higher concentrations of bromide, when sodium tungstate was added to the reaction mixture. Sodium tungstate presumably forms an extremely stable heteropolyacid, poorly reducible by haloids.† However, at the same time care must be taken to maintain a low concentration of hydrogen and iodide ions.

THE TUNGSTATE METHOD

Reagents

All the reagents should be of analytical grade.
Perchloric acid, 10% solution.
Methyl red, 0·1% ethanolic solution.
Sodium tungstate.
Bromine-water, freshly prepared, saturated.
Phenol, 5% solution.
Sodium thiosulphate, 0·01*N* solution, preserved by 1% of *iso*butanol.
Starch, 1% solution of potato starch (decomposed) preserved with 0·1% salicylic acid.
Potassium iodide.

A solution of selenocyanide corresponding to 0·4–4·0 mg of selenium is prepared by weighing accurately and diluted to 40–45 ml. It is transferred into a 100-ml Erlenmeyer flask fitted with a glass stopper, and is neutralised in the presence of methyl red. (When bromide is present, 0·2 g of sodium tungstate should be dissolved in the reaction mixture before neutralisation). The neutral solution is treated with bromine–water until it turns definitely brownish yellow and is allowed to stand for 2–3 minutes; 2–4 ml of phenol solution are added and the contents are allowed to stand for 4–5 minutes and acidified with 2 ml of perchloric acid. After adding 0·1–0·2 g of potassium iodide to the solution and allowing it to stand for 20 minutes, the amount of liberated iodine is measured. When a large amount of sulphate is present, 5 ml of perchloric acid should be added.

1 ml of 0·01*N* $Na_2S_2O_3$ is equivalent to 0·3948 mg of Se.

The effect of tungstate will be dealt with in a subsequent communication.

It was also found to be possible to determine selenocyanide in the presence of bromide by distilling the bromocyanogen formed. This method offers the advantage that the solution can be subjected also to other investigations, after the determination of selenocyanide.

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* It is of interest to note that the equilibrium constant of the reaction selenite-chlorine is recorded as $1{\cdot}4 \,.\, 10^9$.

† This possibility was suggested by E. Pungor.

TABLE 1

Quantity of Se weighed as KSeCN, *mg*	Foreign substances	0·01*N* $Na_2S_2O_3$ consumed, *mg*	Se found, *mg*	Deviation %	Notes
1·961	0·85 g K_2SO_4	4·97	1·962	+0·1	—
		4·96	1·958	−0·2	—
	4·2 g K_2SO_4	4·94	1·950	−0·6	Stronger acidification
		4·96	1·958	−0·2	
	0·75 g KCl	4·96	1·958	−0·2	—
		4·97	1·962	+0·1	—
	1·4 g $NaClO_4$	4·97	1·962	+0·1	—
		4·97	1·962	+0·1	—
	0·3 g KBr	7·5	2·90	+48	—
		6·9	2·67	+36	—
	0·1 g KBr	6·5	2·45	+25	—
		5·7	2·20	+12	—
		6·0	2·32	+18	0·25 g $BaCl_2$
		6·5	2·45	+25	
	0·15 g KBr	4·97	1·962	+0·1	0·20 g Na_2WO_4
		4·96	1·958	−0·2	
	0·3 g KBr	4·96	1·958	−0·2	
		4·95	1·954	−0·4	
	0·6 g KBr	4·95	1·954	−0·4	
		4·96	1·958	−0·2	
	0·15 g KBr	4·97	1·962	+0·1	BrCN removed by distillation
		4·96	1·958	−0·2	
	0·3 g KBr	4·98	1·966	+0·3	
		4·97	1·962	+0·1	
	0·6 g KBr	4·97	1·962	+0·1	
		4·97	1·962	+0·1	

THE DISTILLATION METHOD

Reagents

With the exception of sodium tungstate, the reagents are as used in the tungstate method. In addition a concentrated solution of phosphoric acid (80%) is required.

A solution of selenocyanide corresponding to 0·4–4·0 mg of selenium, accurately weighed, is neutralised in the presence of methyl red in a 100-ml round bottomed flask[4] fitted with a glass condenser connected with a ground glass joint. Excess bromine–water is added. Some glass beads are put in the distilling flask, the joints are lubricated with concentrated phosphoric acid and the flask is connected with the condenser. A 100-ml glass-stoppered Erlenmeyer flask containing 30 ml of water or preferably a 100-ml glass-stoppered measuring flask with a neck narrowed at one point[5] serves as receiver. The tube of the condenser touches the bottom of the receiver flask. The reaction mixture is heated by a small flame, using efficient condensing, and distillation is continued for 4–5 minutes. The tube of condenser is then raised to 1–2 cm above the distillate, and distillation is continued for further 1–2 minutes, in order to wash the condenser. Now the distillate, which contains bromine in addition to bromocyanogen, is treated with 2–4 ml of phenol solution and allowed to stand for 5 minutes; 2 ml of perchloric acid and about 0·1 g of potassium iodide are added. After allowing the liquid to stand for 20 minutes, the amount of liberated iodine is measured with a 0·01*N* solution of sodium thiosulphate.

1 ml of 0·01*N* $Na_2S_2O_3$ solution is equivalent to 0·3948 mg of Se.

The results obtained are shown in Table I.

Zusammenfassung—Das früher angegebene Verfahren zur Bestimmung von Selen über Selenocyanid wurde bezüglich störender Wirkung von Anionen gründlich untersucht. Sulfate, Chloride, Perchlorate übten keinen störenden Einfluss auf die Bestimmung aus. In Gegenwart von Bromiden konnte die störende Einwirkung durch Hinzugabe von Komplexbildner, wie das Natriumwolframat behoben werden. Sehr gute Resultate konnten durch das Abdestillieren des zur jodometrische Bestimmung gelangenden BrCN erzielt werden.

Résumé—Les auteurs ont étudié l'influence gênante de certains anions dans le dosage iodométrique du sélénocyanure. Les sulfates, chlorures et perchlorates ne faussent pas les résultats mais en présence de bromure le sélénocyanure est oxydé seulement partiellement par le brome en sélénite. Dans ce dernier cas les résultats sont donc trop élevés. On peut cependant éliminer l'action gênante des bromures par le tungstate de sodium ou en déterminant, après distillation, le bromure de cyanogène formé.

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CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—III

MICRODETERMINATION OF SELENITE THROUGH BROMOCYANOGEN

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Summary—At a suitable pH selenite can be reduced by ascorbic acid. On converting it into selenocyanide it is possible to determine it precisely on the micro scale by iodometry. The excess of reductant is eliminated by bromine, and the interference of the bromide formed is eliminated by tungstate or by distillation.

In earlier communications, the iodimetric microdetermination of elementary selenium through selenocyanide was dealt with in detail. By this method, it is possible to determine other selenium compounds as well, since these can relatively easily be converted into elementary selenium.

Quadrivalent selenium in selenium dioxide can be converted into elementary selenium by repeated evaporations with hydrazine hydrate and it is possible to remove the excess of the reducing agent in a simple way.[1] When other substances such as acids or bases are present in addition to selenium dioxide, the excess of reducing agent cannot be removed by simple evaporation alone. Attempts to eliminate excess reducing agent by raising the amount of bromine used for the bromination of selenocyanide resulted in an appreciable increase of the concentration of bromine in the solution.

A method for the elimination of interference from bromide has already been described.[2] On the basis of our experiments, the problem may be solved in another way after consideration of the following points:

(1) reducing quadrivalent selenium satisfactorily,
(2) adjusting the pH value, after reduction, to an adequate degree,
(3) dissolving the reduced elementary selenium, and
(4) removing excess cyanide.

These problems are interconnected. The adjustment of pH is difficult. Selenite can only be reduced to elementary selenium in an acid medium, but higher pH values would be desirable to facilitate the dissolving of elementary selenium in potassium cyanide. The simplest method is to adjust the solution before reduction, in the presence of methyl red, to give a neutral or acid reaction, and to make the solution alkaline after reduction, in the presence of sufficient potassium cyanide to dissolve the precipitated selenium. The pH value not exceeding 8 required for the elimination of cyanide by boiling, is secured by the addition of boric acid.

A reducing agent is therefore required which is capable of reducing selenite quantitatively at a pH value of about 5. Hydrazine sulphate or ascorbic acid meet this requirement. It is desirable that excess reducing agent should instantaneously be oxidized by bromine, and that in the course of the bromination only products which do not react with iodide or iodine should form. In some cases hydrazine sulphate was observed to interfere so that only ascorbic acid proved suitable.

At a pH value of about 5, selenite is not instantaneously reduced by ascorbic acid, and if the reaction is hastened by heating, selenium is converted into its crystalline modification which is insoluble in a solution of potassium cyanide.* At room temperature reduction proves to be complete in 10 minutes when 50 mg of ascorbic acid are added to 10 ml of solution.

The colloidal selenium formed during reduction in the cold dissolves in a solution of potassium cyanide in a few seconds, and with the concentration examined 50 mg of potassium cyanide are satisfactory for this purpose. Larger quantities of cyanide are only needed when the solution remains slightly acidic before reduction.

On diluting the solution, excess cyanide can easily be removed by boiling the solution with boric acid.

The selenocyanide content of the resulting solution can be determined by the tungstate or the distillation methods previously described.

THE TUNGSTATE METHOD

Reagents

In addition to the reagents listed previously for the tungstate method[2], the following are necessary:

Sodium hydroxide, 20% solution.

Ascorbic acid, 5% solution freshly prepared.

Potassium cyanide, 5% solution freshly prepared.

Boric acid.

The solution of accurately weighed selenite, containing 0·4–4·0 mg of selenium, is neutralised in a 100-ml glass-stoppered Erlenmeyer flask in the presence of one drop of methyl red, diluted to 10 ml, and treated with 1 ml of ascorbic acid solution; the precipitated selenium is dissolved by the addition of 1 ml of a 5% solution of potassium cyanide and allowing the solution to stand for 10 minutes. When selenium has completely dissolved, 0·5 g of boric acid is added to the reaction mixture, its volume is increased to about 35 ml and the liquid is kept boiling for 10 minutes in order to remove excess cyanide. The evaporated water is periodically replaced. On cooling, the determination of the selenocyanide is completed as described elsewhere.[2]

The results obtained by the tungstate method are presented in Table I.

Some alterations to the earlier procedure are necessary for the distillation method, owing to the presence of dehydroascorbic acid. At higher temperature, under the conditions described, dehydroascorbic acid (more correctly, the product formed when ascorbic acid is oxidized by bromine) is capable of reducing selenium compounds of higher oxidation state (to elementary selenium when pH values are sufficiently low). During this process, compounds form which interfere with the iodometric measurements. This interference can, however, be eliminated when the oxidizing property of the medium is maintained throughout the distillation. An excess of a mixture of potassium bromate and potassium bromide may be used for this purpose.

THE DISTILLATION METHOD

Reagents

Most of these are as used in the tungstate method.[2] Sodium tungstate and bromine water are not required. Additional reagents are a solution containing 1% potassium bromate and 0·5 potassium bromide, 50% sulphuric acid and concentrated sulphuric acid.

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* According to the investigations of Brintzinger,[3] a dilute solution of selenite reacts with ascorbic acid at temperatures below 50°, with precipitation of colloidal selenium.

TABLE 1. RESULTS BY THE TUNGSTATE METHOD

Na_2SeO_3 weighed *mg*	$0{\cdot}01N$ $Na_2S_2O_3$ consumed		Na_2SeO_3 found *mg*	Δ, %
	tests, *ml*	mean value *ml*		
8·243	9·49 9·48 9·46	9·48	8·198	−0·55
4·121	4·76 4·77 4·75	4·76	4·116	−0·12
1·652	1·91 1·91 1·90	1·91	1·652	0
0·818	0·96 0·95 0·95	0·95	0·822	+0·49

TABLE II. RESULTS BY THE DISTILLATION METHOD

Na_2SeO_3 weighed, *mg*	$0{\cdot}01N$ $Na_2S_2O_3$ consumed		Na_2SeO_3 found, *mg*	Δ, %
	tests, *ml*	mean value, *ml*		
8·243	9·54 9·58 9·57	9·56	8·264	+0·29
4·121	4·78 4·79 4·78	4·78	4·134	+0·32
1·652	1·93 1·92 1·92	1·92	1·660	+0·48
0·818	0·95 0·96 0·96	0·96	0·830	+1·46

Weighing, reduction, preparation of the cyanide solution and removal of excess cyanide are carried out as described earlier,[2] but these operations may be carried out in the 100-ml distillation flask. After removal of cyanide by boiling, the reaction mixture is treated with 10 ml of the bromate–bromide solution and 2 ml of sulphuric acid, the joints are greased with concentrated sulphuric acid, and the flask is connected to the condenser. The distillation is then concentrated as before.

Some results obtained by the distillation method are presented in Table II.

Zussammenfassung—Das Selenit kann bei entsprechendem pH-Wert der Lösung durch Askorbinsäure zu elementarem Selen reduziert werden. Letzeres in Selenocyanid übergeführt, welches endlich unter Verwendung von Wolframat, oder nach einer Destillation jodometrisch ermittelt werden kann.

Résumé—A un pH convenable, le sélénite peut être réduit par l'acide ascorbique. En le transformant en selénocyanure il peut être dosé avec précision par iodométrie à l'échelle micro. L'excès du réducteur est éliminé par le brome et l'influence gênante des bromures formés est éliminée comme précédemment.

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CONTRIBUTIONS TO THE CHEMISTRY OF SELENIUM AND SELENIUM COMPOUNDS—IV

DETECTION AND DETERMINATION OF MINUTE AMOUNTS OF SELENITE IN THE PRESENCE OF SELENATE

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Summary—In the absence of halides, and at a low hydrogen ion concentration, selenite is reduced by ascorbic acid whereas selenate remains unchanged. By utilising this reaction, 0·01% of selenite can be detected in selenate preparations. The method also lends itself to quantitative determinations, since the reduced selenite may be converted into selenocyanide and determined by iodometry. It is possible to determine 1% of selenite in selenates by this method with a relative error of ±1%.

MÜLLER[1] has described the detection of selenite in the presence of selenate by reduction with sulphur dioxide, selenate remaining unchanged. The ratio of selenite to selenate is not mentioned, and only the limits of detection for the test (5 mg Se per litre) are given.

We find that the method is suitable for detecting selenite in the presence of a relatively small amount of selenate, but that when the quantity of selenite falls below 0·1 mg and that of selenate rises above 20 mg the method is unreliable.

Elsewhere[2] we have shown that the reduction of selenate to selenite (and through selenite to elementary selenium) is promoted by high hydrogen ion concentration, the presence of halide ion, and increased temperature; in moderate concentrations selenate is reduced to a negligible extent by ascorbic acid at room temperature in a nearly neutral solution free from halide, even over an extended period of time, but in identical conditions the precipitation of selenium from minute amounts of selenite (10 μg) can be observed visually in 5–10 minutes. On this basis a method is proposed for the detection of selenite in the presence of selenate.

Procedure. The test solution should contain not more than 0·1 g of Na_2SeO_4. Neutralise the solution, adjust the pH to a value of 6 using indicator paper, dilute to a volume of about 10 ml and treat with 1 ml of 5% ascorbic acid solution. Set aside for 10 minutes. Carry out a blank test in exactly the same way.

By this procedure the presence of 0·01% of selenite in selenate can be reliably indicated.

No methods described in the literature proved to be suitable for the determination of minute amounts of selenite in the presence of selenate. The thiosulphate method of Norris and Fay[3] can only be used on the macro scale, and the iodometric method of Klasson and Mellquist[4] does not yield accurate results, even when the experimental conditions are strictly maintained. Other methods based on the oxidation of selenite or on gravimetry cannot be considered as micro methods.

We have obtained excellent results by applying the tungstate-ascorbic acid reduction method to determination of selenite in the presence of selenate, and find that 0·1 g of selenate does not interfere, nor do sulphate, perchlorate or small amounts of chloride or bromide.

The sample may contain from 0·8 to 8·0 mg sodium selenite and from 0 to 100 mg of sodium selenate, and is treated precisely as described previously.[2] The results summarised in Table I show that 1 % of selenite can be determined in the presence of sodium selenate with a relative error of 1 %.

TABLE 1

Na_2SeO_3 *mg*	Na_2SeO_4, *mg*	Approx. mole ratio	$0{\cdot}01N$ $Na_2S_2O_3$ consumed		Na_2SeO_3 found, *mg*	Deviation %
			tests, *ml*	mean value, *ml*		
8·088	1	10 : 1	9·32 9·34 9·34	9·33	8·069	−0·21
4·044	5	1 : 1	4·67 4·66 4·66	4·66	4·030	−0·35
0·806	10	1 : 10	0·93 0·94 0·94	0·94	0·813	+0·88
	100	1 : 100	0·92 0·92 0·94	0·93	0·804	−0·25

The distillation method for the determination of selenite described at the same time as the tungstate method has also been examined and found to permit the determination of both selenite and selenate in the presence of each other. Details of this will be presented in a subsequent communication.

Zusammenfassung—In Abwesenheit von Halogeniden werden nur die Selenite bei Zimmertemperatur bei niedrigem pH-Wert der Lösung zu elementarem Selen reduziert; Selenate dagegen nicht. So kann noch 0,01 % Selenit neben Selenat nachgewiesen und jodometrisch über Selenocyanid bestimmt werden. Die Bestimmungsgrenze des Selenits in Selenat beträgt etwa 1 %.

Résumé—En l'absence d'halogénures et aux faibles concentrations d'ions hydrogène, le sélénite est réduit par l'acide ascorbique alors que le séléniate ne réagit pas. En utilisant cette réaction, on peut déceler 0,01 % de sélénite dans les préparations de séléniate. La méthode se prête aussi aux dosages quantitatifs par réduction du sélénite en sélénocyanure et par dosage iodométrique de celui-ci. Par cette méthode, on peut déterminer 1 % de sélénite dans le séléniate avec une erreur relative de ±1 %.

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THE DETERMINATION OF ULTRA-MICRO QUANTITIES OF SILVER IN PLATINUM SPONGE BY NEUTRON-ACTIVATION ANALYSIS

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Summary—The increasing availability of nuclear reactor facilities makes analysis by neutron-activation an important method for more widespread use in trace element analysis. The technique is advantageous for the determination of submicrogram quantities of silver in platinum sponge, and its application in this connection is described.

Activation of samples of platinum sponge has been carried out by neutron irradiation in the Harwell Pile BEPO for a period of one month, and silver has been assayed by measurements of the radionuclides ^{110m}Ag—^{110}Ag. Radiochemical separation after the addition of carrier has been based mainly on precipitations of silver as chloride, sulphide, oxide, and iodate, and on electrolytic deposition. The silver has been finally precipitated as the iodate and counted with a NaI crystal γ-scintillation counter. Chemical yields have been determined gravimetrically.

In order to avoid errors due to self-shielding, standards have been made by adding small known amounts of silver to analytical samples.

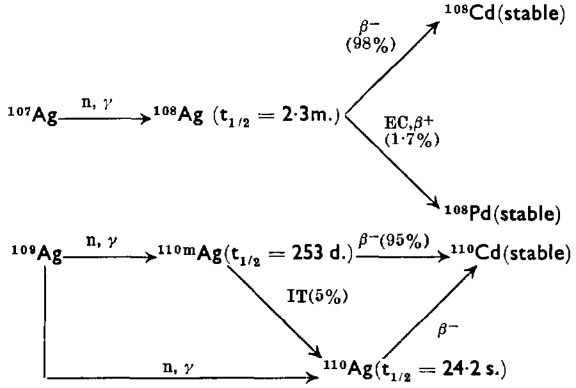
The precision of analyses has been better than ±10 per cent, and the method described may be applied to the analysis of platinum containing as little as 0·02 ppm Ag. The ultimate sensitivity could be considerably enhanced by employing larger analytical samples and the Harwell Pile DIDO for irradiation.

INTRODUCTION

IN the production of precious metals it is necessary to have an accurate specification of trace impurities. Some of the impurities of consequence may be present in amounts below the sensitivity of conventional methods of analysis.

In the present work, neutron-activation[1–5] has been applied to the determination of silver in platinum sponge. The Harwell Pile BEPO has been used as the neutron source. It has been estimated[5] that under ideal circumstances the use of this reactor will enable the determination of as little as *c.* 5×10^{-9} g of silver with a precision of ±10%

Silver has two stable isotopes ^{107}Ag (% abundance 51·35) and ^{109}Ag (% abundance 48·65), which on irradiation with thermal neutrons undergo the nuclear reactions—



The thermal neutron-activation cross sections for the stable silver isotopes are[6]:

^{107}Ag(n,γ)^{108}Ag $\sigma = 44$ barns
^{109}Ag(n,γ)^{110m}Ag $\sigma = 2{\cdot}8$ „
^{109}Ag(n,γ)^{110}Ag $\sigma = 110$, „

and a summary of nuclear data for the different radioisotopes of silver produced in the nuclear reactions[7] is given in Table I.

TABLE I. SUMMARY OF NUCLEAR DATA FOR RADIOISOTOPES OF SILVER

Radioisotope	Half-life	Radiations and energies, *MeV*
^{108}Ag	2·3 min.	β^- 1·77; (EC; γ 0·43, 0·60; β^+)
^{110m}Ag–^{110}Ag	253 days	β^- 0·530 (35 %), 0·087 (58 %), 2·12 (3 %), 2·82 (3 %); γ 0·116 to 1·51
^{110}Ag	24·2 sec	β^- 2·16 (60 %), 2·84 (40 %); γ 0·66, 0·94 (weak), others.

For the present purpose, a procedure involving chemical separation and radiometric assay of the radionuclides ^{110m}Ag—^{110}Ag from neutron irradiated samples of platinum has been developed.

EXPERIMENTAL

Samples for analysis

The material analyzed consisted of platinum sponge supplied by the Mond Nickel Co. This was given no chemical treatment before irradiation. Samples consisting of *c.* 0·3 g of small fragments were weighed out accurately into irradiation containers made from 4-mm internal diameter silica tubing, which were then sealed. Just as in any other sensitive analytical method, extensive precautions must be taken to avoid contamination at this stage.

Neutron irradiation of samples and standards

In order to avoid self-shielding differences with samples and standards,[5] standards were prepared by adding known small quantities of silver to platinum samples to be analyzed. This was done by adding aliquot portions of a dilute standard solution of silver, and a drop of wetting-agent, to 0·3 g samples of the platinum sponge in silica irradiation tubes. The liquid in the tubes was allowed to soak into the metal sponge, and then was carefully evaporated to dryness, after which the tubes were sealed.

Standards containing the added silver and samples to which no silver had been added, were packed with glass wool into a standard 3 in. × 1 in. aluminium can for irradiation in BEPO. Irradiation was for one month. On delivery from Harwell after irradiation, the samples and standards were analyzed radiochemically for ^{110m}Ag—^{110}Ag by the procedure described below.

Chemical separation

A radiochemical separation procedure using carrier chemistry was used to secure the necessary separation of silver. In order to attain solution of the samples and satisfactory separation of silver, a procedure had to be developed which was rather different from that employed by Morris and Killick[8] for the radioactivation analysis of silver in galena and blende.

In the present work, irradiated samples and standards have been dissolved in *aqua regia.* Silver has been initially separated as the ammine complex followed by precipitation of the chloride from nitric acid solution. The silver has been purified further by ferric hydroxide scavenging and silver sulphide precipitation, both carried out in ammoniacal solution. After a further precipitation of the chloride, the silver has been purified by electrolysis,[9] and has finally been converted to the iodate $AgIO_3$, in which form it has been counted.

The efficiency of silver chloride precipitation and of electrodeposition as decontamination steps for silver has been indicated by the tracer tests of Sunderman and Meinke.[9]

Reagents

Ag carrier: 10 mg Ag/ml (added as $AgNO_3$ in very dilute HNO_3) standardised.
Fe^{III} *carrier:* 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl).
Aqua regia: 4 parts conc. HCl+1 part conc. HNO_3 (v./v.).
HCl; *M.*
HCl; 6*M.*
HNO_3; 6*M.*
HNO_3; conc.
Cyanide plating solution: mix 7 ml of 3*M* NaCN with 1 ml 5*M* NaOH.
H_2SO_4; conc.
KIO_3; saturated solution.
NaOH; 6*M.*
NH_4OH; 6*M.*
$(NH_4)_2S$; saturated solution.
Manoxol OT; (British Drug Houses Ltd.), 0·1% solution in water.
Ethyl alcohol; 95%.

Preparation and standardisation of silver carrier

Dissolve 15·75 g of $AgNO_3$ in a minimum amount of H_2O, add a few drops of HNO_3, and dilute the solution to 1 litre.

Pipette exactly 5 ml of the carrier solution into a 50-ml centrifuge tube and dilute to 20 ml with H_2O. Add 1 ml of saturated KIO_3 solution and stir to coagulate the precipitate which forms. Add an additional drop of KIO_3 to test for completeness of precipitation. Filter the precipitate into a weighed sintered-glass crucible of grade 3 or 4. Wash the precipitate with 5 ml of 95% ethyl alcohol and dry in an oven at 110° for 15 min. Cool and weigh as $AgIO_3$.

Radiochemical separation procedure

Step 1: Remove the silica tubes from the can, open them at the constriction, and transfer the solid samples to 50-ml beakers. Wash out the tubes with a little warm dil. HNO_3 and transfer the washings quantitatively to the beakers.

Step 2: To a sample in a 50-ml beaker with a watch glass as cover add 2 ml of standard Ag carrier and 5 ml of *aqua regia*. Dissolve the platinum by heating on a water bath. Evaporate carefully to small volume under an infrared lamp, and then add 10 ml of distilled H_2O. Stir for 5 min. Add 2 ml of conc. NH_4OH dropwise with vigorous stirring. Digest at 60° for 10 min and allow the orange–yellow precipitate of ammonium chloroplatinate to settle. Decant off the supernate into a clean 50-ml centrifuge tube, add a further 1 ml of conc. NH_4OH to the residue in the beaker, digest, and decant the supernate into the centrifuge tube. Filter the solution into a clean 50-ml centrifuge tube. (Note *a*).

Step 3: Add a few drops of Manoxol OT solution and heat to boiling (Note *b*). Add 6*M* HNO_3 drop by drop until precipitation of AgCl is complete. Heat until the AgCl has coagulated. Centrifuge and discard the supernate.

Step 4: Wash the precipitate three times with 10-ml portions of hot H_2O. Dissolve the AgCl in 2 ml of conc. NH_4OH (Note *c*). Dilute to 20 ml with H_2O and add 1 ml of Fe^{III} carrier. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube, and discard the precipitate.

Step 5: To the solution add 1 ml of saturated $(NH_4)_2S$ solution. Stir vigorously and centrifuge. Discard the supernate.

Step 6: Dissolve the Ag_2S precipitate by heating with 1 ml of conc. HNO_3. Dilute to 20 ml with H_2O, centrifuge, and discard any S residue.

Step 7: To the solution add a few drops of Manoxol OT solution and heat to boiling. Add 6*M* HCl drop by drop until precipitation of AgCl is complete. Heat until the AgCl has coagulated. Centrifuge and discard the supernate.

Step 8: Dissolve the AgCl in 8 ml of cyanide plating solution (Note *d*). Mix the solution thoroughly transfer to a Pregl micro-electrolysis apparatus and electrolyse at 4 volts for 15 min. When electrolysis is complete, remove the electrodes and wash the cathode with H_2O from a wash bottle for 1 min.

Step 9: Dissolve the Ag completely off the cathode with conc. HNO_3 and transfer the solution to a clean 50-ml centrifuge tube. Add 10 ml of H_2O. Repeat Steps 7 and 8.

Step 10: Dissolve the Ag completely off the cathode with conc. HNO_3 and transfer the solution to a clean 50-ml centrifuge tube. Make the solution alkaline with 6*M* NaOH, and add 3 drops in excess. Centrifuge the Ag_2O precipitate and discard the supernate. Dissolve the Ag_2O in 4 drops of conc. H_2SO_4 and evaporate completely to dryness (Note *e*). Cool.

Step 11: Add 20 ml of H_2O and boil until a clear solution is obtained, then add 1 ml of saturated KIO_3 solution. Centrifuge and discard the supernate.

Step 12: Dissolve the $AgIO_3$ precipitate in 4 drops of conc. NH_4OH. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube.

Step 13: Add 3 drops of conc. H_2SO_4 to the solution. Centrifuge the $AgIO_3$ precipitate and wash twice with H_2O and once with 5 ml of 95% ethyl alcohol.

Step 14: Slurry the precipitate with 95% ethyl alcohol on to a weighed aluminium counting tray (A.E.R.E. cat. No. 4-3/1068), by using a transfer pipette. Make sure that the distribution of the precipitate on the tray is uniform. Dry at 110° for 15 min and weigh to establish the chemical yield (20 mg Ag $\equiv$ 52·43 mg $AgIO_3$).

Notes

(*a*) The procedure must be followed carefully to ensure complete exchange of radiosilver and carrier.

(*b*) The addition of Manoxol OT helps to coagulate the AgCl and to prevent its adherence to the walls of the tube.

(*c*) A little heating may be necessary.

(*d*) See reagents.

(*e*) It is not necessary to remove the last traces of H_2SO_4 on the walls of the tube.

Counting of the isolated silver iodate precipitates

In the present work the final precipitates of $AgIO_3$ were counted with a NaI(Tl) γ-scintillation counter type 1186 A, fitted with conventional associated electronic equipment. Each sample was placed on shelf 2 of the lead castle, a standard Al—Pb sandwich absorber being inserted on shelf 1 between the sample and the detector. A statistical accuracy of 0·5% was achieved by measuring a total of 40,000 counts, where practicable. In cases where the activity was low, counting was carried out for a period of 40 min. All measured activities were corrected for background and chemical yield. No paralysis correction was necessary.

The counting rates of samples were measured over a period of two weeks, and the decay corresponded to the measurement of ^{110m}Ag—^{110}Ag activity, no short-lived contaminants being detected unless the discriminator bias was set low.

As a check, the γ- spectra of precipitates were recorded using an IDL γ-scintillation spectrometer of the recording type, and no photoelectric peaks other than those due to ^{110m}Ag—^{110}Ag were detectable (Fig. 1). Spectra were also measured on a manually operated IDL γ-spectrometer fitted with a scaling unit, enabling better sensitivity and counting statistics. In this case also, only peaks due to ^{110m}Ag—^{110}Ag could be detected.

Assay of the precipitates by Geiger–Müller counting was not desirable, since with this type of detector decay measurements showed the presence of a very small trace of contaminant, believed to be radioplatinum.

RESULTS

If A_1 is the silver activity (corrected for background and chemical yield) for a standard containing w μg of added Ag, and A_2 is the corrected activity of a corresponding sample of the same weight but with no added Ag, it follows that an activity of A_1–A_2 corresponds to w μg of Ag. The silver content of samples may therefore be calculated from their corrected counting rates.

Typical analysis results obtained by the neutron-activation method are shown in Table II.

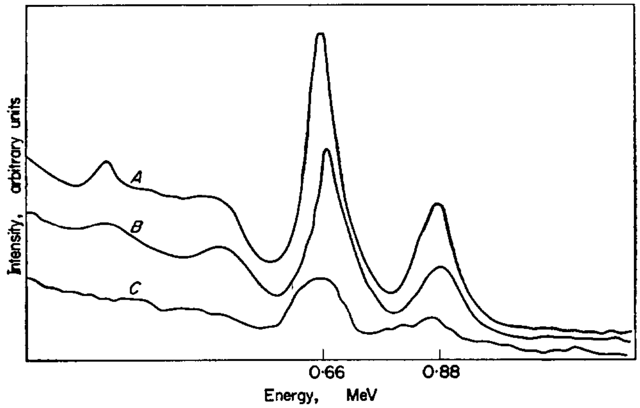


FIG. 1. Gamma spectra. A, pure ^{110m}Ag—^{110}Ag sample. B, final precipitate from a platinum analysis standard. C, final precipitate from a platinum analysis sample.

DISCUSSION

Attention must be given to possible errors caused by the presence of elements other than silver in samples, which may give rise to the radionuclides ^{110m}Ag—^{110}Ag on neutron irradiation. The elements cadmium and indium demand consideration. These elements could possibly give rise to ^{110m}Ag—^{110}Ag activity by the following nuclear reactions—

$$^{110}Cd(n,p)^{110m}Ag$$

$$^{113}In(n,\alpha)^{110m}Ag$$

These nuclear changes are liable to occur with fast neutrons, which may be present to an extent of *c.* 10% of the slow neutron flux in the case of irradiations used in the present work. An estimate of possible interference has been made by irradiating small samples of pure CdO and In_2O_3, together with pure Ag standards in the Pile. The silver activity of the samples was chemically separated, and counted as before. The results indicated that if a sample of platinum sponge contained 1 ppm of cadmium and 1 ppm of indium, the maximum spurious silver content would be only *c.* 0·00004 ppm.

Any interference of consequence due to the production of silver radionuclides other

TABLE II.—SILVER CONTENT OF SAMPLES OF PLATINUM SPONGE DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample C Pt 58	Sample C Pt 46
0·48 ppm	0·24 ppm
0·43	0·24
0·44	0·27
0·45	0·28
0·41	0·29
0·40	0·26
Av. 0.44	Av. 0·26

than ^{110m}Ag—^{110}Ag should have been apparent from energy and decay measurements made on the counted final precipitates from platinum samples.

The neutron-activation method described in this paper may be applied to the analysis of samples of platinum containing as little as 0·02 ppm Ag.* The ultimate sensitivity of the method could be considerably enhanced by employing larger samples or the Harwell Pile DIDO as neutron source.

Precision (standard deviation) of radio-activation analyses has always been better than $\pm 10\%$.

Since platinum apparently can only be dissolved in *aqua regia*, other methods of analysis requiring the bringing of samples into solution would be likely to be bedevilled by problems of silver adsorption, even if the method potentially provided satisfactory analytical sensitivity. Errors due to contamination of reagents would also have to be taken into account.

In addition, conventional emission spectrographic methods do not provide sufficient sensitivity for the reliable determination of silver in platinum.

Neutron-activation analysis clearly has a number of unique advantages for the determination of silver and other trace elements in platinum, and only quite small samples of the precious metal are required for accurate analysis.

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Zusammenfassung—Je mehr Reaktoren zur Verfügung stehen, desto höhere Bedeutung kommt der Neutronenaktivierungsanalyse für breite Anwendung bei Spurenanalyse zu. Die Methode ist von Vorteil bei der Bestimmung von Submikrogrammengen von Silber in Platinschwamm. Die Anwendung der Methode auf dieses Problem wird beschrieben.

Die Aktivierung von Platinschwammproben erfolgte durch Neutronenbestrahlung im Harwell-Reaktor BEPO über einen Zeitraum von einem Monat. Die Messung basierte auf dem Vorgang ^{110m}Ag–^{110}Ag. Radiochemische Trennung nach Zugabe eines Trägers erfolgte durch Abscheidung des Silbers als Chlorid, Sulfid, Oxyd und Iodat, sowie elektrolytisch. Das Silber wurde zuletzt als Jodat gefällt und die Zählung mit einem NaI Gamma-Scintillations-Zähler durchgeführt. Chemische Analysen wurden gravimetrisch durchgeführt.

Um Fehler durch Selbstabschirmung zu vermeiden, wurden Standardproben durch Zugabe kleiner, bekannter Silbermengen zu analytischen Proben hergestellt. Reproduzierbarkeit der Methode ist besser als $\pm 10\%$. Die Methode kann für die Bestimmung von bis herab zu 0,02 ppm Ag verwendet werden. Die analytische Empfindlichkeit konnte erheblich gesteigert werden durch Verwendung grösserer Proben und Bestrahlung im Harwell-Reaktor DIDO.

Résumé—Les possibilités d'utilisation croissantes du réacteur nucléaire font de l'analyse par activation par neutrons une méthode importante dont l'emploi doit être plus répandu dans l'analyse de traces d'éléments. La technique est avantageuse pour le dosage de submicrogrammes d'argent dans la mousse de platine, et l'auteur décrit l'application à ce cas.

L'activation d'échantillons de mousse de platine a été réalisée par l'irradiation par neutrons dans la pile BEPO de Harwell et l'argent a été dosé par la détermination des radio éléments ^{110m}Ag—^{110}Ag.

La séparation radiochimique après addition d'un entraineur a été basée principalement sur des précipitations de l'argent à l'état de chlorure, sulfure, oxyde et iodate et sur le dépôt électrolytique. L'argent a finalement été précipité à l'état d'iodate et dosé avec un compteur gamma à scintillation à cristal de NaI. On a déterminé les rendements chimiques par gravimétrie.

Afin d'éviter des erreurs dues à l'absorption propre on a fait des étalons en ajoutant de faibles quantités connues d'argent à des échantillons analytiques.

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* The sensitivity limit has been set at a content sufficient to give 40 counts/min above the γ-counter background.

La précision des analyses est meilleure que ±10%, et on peut appliquer la méthode décrite à l'analyse de platine contenant des quantités aussi faibles que 0,02 p.p.m. d'argent. On pourrait améliorer considérablement cette dernière sensibilité en employant des échantillons analytique splus importants et la pile DIDO de Harwell pour l'irradiation.

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THE WET OXIDATION OF BONE.

DIGESTION WITH 100 PER CENT SULPHURIC ACID FOLLOWED BY THE ADDITION OF DIOXONIUM PERCHLORATE

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Summary—Organic materials rich in fat, such as bone and bone marrow, introduce complications in wet ashing by previously described procedures. In the accompanying detailed procedure, 100% sulphuric acid and 73.60% perchloric acid serve as oxidants with vanadium as catalyst. Reagent preparation, apparatus design, and illustrative reactions are described.

INTRODUCTION

THE wet oxidation of bone, in preparation for the trace element determination of metallic components, presents unusual operational prerequisites. The presence of fat as a principal component in both the solid composition and the bone marrow complicates destructive oxidation. The trace element estimation of lead or beryllium are illustrative. Medical autopsy and forensic investigations of industrial hazards are frequently involved.

The regular procedures of wet ashing require modification. For bone tissue and bone marrow a two-stage oxidation reaction is requisite.

A preliminary oxidation employing 100% sulphuric acid as oxidant is applied. The thoroughly carbonized sample thus treated is subjected to a second stage reaction. The completion of destructive oxidation is provided by the addition of 73.6% perchloric acid. The first stage involves boiling temperatures of 300° to 325°. The resulting reaction mixture is thus effectively carbonized. The second stage of completed oxidation is operative at 200° to 210°. A milligram of vanadium is added as catalyst. Total reaction time is 30 minutes or less for controlled oxidation. The process is at no disadvantage because of associated hazard.

PREVIOUS STUDIES IN WET OXIDATION

Mixed nitric and perchloric acids in wet oxidation procedures for a wide variety of natural and synthetic organic compositions, has been described.[1] From this work and publications therein cited, routine analytical procedures for a great number of trace metals and major constituents have been applied.

For the wet oxidation of organic materials predominantly composed of cellulose proteins, or sugars, selected and maintained concentrations of perchloric acid alone are admirably adequate.[2] By this procedure selected graded oxidation potentials may be rigidly controlled. The trace element determination of copper in food packaging paper is illustrative.

Organic compositions such as alkaloids and other heterocyclic ring nitrogen compounds, gas-mask canister carbon, decolorizing carbon, or ion-exchange resins require high oxidation potentials for their rapid oxidation. Digestion with mixed sulphuric and perchloric acids serves best.[3] The very highest oxidation potentials, graded in magnitude, and continuously controlled, are thus made operative.

In broad scope, the problem in wet oxidation procedures demands oxidation potentials of 0.8 to 2.0 volts or more. Reaction potentials must be rigidly controlled at selected intermediate values depending upon the type of organic matter to be oxidized.

Chromium, vanadium and molybdenum have been selectively applied as reaction catalysts.

Nitric, sulphuric and perchloric acids are the most important oxidants. Their individual, simultaneous, and stepwise application accounts for a wide diversity of experimental conditions. Selective use, order of addition, and the temperatures involved are important operational variables.

The procedures are free of hazard, rapid in prosecution, and precise in estimation of either trace metals or macro magnitude, non-volatile components. Because of their use, dry ashing procedures are largely losing favour.

THE PRESENT STUDY

The present research involves the wet ashing of bone tissue, bone marrow, and bone-adherent muscle tissue. The problem is complicated by the presence of fat as a major constituent. Such material in the process of wet oxidation, following previously described procedures, requires the oxidation of samples of limited size if uncontrolled reaction intensity is to be avoided. Therefore recourse is had to a procedure involving a two-stage oxidation.

The first reaction involves the decomposition of organic matter to form carbon, or degradation carbonaceous products suspended in or soluble in mineral acid. This is accomplished by high temperature digestion with concentrated sulphuric acid. The second stage involves the addition of concentrated perchloric acid at materially lowered temperature. The oxidation of carbon and acid-soluble degradation products of the preliminary digestion is thus rapidly completed. A few milligrams of vanadium serves to catalyze the second-stage reaction.

EXPERIMENTAL

Reagents employed

100% *sulphuric acid*: Made by mixing 96–97% (reagent grade) sulphuric acid with the necessary amount of 15–18% fuming sulphuric acid. A weight of 337.5 g of reagent grade acid is added to 453 g of the oleum. By analysis the resulting acid was found to be 99.5% H_2SO_4. M.p. 10.5°c. Sp.Gr. (25°/4°) = 1.837. For preparation of 100% acid, employing oleum of different SO_3 content, the following formula, as devised by Gerster,[4] is applicable:

$$X = 100(b - a)/(a - c)$$

where X = quantity of sulphuric acid to be added to 100 parts of oleum,
a = total SO_3 per 100 parts of the acid desired,
b = total SO_3 per 100 parts of the original oleum,
c = total SO_3 per 100 parts of the acid used for dilution.

If the SO_3 content of the oleum is not known a close approximation to the desired 100% sulphuric acid can be made by determining the boiling point of a given reagent grade acid after the addition of increasing amounts of oleum. Sulphuric acid of 100% H_2SO_4 content has a boiling point of 325° at approximately 750 mm atmospheric pressure. By examination of the results in Fig. 1 this procedure is seen to be less accurate because of the limited increase in boiling point with increase in concentration of SO_3.

Dioxonium perchlorate (*73.6% perchloric acid*): Made by vacuum distillation of 72.5% acid (the perchloric acid-water azeotrope) at 2–7 mm pressure as described by Smith and Koch.[5]

Vanadium catalyst: Ammonium vanadate or vanadic oxide.

Apparatus assembly

The apparatus, as originated by Bethge,[2] and employed in previous procedures in wet oxidations, was again employed. To provide for the disposal of evolved SO_2 from the oxidation of organic matter by sulphuric acid, the top terminal of the water cooled condenser is fitted with an adaptor. A small-bore rubber tube conducts away the SO_2 which is vented into the sink drain for absorption in running water. The Bethge apparatus, manipulations, and manner of use, have been previously described.[2]

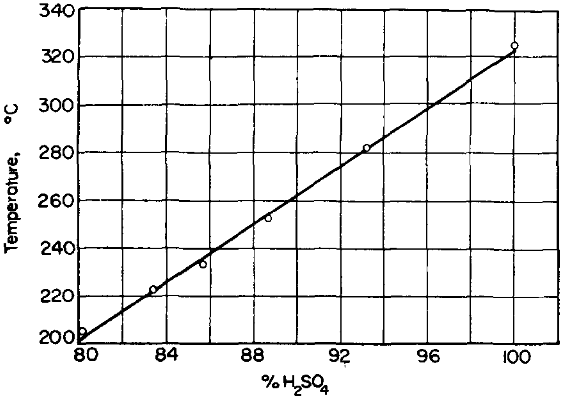

FIG. 1.

Test sample selection

Small diameter fore-leg bone of young beef carcase was cut into 5 mm thick discs. No attempt was made to remove adhering cartilege. The bone centre was left intact. These bones slices were then diced into fragments of 10-mm maximum dimension.

Bone samples from beef of varying ages were not tested. The presence of soft marrow in bone from very young animals would react towards boiling 100% sulphuric acid with similar formation of precipitated carbon and soluble carbon degradation products. The second stage of oxidation, following the addition of perchloric acid, would not be altered materially in carbonaceous residue.

Digestion of sample

Three samples, 0.5, 1.6, and 3 grams, were consecutively wet ashed. The larger the sample taken the lower the boiling temperature becomes for a given volume of sulphuric acid in the first stage of oxidation. This is due to dilution by the resulting reaction products. For the larger sample weights the volume of sulphuric acid should be increased. Otherwise the boiling temperature falls materially below 325°.

The sulphuric acid digestion is complete when SO_2 is no longer evolved. Further digestion for the first stage reaction is then of little value. The heating is then discontinued and the reaction temperature allowed to fall to approximately 200°. The second stage of oxidation, following the addition of 73.6% perchloric acid, is rapid and exothermic.

The results of the digestions are given in Tables I, II, and III.

REACTION CHARACTERISTICS

100 per cent sulphuric acid is employed in the first stage destructive carbonization reaction to shorten the required reaction time. The boiling temperature should be in the range 315° to 325°. Increase in sample weight requires increase in sulphuric acid.

Reaction degradation products lower the boiling temperature. This is illustrated by the results in Tables I, II, and III.

The use of 100% H_2SO_4 prevents formation of insolubles in the wet ash residue. The use of lesser concentrations accompany their precipitation.

Boiling 100% H_2SO_4 requires 300 minutes for the complete wet ashing of 0.5 g of chrome tanned leather, and 240 minutes for 1 g of cellulose at 325°.

TABLE I. WET OXIDATION OF 0.5-G SAMPLE OF BONE

10 ml of 100% H_2SO_4 plus 1.0–2.0 mg of vanadium in first-stage reaction.
5 ml of 73.6% $HClO_4$ for the second stage of digestion.
Bethge apparatus with 250-ml reaction flask and SO_2 disposal vent.

100% H_2SO_4 digestion			73.6% $HClO_4$ digestion		
Reaction time, *min*	Temp, *degrees C*	Reaction effects	Reaction time, *min*	Temp, *degrees C*	Remarks
Start	28		21	195	$HClO_4$ 73.6% added
3	210	Reactants darken	22	160	Reaction exothermic
4	240	Minimum side wall deposit	23	201	Reaction complete
5	306	Solution dark chocolate colour	24	210	Solution clear
6	313	Solution in ebullition			
7	318	Exothermic reaction			
8	323				
10	317	Exothermic reaction completed			
12	318				
15	319	Discontinue heating			

In the preliminary oxidation period some volatile reaction product, which escapes through the SO_2 reaction drain tube, is evolved in the wet ashing of bone. The product condenses to a fluffy white, water-insoluble material of undetermined structure.

By elevating the temperature slowly during sulphuric acid digestion, cleaner reaction-flask walls result. This advantage is minor. Boiling 100% sulphuric acid refluxes these black deposited products down the flasks walls rapidly. This stage of reaction demands no attention.

If desired, the addition of 73.6% perchloric acid may be made in 1-ml portions. By this modification less acid is often required. Little additional reaction time is thus consumed.

OTHER APPLICABLE REACTIONS

Biological tissues such as heart, lung, liver, hair collagen or fat-free protein structures (or blood fibrin) may be wet ashed without complications following procedures previously described.[1,2] Fat-laden materials require the procedure as described because their perchloric acid degradation products, or their original structure, makes them acid-immiscible. Neither, in this case, is the presence of nitric

TABLE II. WET OXIDATION OF 1.6-G SAMPLE OF BONE

10 ml of 100% H_2SO_4 plus 1–2 mg of vanadium in first-stage reaction.
5 ml of 73.6% $HClO_4$ for the second stage of digestion.
Bethge apparatus with 250-ml reaction flask and SO_2 disposal vent.

100% H_2SO_4 digestion			73.6% $HClO_4$ digestion		
Reaction time, *min*	Temp, *degrees C*	Reaction effects	Reaction time, *min*	Temp, *degrees C*	Remarks
Start	26		18	210	73.6% $HClO_4$ added
4	250	Reactants black	19	178	Heat continued
5	266	Reaction refluxing	20	205	Solution red-brown
6	272	Inside flask walls clearing	21	209	Reaction exothermic
8	288	Exothermic effect shown	22	211	Turbid solution White deposit
10	283	Exothermic reaction over	23	214	Reaction complete
12	284				
14	285	SO_2 evolution over			
15	286	Discontinue heating			

TABLE III. WET OXIDATION OF 3.0-G SAMPLE OF BONE

15 ml of 100% H_2SO_4 plus 1–2 mg of vanadium in first-stage reaction.
5 ml of 73.6% $HClO_4$ for the second stage of digestion.
Bethge apparatus with 250-ml reaction flask and SO_2 disposal vent.

100% H_2SO_4 digestion			73.6% $HClO_4$ digestion		
Reaction time, *min*	Temp, *degrees C*	Reaction effects	Reaction time, *min*	Temp, *degrees C*	Remarks
Start	27		18	222	
1	50	Solution dark brown	19	196	73.6% $HClO_4$ added
2	165	Slight foaming	19.5	180	Heat continued
3	215	Solution black	20	205	Solution red-brown
5	268	Solution refluxing	21	213	Reaction exothermic
8	295	Inside flask walls clear	22.5	215	No turbidity formed
10	312		23	215	Reaction complete
12	322				
15	323	Discontinued heating			

acid a solution to the problem. Such two-phase systems, with fats supernatant in contact with boiling perchloric acid and its fumes, do not oxidize smoothly. Fires are ordinarily produced. Fumes of boiling perchloric acid in the presence of volatilized fat may lead to uncontrolled reaction kinetics. The use of boiling 100% sulphuric acid in a single stage reaction obviates this complication.

It is reasonable to apply the method as described to the wet ashing of cream, butter, cheese, lecithin or egg yolk.

Zusammenfassung—Stark fetthaltiges, organisches Material, wie Knochen und Knochenmark, verursacht Schwierigkeiten bei der nassen veraschung nach bekannten Methoden. In der hier vorgeschlagenen Methode werden 100%ige Schwefelsäure und 73.6%ige Perchlorsäure unter Zugabe von Vanadin als Katalysator verwendet. Bereitung der Reagenzien, verwendete Apparatur sowie Reaktionsbeispiele werden mitgeteilt.

Résumé—Des matériaux organiques riches en graisse comme l'os et la moelle, introduisent des complications dans la minéralisation par voie humide dans le cas des méthodes décrites précédemment. Dans le mode opératoire détaillé décrit ici, on utilise comme oxydants de l'acide sulfurique à 100% et de l'acide perchlorique à 73,60% avec le vanadium comme catalyseur. On décrit la préparation du réactif, l'étude de l'appareil et des exemples de réactions.

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THE APPLICATION OF ZONE ELECTROPHORESIS AND POLAROGRAPHY TO THE ANALYSIS OF COMPLEXONE MIXTURES

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Summary—A method of differentiating various types of polyaminocarboxylic acids (complexones) by paper electrophoresis of their cupric chelates at pH 5 is described; some migration rates are noted. The separated chelates may be removed from the pherogram and examined by polarography in 0·4*M* acetic acid. In many cases the $E_{\frac{1}{2}}$ values and the electrophoretic migration rate (M_r) serve to characterise the complexone. By the use of a standard curve relating observed $\Delta E_{\frac{1}{2}}$ values to known log *K* values, an estimate of the stability of the copper chelate may be obtained.

INTRODUCTION

In the course of work on the synthesis of new complexones[1,2] it was found necessary to evolve some method of evaluating the final products and intermediate derivatives. The two common methods of preparation of complexones, the chloroacetic acid condensation with the amine, and the hydrolysis of the corresponding nitrile, both yield partially substituted products. Previously, unless the product was isolated, information about the complexone could not be obtained. The proposed method of investigation now enables the copper chelates of the complexones to be isolated by zone electrophoresis on paper and their approximate stabilities to be determined polarographically; this proves especially useful with acid soluble complexones. The method may also be used to follow the reaction of sterically crowded amines, e.g. *cyclo*hexane-*cis*-1 : 2-diamine,[2] with chloroacetic acid, and the hydrolysis of recalcitrant nitrile intermediates, for example, 4-methylcyclohexane-1 : 2-diamine-N : N : N′ : N′-tetra-acetonitrile.[1,2] The electrophoresis technique enables synthetic mixtures containing, for example, IDA, NTA, and EDTA to be separated and characterised.

ELECTROPHORESIS

EDTA has been used in the electrophoretic separation of cations,[3] but the separation of complexones has not been reported. In early experiments we separated several complexones by electrophoresis at pH 5 and pH 10, but found difficulty in detecting their position, either by ninhydrin or by some weak, coloured calcium complex, such as calcium-phthalein complexone. Subsequently we followed the migration of the copper^{II} chelates which have the advantage of being blue in colour. An increase in sensitivity was obtained by spraying the paper with acidified potassium ferrocyanide solution, or with a solution of dithio-oxamide. The more stable copper chelates are only slowly developed by this latter reagent. The migration of ferric chelates was also examined,[4] but apart from the possibility of improved separation of mono- and di-carboxylic acids, they offered no advantages in our experiments.

The effect of compounds such as glycollic acid, ethylenediamine and cyanide ion, which might be expected to be present with complexones in reaction mixtures was examined. No interference was observed from glycollic acid or ethylenediamine, both of which yielded almost stationary spots. On the other hand, cyanide ion caused streaking due to the formation of a variably charged anionic complex with copper.

When a suitable technique had been evolved the migration rates of the chelates were determined relative to Cu^{II}-IDA, which was adopted as standard with an arbitrary migration rate of 1 relative to the origin. End-osmotic and capillary flow, and hence the true position of the origin, was determined by the use of glucose. The migration rates of a number of copper chelates were determined in order to establish empirically the relationship between migration rate and the number of carboxylic acid groups in the complexone molecule. This enabled a preliminary classification of known complexones to be made. The resolution of mono- and di- acids in admixture is often incomplete. This problem was not pursued further since complexones are classified as derivatives of iminodiacetic acid.

These migration rates are listed in Table 1; where

$$M_I = \frac{\text{Distance moved by chelate relative to glucose}}{\text{Distance moved by IDA chelate relative to glucose.}}$$

The distances were measured from the leading edges of the spots, i.e. the anode edge of the chelate spots and the cathode edge of the glucose spots. Complexones which contain more than two co-ordinating centres, *e.g.* diethylenetriaminepentaacetic acid, (DTPA), have a tendency to give more than one spot; these complexones clearly yield two migrating species (M_{I_1}, M_{I_2}) in the presence of excess copper solution, and generally the resulting spots are less well defined due to streaking. These results are also listed in Table I.

As a result of this investigation the complexones have been divided into three groups depending on their migration rates. With the exception of Chel ME, Chel DE, and DTPA, all of which gives two spots, the number of carboxylic acid groups in the molecule is equal to the group number plus one. It must be emphasised that the variation in M_I values within the group is not very significant due to a potential experimental error of $\pm 10\%$. The appearance of two migratory species from a single complexone in the presence of excess copper solution is indicative of more than two co-ordination centres in the molecule.

POLAROGRAPHIC EXAMINATION OF CHELATES ISOLATED BY ELECTROPHORESIS

We have previously shown that the polarographic half-wave potentials of the copper chelates of complexones in solution are directly related to the stability of these chelates.[5] In the present study we have therefore extended this relationship to the copper chelates separated by paper electrophoresis. In this manner data were obtained on very small amounts of material.

The elution of the copper chelates from the paper with water proved simple, and duplicate determinations showed uniform extraction. Under the experimental conditions used, the half-wave potential of a copper chelate depends on its concentration.[5] In dealing with solutions containing 50% excess of EDTA the half-wave potential of the EDTA chelate of copper changes 80–90 mV per 10-fold change in chelate concentration over the range 10^{-2}–$10^{-4}M$. The relationship is almost linear, *cf* Fig. 1.

Thus a controlled concentration of chelate solution must be obtained for polarography. It proved most convenient to control the addition of the copper sulphate solution to the electrophoresis paper; excess complexone was, of course, necessary to ensure migration of all the copper as chelate. An excess of complexone also modifies the value of the half-wave potential of the chelate wave, but fortunately the excess is separated from the copper chelate by the electrophoresis. The whole range of complexone/copper chelates were isolated individually on paper to simulate experimental conditions, and then eluted. During elution the residual buffer from the electrophoresis electrolyte went into solution thus raising the pH of the final solution on which the polarogram was determined to *ca* 2·8. The $E_{\frac{1}{2}}$ values obtained are listed in Table I; the accuracy is ±20 mV. As the DHEG/Cu^{II} did not appear on our pherograms, we used IDA/Cu^{II} ($E_{\frac{1}{2}} = 0$, $\log K = 10{\cdot}6$) in this instance to establish an arbitrary zero, in the plot of the measured change in half-wave potential ($\Delta E_{\frac{1}{2}}$) versus the known difference in stability constant ($\Delta \log K$). Some values of log *K* were obtained from polarographic data.[5]

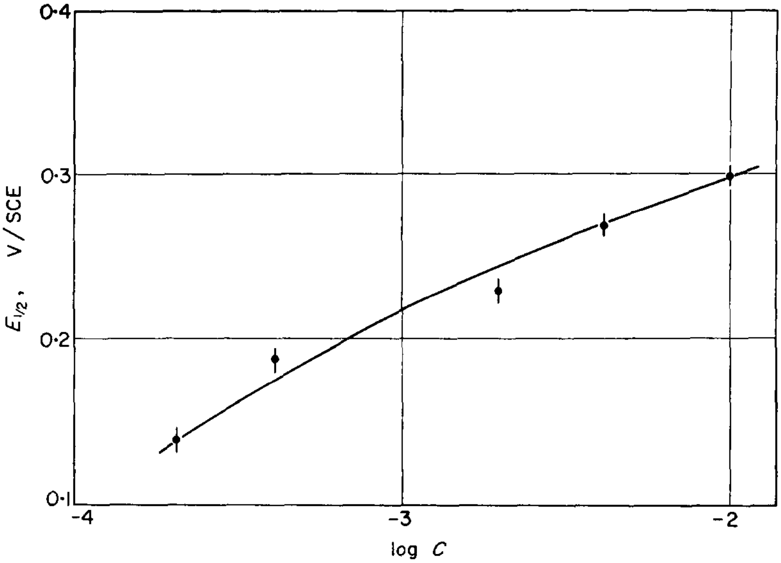

FIG. 1. Variation of $E_{\frac{1}{2}}$ of Cu^{II} chelate of EDTA with concentration. The concentrations of gelatin and acetic acid were kept constant at 0·025 % and 0·4*M* respectively.

The curve produced has a slope almost identical with that obtained from the copper chelates in solution.[5] The use of this curve is restricted to simple complexones, since some complexones with three or more co-ordinating centres behave differently, *e.g.* Chel ME, gives a lower $E_{\frac{1}{2}}$ value and HEEDTA has a much higher $E_{\frac{1}{2}}$ value than expected. It is possible, however, to determine the $\Delta E_{\frac{1}{2}}$ values of new complexones with two co-ordination centres and to obtain the approximate log *K* value from the graph. In Fig. II the curve has been extrapolated as a straight line beyond the value for CDTA; results obtained from this latter part of the curve must be treated with due caution.

TABLE 1

Group	Complexone	Migration Rates		$E_{\frac{1}{2}}$ Value of Cu^{II} Chelate *mV*	$E_{\frac{1}{2}}$ Value of Cu^{II} Chelate From Pherogram *mV*	$E_{\frac{1}{2}}$ Value of Cd Chelate *mV*
		M_{I_1}	M_{I_2}			
One	DHEG	—	—	0·02	—	
	IDA	1·0		0·06	0·00	0·60
	MIDA	1·2		0·08	0·03	
	UDA*	1·0	2·4	0·16	0·00	
	CHEL 138	1·3		0·16		
		1·8				
	CHEL 138†	Streak	1·5			
Two	HEEDTA	2·6		0·23 (l)	0·22	
	AADA‡	2·7		0·08	0·04	
	CHEL ME*	3·0	1·1	0·10	0·06	
	NTA	3·1		0·11	0·05	0·60
	CHEL DE*	3·2	1·1	0·11	0·06	
Three	CPDTA	3·6		0·24 (l)	0·13	0·93
	CDTA	3·6		0·32 (s)	0·27	1·04
	CHDTA	4·0		0·42	0·37	1·08
	DPTA*	4·0	2·4	0·11	0·07	
	EDTA	4·0		0·23 (s)	0·14	0·82
	DTPA	4·1	2·5	0·21	0·13	
	EDAP	4·2		0·27 (l)	0·18	~
	MEDTA	4·3		0·29 (l)	0·24	0·88
	2:3-BDTA	4·3		0·41 (l)	0·33	0·97

Key to Table

IDA—Iminodiacetic acid
MIDA—Methyliminodiacetic acid
NTA—Nitrilotriacetic acid
UDA—Uramil-N:N-diacetic acid
EDTA—Ethylenediamine-N:N:N′:N′-tetra-acetic acid
MEDTA—1:2-Propanediamine-N:N:N′:N′-tetra-acetic acid
§ EDAP—Ethylenediamine-N:N′-diacetic acid-N:N′-di-β-propionic acid
§ DPTA—1:3-Propanediamine-2-ol-N:N:N′:N′-tetra-acetic acid
DTPA—Diethylenetriamine-N:N:N′:N″:N″-penta-acetic acid
¶ 2:3-BDTA—2:3-Butanediamine-N:N:N′:N′-tetra-acetic acid
DHEG—Di-(2-hydroxyethyl)glycine
AADA—*o*-Carboxyphenyliminodiacetic acid
§ Chel ME—2:2′Bis-[di(carboxymethyl)amino]diethyl ether
§ Chel DE—1:2 Bis-[2-di(carboxymethyl)aminoethoxy]ethane
§ Chel 138—N:N′-Ethylene bis-[2-(*o*-hydroxyphenyl)]glycine
HEEDTA—N-(2-Hydroxyethyl)ethylenediamine-N:N′:N′-triacetic acid
¶ CPDTA—*Cyclo*pentane-*trans*-1:2-diamine-N:N:N′:N′-tetra-acetic acid
CDTA—*Cyclo*hexane-*trans*-1:2-diamine-N:N:N′:N′-tetra-acetic acid
¶ CHDTA—*Cyclo*heptane-*trans*-1:2-diamine-N:N:N′:N′-tetra-acetic acid

* Major migrating species with excess chelating agent is M_{I_1}. (s) and (l) "reversed current" small or large respectively. ~ Not reproducible.

† Excess copper.

‡ Cu^{II} chelate has distinct green-blue colour on the pherogram.

§ Supplied by The Geigy Company Ltd.

¶ Synthesised by the authors.[1,2]

The experimental procedure must be modified for use with mixtures of complexones, since under these conditions it is not possible to control the amount of any particular copper chelate constituent moving along the paper. It should be possible in an identical experiment to ascertain the amount of copper chelate present, from he diffusion current, and in the final determination the concentration of copper chelate in the acetic acid solution may then be adjusted to be comparable with that used to establish the standard curve.

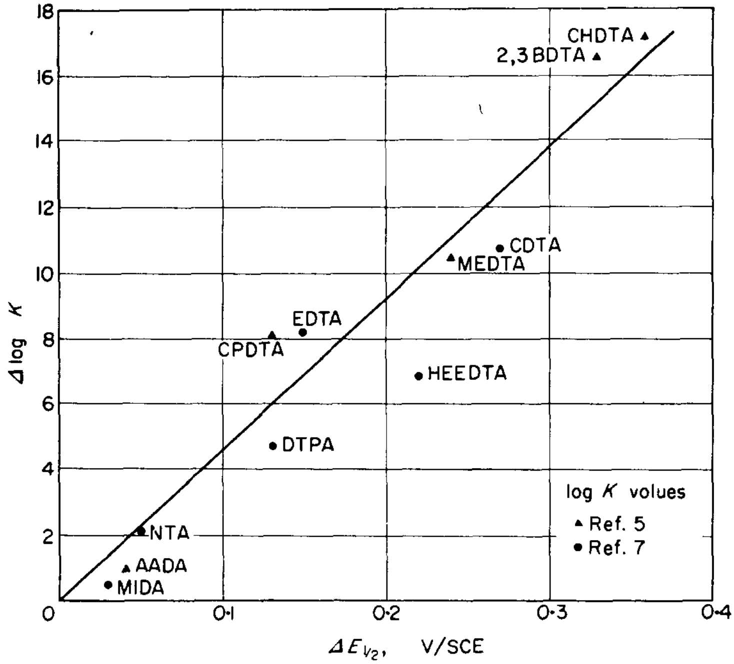

FIG. 2. Variation of $\Delta E_{\frac{1}{2}}$ with Δ log K for complexones isolated from pherograms.

Whilst we have been primarily interested in the evaluation of new complexones, and their intermediates, which are simple analogues of EDTA, we consider the proposed method of direct application to the analysis of complexones both singly and in admixture. The electrophoresis experiment gives a "group" analysis, and within the group most of the individual complexones may be characterised by the half-wave potential of the eluted copper chelate. In a few cases where ambiguous results may be obtained, *e.g.* with EDTA and CPDTA, these complexones can be characterised by the $E_{\frac{1}{2}}$ value of the polarogram of the cadmium chelates, by the colour intensity of the copper chelates or by the nature of the reduction wave.[5]

The $E_{\frac{1}{2}}$ values of some Cu^{II} and Cd chelates, the determination of which is described elsewhere,[5] are listed in Table I. Some of these reduction waves exhibited the phenomenon of "reversed current",[5] this is indicated in the Table. The reduction waves of *eluted* copper chelates displayed only a little "reversed current", and it is thought that the phenomenon is a function of the complexone when it is present in excess.

It should prove possible to extend the method to give a quantitative analysis.

EXPERIMENTAL

Paper electrophoresis

Reagents:

pH 5 Buffer: 96 g of hydrated sodium acetate and 17·7 g of glacial acetic acid were dissolved in 1 litre of water, and the solution was made up to 5 litres with distilled water.

Copper sulphate A.R.: 0·2*M* aqueous solution.

Complexone solutions. 0·1*M* aqueous solutions of the sodium salts.

Glucose: 0·2*M* aqueous solution.

Potassium ferrocyanide solution: 2% aqueous solution acidified to the extent of *ca.* 0·1% with concentrated hydrochloric acid before use.

Aniline hydrogen phthalate: 8·3 g of phthalic acid were dissolved in 75 ml. of hot water and 475 ml. of *n*-butyl alcohol; 4·65 g. of aniline were added and the solution was well shaken.

Dithio-oxamide: 0·1% solution in ethanol.

Whatman No. 3 *Paper.*

Apparatus: The simple type of apparatus used is based on that of Kunkel and Tiselius.[6] A stabilised power-pack capable of giving about 75 ma. at 1000 V d.c. was used. 0·5 ml Agla syringe pipette.

Measurement of migration rates

20 μl of the copper sulphate solution were added to the cathode end of the paper from an Agla syringe in two lots of 10 μl each. About three micro-equivalents each of IDA and the complexone, and one drop of the glucose solution were added. The paper was dried after the addition of each spot. The migration rates of di-carboxylic acid complexones were measured by reference to IDA and glucose on a separate track on the same paper. The paper was soaked in buffer solution, blotted, and clamped tightly between glass plates 45 cm long. A potential of 1000 V was applied to the paper for a period of about 2 hr. After the paper had been dried, the area about the origin was sprayed with the solution of aniline hydrogen phthalate and heated for some minutes to develop the glucose spots. The paper was then sprayed with ferrocyanide solution and again dried by heating. On exposure to light over a period of time the paper becomes discoloured, and is thus best stored in the dark. Alternatively the paper may be sprayed with a solution of dithio-oxamide.

Isolation of known copper chelates for elution and polarographic examination

10 μl of the copper sulphate solution was applied to the paper as above. Excess of complexone was added and each spot was dried before the addition of the next. Electrophoresis was carried out as before, the paper was dried, and the spots later removed for polarography.

The qualitative analysis of simple complexone mixtures

The mixture of complexones or reaction liquor containing complexones and intermediates was spotted on the paper, and excess copper sulphate solution was added. Electrophoresis was carried out as described above, and the paper was sprayed with ferrocyanide solution. The migration rates of new complexones containing three or more carboxylic acid groups were determined by reference to IDA and glucose on the same track; when dealing with mono- and di- acids the IDA reference spot was run on a separate track on the same paper. In a subsequent experiment the quantities of reagents were adjusted where possible to give spots of the copper chelates containing the equivalent of 10 μl of 0·2*M* Cu^{II} solution, which were removed, eluted and examined polarographically.

Polarography

Reagents:

Acetic acid solution: 0·8*M* Aqueous solution containing—

Gelatin: 0·05% freshly prepared before use.

Apparatus:

Tinsley Recording Polarograph Mark 19, with dropping mercury electrode (drop time 5·2 sec, under an open head of mercury of 37 cm) and a saturated calomel electrode with a potassium chloride bridge as a reference electrode. E.I.L. Direct Reading pH Meter.

The polarographic examination of eluted pherograms

The copper chelates separated by electrophoresis were cut out from the paper and placed in 5 ml of distilled water in a 20-ml beaker, and allowed to stand for thirty minutes with occasional stirring. 5 Ml of the 0·8*M* acetic acid solution were then added and the paper was removed from the beaker. The pH of the solution was measured (to ensure that it was 2·8 ± 0·1) and the solution was then polarographed, using a damping of 1, a counter current of 2, a sensitivity of 1·5 μA, and a chart scale of 1 V/4″. The half-wave potentials were measured from the curve drawn through the points given by the current at maximum *drop* size.

The polarographic determination of Cu^{II} and Cd chelate stabilities has been described elsewhere.[5]

Acknowledgement—We are grateful to the Geigy Company, Ltd., for supplying certain of the samples used and for the provision of a research grant to one of us (W. H.). We also wish to record our thanks to Professor R. Belcher and Dr. A. B. Foster of this Department for their interest and helpful advice.

Zusammenfassung—Eine Methode zur Unterscheidung verschiedener Polyamincarboxysäuren (Komplexone) durch Papierelektrophorese ihrer Kupferchelate bei pH 5 wird beschrieben. Die getrennten Chelate werden vom Pherogram gelöst und in 0,4 n Essigsäure polarographisch untersucht. Wanderungsgeschwindigkeiten werden in einigen Fällen mitgeteilt. Diese, sowie das Halbstufenpotential sind manchmal zur Charakterisierung des Komplexons ausreichend. Durch Anwendung einer Eichkurve kann auf Grund bekannter Beziehungen zwischen $E_{1/2}$ und log *K*-werten eine grobe Abschätzung der Stabilität der Kupferchelate erfolgen.

Résumé—Une méthode permettant de différencier divers types d'acides polyaminocarboxyliques (complexons) par électrophorèse sur papier de leurs chelates cuivriques à pH 5 est décrite; quelques vitesses de migration sont indiquées. Les chelates ainsi séparés peuvent être rédissous du pherogramme et étudiés par polarographie dans l'acide acétique 0,4 *M*. Dans beaucoup de cas les valuers de $E_{1/2}$ et la vitesse de migration électrophorétique (M_I) sont utilisées pour caractériser le complexon. Par l'emploi d'une courbe d'étalonnage reliant les valeurs de $E_{1/2}$ observées aux valeurs connues de log *K*, on peut obtenir une estimation de la stabilité du chelate de cuivre.

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UNTERSUCHUNG EINIGER ALS REDOXINDICATOREN ANWENDBAREN VARIAMINBLAUDERIVATEN

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Zusammenfassung—Es wurde über die ausführliche elektrochemische Untersuchung der als Indicatoren verwendbaren mit verschiedenen elektrophylen und nukleophylen Gruppen substituierten Derivate des 4-Amino-4′-methoxy-diphenylamins (Variaminblau) berichtet. Der reversible Redoxvorgang dieser Verbindungen ist zweielektronig, ihr Oxydationsmechanismus entspricht dem des Variaminblaus, d.h. ihre oxydierte Form entspricht dem entsprechend substituierten Derivat des Chinon-p-anisil-diimins. Bei der Oxydation des 2-Methyl- und 2-Methoxyproduktes entsteht auch ein intermediäres semichinoidales Oxydationsprodukt. Die Instabilität der Systeme in saurer Lösung ist durch den Zerfall der oxydierten Form verursacht. Mit Hilfe der Elektrodengleichungen können die Redoxpotentiale für beliebigen pH-Wert berechnet werden. Die Brechpunkte der E_0'-pH-Kurven geben die Säure-Basendissociationskonstanten der oxydierten und reduzierten Formen. Nukleophyle Substituenten erhöhen, elektrophyle Substituenten erniedrigen die Basicität des Variaminblaumoleküls.

DIE ausgezeichneten Eigenschaften des Variaminblaus /4-Amino-4′-methoxy-diphenylamin/ als Redoxindicator[1–21] und als colorimetrisches Reagens[22–27] gaben uns den Gedanken seine verschieden substituierten Derivate herzustellen.[28,29] Es war zu erwarten, dass diese Derivate sich als Redoxindicatoren ebenfalls gut bewähren und dass sie ein von der Grundverbindung abweichendes Umschlagspotential besitzen werden. Die Untersuchungen von Fieser und Thompson,[30] Fieser und Fieser[31] und anderen[32] zeigten, dass elektrophyle Substituenten das Redoxpotential der Grundverbindung in positive, nukleophyle Substituenten dagegen in negative Richtung verschieben. Ähnliche Potentialverschiebung beobachteten auch wir im Falle einiger Derivate des Variaminblaus, wie darüber schon berichtet wurde.[29] Im folgenden werden die Ergebnisse der ausführlichen physico-chemischen Untersuchung der als Redoxindicatoren verwendbaren Derivate des Variaminblaus mitgeteilt. Diese Versuche breiteten sich auf die Bestimmung der Funktion Redoxpotential-pH, der Zahl der im Vorgang beteiligten Elektronen, der Säure-Basendissociationskonstanten der reduzierten und oxydierten Formen aus. Es wurde weiterhin die Reversibilität der Vorgänge und die Möglichkeit der Bildung von intermediären Produkten untersucht.

EXPERIMENTELLER TEIL

Die Redoxpotentiale wurden teilweise polarographisch, teilweise potentiometrisch bestimmt. Die polarographischen Messungen wurden mit einem Polarograph Typ Heyrovsky V 301 im Kalousek-Gefäss unter Anwendung einer tropfenden Quecksilberelektrode und einer Quecksilber (I) sulphatvergleichselektrode in Stickstoffatmosphäre durchgeführt. Die Elektroden wurden anodisch-kathodisch polarisiert. Die Quecksilberniveauhöhe (h) betrug 50 cm. Die Daten der angewandten Kapillare waren: $m = 7{,}2$ mg/s, $t = 1{,}84$ s. Die zur Untersuchung von instabilen Systemen sehr geeignete schnelle polarographische Methode ersetzten wir nur dann mit einer potentiometrischen, wenn unter den gegebenen Verhältnissen keine Stufe erhalten werden konnte. Die potentiometrischen Titrationen erfolgten ebenfalls in Stickstoffatmosphäre zwischen einer Indicatorenelektrode aus Platin und einer Vergleichselektrode aus gesättigtem Kalomel. Zur Oxydation diente in saurer Lösung 0,01 n

Bromwasser, in alkalischer Lösung ausserdem noch eine 0,01 n Kaliumhexacyanoferrat(III)lösung. Bei instabilen Systemen wurde nach der stufenweisen Methode gearbeitet.[29]

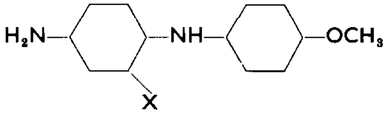
Die optischen Messungen—u.zw. die Aufnahme der Absorptionskurven und der Zusammenhänge zwischen Extinktionskoeffizient und pH zur Bestimmung der Säure-Basendissociationskonstanten der farbigen oxydierten Formen[33,34]-wurden mit Hilfe des Pulfrich Photometers unternommen.

Über die Erzeugung der Indicatoren berichteten wir schon vorangehend.[29] Die 2-Amino, 2-Methyl- und 2-Methoxyderivate wurden in 0,005 m alkoholischer, die 2-Sulfonsäurederivate in 0,001 m schwach alkalischer, das 2-Carbonsäureanilid in 0,0025 m schwach saurer Lösung benützt in Pufferlösungen gemäss Britton-Robinson.[35] Die pH-Messungen wurden mit Wasserstoffelektrode durchgeführt.

ALLGEMEINE CHARAKTERISIERUNG DER INDICATOREN

Das Verhalten folgender Indicatoren wurde näher untersucht:

Generalformel:



I. 4-Amino-4′-methoxy-diphenylamin (Variaminblau)

$X = —H$

II. 2,4-Diamino-4′-methoxy-diphenylamin

$X = —NH_2$

III. 4-Amino-2,4′-dimethoxy-diphenylamin

$X = —OCH_3$

IV. 4-Amino-2-methyl-4′-methoxy-diphenylamin

$X = —CH_3$

V. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure

$X = —SO_3H$

VI. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anilid

$X = —SO_2—NH—C_6H_5$

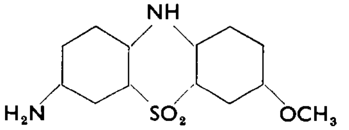
VII. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anisidid

$X = —SO_2—NH—C_6H_4—OCH_3$

VIII. 4-Amino-4′-methoxy-diphenylamin-2-sulfonsaurer Methylester

$X = —SO_3CH_3$

IX. 2-Amino-7-methoxy-phenthiazin-9-dioxyd



X. 4-Amino-4′-methoxy-diphenylamin-2-carbonsäure-anilid

$X = —CO—NH—C_6H_5$

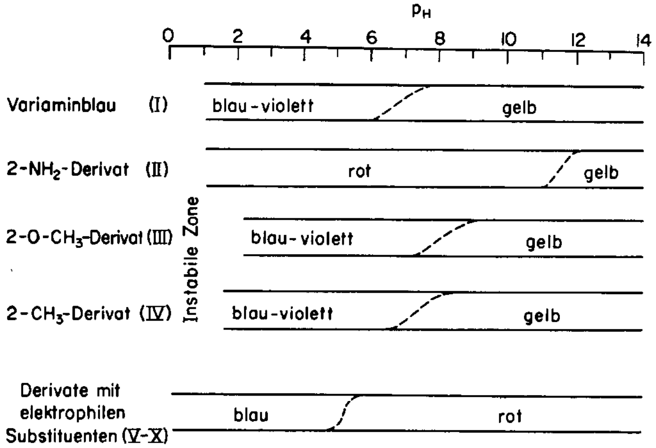
XI. Variaminblau-pikrat

1 Mol Variaminblau + 2 Mol Pikrinsäure

Die Oxydation der in Leukoform leicht präparierbaren farblosen, oder schwach gelblichgrünen Verbindungen ist mit einer intensiven Farbänderung verbunden, worüber Tab. I. eine Übersicht gibt.

In saurem Medium färbt sich die wässrige oder alkoholische Lösung des Variaminblau (I), der 2-Methoxy (III) und 2-Methyl (IV) Derivate auf Einwirkung einer geringfügigen Menge an Oxydationsmittel auf blau. Die Farbe der Holochinone* ist violett. Das Absorptionsmaximum des blauen Oxydationsproduktes fällt zwischen 570–610 mμ, während das der Holochinone gegen die kürzeren Wellenlängen verschoben ist. Auf Einwirkung von überschüssigen starken Oxydationsmitteln entsteht ein rotes Oxydationsprodukt. In alkalischem Medium kommt nur ein gelbes Oxydationsprodukt zustande. Die Holochinone des 2-Aminoderivates (II) sind rot und gelb. Die in saurem Medium beobachtbare blaue Färbung verschwindet augenblicklich. Die Holochinone der 2-Sulphonsäuregruppe (V–IX) und des Variaminblau-2-carbonsäureanilids (X) sind blau und rot. In den mit S-förmigen Kurven bezeichneten pH-Intervallen bilden sich die Mischfarben der aufgezählten sauren und alkalischen Grenzfarben aus.

Tabelle I



Die nukleophyle Substituenten enthaltenden Leukoderivate (II–IV) geben im pH-Bereich 3–14 gut auswertbare anodische polarographische Oxydationsstufen. Bei niedrigeren pH-Werten als 3 wirkt die anodische Auflösung des Quecksilbers auf die Ausbildung der Stufen störend ein. Die Stufenhöhen sind mit der Konzentration und $\sqrt{h}$ direkt proportional, d.h. es handelt sich hier um Diffusionsstufen. Von den mit elektrophylen Gruppen substituierten Derivaten geben die Mitglieder der Variaminblau-2-sulphonsäuregruppe (V–IX) nur in stark alkalischem Medium eine polarographische Stufe, das Variaminblau-2- carbonsäureanilid (X) ist polarographisch inaktiv.

ZAHL DER IM REDOXVORGANG BETEILIGTEN ELEKTRONEN, REVERSIBILITÄT UND OXYDATIONSMECHANISMUS

Die Äquivalenzpunkte der oxydimetrischen potentiometrischen Titrationen deuteten ähnlich dem Variaminblau auf einen zweielektronigen Redoxvorgang.[1,28,36,37] Mit voller Sicherheit konnte man diese Frage jedoch nur auf polarographische Weise entscheiden. In gleicher Konzentration stimmt die Höhe der anodischen Oxydationsstufe des Leukovariaminblaus und dessen Derivate miteinander beinahe überein (Abb. 1,2). Der ungefähr 30 mV betragende Neigungswinkel der durch mathematische Analyse der polarographischen Stufen erhaltenen $\log(i/i_d - i) - V$ Funktionen weist ebenfalls auf einen zweielektronigen Redoxvorgang. Mit den nukleophylen Substituenten enthaltenden Derivaten, die gut auswertbare Stufen geben, wurden auch polarometrischen Titrationen unternommen; der Äquivalenzpunkt der Titrationen der Leukofarbstoffe entspricht ebenfalls einer zweielektronigen Oxydation (Abb. 3).

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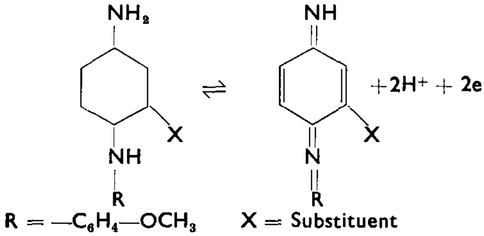
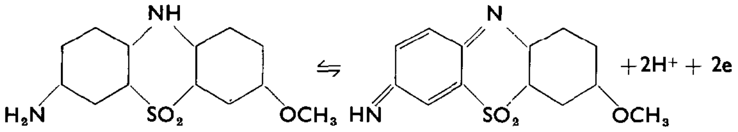
* Unter Holochinon verstehen wir diejenige oxydierte Form, die auf Einwirkung von einer zweielektronigen Oxydation entsprechenden Mengen des Oxydationsmittels entsteht.

Die Reversibilität der Redoxvorgänge ist in erster Linie durch die Linearität des erwähnten log $(i/i_a - i) - V$ Zusammenhanges bewiesen. Das Halbstufenpotential der anodischen Oxydationsstufe der mit nukleophylen Gruppen substituierten Derivate stimmt mit dem Halbstufenpotential der kathodischen Reduktionsstufe der in der Lösung oxydierten Formen gut überein. Im Falle von Verbindungen mit elektrophylen Substituenten konnte man diese Identität nicht nachweisen. Die potentiometrischen Untersuchungen, weiterhin die mathematische Analyse der anodischen Oxydationsstufen weisen aber auch in diesem Falle eindeutig auf einen reversibilen Redoxvorgang.

Ähnlich dem Variaminblau lässt sich auch für die substituierten Produkte folgender potentialbestimmender Vorgang aufschreiben:



Im Falle von 2-Amino-7-methoxy-phenthiazin-9-dioxyd (IX) ändert er sich folgendermassen:



Wir können also auch ohne jegliche präparative Beweise behaupten, dass die vollständig oxydierten Formen (Holochinone) der Derivate nur dem Chinon-p-anisil-diimin entsprechende substituierte bzw. ringgeschlossene Produkte sein können.

Die Oxydation des 2-Methyl-(IV) und des 2-Methoxyproduktes (III) verläuft in saurer Lösung bis pH-Wert 6 ähnlich dem Variaminblau unter Bildung eines intermediären semichinoidalen Oxydationsproduktes. Die vom Holochinon abweichende Farbe des im geringen Masse oxydierten Farbstoffes und die mehr als 14 mV betragenden Indexpotentiale der Titrationskurven zeigen ebenfalls, dass hier ein Semichinon zustandekommt.[38] Die Index-potentiale sind innerhalb der Konzentrationen $1 \cdot 10^{-3}$–$2 \cdot 10^{-4}$ Mol/Liter von der Farbstoffkonzentration unabhängig, das Übergangsprodukt besteht folglich aus freien Radikalen. Die aus freien Radikalen bestehende Struktur wird durch die Zahl der mesomeren Möglichkeiten stabilisiert. In Tab. II sind die charakteristischen Daten der Semichinonbildung dargelegt.

Im Falle von elektrophylen Substituenten wurde keine Semichinonbildung beobachtet (V–X). Die elektrophylen Substituenten üben hier wahrscheinlich eine Anziehung auf das einsame Elektron der aus freien Radikalen bestehenden Struktur aus, wodurch die Zahl der mesomeren Möglichkeiten abnimmt, deshalb die Stabilität der Struktur aufhört.

Die auf Einwirkung des überschüssigen Chlor- und Bromwassers entstehende rote Verbindung ist ein zerstörtes Oxydationsprodukt. Die aus der konzentrierten

Lösung des Variaminblau-2-carbonsäureanilid (X) präparierte dunkelviolette Verbindung löst sich in Alkohol mit roter Farbe, wirkt oxydierend und färbt die Lösung des Leukofarbstoffes blau. Laut Analysenergebnisse enthält diese Verbindung keine Halogene und ihr 2,85%-iger Stickstoffgehalt ist wesentlich geringer als der des Holochinons.

Die in die Variaminblaureihe gehörenden Redoxsystéme zeigen ebenfalls die der Diamin-diiminsysteme typisch eigene Instabilität, die in erster Linie durch den Zerfall der oxydierten Form verursacht wird.[39–41]

TABELLE II

Verbindungen	$E_{i\ 25\%}$ mV 20°C	k	$(s/a)_{max}$
4-Amino-2,4′-dimethoxy-diphenylamin (III)	16	$8{,}4 \cdot 10^{-2}$	0,12
4-Amino-2-methyl-4′-methoxy-diphenylamin (IV)	15	$2{,}9 \cdot 10^{-2}$	0,07

E_i = Indexpotential
k = Semichinonbildungskonstante
$(s/a)_{max}$ = Maximale Menge des entstandenen Semichinons im Verhältn zuris Gesamtfarbstoffkonzentration.

Laut unserer polarographischen Untersuchungen zerfallen die Holochinone der verschiedenen Derivate sogar in Stickstoffstrom, wobei teilweise Zersetzungprodukte mit negativeren Halbstufenpotentialen entstehen. Die Potentialstabilität der halboxydierten Indicatorsysteme ist ebenfalls veränderlich. Die Zersetzung der oxydierten Formen geht mit Farbänderung vor sich, sodass dieser Erscheinung bei der praktischen Anwendung der Indicatoren eine bedeutende Rolle zukommt. Mass und Geschwindigkeit der Zersetzung ist vom pH und von dem Substituenten selber abhängig. In einem mittelmässig sauren Medium (pH $\sim$ 2–6) ändert sich das Potential und damit die Farbe der halboxydierten Systeme des Variaminblau (I), der 2-Methoxy- (III) und 2-Methyl- (IV) derivate nur kaum, was mit dem Entstehen stabiler semichinoidaler Radikale sich erklären lässt. Die in stark saurem Medium ($pH < 2$) beobachtbare, mit einer raschen Entfärbung verbundene Zersetzung lässt sich wahrscheinlich auf die Hydrolyse des chinondiiminartigen Moleküls auf Chinon und Ammoniak zurückführen. Im Laufe von in saurem Medium durchgeführter Farbstoffoxydation gelang es tatsächlich nach einer gewissen Zeitdauer in der Lösung NH_4^+ Ionen nachzuweisen. Es ist möglich, dass dieser Vorgang durch die bei niedrigeren pH-Werten erfolgende zweite Protonenaufnahme des Moleküls gefördert wird, da die dadurch entstehende, aufgelockerte Struktur des Moleküls die Substitution der $=NH_2^+$- Gruppe auf $=OH^+$-Gruppe ermöglicht. Die Potentiale der elektrophyle Substituente enthaltenden Derivate (V–X) nehmen mit der Zeit allmählich ab u.zw. mit der vom pH abhängigen Geschwindigkeit linear. Der Potentialfall wird vom allmählichen Verblassen der blauen Farbe begleitet. Diese Verbindungen lassen sich im pH-Bereich 2–5 als Indicatoren anwenden.

REDOXPOTENTIAL-pH FUNKTIONEN

Im Sinne des Oxydationsmechanismus ist das Redoxpotential der Indicatorsysteme pH-abhängig. Die erhaltenen Ergebnisse sind in Abb. 4 und 5 graphisch dargestellt. Die Kurve E_0'-pH der Mitglieder der Variaminblau-2-sulphonsäuregruppe (V-IX) konnten nur im pH-Bereich 1–7 ermittelt werden. In mehr alkalischem Medium zufolge der Instabilität dieser Systeme können nämlich sogar mit Hilfe der stufenweisen potentiometrischen Methode keine verlässlichen Ergebnisse erzielt werden. Im Falle des Variaminblau-2-carbonsäureanilids (X) konnte der Zusammenhang nur bis pH ~5 festgestellt werden, da schon bei pH = 4,7 die freie Base der reduzierten Form selbst in dünnen Lösungen auszuscheiden beginnt. Das Verhalten des Variaminblaupikrats in saurem Medium stimmt mit dem des Variaminblaus überein.

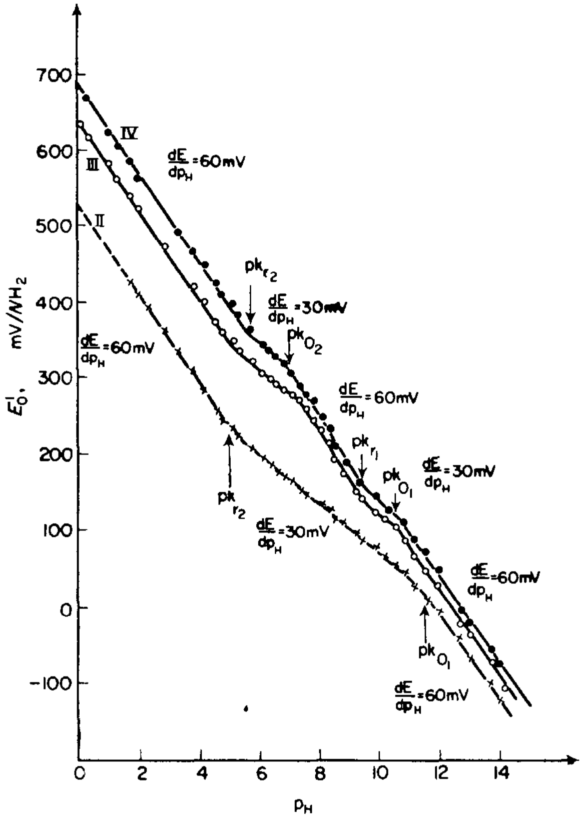


Abb. 4. E_0'-pH-Kurven der nukleophyle Substituenten enthaltenden Derivate. 4-Amino-2-methyl-4′-methoxy-diphenylamin (IV), 4-Amino-2,4′-dimethoxy-diphenylamin (III), 2,4-Diamino-4′-methoxy-diphenylamin (II).

Die durch die linearen Strecken mit verschiedenen Neigungswinkeln der E_0'-pH Kurven gegebenen Knickpunkte entsprechen den Säure-Basendissociationskonstanten der reduzierten und oxydierten Formen. Im Falle der Variaminblau-2- sulphonsäure (V) wurde keine bajonettartige Knickung beobachtet, was dem kleinen Unterschied zwischen pK_0 und pK_r zuzuschreiben ist. Auf optischem Wege ergab sich der pK_0-Wert zu 4,1. Die Dissociationskonstanten der mit Farbänderung verbundenen

Protonenabgabe der oxydierten Formen wurden auch bei den übrigen Derivaten auf optischem Wege kontrolliert. Die erhaltenen Werte stimmen mit den durch die entsprechenden Knickpunkte dargestellten Werten gut überein. Die Grössenordnung einiger Werte wurde auf qualitativem Wege bewiesen. So z.B. die Farbänderung der oxydierten Form des 2-Aminoderivates (II) erfolgt in stark alkalischem Medium in

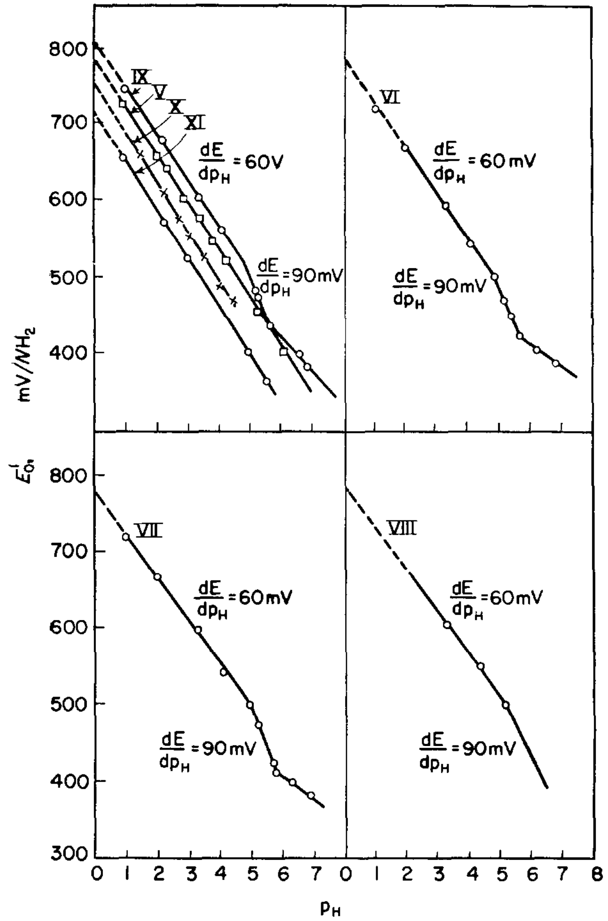


ABB. 5. E_0'-pH-Kurven der elektrophyle Substituenten enthaltenden Derivate. 2-Amino-7-methoxy-phenthiazin-9-dioxyd (IX), Variaminblau-2-sulfonsäure (V), Variambinblau-2-carbonsäureanilid (X), Variaminblaupikrat (XI), Variaminblau-2-sulfonsäureanilid (VI), Variaminblau-2-sulfonsäureanisidid (VII), Variaminblau-2-sulfonsäuremethylester (VIII).

der Nähe des beobachteten Knickpunktes; die pK_{r1} -Werte der 2-Methoxy (III) und 2-Methyl (IV) Derivate müssen höher sein als die Konstante des Variaminblaus, weil in der Lösung ihrer salzsauren Salze die Ausscheidung der freien Base auf die Zugabe von grösserer Laugenmengen beginnt als im Falle des Variaminblaus.

Die Elektrodengleichung der untersuchten Derivate hat folgende Formel:

$$E = E_0 + 30 \log \frac{[ox]t}{[red]_t} + 30 \log \frac{K_{r1}K_{r2} + K_{r2}[H^+] + [H^+]^2}{K_{01}K_{02} + K_{02}[H^+] + [H^+]^2} - 60 \text{ pH} \quad \text{bei } 30°\text{C}$$

Beim 2-Aminoprodukt (II) und bei den 2-Sulfonsäureverbindungen (V–IX), wo die

Gültigkeit der Gleichung versuchsmässig nur zwischen den pH-Werten 0 und 7 bewiesen werden konnte, lässt sich diese Gleichung vereinfacht schreiben:

$$\mathrm{E} = \mathrm{E}_0 + 30 \log \frac{[\mathrm{ox}]_t}{[\mathrm{red}]_t} + 30 \log \frac{\mathrm{K}_r + [\mathrm{H}^+]}{\mathrm{K}_0 + [\mathrm{H}^+]} - 60\ \mathrm{pH} \quad \text{bei } 30^\circ\mathrm{C}$$

Das Redoxpotential des Variaminblau-2-carbonsäure-anilids (X) und des Variaminblaupikrats (XI) ändert im pH-Gebiet 0–5 je ein pH-Wert mit 60 mV:

$$\mathrm{E} = \mathrm{E}_0 + 30 \log \frac{[\mathrm{ox}]_t}{[\mathrm{red}]_t} - 60\ \mathrm{pH} \quad \text{bei } 30^\circ\mathrm{C}$$

Die Dissociationskonstanten der Gleichungen sind Dissociationskonstanten gemäss der Brönstedschen Theorie aus welchen die üblichen basischen Dissociationskonstanten mit Hilfe des Ausdrucks

$$\mathrm{K}_r \cdot \mathrm{K}_{br} = 10^{-14} \quad \text{bzw. } \mathrm{p}K_r + \mathrm{p}_{br} = 14$$

ermittelt werden können. Die Dissociationskonstanten sind also folgendermassen definiiert:

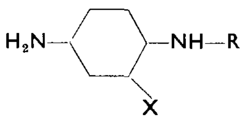
$$\text{red H}_2^{++} \leftrightharpoons \text{red H}^+ + \mathrm{H}^+ \qquad \mathrm{K}_{r2} = \frac{[\text{red H}^+] \cdot [\mathrm{H}^+]}{[\text{red H}_2^{++}]}$$

$$\text{red H}^+ \leftrightharpoons \text{red} + \mathrm{H}^+ \qquad \mathrm{K}_{r1}\mathrm{K}_r = \frac{[\text{red}] \cdot [\mathrm{H}^+]}{[\text{red H}^+]}$$

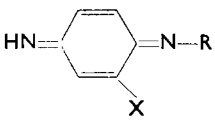
$$\text{ox H}_2^{++} \leftrightharpoons \text{ox H}^+ + \mathrm{H}^+ \qquad \mathrm{K}_{02} = \frac{[\text{oxH}^+] \cdot [\mathrm{H}^+]}{[\text{ox H}_2^{++}]}$$

$$\text{ox H}^+ \leftrightharpoons \text{ox} + \mathrm{H}^+ \qquad \mathrm{K}_{01}\mathrm{K}_0 = \frac{[\text{ox}] \cdot [\mathrm{H}^+]}{[\text{ox H}^+]}$$

red =



ox =



Die charakteristischen elektrochemischen Daten der Derivate u.zw. die Redoxnormalpotentiale und die Dissociationskonstanten der reduzierten und oxydierten Formen sind in Tab. III. zusammengestellt. Die E_0-Werte sind aus den in mässig sauren Lösungen erhaltenen linearen Zusammenhangen extrapolierte Werte. Die mit * bezeichneten $\mathrm{p}K_0$-Werte sind Mittelwerte der durch die Brechpunkte gegebenen und auf optischem Wege erhaltenen Ergebnisse oder auf rein optischem Wege ermittelte Werte.

Wie es aus der Tabelle ersichtlich ist, gestalten nukleophyle Gruppen die Grundmolekel basischer. Infolge der Zunahme der Elektronendichte ist das einsame Elektronenpaar der Stickstoffatome durch den aromatischen Ring weniger in Anspruch genommen, so, dass die Protonenaufnahme auch schon in weniger saurer Lösung erfolgen kann. Der Zusammenhang zwischen den nukleophylen Charakter und der Zunahme der Basicität kann besonders gut bei den Dissociationskonstanten der oxydierten Formen beobachtet werden. Die elektrophylen Substituenten erniedrigen

TABELLE III

Verbindungen	E_0 mV/n H_2 pH = 0	pK_{r1}	pK_{r2}	pK_{o1}	pK_{o2}
2,4-Diamino-4′-methoxy-diphenylamin (II)	532	kein Brechpunkt	5,0	11,5	kein Brechpunkt
4-Amino-2,4′-dimethoxy-diphenylamin (III)	636	9,6	5,2	10,6	7,5*
4-Amino-2-methyl-4′-methoxy-diphenylamin IV	686	9,4	5,7	10,5	7,0*
4-Amino-4′-methoxy-diphenylamin (I)	712	5,9	unmessbar	6,6	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-carbonsäure-anilid (X)	754	≈4,7	unmessbar	≈5,5*	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure (V)	776	—	unmessbar	4,1*	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anisidid (VII)	780	5,9	unmessbar	5,0	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsaurer Methylester (VIII)	786	—	unmessbar	5,1	unmessbar
4-Amino-4′-methoxy-diphenylamin-2-sulfonsäure-anilid (VI)	788	5,7	unmessbar	4,7	unmessbar
2-Amino-7-methoxy-phenthiazin-9-dioxyd (IX)	800	5,8	unmessbar	4,7	unmessbar

aus demselben Grund die Basicität der Grundmolekel. Die mit mehreren Grössenordnungen erfolgende Änderung der Basicität weist darauf, dass hier nicht nur polare, sondern auch sterische Effekte zur Rolle kommen. Die pK_r und pK_0 Werte der Glieder der 2-Sulfonsäuregruppe (V–IX) ändern untereinander kaum. Dies beweist, dass die auf den aromatischen Ring ausgeübte elektrophyle Wirkung der Sulfonsäuregruppe durch weitere Bindungen ausser dem Kern mehr kaum beeinträchtigt wird.

Verfasser danken Frau I. Kucsera und M. Tésy, weiterhin Herrn T. Meisel für die Mithilfe bei den Untersuchungen.

Summary—A report is presented of a detailed electrochemical investigation of substituted derivatives of 4-amino-4′-methoxydiphenylamine (Variamin Blue) as indicators for use with different electrophilic and nucleophilic groups. The reversible "redox" process of these compounds corresponds to two electrons, and their oxidation mechanism corresponds to that of Variamin Blue, *i.e.*, their oxidised form corresponds to the correspondingly substituted derivative of quinone-*p*-anisil-di-imine. In the oxidation of 2-methyl- and 2-methoxy-products an intermediate semi-quinoidal oxidation product also occurs. The instability of the system in acid solution is brought about by the decomposition of the oxidised form. By means of electrode equations the "redox" potentials at desired pH values can be calculated. The point of inflection of the E_0'-pH curves gives the acid-base dissociation constants of the oxidised and reduced forms. Nucleophilic substituents raise, and electrophilic substituents lower the basicity of the Variamin Blue molecules.

Résumé—Les auteurs présentent une étude électrochimique détaillée des dérivés substitués de l'amino-4 méthoxy-4′ diphénylamine (blue de variamine), dérivés utilisés comme indicateurs et comportant différents groupements électophiles et nucléophiles. Le comportement reversible du point de vue oxydo-réduction, de ces composés correspond à l'échange de deux électrons et le mécanisme de leur oxydation correspond à celui du bleu de variamine, c'est à dire que les formes oxydées de ces dérives correspondent aux dérivés substitués correspondants de la p.anisil di-imine-quinone. Dans l'oxydation des composés méthyl-2 et méthoxy-2, on obtient aussi un produit d'oxydation semi-quinonique intermédiaire. L'instabilité du système en solution acide est due à la décomposition de la forme oxydée. Au moyen d'équations relatives aux phénomènes aux électrodes, les potentiels "redox" pour différents pH ont été calculés. Le point d'inflection des courbes E_0'-pH fournit les constantes de dissociation des formes oxydées et réduites. Les substituants nucléophiles augmentent le caractère basique des molécules de bleu de variamine, alors que les substituants électrophiles le diminuent.

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ORGANIC ANALYSIS—XV.* THE INFRARED SPECTRA OF THE TETRALIN SERIES

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Summary—The out-of-plane CH deformation vibrations of the aromatic ring of the tetralin series normally appear in almost the same frequency region as in the corresponding benzene series, and their frequencies are regularly shifted by the type of substituents attached to the aromatic ring with a few exceptions.

All compounds which have an isolated CH group in the aromatic ring exhibit fairly strong absorption bands around the 800 cm^{-1} region, which may be associated with the aromatic ring.

Carbonyl and hydroxyl groups in the *peri*-position of tetralone are strongly chelated, showing frequency shifts in their stretching vibrations.

THE out-of-plane CH deformation vibrations of aromatic ring have been studied in detail in correlation to the position and type of substituents in the benzene,[1] pyridine,[2,3] naphthalene,[1,4,5] and quinoline[6] series, but no systematic study has appeared of the tetralin series in the literature. In this work, the infrared spectra of 61 compounds of tetralin series have been measured, and their out-of-plane CH deformation vibrations have been discussed. In the tetralone and 8-hydroxy-tetralin-7-acetic acid lactone derivatives, the C=O stretching vibrations were also discussed in relation to OH stretching vibrations.

RESULTS AND DISCUSSION

1. *Out-of-plane* CH *deformation vibrations*

The out-of-plane CH deformation vibrations of the aromatic ring of the tetralin series produced, generally, strong bands in almost the same region as the corresponding benzene series. Their frequencies showed regular shifts with the type of substituents present in the aromatic ring; and in general, strong electron-attracting substituents exerted shifts towards longer frequencies, and electron-donating substituents towards shorter frequencies. The substituents attached to the saturated ring gave no regular shift of the frequencies. These are shown in Table I and discussed in detail as follows.

1.1. *Four adjacent ring hydrogen atoms.* A few compounds thus substituted are shown in Table I, and exhibited strong absorption bands in the 740–770 cm^{-1} region. In agreement with Jones *et al.*,[7] who noted that the out-of-plane CH deformation vibrations of tetralin absorbed almost the same range of frequencies as *ortho*-disubstituted benzene derivatives, the above data coincided well with the 735–770 cm^{-1} region, which was proposed for *ortho*-disubstituted aromatics.[1]

1.2. *Three adjacent ring hydrogen atoms.* Compounds examined which had three adjacent hydrogen atoms were confined to derivatives of 8-tetralone and of the 8-hydroxy-7-acetic acid lactone. These compounds each had one strong band in the 785–815 cm^{-1} and 730–760 cm^{-1} regions, respectively, as shown in Table I. These

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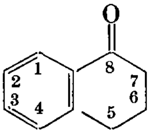
* Part XIV: *Chem. Pharm. Bull.* (*Tokyo*), in press.

bands correspond to those of the benzene series thus substituted, which appear in the 750–810 cm^{-1} and 680–725 cm^{-1} regions[1] or in the liquid state in the 780–830 cm^{-1} and 700–750 cm^{-1} regions.[8]

The two bands had variable intensities. The frequency of the higher component of the pair in the 8-tetralones varied with the substituent in the order $NO_2 > NHAc > OAc > OH$. This order agrees with the results obtained by Kross *et al.*[9] in mono-substituted and *para*-disubstituted benzene derivatives. Somewhat similar

TABLE I. OUT-OF-PLANE CH DEFORMATION FREQUENCIES
Tetralone-(8) derivatives



Substituent					Adjacent hydrogen atoms	δCH (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(7)}$			
H	H	H	H	H	4	761*	
H	H	H	H	CO_2Et	4	771	
H	H	H	NO_2	H	3	815	759
NO_2	H	H	H	H	3	812	743
H	H	H	NHAc	H	3	808	735
H	H	H	OAc	H	3	807	737
H	H	H	OH	H	3	800	730
OH	H	H	H	CH_2CO_2H	2	824	
OMe	H	H	OMe	CH_2CO_2H	2	822	
OAc	H	H	OAc	H	2	842	
OH	H	H	OAc	H	2	842	
OH	H	H	OH	H	2	825	
OMe	H	H	OMe	H	2	812	
H	OH	H	H	CH_2CO_2H	2	833	
H	OMe	H	H	CH_2CO_2H	2	818	
H	NHAc	H	H	H	2	836	
H	NO_2	H	H	H	2	831	
H	OH	H	H	H	2	822	
H	H	OH	H	H	2	822	
H	OMe	H	H	H	2	821	
H	Me	H	H	H	2	815	

Tetralin derivatives

Substituent				Adjacent hydrogen atoms	δCH (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
H	H	H	H	4	744*
OAc	H	H	OAc	2	844
H	OH	H	H	2	822

8-Hydroxytetralin-7-acetic acid lactone derivatives

Substituent				Adjacent hydrogen atoms	δCH (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$			
H	H	H	H	4	753	
H	H	H	NO_2	3	803	741
H	H	H	OAc	3	795	736
H	H	H	OH	3	787	746
OH	H	H	OH	2	821	
OAc	H	H	OAc	2	848	
H	OAc	H	H	2	833	

* Liquids; others in Nujol.

effects in the order of frequencies with substituent are apparent in the lower frequency component of the pair of bands in the 8-tetralones, and in the higher frequency component in the lactones.

1.3. *Two adjacent ring hydrogen atoms.* All compounds examined which had two adjacent hydrogen atoms in the 1:2, 2:3 or 3:4 positions absorbed strongly within the 810–850 cm^{-1} region. The frequency depended on the substituent, in the order OAc > OH $\geqslant$ OMe, but the order NO_2 > NHAc > OAc > OH remarked on above (in Section 1.2) was modified to NHAc > NO_2 in the tetralones with the two adjacent ring hydrogens.

2. *The* 800 cm^{-1} *absorption*

1:3-, 2:3-disubstituted, and 1:2:3-, and 1:2:4-trisubstituted compounds of the tetralin series which had an isolated CH group exhibited fairly strong absorption bands around the 800 cm^{-1} region as shown in Table II. These bands shifted towards longer frequencies with the nature of the substituents in the order OAc > OH > OMe in 2:3-disubstituted compounds, which coincides with the order obtained in their out-of-plane CH deformation vibrations. With the same substituents, the shift occurred toward longer frequencies in tetralin than it did in tetralone.

No satisfactory assignment was possible for the band, but the above nature of the shift might prove that the band was associated with the aromatic ring of the series. Some other compounds which had no isolated CH group sometimes showed absorption bands around the 800 cm^{-1} region, of variable intensity, but no agreement could be found with the position and number of the substituents.

3. C=O *and* OH *stretching vibrations*

The OH stretching frequencies of this series are shown in Table III. In the tetralone derivatives, the C=O stretching frequencies appeared in almost the same region as in aryl ketones, and are shown in Table IV.

3.1. *Hydroxy-tetralones.* The *peri*-hydroxyl group of the tetralone derivatives caused a large shift to shorter frequency, superimposing the absorption band on the absorption of Nujol. This fact proved that the group was strongly chelated with the carbonyl group. The other hydroxyl groups of tetralone gave no such shift.

Table II. The 800 cm^{-1} absorption

2:3-Disubstituted derivatives

Compound	Substituent		Wave number (cm^{-1})
	$C_{(2)}$	$C_{(3)}$	
Tetralin	OMe	OMe	803
	OH	OH	809
	OAc	OAc	824
	OH	OMe	807
	OH	COMe	808
Tetralone-(8)	OMe	OMe	794
	OH	OH	805
	OAc	OAc	816
8-Tetralone-7-acetic acid	OMe	OMe	797
	OH	OH	806

1:3-, 1:2:3-, 1:2:4-Substituted tetralin derivatives

Substituent				Wave number (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	
OAc	H	OAc	H	823
OH	H	OH	H	812
NO_2	H	NO_2	H	799
NH_2	H	NH_2	H	817
OH	Me	H	OH	833
COMe	OH	OH	H	810
COMe	OMe	OMe	H	773
CHO	OH	OMe	H	776
$CH_2—CH=CH_2$	OH	OMe	H	811
C_3H_7	OH	OH	H	810
C_3H_7	OH	OMe	H	812
Me	OH	OMe	H	814
Br	OH	NO_2	H	798
Br	OMe	NO_2	H	798
Br	OMe	OMe	H	796

1:2:4-Substituted tetralone-(8) derivatives

Substituent				Wave number (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	
OMe	Me	H	OMe	813
OH	Me	H	OH	829

Measured in Nujol.

TABLE III. OH STRETCHING FREQUENCIES
Tetralone-(8) derivatives

Substituent					ν_{OH} (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(7)}$		
OH	H	H	OAc	H		—
OH	H	H	OMe	H		—
OH	H	H	OH	H	3323	—
OH	H	H	OH	CH_2CO_2H	3554	—
OH	Me	H	OH	H	3280	—
H	OH	OH	H	H	3529	3206
H	OH	H	H	H		3237
H	H	H	OH	H		3209
H	OH	OH	H	CH_2CO_2H	3415	3253

Tetralin derivatives

Substituent				ν_{OH} (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
H	OH	OH	H		3562
H	OH	OMe	H		3425
OH	H	OH	H	4072	3471

8-Hydroxytetralin-7-acetic acid lactone derivatives

Substituent				ν_{OH} (cm^{-1})	
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
OH	H	H	OH	3575	3287
H	H	H	OH		3361
H	OH	H	H		3405

Measured in Nujol.

Table IV shows that the C=O stretching vibrations of the *peri*-hydroxytetralone derivatives appear around 50 cm^{-1} lower in frequency than that of tetralone, showing that the vibrations are strongly influenced by hydrogen bonding. This shift is larger than the frequency shift of 40 cm^{-1} in *peri*-hydroxyanthraquinone,[10] and of 16–25 cm^{-1} in *peri*-hydroxynaphthoquinone. Other hydroxytetralones than the *peri*-hydroxy-derivatives also showed frequency shifts of about 35 cm^{-1} in C=O stretching vibrations, which might be caused by inter-molecular hydrogen bonding.

3.2. *γ-Lactones.* The C=O stretching vibrations of the γ-lactone in 8-hydroxytetralin-7-acetic acid lactones appeared in a frequency range of 1725–1790 cm^{-1}, and were fairly strongly affected by substituents attached to the aromatic ring. Table V

TABLE IV. C=O STRETCHING FREQUENCIES
Tetralone-(8) derivatives

Substituent					$\nu_{C=O}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(7)}$		
H	H	H	H	H	1684	0*
OH	H	H	OH	H	1612	−72
OH	H	H	OAc	H	1634	−50
OH	H	H	OMe	H	1637	−47
OAc	H	H	OAc	H	1695	+11
OMe	H	H	OMe	H	1679	−5
H	H	H	NO_2	H	1679	−5
NO_2	H	H	H	H	1693	+9
H	OH	H	H	H	1652	−32
H	OMe	H	H	H	1682	−2
H	Me	H	H	H	1679	−5
H	NO_2	H	H	H	1684	0
H	H	OH	H	H	1649	−35
H	OH	OH	H	H	1653	−31
H	OMe	OMe	H	H	1662	−22
H	OAc	OAc	H	H	1684	0
OMe	Me	H	OMe	H	1683	−1
OH	Me	H	OH	H	1618	−66
H	H	H	OH	H	1647	−37
H	H	H	OAc	H	1685	+1
H	OH	H	H	CH_2CO_2H	1663	−21
H	H	H	H	CO_2Et	1680	−4

* Liquid; others in Nujol.

TABLE V. C=O STRETCHING FREQUENCIES
8-Hydroxytetralin-7-acetic acid lactone derivatives

Substituent				$\nu_{C=O}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})
$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$		
H	H	H	H	1764	0
H	H	H	OH	1726	−38
OH	H	H	OH	1726	−38
H	OH	H	H	1742	−22
H	H	H	NO_2	1780	+16
H	NO_2	H	H	1789	+25
OAc	H	H	OAc	*ca.* 1770	*ca.* +6
H	H	H	OHc	*ca.* 1770	*ca.* +6
H	OAc	H	H	*ca.* 1770	*ca.* +6

Measured in Nujol.

shows their frequencies and shifts from the unsubstituted lactone. In the hydroxyl compounds, the shifts were 20–40 cm^{-1} towards lower frequencies, but were smaller in all cases where the hydroxyl group was acetylated, overlapping the absorption band of the C=O band of the acetyl group. This fact suggests that inter-molecular hydrogen bonding might be present in these compounds.* On the other hand, a nitro group attached to the aromatic ring exerted a shift towards the higher frequency region as may also be seen in the Table.

EXPERIMENTAL

Samples were previously[11] prepared in the writer's laboratory.

Infrared spectra were measured with Koken Model DS-201 and -301 recording infrared spectrophotometers using a NaCl prism.

Zusammenfassung—Die Infrarotspektren von 61 Verbindungen der Tetralinreihe wurden gemessen. Die Deformationsschwingungen der abstehenden CH-Gruppen wurdendiskutiert. Sie erscheinen im allgemeinen nahezu im gleichen Frequenzbereich wie die der entsprechenden Benzolreihe. Nur mit wenigen Ausnahmen werden ihre Frequenzen durch Substituenten regulär verschoben. Alle Verbindungen mit einer isolierten CH-Gruppe im aromatischen Ring zeigten eine ziemlich starke Absorptionsbande im 800 cm^{-1} Bereich. Carbonyl- oder Hydroxylgruppe in peri-Stellung im Tetralon sind stark cheliert und zeigen eine Frequenzverschiebung in den Streckschwingungen.

Résumé—Les spectres infra rouges de 61 composés des séries de la tétraline ont été déterminés et leurs vibrations "relatives" à la déformation des CH non plans ont été discutées. Celles-ci apparaissent, en général, à peu près dans le même domaine de fréquence que dans le cas des séries benzéniques correspondantes; à quelques exceptions près leurs fréquences varient régulièrement avec les substituants. Tous les composés comportant un groupement Ch isolé dans le cycle aromatique présentent, dans la région 800 cm^{-1}, des bandes d'absorption assez fortes qui peuvent être associées au cycle aromatique.

Le groupement carbonyl ou hydroxyl de la tétralone, placé en péri, est fortement chelaté et présente une variation de fréquence pour les vibrations de valence.

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* This assumption is supported by the fact that the C=O stretching frequency (1773 cm^{-1}) of γ-butyrolactone shifted to 1744 cm^{-1} when it was measured in phenol solution.

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UTILIZATION OF TERNARY AND ION-ASSOCIATION COMPLEXES IN CHEMICAL ANALYSIS—I

SELECTIVE EXTRACTION AND COLORIMETRIC DETERMINATION OF TRACES OF IRON AS "FERROÏN IODIDE"

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Summary—The complex cation $Fe(Phen)_3^{2+}$ [Phen = 1:10-phenanthroline] reacts with certain anions forming slightly dissociated usually insoluble compounds, extractable by organic solvents, in particular chloroform and nitrobenzene, The iodide complex $Fe(Phen)_3I_2$ ("ferroïn iodide") has proved very suitable for the extraction and colorimetric determination of bivalent iron. High selectivity of the method is ensured by the addition of EDTA* which masks all the elements which require consideration in practice.

ONE of the most sensitive colorimetric determinations of traces of bivalent iron, using with 1:10-phenanthroline, is interfered with in many practical applications by the presence of certain cations. Phenanthroline is not a specific reagent for bivalent iron, and over a comparatively wide range of pH it reacts also with several other cations, forming soluble or insoluble, and usually also coloured complexes. Therefore the determination of iron is interfered with, for example, by the presence of silver, univalent and bivalent mercury (insoluble complexes) as well as by the presence of copper, cadmium, and cobalt (soluble, usually coloured complexes). Any colour of the test solution, whatever its cause, will interfere with the determination of iron because we must develop the colour reaction with phenanthroline directly in the solution. The phenanthroline complex with bivalent iron, $Fe(Phen)_3^{+2}$ is, however, not extractable by the usual organic solvents (in the presence of *e.g.* nitrates and sulphates). Therefore a way has been sought of improving this method. The extractability of the perchlorate complex of "ferroïn" by nitrobenzene makes possible, according to Margerun and Banks,[1] the determination of traces of iron in the presence of vanadium, chromium, manganese, nickel and zinc. The determination is interfered with according to these authors, by the presence of copper and cobalt which are also extracted as similar complexes into nitrobenzene. A short time ago Diehl and Buchanan[2] utilized the extraction of the phenanthroline-cyanide complex of bivalent iron $Fe(Phen)_2(CN)_2$ by chloroform or nitrobenzene for the colorimetric determination of iron in the presence of copper. The disadvantage of this method is that for each concentration of copper it is necessary to prepare a special calibration curve.

Many experiments have also been made to mask the interfering elements by complex-forming materials. An example is the determination of traces of iron in metallic bismuth suggested by Holmes[3] who uses ethylenediaminetetra-acetic acid for the screening of bismuth (adding it after the reduction of iron in acid medium before adding the phenanthroline).

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* EDTA = Ethylenediaminetetra-acetic acid.

The endeavour to improve the original colorimetric method of the determination of bivalent iron has also led many authors to study a wide range of derivatives of 1:10-phenanthroline. Smith and McCurdy,[4] for example, recommend for the colorimetric determination of copper and iron the as yet not readily available reagent 4:7-diphenyl-1:10-phenanthroline the complex of which, with copper and bivalent iron, is readily extractable by chloroform and nitrobenzene and has, in addition, a considerably higher extinction coefficient than "ferroïn" proper. According to the authors, cobalt, which is not extracted, should not interfere in this case. Because of the price of this reagent it cannot be expected that this method will have an extensive use in routine analysis.

In the course of a systematic study of the ternary complexes of phenanthroline of the type $Me(Phen)_3X_2$ (where $X = Cl$, Br, I and CNS) we have also paid attention to the corresponding complexes of bivalent iron. Their comparatively slight solubility in water is already known from the paper by Blaue[5] who prepared many of them in solid form and analysed them. The iodide complex (subsequently called "ferroïn iodide") is very slightly soluble, and relatively undissociated. By preliminary experiments we have not only verified Blaue's results but have also confirmed our expectation that these ternary complexes are soluble in a number of organic solvents. The early experiments have proved that "ferroïn" can be quantitatively extracted by chloroform over a wide range of pH in the presence of iodide or sulphocyanide. Similar chloride and bromide complexes are not extracted. The increase of the selectivity of the "ferroïn iodide" extraction almost to the extent of absolute specificity was obtained with EDTA acid with which it is possible to screen practically all interfering bivalent to quadrivalent elements, under suitable conditions, without influencing the necessary reduction of tervalent iron to bivalent iron before the appropriate colorimetric determination.

EXPERIMENTAL

Reagents and solutions

Standard solutions of ferrous and ferric iron (0·05 molar) were prepared from reagent grade ferrous ammonium sulphate and ferric ammonium sulphate respectively. Their titres were determined gravimetrically. Solutions of $1 \cdot 10^{-3}$ and $1 \cdot 10^{-4}$ molar concentration were prepared by dilution.

Solutions of 1:10-phenanthroline ($5 \cdot 10^{-2}$ and $1 \cdot 10^{-3}$ molar) were prepared by dissolution of a precisely weighed and calculated quantity of 1:10-phenanthroline, Guaranteed Reagent (Lachema, National Corporation, Brno) in warm redistilled water acidified by a minimum quantity of nitric acid. The resulting pH of the solutions was 3 to 5.

Solutions of various metal salts were also prepared from reagent grade chemicals. The concentration of these solutions was controlled complexometrically.

The disodium salt of ethylenediaminetetra-acetic acid (EDTA) was used in solid form. The product "Chelaton 3" (Lachema, National Corporation, Brno) was employed.

30% solutions of potassium iodide and 20% solutions of potassium thiocyanate were also prepared from reagent grade chemicals.

Apparatus

The adjustment of the pH of the solutions was controlled potentiometrically with a glass electrode. The measurement was carried out with a pH meter, (Kovodružstvo, Praha).

The colorimetric measurement was carried out by a deflection photometer (Laboratorní potřeby, National Corporation, Praha) with the use of suitable filter.

The spectrophotometric measurements were carried out on a spectrophotometer (Uvispek, Hilger, London).

EXTRACTION OF BIVALENT IRON IN THE FORM OF ITS TERNARY COMPLEX WITH PHENANTHROLINE AND IODIDE

As mentioned in the introductory part it is possible to extract the red-orange complex of ferrous iron with 1:10-phenanthroline ("ferroïn") in the presence of excess of iodide ions by organic solvents, in particular by chloroform. In order to ascertain the basic optical properties of the chloroform solutions of various ternary complexes of bivalent iron the following series of tests was carried out:

A solution containing bivalent iron was mixed in a 100-ml beaker with phenanthroline solution, potassium iodide solution, and ammonium thiocyanate solution, diluted with water to approximately 25 ml and 25 ml of chloroform were added. The solution was thoroughly stirred by a magnetic stirrer. The chloroform layer was separated from water in a separating funnel with a long stem, then poured through a folded filter paper into a 25-ml measuring flask. The filter was rinsed with chloroform which was also collected into the flask. After adjustment to the mark the solution was measured photometrically in a 1-cm cell. If not otherwise mentioned the procedure was the same in all further measurements. The basic spectra are shown in the graphs of Fig. 1.

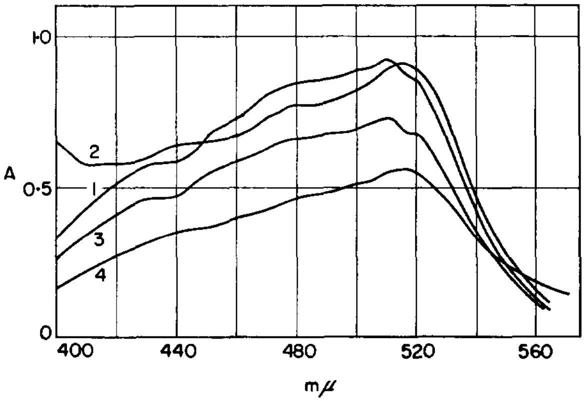

FIG. 1. Absorption spectra of complexes of ferrous iron (4 × $10^{-5}M$). (1) aqueous solution of "ferroïn," (2) chloroform solution of "ferroïn iodide", (3) aqueous solution of "ferroïn" thiocyanate (4) chloroform solution of "ferroïn thiocyanate."

Here curve (1) represents the absorption spectrum of "ferroïn" (the solution of "ferroïn iodide" in water has the same form) curve (2) represents the absorption spectrum of "ferroïn iodide" in chloroform, curve (3) the spectrum of "ferroïn thiocyanate" in water and finally curve (4) the spectrum of "ferroïn thiocyanate" in chloroform. All the measurements were made under the same conditions of concentration.

From the form of curves (1) and (2) it is evident that the extinction coefficient of "ferroïn" in water and of "ferroïn iodide" in chloroform is practically the same (in the range of maximum absorption); a change of the absorption occurs only in the region of shorter wave lengths and a slight shift of the absorption maximum, from 510 to 515 mμ, takes place. The absorption spectra of the aqueous and chloroform solutions of "ferroïn thiocyanate", however, differ from each other [curves (3) and (4)]. The shift of the absorption maximum is small but at the same time the decrease of the extinction coefficient is considerable. Because of the lower sensitivity the extinction of iron in the form of phenanthroline–thiocyanate complex has not been studied more closely.

DEPENDENCE OF THE EXTRACTION OF "FERROÏN IODIDE" ON THE CONCENTRATIONS OF 1:10-PHENANTHROLINE, IODIDE, ON pH AND ON THE TYPE OF THE ORGANIC SOLVENT USED.

Influence of the concentration of 1:10-*phenanthroline*

This has been followed by the method of the shift of balance (the so-called titration curve was measured). To a constant quantity of ferrous iron an increasing quantity of phenanthroline of the same molarity was added. The extraction was carried out with chloroform in the presence of a constant large excess of potassium iodide and by the same procedure as described in the preceding paragraph. Fig. 2 shows the curve obtained from the extinction values at 515 mμ.

From the form of the curve it is immediately evident that the extraction of "ferroïn iodide" (that is, the extinction of the extract) is constant above the ratio Fe^{+2} : Phen = 1 : 6. It is known that water solutions with excess of phenanthroline contain only complex with a ratio of components 1 : 3, *i.e.* with the composition $Fe(Phen)_3^{2+}$. The two breaks in the curve prove that the complex $Fe(Phen)_3I_2$ is extracted and, in the presence of excess of phenanthroline, also another complex containing also three further molecules of phenanthroline. (Note the sharp break on the curve in the proximity of the ratio 1 : 6). It is at present not possible without a more detailed study to decide how the further three molecules of phenanthroline are bonded. In nonaqueous (chloroform) medium a different behaviour of "ferroïn iodide" from that in water may be expected; but the presupposition that a solvate of the type $Fe(Phen)_3I_2.3$ Phen is being formed is hardly likely in view of the sharpness of the break in the proximity of the ratio 1 :6, which proves the comparatively considerable stability of the bonding of the further three molecules of phenanthroline in the extracted complex. A more detailed study of this question has not yet been carried out.

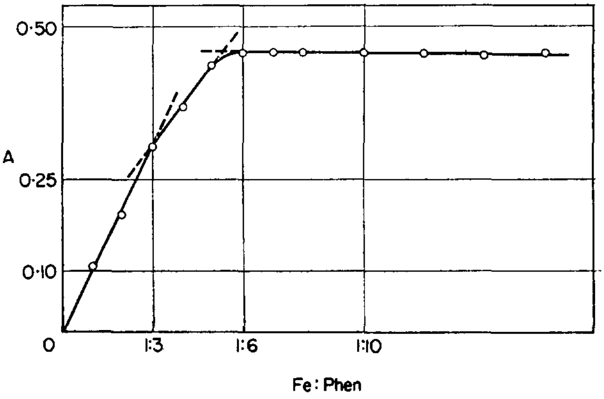

FIG. 2. Extinction of "ferroïn iodide" extract vs. excess of phenanthroline (titration curve). 25 ml of solution containing 1 ml of 1 × $10^{-3}M$ Fe^{2+}, 1 to 10 ml of 1 × $10^{-3}M$ 1:10-phenanthroline and 5 ml of 30% solution of KI extracted by 25 ml of chloroform.

Influence of KI *concentration*

A constant quantity of ferrous iron (4 · $10^{-5}M$) was extracted from solutions containing different amounts of potassium iodide in the presence of a constant quantity of phenanthroline and the light

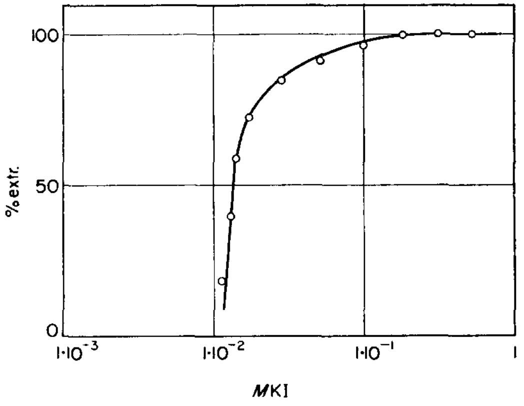

FIG. 3. Extraction (in %) of "ferroïn iodide" vs. concentration of iodide. Concentration of iron: 4 × $10^{-5}M$, of phenanthroline: 4 × $10^{-4}M$.

absorption of chloroform extracts was measured again. Fig. 3 shows the per cent extraction of bivalent iron as "ferroïn iodide" in relation to the molarity of the present potassium iodide. From the graph it is evident that only high concentrations of iodide (5000 times more than the iron) suppress the dissociation of small amounts of the complex $Fe(Phen)_3I_2$ so much that its quantitative formation as well as its quantitative extraction in chloroform is made possible. The removal of the complex from the water phase obviously influences this balance favourably.

Influence of pH

The completeness of the extraction in relation to the pH of the water solution was studied by preparing a water solution of "ferroïn iodide" under constant concentration conditions (the original pH being approximately 4), the pH of the solution being adjusted with 0·1*N* hydrochloric acid or 0·1*N* sodium hydroxide, controlling potentiometrically with a glass electrode to the required value; the solution was diluted to 25 ml and extracted by the already described method with 25 ml of chloroform. From the curve in Fig. 4 it is evident that the extraction is quantitative in the range pH 2·5–10 which in practice is the pH range of stability of "ferroïn".

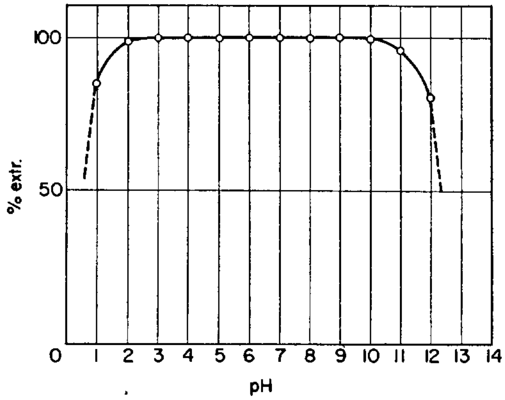

FIG. 4. Extraction (in %) of "ferroïn iodide" vs. pH. Concentration of iron: 4 × $10^{-5}M$, of phenanthroline: 4 × $10^{-4}M$ and of potassium iodide: 2 × $10^{-1}M$.

Influence of the organic solvent

Besides chloroform, other solvents were also used for the extraction. The complex is only partly extracted by alcohols (aliphatic and aromatic). Ketones, hydrocarbons, tributylphosphate, carbon tetrachloride, carbon bisulphide or monochlorobenzene do not extract "ferroïn iodide" at all.

REDUCTION OF FERRIC IRON AND EXTRACTION OF "FERROÏN IODIDE" IN THE PRESENCE OF EDTA

It is known that the colorimetric determination of iron as "ferroïn" is interfered with by the presence of all elements forming sufficiently stable complexes with 1:10-phenanthroline. This is also the case in its determination as "ferroïn iodide" where, in addition, elements reacting with iodide, *e.g.* copper, lead etc., interfere. The interfering influence of all these elements can be totally eliminated by screening with EDTA. It was, of course, necessary to determine whether an excess of EDTA might not interfere in the extraction of bivalent iron. In normal analytical practice, however, iron is encountered in tervalent form. Therefore it was also necessary to study the conditions of the reduction of tervalent iron in the presence of high EDTA concentrations. That increase of selectivity in the colorimetric determination of iron is possible by using EDTA can be seen from Fig. 5, which shows the dependence on pH of the apparent stability constants[6,7,8] (conditions constant) of all four complexes $Fe(Phen)_3^{+2}$ (curve 2), $Fe(Phen)_3^{3+}$ (curve 3), FeY^{-2} (curve 4) and FeY^{-1} (curve 1). (Y = anion of EDTA). From curves (1) and (3) it is evident that the complex of tervalent iron with EDTA is much more stable than with phenanthroline. Curves (2) and (4), on the contrary, prove that, for example, at pH 5–6 the stability constant of "ferroïn" is approximately 15 times higher in order than the stability constant

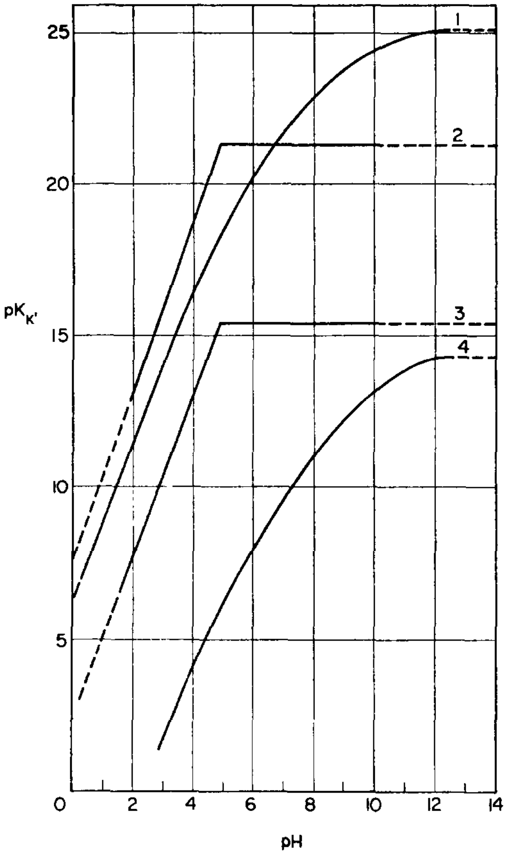

Fig. 5. Apparent stability constant vs. pH. (1) FeY^-; (2) $Fe(Phen)_3{}^{2+}$; (3) $Fe(Phen)_3{}^{3+}$; (4) FeY^{2-}

of the iron complex with EDTA. Therefore the formation of "ferroin" in the presence of EDTA must follow a completely smooth course at the given pH assuming that the tervalent iron compounded in a complex with EDTA is quantitatively reduced. A series of tests was therefore carried out on the reduction of the complex FeY^{-1} in the presence of phenanthroline which, according to the equation (1), should in fact encourage the reduction of tervalent iron:

$$FeY^- + 3\,Phen + e^{-1} + 2H^{+1} \rightleftharpoons Fe(Phen)_3{}^{+2} + H_2Y^{-2} \qquad (1)$$

Hydroxylamine has proved satisfactory for the reduction of iron, especially at increased temperature (approximately 50°). Tests have confirmed our theoretical assumption that the reduction of tervalent iron is quantitative in the presence of practically any amount of EDTA if a sufficient quantity of phenanthroline is simultaneously present and the pH of the solution is suitable (influence of pH on the redox potential of the system). In solutions of pH 5–8 at a temperature of approximately 50° the reduction of iron is smooth and quantitative in the presence of about twenty times as much phenanthroline as iron. A sufficient excess of hydroxylamine is used for the reduction. The extraction of the already formed "ferroïn iodide" is also not interfered with by the presence of EDTA. Proof of this is found in Fig. 6. The points on the calibration curve marked with a circle indicate the extinction values for the "ferroïn iodide" extract, and those marked with a square show the extinction of "ferroïn iodide" in the presence of 1 g of EDTA in 25 ml of aqueous phase.

The calibration curve was obtained by the following series of tests: a solution containing ferric ammonium sulphate (0·44–3·79 μg in 1 ml) was diluted to about 10 ml, the pH value was adjusted with aqueous ammonia (1 : 1) to pH 7–8 (glass electrode). After addition of 5 ml of 10% solution of hydroxylamine hydrochloride (previously neutralized to pH 7–8) and of 4 ml of 0·05 molar phenanthroline

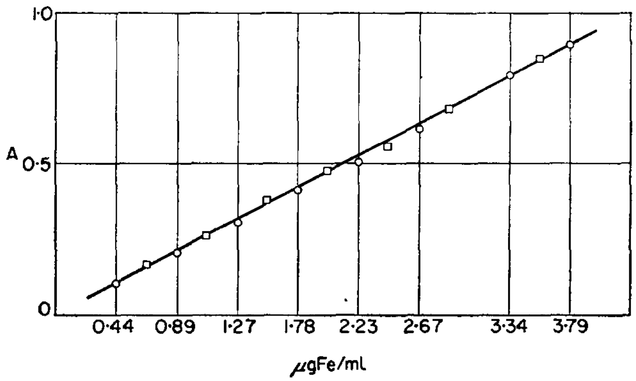

FIG. 6. Calibration curve for the determination of iron as "ferroïn iodide" ○ for "ferroïn iodide" ☐ for "ferroïn iodide" in the presence of EDTA.

the solution was heated to 40° to 60°. After 2 minutes the solution was cooled to room temperature, 5 ml of 30% solution of potassium iodide were added, the solution was diluted to 25 ml and extracted with 25 ml of chloroform as described above. The light absorption was measured on a colorimeter with the use of a 510 mµ filter. A series of tests with solutions containing 1 g of EDTA (EDTA is dissolved only after adjusting the pH of the solution) was carried out in the same manner.

TABLE I. DETERMINATION OF IRON BY EXTRACTION OF "FERROÏN IODIDE" WITH CHLOROFORM IN THE PRESENCE OF A NUMBER OF METALS*

Present		Found	
Fe µg/ml	Other metal mg/ml	Fe µg/ml	Error in %
0·66	—	0·68	+3·3
1·32	—	1·31	−0·7
1·98	—	1·95	−1·5
2·64	—	2·64	0·0
3·33	—	3·30	−1·0
3·96	—	3·91	−1·2
2·64	2·3 Ni	2·66	+0·8
2·64	2·7 Zn	2·64	0·0
2.64	3·1 Mn	2·67	+1·2
2·64	2·0 Cr	2·68	+1·4
2·64	29·0 Bi	2·64	0·0
2·64	28·0 Pb	2·66	+0·8
2·64	2·7 Al	2·62	−0·8
2·64	21·0 U	2·64	0·0
2·64	1·9 Ti	2·67	+1·2
2·64	9·1 Zr	2·62	−0·8
2·64	26·0 Th	2·61	−1·2
2·64	11·0 Cd	2·68	+1·2
2·64	8·0 Cu	2·64	0·0
2·64	4·6 Co	2·68	+1·4

* The stated results are the mean value of three determinations.

DETERMINATION OF TRACES OF IRON IN THE PRESENCE OF OTHER ELEMENTS

By the method just described it is possible to determine traces of iron in the presence of a range of elements if they are screened by EDTA; this also prevents hydrolysis of certain elements which would otherwise not interfere in the determination. Both the masking and the extraction can be carried out in the pH range 5–8. Copper and cobalt are an exception. Copper can be completely masked against phenanthroline by means of EDTA at pH 7–8 (it is possible also at higher pH but here the sensitivity of the reaction of phenanthroline with ferrous iron decreases). Small quantities of cobalt are screened by EDTA at pH values above 9. Higher concentrations, however, interfere at this pH since the phenanthroline-iodide complex of cobalt is formed and this is also extractable. A subsequent paper will discuss the selective extraction and analytical utilization of this complex. In the presence of cobalt it is therefore necessary to modify the procedure by previously converting the cobalt into the complex of tervalent cobalt with EDTA. In the presence of copper it is sufficient to adjust the pH of the solution to a value of 7–8 before the reduction with hydroxylamine.

TABLE II. DETERMINATION OF IRON IN METALS AND ALLOYS

Sample	Composition, %	Content of Fe, %	Found, Fe,* %
Pure "cobalte"	99·40 Co, 0·42 Ni 0·03 Cu, 0·04 Cr 0·22 Si, traces of P, S, As	0·10	0·096
Bronze	58·4 Cu, 39·20 Zn 1·02 Pb, 0·12 Ni 0·33 Al, 0·01 Mn 0·02 Si, 0·48 Sn 0·02 Mg, 0·01 Ag	0·40	0·403
Waspaloy NBS, No. 349	57·14 Ni, 19·45 Cr 13·95 Co, 4·03 Mo 3·11 Ti, 1·25 Al 0·30 Si, 0·42 Mn 0·006 Cu, 0·077 Zr 0·0043 B, 0·074 C traces of P and S	0·142	0·138

* The stated results of the determination of iron are the mean value of three determinations.

DETERMINATION OF TRACES OF IRON IN THE PRESENCE OF COBALT

Procedure: To 5 ml of the solution (2 to 20 μg per 1 ml) add an amount of EDTA sufficient to bond cobalt (and other elements), adjust the pH to 7–8 and add several drops of 10% hydrogen peroxide. Oxidize the cobalt to the tervalent form (CoY^{-1}) and simultaneously remove the excess of peroxide by boiling for several minutes. After cooling to approximately 50° add 5 ml of 10% hydroxylamine hydrochloride solution (pH 7–8) and 4 ml of 0·05 molar phenanthroline. After cooling proceed as already mentioned. Table I shows typical results for the determination of traces of iron in the presence of various elements.

PRACTICAL APPLICATION

The suggested method has proved satisfactory in certain samples—"pure cobalt", bronze and a special alloy. After dissolution of the sample in nitric acid or in *aqua regia* the solution was adjusted to a suitable volume. In an aliquot (usually 5 ml) iron was determined by the method described. Oxidation with hydrogen peroxide was carried out in samples containing cobalt. The results are given in Table II.

Acknowledgement—The authors wish to thank Dr. K. L. Cheng, Metals Division, Kelsey-Hayes Comp., Utica, N.Y. for supplying a sample of the alloy Waspaloy used in this work.

Zusammenfassung—Das komplexe Kation $Fe(Phen)_3^{2+}$ (Phen = 1,10-Phenantrolin) reagiert mit gewissen Anionen unter Bildung schwach dissoziierter oder praktisch unlöslicher Verbindungen, die mit organischen Lösemitteln (vorwiegend Chloroform und Nitrobenzol) ausgeschüttelt werden können. Der Komplex $Fe(Phen)_3J_2$ ("Ferroinjodid") hat sich fur die Extraktion und photometrische Bestimmung von zweiwertigem Eisen als äusserst brauchbar erwiesen. Hohe Selektivität der Methode wird durch Zugabe von ÄDTA erreicht, wodurch alle üblichen Störmetalle ausgeschaltet werden.

Résumé—Le cation complexe $Fe(Phen)_3^{2+}$ (où Phen = 1:10 phenanthroline) réagit avec certains anions en donnant des composés peu dissociés et pratiquement insolubles, extractibles par des solvants organiques principalement par le chloroforme et le nitrobenzène. Le complexe iodure $Fe(Phen)_3I_2$ (iodure de ferrïone) s'est révélé tres adapté pour l'extraction et le dosage colorimétrique du fer divalent. La grande sélectivité de la méthode est augmentée par l'addition de EDTA qui élimine tous les éléments dont on doit tenir compte en pratique.

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ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—III.

SPECTROPHOTOMETRIC STUDY ON THE HAFNIUM-XYLENOL ORANGE COMPLEX

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Summary—Hafnium reacts similarly to zirconium with Xylenol Orange. The hafnium-Xylenol Orange complex shows almost identical maximum absorption as the zirconium-Xylenol Orange complex at 535–540 mμ. The reagent gives a more sensitive reaction with hafnium than with zirconium. The molar absorption of the hafnium-Xylenol Orange complex was found to be 48,700 at 540 mμ. The formation constant of the hafnium complex was calculated as 3.2×10^6 in $0.3N$ perchloric acid. The conditions for using Xylenol Orange as a reagent for determining hafnium have been studied. Only zirconium or hafnium gives a purplish-red colour reaction with Xylenol Orange in $0.8N$ perchloric acid in the presence of hydroxylamine hydrochloride, which masks both iron and bismuth. Hafnium may be distinguished from zirconium since zirconium can be masked by hydrogen peroxide. Beryllium may be used as a demasking agent in the determination of zirconium or hafnium in the presence of fluoride.

INTRODUCTION

IN previous papers,[1,2] Xylenol Orange has been successfully used as a sensitive and selective reagent for zirconium. The zirconium-Xylenol Orange complex has been investigated spectrophotometically.[3] Recently this laboratory needed a sensitive method for determining small amounts of hafnium in high temperature alloys. This paper describes the results of a spectrophotometric study on the hafnium-Xylenol Orange complex and the application of this reagent to the determination of trace amounts of hafnium.

EXPERIMENTAL

Reagents

Xylenol Orange solution: 0.05% aqueous solution. This gave a concentration of $8 \times 10^{-4}M$. A $4 \times 10^{-5}M$ solution in $0.8N$ perchloric acid was prepared by appropriate dilution.

Standard hafnium solution: Accurately weighed, 0.1786 g of super-pure hafnium, prepared by the iodide process, was carefully dissolved in a platinum crucible by adding 1 ml of concentrated hydrochloric acid, 5 ml of water, and 2 to 3 drops of hydrofluoric acid. It was covered and gently warmed until all hafnium was in solution. The cover was rinsed with the minimum amount of water into the crucible. The content was evaporated to a few ml on a hot plate which was covered with asbestos. It was evaporated again, after addition of 4 ml of concentrated sulphuric acid, until it was fumed to a volume of approximately 1 to 2 ml. After cooling, 10 ml of water were carefully added, upon which hafnium was precipitated. The crucible was covered and heated until the precipitate was dissolved. After cooling, it was transferred into a 100-ml volumetric flask, rinsed, and made up to volume with $0.3N$ perchloric acid. This solution was presumably to be $0.0100M$. It was found to be 0.0099_4M by EDTA standardization. A solution containing 5 to 10 μg hafnium per ml was prepared by appropriate dilution.

EDTA standardization of hafnium solution: Attempted standardization of the hafnium solution by direct EDTA titration at pH 1 using Xylenol Orange as the indicator gave no sharp end-point whether the titration was carried out at room temperature or at 100°. Addition of a slight excess EDTA and back-titration with a standard copper nitrate solution at pH 3 to 5 using PAN as the indicator gave a gradually fading end-point as copper displaced hafnium. A good end-point with PAN at pH 6 was obtained by using a zinc solution as the back titrant. To 10 ml of approximately $0.01M$ hafnium solution in a porcelain dish or crucible were added 25 ml of $0.005M$ standard EDTA solution. After adjusting the pH to approximately 6 to 7, the solution was back-titrated with a standard $0.005M$ zinc solution using 4 drops of 0.1% PAN solution as the indicator. The end-point change was from yellow to faint pink. In the previous work zirconium was successfully standardized either by the direct EDTA titration at pH 1 using Xylenol Orange as the indicator at 80° or by the EDTA back-titration, with copper as the back titrant, at pH 3 using PAN as the indicator. The stability constants (log K) of the EDTA complexes of zirconium, hafnium, and copper have been reported to be 19.9, 19.2, and 18.8 respectively. From the reported values, it is interesting to note that hafnium behaved differently from zirconium in the EDTA titration under similar conditions.

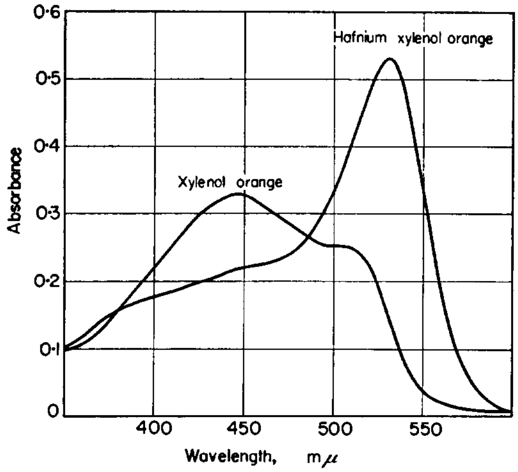


Fig. 1.—Spectra of Xylenol Orange and its hafnium complex.

The absorbance measurements were made with a Cary Spectrophotometer, Model 14, and a Beckman Spectrophotometer, Model DU. A Dyna Cath was used for the mercury cathode separation.

Spectra

Fig. 1 shows that the maximum absorption of the hafnium–Xylenol Orange complex is at 530 mμ in $0.3N$ perchloric acid. A wavelength of 535 mμ is suggested for the measurement since it offers maximum absorption when Xylenol Orange is used as the blank. This wavelength is almost identical with the maximum absorption wavelength of the zirconium–Xylenol Orange complex. It is also noted that in $0.8N$ perchloric acid medium the pure Xylenol Orange solution showed a small peak at 507 mμ and that the zirconium Xylenol Orange complex had a small peak at 340 mμ.

Calibration curve

To 25-ml volumetric flasks were added 0, 1, 2, 4, 6, 8, and 9 ml of $5 \times 10^{-5}M$ hafnium solution and 3 ml of $8 \times 10^{-4}M$ Xylenol Orange solution in $0.3N$ perchloric acid. The flasks were made to volume with $0.3N$ perchloric acid. The absorbance measurements were made at 540 mμ using a reagent blank. Beer's law was followed. For more than 80 μg hafnium in 25 ml the absorbance was slightly off the straight line. By increasing the amount of Xylenol Orange, Beer's law may follow for larger amounts of hafnium. Since the colour develops rapidly and is stable, no particular attention need be paid to the time of standing. Fig. 2 shows calibration curves with and without addition of hydrogen peroxide. Since hydrogen peroxide also diminishes the colour intensity of the hafnium complex, it would therefore be expected that the curve with addition of hydrogen peroxide would be different from that without hydrogen peroxide.

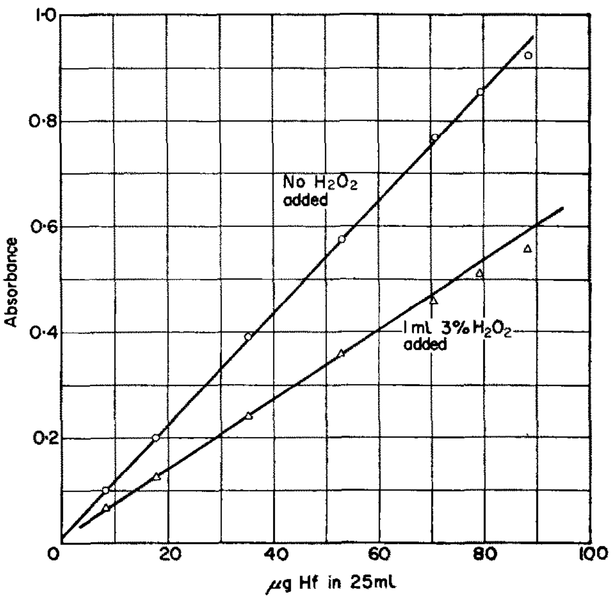


Fig. 2.—Calibration curve.

Specificity

In Part I of this series, the qualitative results of Xylenol Orange in 0.2N sulphuric acid medium indicate that niobium, tin,^{II} and molybdenum also gave light pink or yellow-orange colours as well as hafnium, zirconium, iron^{III}, and bismuth. It was also true that in 0.3N perchloric acid, in the presence of hydroxylamine hydrochloride and 0.8N perchloric acid, only zirconium and hafnium gave a purplish-red colour. Such a colour reaction seems to be highly selective for zirconium or hafnium under the conditions tested. Hydrogen peroxide formed a precipitate or complex with zirconium in 0.5N to 1.0N perchloric acid medium and had less effect on hafnium under similar conditions. Therefore, it was possible to distinguish the two metals. A simple test was conducted: One drop of 0.01M zirconium or hafnium solution (in 0.2N sulphuric acid) was mixed with 4 to 5 drops of 0.8N perchloric acid and one drop of 30% hydrogen peroxide. Zirconium did not give any significant colour change and hafnium gave a red to purplish colour upon addition of one drop of 0.05% Xylenol Orange solution.

Sensitivity

The Xylenol Orange in 0.8N perchloric acid gave a less sensitive colour reaction with hafnium than with zirconium. The molar absorption of the hafnium-Xylenol Orange complex was found to be 25,100 at 535 mμ as compared with 38,800 for that of the zirconium-Xylenol Orange complex at 540 mμ in 0.8N perchloric acid medium. However, in the optimum acid concentration of 0.3N perchloric acid, the molar absorption of the hafnium complex was found to be 48,700, which is much higher than that of the zirconium complex.[3]

Effect of anions

Anions such as EDTA, oxalate, phosphate, thiosulphate, fluoride, and sulphate inhibited the colour of the hafnium complex as well as that of the zirconium complex. As compared with the zirconium complex, the hafnium complex could tolerate less sulphate (see Fig. 3). Large amounts of thioglycollic acid also decreased the absorbance slightly. If 1 ml of 1% thioglycollic acid is used, the same amount of thioglycollic acid should be added in preparing the calibration curve. The interference of fluoride could be eliminated by beryllium. The results of determining zirconium or hafnium in the presence of fluoride are shown in Table I. For amounts of fluoride and zirconium or hafnium studied, the optimum amount of beryllium required is 1.5 millimoles. Apparently fluoride formed a

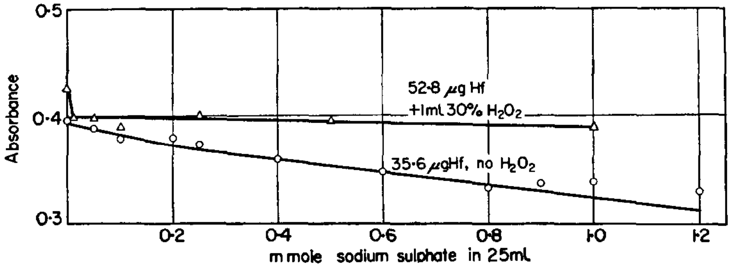


FIG. 3.—Effect of sulphate

TABLE I. DETERMINATION OF ZIRCONIUM AND HAFNIUM IN PRESENCE OF FLUORIDE BY USING BERYLLIUM AS DEMASKING AGENT

Zirconium

Metal present, *millimole* × 10^{-4}	Potassium fluoride added, *millimole* × 10^{-4}	Beryllium chloride added, *millimole* × 10^{-4}	Recovery, %
1.92	10	10	58.2
1.92	10	100	52.8
1.92	10	1,000	72.0
1.92	10	1,500	72.7
1.92	10	10,000	97.7
1.92	10	15,000	100.5
1.92	10	20,000	107.5
none	none	20,000	0.0

Hafnium

1.92	10	10	91.1
1.92	10	100	92.4
1.92	10	1,000	101.6
1.92	10	10,000	105.0
1.92	10	20,000	108.0
3.84	10	1,000	98.5
3.84	20	1,000	89.9
3.84	20	1,500	93.0
3.84	20	10,000	96.5
3.84	20	15,000	105.3
3.84	20	20,000	109.5
none	none	20,000	1.8

stronger complex with zirconium in 0.8*N* perchloric acid than with hafnium in 0.3*N* perchloric acid, and therefore more beryllium was needed to demask fluoride which masked the zirconium colour. Since large amounts of beryllium salt gave a slight blank in the 0.3*N* perchloric acid medium, a blank determination should be made. It was also noticed that large amounts of chloride gave slightly higher absorbance. Aluminium could also be used for demasking fluoride but proved less efficient than beryllium. Under the experimental conditions boric acid could not demask fluoride from the zirconium or hafnium complex.

Effect of acid concentration

The effect of acid concentrations on the colour development of the Xylenol Orange complexes of zirconium was different from that for hafnium, (see Fig. 4 and compare Fig. 3 in reference[1].) The optimum acid concentration for the hafnium complex was $0.3N$ of perchloric acid. Acid concentrations higher than $0.4N$ greatly diminished the colour intensity. The hafnium complex tolerated less, and required a narrower range of acid concentration. The acidity should be carefully controlled, since increase in acidity tended to shift the maximum absorption of the Xylenol Orange solution to a longer wavelength.

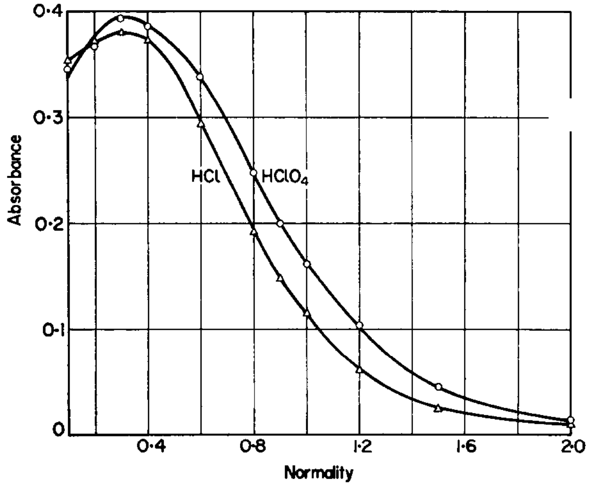


FIG. 4.—Effect of acid concentration.

An attempt was made to determine hafnium in the presence of zirconium through control of acidity. Both the hafnium and zirconium complexes absorb appreciably in $0.5N$ perchloric acid, while in $1.0N$ perchloric acid only the zirconium complex absorbs appreciably. Thus if the colour of a mixture of zirconium and hafnium solution is developed at $0.6N$ acidity and later at $1.0N$ acidity, the difference of the absorbance would represent the amount of hafnium. The actual results obtained were about 20–30% high, probably due to difficulty in control of acidity.

Effect of Xylenol Orange

In $0.3N$ perchloric acid, 3 ml of 0.05% Xylenol Orange are recommended for from 10 to 80 μg of hafnium. Too large amounts of the dye tended to decrease the absorbance. It is possible that in the presence of large excess of the dye, zirconium or hafnium may form a complex other than a 1 : 1 complex. The dye may be expected to vary in purity from lot to lot, and therefore a new calibration curve should be prepared for each fresh lot of dye used.

Formation constant

The mole ratio and the formation constant of the hafnium-Xylenol Orange complex has been determined spectrophotometrically by the same method as that previously reported for the zirconium-Xylenol Orange complex. It is evident that hafnium like zirconium also formed a 1 : 1 complex with Xylenol Orange. The formation constant (K_f) for the hafnium-Xylenol Orange complex in $0.3N$ perchloric acid was calculated from Job's curves, shown in Fig. 5, as 3.2×10^6. It is slightly lower than that of the zirconium-Xylenol Orange complex[3] ($K_f = 4.0 \times 10^7$). It seems to agree with the general trend that hafnium forms a slightly less stable complex than zirconium.

Masking effect of hydrogen peroxide

It was reported previously from qualitative tests that hydrogen peroxide could easily mask the zirconium–Xylenol Orange complex in 0.2*N* sulphuric acid medium, but not the hafnium–Xylenol Orange complex. An extensive investigation was made to see if this masking action could be utilized in the determination of hafnium in the presence of zirconium.

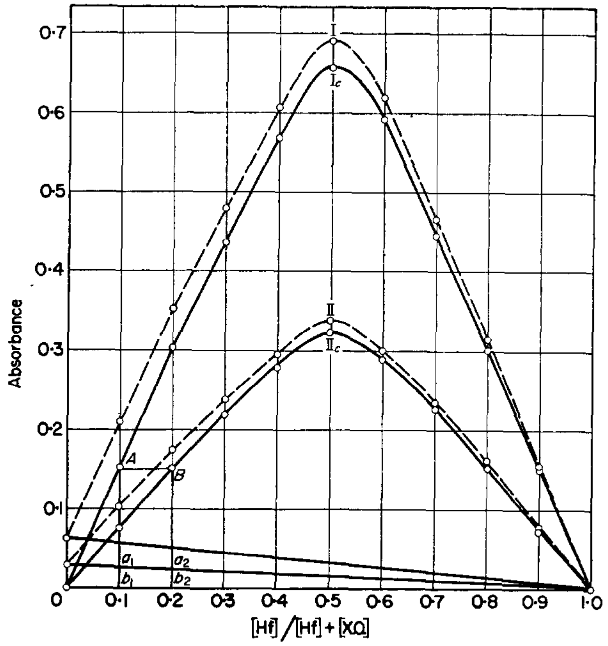


FIG. 5.—Job's curves.
I_c and II_c are corrected curves of I and II respectively.

Effect of hydrogen peroxide on absorbance of pure hafnium solutions: Addition of from 1–4 ml of 15% hydrogen peroxide per 25 ml, before addition of Xylenol Orange to a hafnium solution gave a lower absorbance than that with no hydrogen peroxide added. The absorbance increased gradually with time of standing, reaching a maximum value between 1.5 and 2.0 hours (Fig. 6). Heating hastened the colour development but the colour faded rapidly. A calibration curve prepared from 10 to 80 μg hafnium with 2 ml 15% hydrogen peroxide and 1.5 to 2.0 hours standing also followed Beer's law. But the slope of the curve was lower than that prepared without hydrogen peroxide. When hydrogen peroxide was added after the colour had been developed, the colour decreased with time and merged after about 3 hours with the curve prepared by addition of hydrogen peroxide before the colour had been developed. During the first 10 to 15 minutes, however, the absorbance was essentially constant, thus offering a possibility of measuring the absorbance, which was only slightly lower than that without hydrogen peroxide at its maximum. A calibration curve prepared under this condition also followed Beer's law. Hydrogen peroxide inhibited almost completely the colour development of the zirconium–Xylenol Orange complex regardless of whether the hydrogen peroxide was added before or after the colour development. The absorbance varied only slightly with lapse of time.

Effect of hydrogen peroxide on recovery of hafnium in the presence of zirconium: From the results shown in Fig. 6, it can readily be assumed that the determination of hafnium in the presence of zirconium, or *vice versa*, would be possible. However, the experimental results were not so satisfactory as expected. Table II indicates that the presence of 17.5 μg of zirconium does not show any significant effect on the absorbance of the hafnium–Xylenol Orange complex, but that larger amounts of zirconium decrease the absorbance of the hafnium complex. Various mixtures of hafnium and

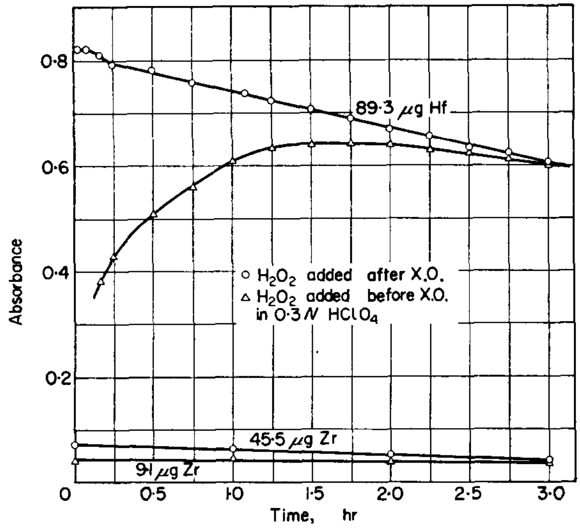
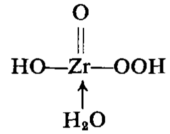


FIG. 6.—Effect of standing.

zirconium were analyzed for hafnium recovery. The results in Table II show that the smallest amount of hafnium (17.5 μg) gave the best recoveries with both curves. By using the curve with 52.5 μg of zirconium added, the average recovery of known amounts of hafnium was approximately ±5%. The present results suggest a new approach to the study of the selective determination of zirconium in the presence of hafnium and *vice versa* through the use of other complexing agents in a manner analogous to the use of Xylenol Orange and hydrogen peroxide.

The masking action of hydrogen peroxide on the zirconium Xylenol Orange complex is probably based on the formation of a relatively stable zirconyl peroxide complex:



$$\begin{array}{c} O \\ \| \\ HO\text{—}Zr\text{—}OOH \\ \uparrow \\ H_2O \end{array}$$

Though the formation constant of zirconyl peroxide is not known, it is presumably not greatly different from that of the zirconium–Xylenol Orange complex because the change in concentration of hydrogen peroxide or Xylenol Orange would shift the following equilibrium,

$$\text{Zr-Xylenol Orange} + H_2O_2 \rightleftharpoons \text{zirconyl peroxide} + \text{Xylenol Orange.}$$

It is rather difficult to understand the fact that the presence of relatively large amounts of zirconium tended to decrease the recovery of hafnium. Further study is needed to ascertain if the masking action of hydrogen peroxide can be applied to the quantitative determination of hafnium in the presence of wide range of zirconium. However, from the present results, it may be applied to the estimation of purity of hafnium metal or its salt when pure hafnium metal is available as a standard.

Effect of sulphate in presence of hydrogen peroxide: When hydrogen peroxide is present, 0.01 to 10 mmole of sulphate gave a constant absorbance for the hafnium–Xylenol Orange complex (Fig. 3). This is different behaviour from that caused by the addition of sulphate to the sample in the absence of peroxide, where the absorbance decreased rapidly. Addition of 0.1 mmole of sulphate gave slightly higher absorbance of the hafnium–Xylenol Orange complex in the presence of peroxide than in the absence of peroxide.

Effect of other compounds in presence of hydrogen peroxide: For the solution containing 68.6 μg hafnium, 35.0 μg zirconium and 1 ml of 30% hydrogen peroxide, approximately 75% to 77%

TABLE II. DETERMINATION OF HAFNIUM IN HAFNIUM AND ZIRCONIUM MIXTURE USING HYDROGEN PEROXIDE AS MASKING AGENT

Mixture, μg		Hafnium found			
		Reference: 17.5 μg Zr		Reference: 52.5 μg Zr	
Hf	Zr	μg	% Recovery	μg	% Recovery
17.15	17.5	18.5	107.0	17.15	100.0
17.15	35.0	19.5	112.5	16.0	96.2
17.15	52.5	18.0	104.2	17.3	101.5
17.15	105.0	16.7	96.5	15.8	94.0
34.3	17.5	39.5	116.0	41.0	117.0
34.3	35.0	38.5	113.2	38.1	110.0
34.3	52.5	34.6	101.4	36.3	105.0
34.3	105.0	28.8	84.7	26.8	80.9
68.6	17.5	73.2	106.4	92.0	131.7
68.6	35.0	67.8	98.6	73.5	105.7
68.6	52.5	62.5	91.0	76.0	108.7
68.6	105.0	50.7	73.3	4815	71.5

recoveries were obtained by addition of 1 ml of 1% gelatine, glycerine, polyvinyl alcohol, sucrose, mannitol, resorcinol, pyrocatechol, pyragallol, *tris*(hydroxymethyl)-aminomethane, acetic acid, or formic acid. By adding 1 ml of 1% ethyleneglycol-bis-(β-aminoethylether) N:N′-tetra-acetic acid or oxalic acid, a recovery of 66.5% or 3.6% was obtained. By addition of 2 to 3 ml of 1% lactic acid, a recovery of 93.5% was obtained.

DETERMINATION OF THE HAFNIUM IN HIGH-TEMPERATURE ALLOY

The determination of hafnium in the presence of zirconium cannot be relied upon at the present time. In the absence of zirconium, however, a method to determine hafnium in the concentration range of 0.01–0.5% has been developed for Udimet 500, a nickel-base alloy containing about 3% Al, 3% Ti, 3–5% Mo, 18–20% Cr, 16–20% Co, 1.0% Fe, and small amounts of C, S, B, Si, Mn and Cu.

Procedure

Weigh samples (see Table III) into 400-ml beakers. Weigh one blank for each different weight of sample taken. (The first ingot has no hafnium addition).

TABLE III

Hf range, %	0.01	0.05	0.1–0.5
Sample needed, *g*	1.0	0.5	0.1

A suitable sample (from 0.1 to 1.0 g) was dissolved in 15 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid on a hot plate. The solution was boiled after cautious addition of 2 g of ammonium persulphate in order to destroy carbides. Ten ml of 1 : 1 sulphuric acid (20 ml for a 1-g sample) were added and evaporated to strong fumes. The evaporation should be carried out slowly, since salts will precipitate and cause bumping if heated strongly. After cooling, about 75 ml of water were added and heated with stirring to dissolve salts. It was transferred to a mercury cathode for electrolysis at 15–20 amperes to a negative spot test for chromium. (Use a 200-ml volume for samples with 20 ml of 1:1 sulphuric acid, and 100 ml for all others). It was transferred to a hot plate, and boiled until all the yellow colour, if any, was discharged. After cooling, approximately 40 mg of titanium (titanium sulphate solution) were added to all samples and blanks weighing less than 0.5 g. It was adjusted to pH 8 to 9 by adding 1 : 1 ammonium hydroxide slowly, with stirring. It was gently boiled on a hot plate and the hydroxides allowed to settle to the bottom. The precipitate was filtered through a fast 11-cm paper (Whatman no. 41-H or S & S no. 589-1H), washed three times with hot 1% ammonium nitrate, and dissolved into a 50-ml beaker with 25 ml of hot 0.8*N* perchloric acid. The filtrate was poured back through the paper into a 100-ml volumetric flask. The beaker and paper were washed with 0.8*N* perchloric acid to a total volume of 40 ml in the flask, making to volume with water. An aliquot of 20 ml was pipetted into a 25-ml volumetric flask. (Use a 10-ml aliquot if the hafnium is about 0.5%). To it were added one ml of 1% sodium chloride in 1% thioglycollic acid and 3 ml of 0.05% Xylenol Orange, and the solution was made to volume with water. (Made to volume with 0.3*N* perchloric acid if a 10-ml aliquot was used). The absorbance was measured at 535 mμ against a dye blank. Determine the amount of hafnium present from a calibration curve prepared under the similar conditions.

DISCUSSION

Since hafnium is a carbide-forming element, the destruction of all carbides in the solution procedure is imperative. Sodium sulphite and hydrogen peroxide were also tried as oxidizers, but the oxidation by these means was sometimes incomplete, thus necessitating a second treatment.

Electrolysis on the mercury cathode will remove iron and molybdenum, which interfere with the colour development, as well as nickel, cobalt, and chromium, which might disturb the absorbance measurement because of their intense colours. Sulphuric acid is preferable to perchloric acid as use of the latter greatly increases the time required for the complete deposition of chromium and molybdenum by mercury cathode.

Titanium peroxide reacted with ammonia to yield a greenish-black precipitate that was not easily soluble in 0.8*N* perchloric acid. This difficulty was eliminated by boiling to destroy the peroxy complex before the ammonia precipitation was made.

Hafnium in trace amounts will not be quantitatively precipitated from ammonia solution, and a suitable co-precipitant should be used. Fortunately, Udimet 500 contains about 3% each of aluminium and titanium, which serve as carriers. For samples weighing less than 0.5 g, addition of extra titanium is necessary to precipitate all the hafnium.

TABLE IV. RECOVERY OF HAFNIUM IN NICKEL BASE ALLOY

% Hf Added	Sample, *g*	Aliquot used	Hf Taken, μg	Hf Found, μg	% Hf Recovered
0.01	1.0	20/100	106	102.5	96.7
0.01	1.0	20/100	106	117.5	110.8
0.05	0.5	20/100	265	245.0	92.5
0.10	0.1	20/100	106	102.5	96.7

Since sulphate interferes with the hafnium-Xylenol Orange colour development, this ammonia precipitation step would also serve the purpose of separation of sulphate. The ammonium nitrate serves to wash any excess sulphate out of the precipitate, and to prevent peptization.

Samples of Udimet 500, Heat no. 2-717-1 with addition of known amounts of hafnium were analyzed. The results are shown in Table IV. Reasonably good recoveries were obtained for the alloy containing 0.01 to 0.1 % hafnium. Further study is needed of the analysis of samples containing over 0.25 % hafnium because low recoveries have resulted by the method described here.

Acknowledgment—The author is indebted to Fran Warmuth for assistance during this study.

Zusammenfassung—Hafnium reagient ähnlich wie Zirkon mit Xylenol Orange. Der Hafnium Xylenol Orange Komplex weist fast übereinstimmende maximale Absorption mit dem Zirkon Xylenol Orange Komplex von 535 bis 540 mμ auf. Das Reagens zeigt eine empfindlichere Reaktion mit Hafnium als mit Zirkon. Die molare Absorption des Hafnium Xylenol Orange Komplexes wurde zu 48,700 bei 540 mμ bestimmt. Die Bildungskonstante des Hafnium Komplexes wurde auf $3,2 \times 10^6$ in 0,3*N* Perchlorsäure berechnet. Die Anwendungsbedingungen für Xylenol Orange als Reagens für die Hafniumbestimmung wurden untersucht. Nur Zirconium oder Hafnium geben eine purpur-rote Farbreaktion mit Xylenol Orange in 0,8*N* Perchlorsäure; dies bei Gegenwart von salzsäurem Hydroxylamin, welches Eisen sowie auch Wismuth abschirmt. Hafnium lässt sich von Zirkon leicht unterscheiden nachdem Zirkon durch Wasserstoffsuperoxid abgeschirmt werden kann. Beryllium kann als Demaskierungsreagens zur Bestimmung von Zirkon oder Hafnium in der Gegenwart von Fluoriden verwendet werden.

Résumé—Le hafnium réagit comme le zirconium avec le Xylénol Orange. Le complexe hafnium–Xylénol Orange présente un maximum d'absorption presque identique à celui du complexe zirconium-Xylénol Orange, vers 535–540 mμ. L'indicateur réagit avec plus de sensibilité avec le hafnium qu' avec le zirconium. On a trouvé l'absorption molaire du complexe hafnium–Xylénol Orange égale à 48,700 à 540 mμ. La constante de formation du complexe de hafnium a été calculée égale à $3,2 \times 10^6$ dàns l'acide perchlorique à 0,3*N*. On a étudié les conditions d'utilisation du Xylénol Orange comme indicateur pour l'analyse du hafnium. Seuls le zirconium et le hafnium donnent une couleur rouge pourpre par la réaction avec le Xylénol Orange dans l'acide perchlorique à 0,8*N*, en présence d'hydroxylamine chlorhydrique qui masque le fer et le bismuth. On peut distinguer le hafnium du zirconium, car le zirconium peut être masqué par l'eau oxygénée. On peut utiliser le beryllium comme agent de démasquage pour l'analyse du zirconium ou du hafnium, en présence de fluorures.

REFERENCES

[1] K. L. Cheng, *Talanta*, 1959, **2**, 61.
[2] *Idem*, *ibid.*, 1959, **2**, 186.
[3] *Idem*, *ibid.*, 1959, **2**, 266.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—I

THE BLOCKING OF INDICATORS AND ITS ELIMINATION

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Summary—The formation with metallochromic indicators of complexes inert to substitution makes certain complexometric titrations impossible. The cations of bivalent copper, cobalt and nickel, in addition to others, show a tendency to form such complexes with for example Eriochrome Black T, Xylenol Orange, Methylthymol Blue. It has been proved that small quantities of *o*-phenanthroline entirely suppress this phenomenon, which is undesirable in complexometry. The presence of *o*-phenanthroline makes it possible reliably to determine copper as well as cobalt complexometrically against Xylenol Orange even at room temperature. The influence of *o*-phenanthroline is explained by the formation of substitution-labile complexes with copper or cobalt, and by the reaction mechanism at the point of equivalence. The influence of other materials on the colour change of the indicator in these titrations is also discussed.

VISUAL titration even in simple complexometric titrations is unfavourably influenced by a number of factors; for example, the high concentration of neutral salts (high ion strength of the solution), the development of intensely coloured complexes with the titrating agent during the titration (complexes of EDTA with Fe, Cu, Cr), or their slow formation at room temperature (Al–EDTA complex). The undesirable influence of neutral salts, as well as the original colour of the solution can to a considerable degree be decreased by dilution of the titrated solution; and the rapidity of the complex formation can be enhanced by increasing the temperature.

One of the most notable interferences in complexometry arises from the formation with the indicators of so-called substitution-stable complexes. In particular, cations with incomplete inner orbits as, for example, Fe^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, tend to form complexes stable with respect to substitution. Such complexes prevent complexometric determination of these elements. Traces of them in the solution also may make it impossible to carry out entirely independent determinations or may have a very unfavourable influence on the colour change of the indicator. It is known, for example, that traces of copper or aluminium have an unfavourable influence on the complexometric determination of magnesium with Eriochrome Black T. Such phenomena often lead to an erroneous assessment of the suitability of a complexometric method.

Hitherto no effective remedy has been found against this undesirable phenomenon. For certain elements, of course, we can choose other indicators which do not form substitution-stable complexes. But such determinations can usually be carried out only in "pure solutions"; as, for example, the determination of copper or nickel with Murexide. In a number of cases we are dependent on the removal of these interfering elements by precipitation or masking in order to be able to determine other elements. (Screening of iron by triethanolamine, of copper by potassium cyanide, etc.) In fact, however, there exists a completely universal method which instead of preventing the formation of these substitution-stable complexes with the indicators, entirely suppresses their unfavourable influence. In this connection the following considerations are of importance:

The character of complexometric titration as an analytical method presupposes rapid reaction, at the most over several seconds. This applies to the principal complexometric reaction:

$$\text{Me} + \text{Y} = \text{MeY} \tag{1}$$

and also to the colour-indication replacement reaction:

$$\text{MeI} + \text{Y} = \text{MeY} + \text{I} \tag{2}$$

(The ionic charges are omitted here for the sake of simplicity).

Indicators forming complexes which are labile with respect to substitution are reliably applicable in most complexometric titrations if they comply also with the other specific requirements (of sensitivity, etc.) Indicators forming complexes which are stable with respect to substitution are unsatisfactory principally on kinetic grounds (equation 2). In principle we can avoid this harmful influence if we substitute for the indication reaction (2) a different mechanism. Recently we described such a possibility in the complexometric determination of iron by Xylenol Orange.[1] In this the slow replacement-reaction of type (2) was substituted, on addition of ferrous salt, by the rapid redox reaction. A more universal method was found during investigation of certain screening agents. It consists in introducing a further complex-forming agent Z in a somewhat higher concentration than that of the indicator. This agent must have the following properties:

(a) Its reaction with the indicator complex

$$\text{MeI} + \text{Z} = \text{MeZ} + \text{I} \tag{3}$$

must be rapid. That is possible especially if the auxiliary complex-forming agent Z has an electronic structure of different type from titrant used.

(b) The stability of the complex MeZ must, under the titration conditions, be approximately the same as the stability of the complex MeY.

If these conditions are fulfilled, the following reaction changes take place during the titration: at the beginning of the titration the solution contains free ions Me, the complex with indicator MeI, and complex MeZ. At first the concentration of Me decreases during the titration according to equation (1); then there follows the reaction:

$$\text{MeZ} + \text{Y} = \text{MeY} + \text{Z} \tag{4}$$

and the liberated complex-forming agent Z then immediately reacts with the indicator complex MeI according to equation (3).

An example of this mechanism is the direct complexometric determination of copper against Xylenol Orange in the presence of a small amount of *o*-phenanthroline as an auxiliary complex-forming agent. Details are given in the Experimental Part.

EXPERIMENTAL

Preparation of standard solutions

The solution of 0.05 molar EDTA and the solutions of 0.05 molar $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Co(NO_3)_2$ were prepared by the usual method. Their concentration (titres) were determined complexometrically.

The solution of 0.001 molar *o*-phenanthroline was prepared by dissolution of the required quantity in re-distilled water. The solution of 0.01 molar *o*-phenanthroline was prepared in the same manner with moderate heat. The 0.05 molar solution was prepared by adding a small quantity of nitric acid.

Xylenol Orange, 0.2% aqueous solution.

Determination of copper

Since *o*-phenanthroline forms a quite stable complex with copper, it was necessary to ascertain the minimum amount which is necessary to accelerate the reaction at the equivalence point. For 100–300 ml of solution 0.5 ml of 0.001 molar solution gave a satisfactorily rapid and sharp colour change of Xylenol Orange in the titration with EDTA. The colour change depends on the concentration of copper as well as on that of the indicator. At low concentrations of copper (several mg) the colour change is from red-violet to yellow, and then to yellow-green. If the content of copper is 10 to 20 mg, the colour before the end-point of the titration is blue to violet and, on addition of 1 to 2 drops of EDTA, it changes to green-yellow. By the addition of 1 ml of 0.001 molar *o*-phenanthroline to the solution being titrated, the theoretical error is 0.003–0.05 ml of EDTA. This is negligible so that it is not necessary to prepare a solution of Cu-phenanthroline (Cu : Phen = 1 : 3) which has the same function as *o*-phenanthroline alone.

Procedure. To a slightly acid solution with at most 30 mg content of copper, add several drops of Xylenol Orange solution, and solid hexamethylenetetramine until a red or red-violet colour develops. Dilute with water to 200–250 ml, add 0.5 ml of 0.001 molar *o*-phenanthroline, and titrate with 0.05 molar EDTA solution to a yellow-green colour.

Determination of copper and lead

The procedure is the same as described above. Ascertain the total content of copper and lead by titration. Add excess of 0.1 molar phenanthroline and after three minutes titrate the liberated EDTA[2] with the solution of 0.05 molar $Pb(NO_3)_2$.

Determination of cobalt

The procedure is the same as that described for the determination of copper. A very sharp colour change is obtained if the titration is carried out at 50°.

The results of the determinations using the procedures here described agreed with other complexometric methods and therefore it is not necessary to give them in tabular form.

DISCUSSION

This example of direct complexometric determination of copper against Xylenol Orange, in the presence of small concentrations of *o*-phenanthroline as an auxiliary complex-forming agent, illustrates how it is possible to eliminate the influence of the formation of substitution—inert indicator complexes. In this case it was proved that the cation $Cu(Phen)_3^{2+}$, bonded in a complex, participates in the indication mechanism at the equivalence point. This cation develops just before the end-point of the titration according to the equation:

$$3Cu(Phen)^{2+} + 2H_2Y^{2-} = 2CuY^{2-} + Cu(Phen)_3^{2+} + 4H^+$$

and is sufficiently labile to substitution in practice to react immediately with EDTA.

Should the principle described in this paper by the equations (3) and (4) be of general validity, we may expect that there exist other compounds whose structure will permit a similar "indicator effect" with other cations with incomplete inner orbits. Further experiments have indicated that this does not only concern compounds which form insoluble complexes. Thus, for example, sodium diethyldithiocarbaminate or cupferron[3] have a similar, if not so marked, influence in the determination of copper here described. In the titration of cobalt against Xylenol Orange the addition of acetylacetone showed a favourable influence. In a similar titration of nickel this effect has not so far been observed although a range of complex-forming substances have been tested. This may be explained by the especially high inactivity of the indicator complex of nickel.

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Zusammenfassung—Die Bildung äusserst reaktionsträger Metallkomplexe mancher metallochromer Indicatoren macht einige komplexometrische Titrationen unmöglich. Von den in Frage kommenden Kationen zeigen die zweiwertigen Ionen von Kupfer, Cobalt und Nickel besonders starke Tendenzen zur Blockierung von z.B. Eriochromschwarz T, Xylenolorange und Methylthymolblau. Es wurde gefunden, dass die Zugabe kleiner Mengen von *o*-Phenanthrolin das störende Blockieren vollständig unterdrückt. In Anwesenheit kleiner Mengen von *o*-Phenanthrolin wird die Titration von Kupfer (II) und Cobalt (II) mit EDTA unter Verwendung von Xylenolorange als Indicator selbst bei Zimmertemperatur möglich. Als Erklärung für die Wirksamkeit des Phenanthrolins wird die Bildung hochaktiver "Hilfskomplexe" gegeben, die (als Zwischenprodukte wirkend) auf die Endpunkstreaktion einen beschleunigenden Einfluss haben. Der Einfluss auch anderer Substanzen auf den Farbwechsel der Indicatoren in derartigen Titrationen wird diskutiert.

Résumé—La formation de quelques complexes de substitution inertes avec des indicateurs colorés de cations métalliques rend impossible un certain nombre de titrages complexométriques. Entre autres cations, le cuivre divalent, le cobalt, et le nickel ont tendance à former de tels complexes avec, par exemple, le noir ériochrome T l'orangé de xylénol, le bleu de méthylthymol. On a montré que de petites quantités d'*o*-phénanthroline suppriment entièrement ce phénomène qui est indésirable en complexométrie. La présence d'*o*-phenanthroline permet de déterminer en toute sécurité, à la fois le cuivre et le cobalt avec l'orangé de xylénol, même à la température ambiante. L'influence de l'*o*-phenanthroline s'explique par la formation de complexes de substitution labiles avec le cuivre ou le cobalt et par le mécanisme de la réaction au point équivalent. L'influence d'autres substances sur le changement de couleur de l'indicateur dans ces titrages est aussi discutée.

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2-MERCAPTOACETIC (THIOGLYCOLLIC) ACID AS A REAGENT FOR ZIRCONIUM

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Summary—Thioglycollic acid has been shown to be a suitable reagent for the quantitative precipitation of zirconium at a pH of about 4.5. A basic zirconyl thioglycollate is formed and therefore the analysis is completed by weighing the zirconium oxide. Interference due to several metal ions is discussed.

RECENTLY we reported the use of thiodiglycollic acid, $S(CH_2COOH)_2$, as a suitable reagent for zirconium.[1] Preliminary experiments showed that under suitable conditions zirconium can be quantitatively precipitated by 2-mercaptoacetic (or thioglycollic) acid. While this reagent is a well known complexing agent,[2,3] no information seems to exist on its use as a precipitant for zirconium. The present communication describes optimum conditions for the determination of zirconium by thioglycollic acid. Interference due to other metal ions is also discussed.

EXPERIMENTAL

Reagents

Reagent grade zirconyl nitrate was used to prepare its solution in water. The acidity with respect to nitric acid in it was maintained at 0.2*N* and the zirconium content was determined by the *m*-nitrobenzoic acid method.[4] Evans' thioglycollic acid, $HS—CH_2COOH$, of 98–99% assay was used without further purification as a 5% aqueous solution.

Procedure

To an aliquot portion of zirconyl nitrate solution diluted to about 150 ml, 10–15 ml of 5% thioglycollic acid and methyl orange indicator were added. A 10% solution of ammonium acetate was now added so as to raise the pH of the system to about 4.5. The system was heated on a hot plate at 85–90° for nearly 15 minutes and the white precipitate filtered after an hour. It was washed with a 5% ammonium nitrate solution, dried, ignited and eventually weighed as ZrO_2.

RESULTS AND DISCUSSION

Results entered in Table I show a fair agreement between the experimental values and those expected on the basis of the standard *m*-nitrobenzoic acid method.

Under the given experimental conditions, alkaline earth metal ions, manganese^{II}, magnesium, beryllium, aluminium, cerium^{III}, lanthanons, chromium^{III}, and iron^{III} do not interfere in the present method of estimating zirconium. Under the same experimental conditions, vanadyl and uranyl ions give with thioglycollic acid blue and orange colours respectively without, however, affecting the accuracy of the results. Tin^{II}, mercury^{II}, zinc, cadmium, titanium^{IV} and thorium give white precipitates, copper^{II} a violet precipitate, lead^{II} a yellow precipitate and nickel^{II} a dirty coloured precipitate. Although cobalt^{II} and bismuth^{III} produce only brown colours with thioglycollic acid, these, in presence of zirconium, are co-precipitated

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appreciably. The above interfering metal ions should therefore be either absent or previously removed.

TABLE I. DETERMINATION OF ZIRCONIUM BY THIOGLYCOLLIC ACID

ZrO_2, g		Difference
By *m*-nitrobenzoic acid	By thioglycollic acid	
0.01770	0.01776	0.00006
0.04425	0.04420	0.00005
0.08850	0.08860	0.0001
0.1327	0.1328	0.0001
0.1770	0.1772	0.0002
0.2212	0.2213	0.0001

The composition of the zirconium complex varies somewhat, but corresponds approximately to a basic salt with the formula

$$ZrO(OH){\cdot}CH_2SH{\cdot}COO.$$

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Zusammenfassung—Thioglykolsaure wurde als geeignetes Fällungsmittel zur quantitativen Niederschlagung von Zirkonium bei pH ca 4.5 gefunden. Ein basisches Zirkonylthioglykolat wird gebildet und daher die Analyse durch Verglühen zu Zirkoniumoxyd abgeschlossen. Störungen durch verschiedene Metallionen werden diskutiert.

Résumé—Les auteurs ont montré que l'acide thioglycollique est un réactif converable pour la précipitation quantitative du zirconium à un pH d'environ 4,5. Il se forme un thioglycollate de zirconyl basique, on complète donc l'analyse par pesée de l'oxyde de zirconium. L'interférence due à différents ions métalliques est discutée.

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ÜBER DAS VERHALTEN VON ISOLIERTEN EINSCHLÜSSEN AUS EISENWERKSTOFFEN BEI HOHEN TEMPERATUREN

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Allgemeines über Probekörper und Schmelzen—Erhitzungsverhalten von Eisen-Mangan-Silikatschlacken in Luft und Argon—Isolate aus Transformatorenblechen und unberuhigten Weicheisenschmelzen.

Zusammenfassung—Es wird an einigen Beispielen gezeigt, dass ein Erhitzungsmikroskop sehr gut zum Studium des Schmelzverhaltens isolierter oxydierter Gefügebestandteile herangezogen werden kann.

WIE in der organischen und pharmazeutischen Industrie die Schmelzpunktsbestimmung sowie andere thermoanalytische Untersuchungen neben der chemischen Analyse ein wesentliches Kriterium der Reinheitsprüfung und Identifizierung bilden, so sollte auch bei der metallkundlichen Analyse[1] neben den bisherigen Analysendaten als ein weiteres auch das Verhalten der isolierten Körper bei hohen Temperaturen näher untersucht und beschrieben werden. Weder die chemische noch die Strukturanalyse erlauben sichere Rückschlüsse auf das Schmelzverhalten eines bestimmten isolierten Oxydkörpers. Aus der Übertragung der Analysenergebnisse in bekannte Drei- und Vielstoffsysteme kann man zwar mit einiger Sicherheit auf das Verhalten während des Schmelzens schliessen. Die Untersuchung isolierte Körper in inerter, oxydierender oder reduzierender Gasatmosphäre kann hier Fortschritte bringen.

Im Schrifttum sind speziell für die Untersuchung von Kohle- und Koksaschen zahlreiche Verfahren vorgeschlagen und in Verwendung.[2] Hier soll als erste Stufe des Studiums isolierter Produkte bei hohen Temperaturen die Verwendung eines Erhitzungsmikroskops betrachtet werden. Vorweggenommen sei aber, dass die hier skizzierte Arbeitsmethode noch nicht die Endlösung für metallkundliche Zwecke darstellt, dass wir aber an einer solchen arbeiten.

Um das Verhalten der Probekörper bei hohen Temperaturen soweit als möglich ausschöpfen zu können, kommt nur ein Verfahren in Frage, das neben einer subjektiven auch eine objektive registrierende Beobachtung und dies sowohl im Auf- als auch Durchlicht und im polarisierten Licht gestattet.

Der Probekörper

Wie die Untersuchungen von W. Radmacher[2] gezeigt haben, kommt der Form des Probekörpers eine besondere Bedeutung zu. Leider sind wir in den meisten Fällen nicht in der Lage, bestimmte, einheitliche Probekörper herzustellen, sondern müssen uns mit den aus der verfügbaren Menge herstellbaren begnügen. Oft aber interessiert gerade ein besonders ausgebildetes (verformtes) Teilchen.[3]

Radmacher hat vier verschiedene Probekörper—zylindrische, würfelförmige sowie symmetrische und unsymmetrische, pyramidenförmige—wie sie nach den

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Normverfahren zur Asche-Schmelzpunktsbestimmung gefordert werden, untersucht und gefunden, dass, je grösser der Probekörper ist, der Temperaturanstieg um so geringer sein muss. Ein Segerkegel z.B. hatte schon weitgehend seine Form verändert, während an anderen, aus dem gleichen Material mit der gleichen Menge hergestellten zylindrischen Probekörpern noch keine merkliche Änderung festzustellen war. Er kommt zu dem Schluss, dass der zweckmässigste Probekörper für die Aschenanalyse ein Zylinder von 7 mm ϕ und 7 mm Höhe ist oder ein Würfel von 7 mm Kantenlänge. Für derartige Körper ist ein durchschnittlicher Materialbedarf von 300 mg angegeben, eine Menge, die bei der metallkundlichen Analyse nur selten anfällt. Wenn 10 mg Substanz für diesen Zweck zur Verfügung stehen, so wird mit Hilfe eines kleinen Gesenkes ein zylindrischer Pressling (etwa 10–15 kg/mm^2 Pressdruck) hergestellt, der 1 mm ϕ und 1–3 mm Höhe aufweist. Die zylindrische Probenform ist der würfelförmigen vorzuziehen, da keine Gefahr der verkanteten Aufstellung besteht und evtl. Flächenmessungen (Volummessungen) leichter durchgeführt werden können. Jedoch kommt dieser Art der Probekörperherstellung zunächst noch geringe Bedeutung zu, da wir selten über soviel Material verfügen und da oft das Verhalten eines einzelnen, ganz bestimmten Körpers interessant ist.

Das *Erhitzungsmikroskop* sowie dessen Bedienung ist in seinen Einzelheiten ausführlich beschrieben worden,[2] so dass sich hier ein weiteres Eingehen darauf erübrigt, da deine wesentlichen Änderungen vorgenommen werden.

Wichtiger ist nach den bisherigen Untersuchungen, einiges zur *Begriffsbestimmung* während des Erhitzens zu sagen, um zum Verständnis der charakteristischen Temperaturpunkte oder -bereiche, die ja auch für den physikalischen Zustand der Probe verantwortlich sind, beizutragen. Es sollen hier in Anlehnung an Radmacher folgende Begriffe gelten:

(1) Der Formänderungspunkt (-bereich) ist jene Temperatur, bei der das erste merkbare Anzeichen einer Formänderung, Abrundung der Kanten, Aufblähen, Veränderung der Oberfläche, Änderung der Farbe oder Durchsichtigkeit usw. eintritt.

(2) Erweichungs- bzw. Sinterungspunkt (-bereich) ist der Punkt (Bereich), an dem der Probekörper *sichtlich* seine Gestalt verliert.

(3) Schmelzpunkt bzw. -bereich ist die Temperatur, bei der die Probe vollständig ihre Form verliert und zu einer mehr oder minder kugeligen Form (Halbkugel, Kugelsegment (s. Bild 3), stehendem oder hängendem Tropfen (s. Bild 5) zusammengeflossen ist.

(4) Fliesspunkt bzw. -bereich ist die Temperatur, bei der sich der Probekörper—natürlich abhängig von Form und Natur seiner Unterlage—gleichmässig ausbreitet, s. Bild 1 rechts oben (Fliesskegel), Bild 3 rechts oben, Bild 5 oben, Bild 6 rechts unten.

Im übrigen sei aber hier darauf hingewiesen, dass die Frage der Schmelzdefinitionen sicher noch einer Diskussion unterworfen sein wird, denn grundsätzlich gibt es bei homogenen Körpern nur einen Punkt, den Schmelzpunkt, und der ist abhängig von der Einheitlichkeit und Reinheit der Verbindung. Besser erfassbar erscheint dieser Punkt dann, wenn z.B. ein anisotroper Körper vollkommen isotrop geworden ist. Wann und ob dies bei den bei der metallkundlichen Analyse anfallenden Proben der Fall bzw. erfassbar ist, bedarf noch der weiteren Untersuchung, ebenso wie die Gleichsetzung des Schmelzverhaltens eines Körpers im Erhitzungsmikroskop mit seinem Verhalten im flüssigen bzw. heissen Metallbad.

Jedoch lassen die Ergebnisse zusammen mit anderen Daten—wie an einzelnen Beispielen gezeigt werden soll, trotzdem Aussagen über wahrscheinlichen Flüssigkeits- und Verformbarkeitsgrad zu. An einigen Beispielen soll über die Schmelzpunktsbestimmung diskutiert werden.

(1) *Ein Isolat aus einem Puddeleisen:* dessen chemische Analyse wie folgt lautet: 24% SiO_2, 5% Al_2O_3, 5% MnO, 66% FeO und Spuren von CaO und MgO zeigte bei der mikroskopischen Betrachtung viele kristallisierte, doppelbrechende und wenige glasige, schwach braun gefärbte Kristalle. Da genügend Probematerial zur Verfügung stand, wurden zwei würfelförmige Presslinge von etwa 2 mm Kantenlänge angefertigt und einmal an Luft und zum anderen in Argon im Erhitzungsmikroskop bei einer durchschnittlichen Temperatursteigerung von etwa 5°/min bis 1000°C und von da an mit 2 bis 3°/min bis zum Schmelzpunkt erhitzt. Es gibt sich ein deutlicher Einfluss der herrschenden Atmosphäre zu erkennen, wie dies sowohl im Bild 1 als auch in Tafel 1 zu sehen ist.

Tafel 1.

Temperatur °C	scheinbare Volumenänderung			
	Luft		Argon	
	%	Bemerkung	%	Bemerkung
20	0		0	
500	0		0	
900	0		10	Sinterung
1000	0		20	Sinterung
1060	0		42	Sinterung
1100	8	Sinterung	46	Sinterung
1150	8	Sinterung	50	Erweichung
1195	8	Sinterung	54	Erweichung
1200	15	Erweichung	54	Erweichung
1230	15	Erweichung	56	Schmelzen
1235	15	Erweichung	63	Schmelzen
1238	18	Erweichung	65	Schmelzen
1240	18	Erweichung	75	Schmelzen
1243	18	Erweichung	84	Schmelzen
1245	18	Erweichung	87	Schmelzen
1300	43	Erweichung		
1330	67	Schmelzen		
1380	77	Schmelzen		
1390	84	Schmelzen		

Fasst man die charakteristischen Temperaturbereiche zusammen, wie dies in Tafel 2 geschehen ist, so ergibt sich folgendes: Alle charakteristischen Bereiche (Sinterung, Erweichung und Schmelzen) beginnen beim Erhitzen an Luft bei wesentlich höherer Temperatur und—was wichtiger erscheint—der Erweichungs- und Schmelzbereich zieht sich über einen breiten Temperaturintervall hin, während gerade diese wichtigen Bereiche in Argonatmosphäre geringer und ausgeprägter sind und daher auch besser erfasst werden können.

(2) *Isolate aus Transformatorenblechen:* Die chemische Analyse war folgende:

Isolat A: 84% SiO_2, 11,4% Al_2O_3, 4,8% CaO; FeO, MgO und $TiO_2 \leqslant 1\%$
Isolat B: 89,5% SiO_2, 8,3% Al_2O_3, 2,9% FeO; CaO, MgO und $TiO_2 \leqslant 1\%$

TAFEL 2.

Atmosphäre	Sinterung °C	Erweichung °C	Schmelzen °C
Luft	1100–1200	1200–1330	1330–1390
Argon	900–1150	1150–1230	1230–1245

Die Röntgenanalyse ergab in beiden Fällen glasige, wenig kristallisierte Körper. Die mikroskopische Untersuchung zeigte ebenfalls vorwiegend glasige Körper, in denen kristallisierte Substanzen entahalten sind, wobei noch bemerkenswert ist, dass —wie Bild 2 zeigt—das Isolat A vorwiegend eckige Kristalle liefert und das Isolat B kugelige.

Da von jeder dieser Proben nur einige Milligramme zur Verfügung standen, konnte keiner der empfohlenen Prüfkörper hergestellt werden. Mit Hilfe eines kleinen Gesenkes, ähnlich wie in der Spektralanalyse verwendet, konnten aus dem Isolat A durch Handdruck ein Quader von 2 mm^2 Grundfläche und 1,3 mm Höhe und vom Isolat B ein solcher mit einer Grundfläche von ebenfalls 2 mm^2 und einer Höhe von lediglich 0,5 mm hergestellt werden.

Das Verhalten dieser beiden Prüfkörper beim Erhitzen im Erhitzungsmikroskop and der Luft zeigt Bild 3. Demnach verhalten sich die beiden Substanzen trotz sehr ähnlicher Silizium- und Aluminiumgehalte keinesfalls gleich, da einmal die prozentuale Volumverminderung wesentlich unterschiedlich ist, zum anderen die Sinterbereiche beim Isolat A in einem Intervall von 200°C, beginnend bei 1200°C, beim Isolat B in einem solchen von 400°C mit dem Beginn bei 1000°C liegen. Der Erweichungsbereich liegt bei Probe A innerhalb 40, bei B innerhalb 110°C. Der Schmelzbereich liegt, wie dies auch Tafel 3 zeigt, zwischen 1440 und 1500°C innerhalb 60°C, bei Probe A wesentlich geringer als der für die Probe B, der zwischen 1510 bis 1540°C im Bereich von 30° wesentlich höher liegt. Das heisst, die kalziumoxydhaltigen, eckigen Kristalle zeigen gegenüber den kalziumoxydfreien, aber eisenoxydhaltigen, kugelförmigen Verbindungen einen niedrigeren Schmelzpunkt.

TAFEL 3.

Isolat	Sinterung °C	Erweichung °C	Schmelzen °C
A	1200–1400	1400–1440	1440–1500
B	1000–1400	1400–1510	1510–1540

Es sei an dieser Stelle hervorgehoben, dass sicherlich die während des Erhitzens erhaltenen Zahlen von der Korngrösse des Produktes und vom Pressdruck, den der

Körper erfahren hat, sowie von den den Körper umgebenden atmosphärischen Bedingungen abhängen.

Trägt man die Analysenwerte vom Isolat A in das Dreistoffsystem SiO_2—CaO—Al_2O_3 ein, so stimmt der Schmelzpunkt von etwa 1460° sehr gut mit der eutektischen Rinne überein. Die chemische Analyse des Isolates B muss naturgemäss in das Dreistoffsystem SiO_2—FeO—Al_2O_3 eingetragen werden, und man liegt damit in der Phasengrenzfläche zwischen Cristobalit und Mullit, wobei schon sehr geringe Mengen von FeO den Schmelzpunkt von ca. 1600° auf 1510° herunterdrücken. Dies stimmt mit dem Verlauf der Schmelzrinne gut überein.

(3) *Isolate aus unberuhigten Weichstählen:*[3] Die chemische Zusammensetzung war folgende:

Isolat C: 38% SiO_2, 20% Al_2O_3, 28% MnO, 13% FeO

Isolat D: 22% SiO_2, 15% Al_2O_3, 48% MnO, 15% FeO

Die Röntgenanalyse zeigte für C einen kristallisierten Körper, der nach der Textur des Diagramms dem Tephroit zugeordnet werden kann, während D auf einen glasigen Körper hinweist. Die mikroskopischen Analysen der Isolate zeigen durchsichtige und undurchsichtige, braunschwarze, mitunter Hohlräume (Isolat C) aufweisende Kugeln, die im Anschliff, wie Bild 4 zeigt, im Innern entweder Blasen oder Auskristallisationen (Isolat D) beinhalten.

Das Verhalten derartiger Kugeln im Erhitzungsmikroskop geht aus Bild 5 hervor. Diese Kugeln wurden auf einen aus dünnem Platindraht hergestellten Träger gebracht und nebeneinander in das Mikroskop eingesetzt. Während des Erhitzens verhielt sich die durchsichtige Kugel wesentlich anders als die undurchsichtige, und zwar derart, dass sie oberhalb 400°C ihre Durchsichtigkeit verlor, bei etwa 800°C sich aufzublähen begann, bei 1230°C unter kräftiger Volumzunahme zu schmelzen begann und bei 1260°C den Schmelzpunkt erreichte. Unmittelbar darauf erfolgte ein nahezu vollständiger Zusammenbruch des Probekörpers, um bei 1300°C eine neuerliche, wenn auch geringere Aufblähung zu erfahren und um bei 1340°C neuerlich und vollständig zusammenzubrechen. Die undurchsichtigen Kugeln hingegen begannen erst bei über 1000°C sich aufzublähen, wiesen an und für sich eine wesentlich geringere prozentuale Volumzunahme auf, erreichter aber bei der gleichen Temperatur wie die durchsichtigen Kugeln ihren Schmelzpunkt, wurden dann ohne wesentliche Volumänderung dünnflüssig und sackte langsam durch die Öse des Platindrahtes durch. Wieweit ein derartiges Verhalten mit der Viskosität dieser Kugel in Zusammenhang steht und daraus rückschliessend das Verhalten der Kugeln im Schmelzfluss beurteilt werden darf, muss späteren Untersuchungen vorbehalten bleiben. Hier können die Arbeiten von F. Johannsen und W. Wiese[4] wertvolle Hinweise geben.

(4) Ein weiteres interessantes Beispiel einer Schmelzpunktsbestimmung zeigt Bild 6, in dem auf der linken Bildseite eine Isolierungsprobe mit nadelförmigen Einschlüssen zu sehen ist, deren chemische Analyse wie folgt lautet: 13% FeO, 26% SiO_2, 42% MnO und 19% Al_2O_3. Das Röntgendiagramm zeigte wiederum den tephroitartigen Charakter der Einschlüsse und der Schmelzpunkt einer einzelnen Nadel, der auf 2°C genau erfassbar war, lag bei 922°C, wobei die Erweichung bei 900°C erfolgte. In diesem Falle wurde aus dem Gesamtisolat mit Hilfe des

Mikromanipulators[5] eine Nadel ausgesucht und diese, wie im Bild 6, Mitte oben (Ausgangszustand), zu sehen ist, schräg durch den Platindrahthalter gesteckt.

Überträgt man die chemische Analyse in vereinfachter Weise in das Dreistoffsystem $MnO—FeO—SiO_2$, wobei Aluminiumoxyd und Siliziumdioxyd addiert werden, so kommt man in ein Gebiet mit Schmelzpunkten von 1200°C. Überträgt man aber die chemische Analyse in das Dreistoffsystem $MnO—Al_2O_3—SiO_2$ unter Zusammenfassung von FeO und MnO, so kommt man in ein Gebiet, welches im reinen Dreistoffsystem Schmelzpunkte von etwa 1140°C aufweist, so dass man sehr wohl im Vierstoffsystem einen noch niedrigeren Schmelzpunkt erwarten darf. Es steht auf alle Fälle fest, dass sich Körper, die bei 900°C erweichen und bei 920°C schmelzen, sehr wohl beim Walzen verformen[3] lassen.

Summary—The value of a heating microscope for the investigation of the melting behaviour of isolated oxidised structural components in ferrous materials is illustrated by examples.

Résumé—On illustre par des exemples l'intérèt du microscope chauffant pour l'étude de la fusion de composés isolés à l'état oxydé dans des matériaux ferreux.

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PRELIMINARY COMMUNICATION

New redox systems—I. Oxidation of bivalent cobalt with iron^{III} chloride in 1:10-phenanthroline solutions

(*Received* 12 *September* 1959)

In the study of the properties of ferric iron and of bivalent and tervalent cobalt with 1:10 phenanthroline a reaction of considerable theoretical interest has been observed. In a weakly acid solution of bivalent cobalt and ferric salt (optimum pH 3), on addition of 1:10 phenanthroline solution, the tervalent iron is reduced to the bivalent state which is simultaneously bound by the phenanthroline present to form the intensely red ferroïn complex. This colour reaction, which can be used for the very sensitive detection of cobalt, arises only because of the existence of phenanthroline complexes of iron and cobalt in both valency states, with stability constants which permit the reaction.

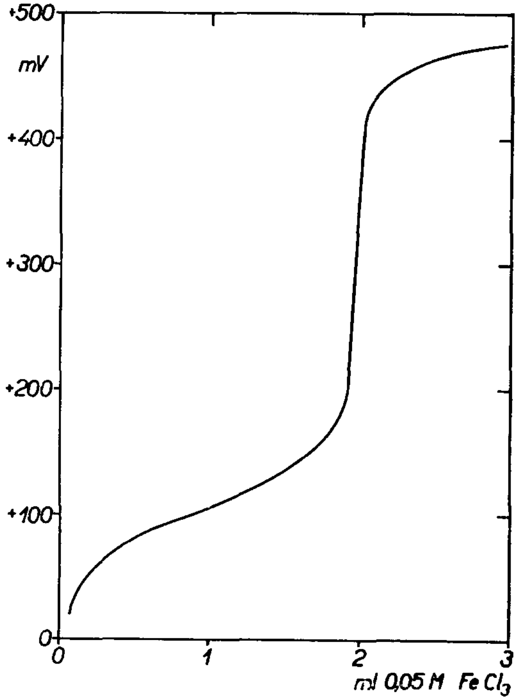

FIG. 1

2 ml of 0·05M Co
25 ml of 0·05M 1:10-phenanthroline
20 ml of buffer (formic acid with ammonium formate, pH 3)
Titrated with 0·05M FeCl$_3$; Pt electrode and saturated calomel electrode.

The redox character of the reaction was verified by potentiometric titration of a solution containing cobaltous salt and 1:10-phenanthroline with 0·05M ferric chloride. The titration curve and the appropriate data are given in Fig. 1. The reaction is rapid and quantitative at pH 3. The redox potential for the couple

$$\mathrm{Co^{II}(Phen)_3Cl_2 + Cl^- = Co^{III}(Phen)_3Cl_3 + e}$$

was determined by analysis of the potentiometric curve and the value 0·38 V found, in excellent agreement with the value 0·37 V reported by Paglia and Sironi[1] for these complexes prepared synthetically.

The reaction was also followed spectrophotometrically and found to be stoichiometric provided the ratio of phenanthroline to total iron plus cobalt was at least 6 to 1. From the known composition of all the complexes concerned, the reaction can be formulated as

$$\mathrm{[Fe_2(Phen)_4(OH)_2]^{2+} + 2Co(Phen)_3{}^{2+} + 2HPhen^+ \rightleftharpoons 2Fe(Phen)_3{}^{2+} + 2Co(Phen)_3{}^{3+} + 2H_2O}$$

(Tervalent iron forms with 1:10-phenanthroline in acid solution a binuclear complex of different composition from the complexes of other metals.[2,3])

Analytical applications

Preliminary tests show that the reaction can be used for the highly selective oxidimetric determination of cobalt. The end-point can be detected potentiometrically or spectrophotometrically. Traces of cobalt—several μg per ml—can be indirectly determined colorimetrically as ferroïn. In solutions coloured by ions such as Ni or Cr, the ferroïn produced in the reaction can be extracted as its perchlorate with chloroform or nitrobenzene and then determined colorimetrically.[4]

The reaction is being further studied in its theoretical as well as its analytical aspects and the results will be published in this journal.

Acknowledgement—We wish to thank Dr. R. A. Chalmers for helpful discussion of the paper.

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SHORT COMMUNICATIONS

Vereinfachte Schnellmethode zur Sulfatbestimmung durch Ionenaustausch

(*Received* 20 *April* 1959)

Es wurden Austauschadsorbentien seit langem zur Sulfatanalyse verwendet, Grössten Teils dienen sie zur Beseitigung der störenden Komponenten. So verfährt auch Bahrdt[1] in seiner Schnellmethode, indem er den Sulfatgehalt von Naturwässern mit bestimmter Menge einer $BaCl_2$ Lösung versätzt, und den Überschuss von $BaCl_2$ mit K-Palmitat titriert. Da Ca und Mg bei der $BaSO_4$-Abscheidung stören, wird die zu analysierende Lösung durch eine Na-Permutit-Säule filtriert. Unabhängig von Bahrdt, aber in ähnlicher Weise arbeiten Kehren und Stommel.[2]

Die gravimetrische Bestimmung von $BaSO_4$ Niederschläge wird durch manche Ionen gestört, so sind grössere Mengen Na oder Fe nachteilig. Lässt man die Lösung durch ein H^+-Austauscherbett fliessen, so werden diese Nachteile beseitigt.[4,5] Interessant ist die "Auflösung" von $BaSO_4$[6] durch die Verschiebung des Lösungsgleichgewichtes mittels Kationenaustauscher. Der Sulfatgehalt kann volumetrisch, als freie Schwefelsäure ermittelt werden. Funasaka[7] bestimmt den Sulfatgehalt, indem er ihn in die Chloridform konvertiert, und potentiometrisch titriert. Gabrielson[8] bedient sich zur $PbSO_4$ Analyse mit H^+ Austauscher: die freie Schwefelsäure wird alkalimetrisch gemessen. In den erwähnten Methoden sind teils reine Sulfatlösungen nötig, die ohne weiteres gemessen werden können, teils sind Reinigungsoperationen erforderlich, die mühsam und zeitraubend sind, evtl. die Genauheit gefährden.

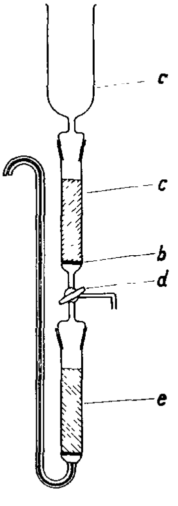

FIG. 1.

Unsere Arbeit über das physikalisch-chemische Verhalten unserer permselektiven Membranen[9] erforderte eine Vielzahl von $CuSO_4$-Bestimmungen, undzwar mit getrennter Sulfatanalyse. Wir suchten ein schnelles Routinverfahren, womit der SO_4-Gehalt neben Cu^{++} Ionen genau und einfach ermittelt werden kann.

Wir konvertieren die SO_4-Ionen an einem Anionenaustauscher stöchiometrisch in Chlorid und titrieren nach Mohr. In Spezialfällen, wenn die Lösung sauer anfällt, benützen wir die Volhardtsche Methode. Die störenden Kationen werden an einem Na^+-Austauscher zu Na^+ Ionen ausgetauscht, so sind die Umstände gleichgestellt. Enthält die Ausgangslösung auch Cl' Ionen, so muss dessen Gehalt vor dem Anionenaustausch mit einer Titrierung auch bestimmt, und dieser Wert vom Endresultat abgezogen werden. Evtl. vorliegender PO_4 Gehalt wird durch Magnesia-Mixture beseitigt. Der Niederschlag wird nicht filtriert: teils setzt er sich bei der Dekantierung ab, teils bleibt er über den Kationenaustauscher stecken und wird mit der Regeneriersäure abgewaschen.

Zur Ausführung der Bestimmungen entwickelten wir einen Apparat, in dem der ganze Prozess in einem Schritt vor sich geht (Abb. 1).

Die Behandlung des Apparates ist insofern einfach, dass mit einem Hahn die ganze Regulierung eingestellt wird, bloss die Lösungen werden eingeschüttet. Der Schwanenhals verhütet den Ablauf der Lösung vom Harz.[10] Die Methode gibt, mit kommensurablen Ionenverhältnissen in mässig verdünnten Lösungen eine Genauheit von rund ±1% rel. (Tab. I) Die Wiederbelebung geschieht mit Kochsalzlösung oder Salzsäure, die den Kationenaustauscher in die Na^+-bzw. H^+ Form, den Anionenaustauscher in die Cl' Form umwandeln, also in einem Schritt beide Harzbette regenerieren doch können mehrere Bestimmungen nacheinander ohne Regenerirerung durchgeführt werden (Tab. II).

TABELLE I

No.	Volum *ml*	Einwage $CuSO_4$ *mg*	Gemessen $CuSO_4$ *mg*	Titrierung 0,05*N* $AgNO_3$ *ml*	Fehler %
1	4	15,963	16,043	4,02	+0,5
2	4	15,963	15,833	3,97	−0,7
3	4	15.963	16,163	4,05	+1,2
4	4	15,963	16,043	4,02	+1,5
5	5	7,981	7,851	1,98	−1%
6	5	7,981	8,021	2,01	+0,5
7	5	7,981	7,981	2,00	0
8	5	7,981	8,061	2,02	+1,0

Das Harz wurde vor jeder Bestimmung regeneriert

TABELLE II

No.	Volum *ml*	Einwage $CuSO_4$ *mg*	Gemessen $CuSO_4$ *mg*	Titrierung 0,05*N* $AgNO_3$ *ml*	Fehler %
1	5	7,981	8,101	2,03	+1,5
2	5	7,981	7,851	1,98	−1
3	5	7,981	8,061	2,02	+1
4	5	7,981	7,981	2,00	0,0
5	5	7,981	8,021	2,01	+0,5

Die fünf Bestimmungen liefen ohne Zwischenregenerierung

EXPERIMENTELLER TEIL

Die Bestimmung verläuft wie folgt: Die zu analysierende Lösung, befreit von PO_4, CrO_4, WoO_4, MoO_4 od.dgl., wird im Normalkolben auf eine Konzentration von rund 0,01–0,05*N* verdünnt, einen evtl. Niederschlag (der doch kein SO_4'' enthalten darf) lässt man absetzen und aus der spiegelklaren Lösung messt man 2–6 ml (= 5–10 mg SO_4) in den Apparat (Abb. 1) für den Austauschvorgang ein.

Der Apparat ist in Na^+ bzw. Cl' Form, ionenfrei und mit demineralisiertem Wasser bis zum Schwanenhals gefüllt, zur Analyse bereit. Die obenerwähnte analysierende Lösung bringt man in den Vorraum (*a*), wobei der T-Hahn (*d*) geschlossen ist. Es wird darauf geachtet, dass die Lösung den Trichter (*a*) nur in dem erforderlichen Masse benetze, um leichte Nachspülmöglichkeit zu sichern.

Der Austausch verläuft mit einer Geschwindigkeit von rund 1 Tropfen/sec, also im abgebildeten Apparat (D = 7 mm, 1,5 ml. Harz) 2 ml in der Minute, = 5 cm/Min (3 m/h), bzw. 1,33 ml/ml/Min Durchsatz. Die Durchflüssgeschwindigkeit wird mit dem T-Hahn (*d*) reguliert, doch stellt sich das erwähnte Wert bei völliger Öffnung des Hahnes ein, falls die Kapillare 1 mm ϕ hat, die (*b*) Filterplatten aus G 1 Sinterglas und das Austauschmaterial aus einem Perlenpolymerisat von 0,1–0,2 mm ϕ bestehen.

Nachdem die Sulfatlösung durchgeflossen ist, wird der Apparat mit einmal 10 und einmal 5 ml ionenfreiem Wasser durchgespült und die gesamte Flüssigkeit mit 0,05 N $AgNO_3$ nach Mohr titriert.

Die gesamte Bestimmung verläuft in 20 Minuten.

Wenn die analysierende Probe auch Cl' Ionen entält, wird der Austauschprozess zweimal unternommen, einmal durch den Seitenweg (*d*), wobei darauf streng zu achten ist, das die Oberfläche der Flüssigkeit ständig über dem Harzschicht (*c*) bleibe, und einmal in der erwöhnten Weise, Beide gesammelten Flüssigkeiten unterliegen einer Mohr' schen Titrierung, wobei man mit der Differenz zu rechnen hat.

Materialien

Kationenaustauscher (*c*): *Mykion PS*, p.a., Polystyrolsulfonsäure Harzperlchen, 0,1–0,2 mm ϕ, Kapazität: 4,7 mAequ/g, 1,8 mAequ/ml (Farbstoff-Fabrik Füzfö, Ungarn).

Anionenaustauscher (*e*): *Mykion PA*, p.a., Polystyrolbenzyl-ammonium Harzperlchen, Typ II, 0,1–0,2 mm ϕ, Kapazität: 2,7 mAequ/g, 1,2 mAequ/ml (Farbstoff-Fabrik Füzfö, Ungarn).

Reagenzien: p.a. bzw. puriss. Präparate, der Firma Merck.

Wasser: Entionisiertes budapester Leitungswasser.

Beschickung des Apparates: Der mit Lauge und Säure durchgespülte Apparat, wird mit Wasser ausgewaschen und gefüllt. Die Harze werden in einem Becher mit Wasser aufgeschwämmt, 24 Stunden lang öfters mit neuem Wasser versetzt, dreimal mit Lauge und Säure (0,5.*N*–1.*N*) behandelt und in Na^+ bzw. Cl' Form so eingefüllt, dass die Behälter auch unter der Sinterplatten keine Luftblasen enthalten sollen. Danach erfolgt eine Regenerierung.

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Anhydrous magnesium perchlorate desiccant with added indicator

(*Received* 10 *August* 1959)

ANHYDROUS magnesium perchlorate as a new desiccant was first described by Willard and Smith[1] in 1922. The first application as desiccant was that of Smith, Brown and Ross.[2] Comprehensive einen evtl. Niederschlag (der doch kein SO_4'' enthalten darf) lässt man absetzen und aus der spiegelklaren Lösung messt man 2–6 ml (= 5–10 mg SO_4) in den Apparat (Abb. 1) für den Austauschvorgang ein.

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Anhydrous magnesium perchlorate desiccant with added indicator

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ANHYDROUS magnesium perchlorate as a new desiccant was first described by Willard and Smith[1] in 1922. The first application as desiccant was that of Smith, Brown and Ross.[2] Comprehensive studies of its preparation and properties were made by Smith and Rees,[3] Smith, Rees and Hardy[4] and Smith,[5] the latter study being that of its commercial application to the dehydration of air for use in liquefaction and fractionation to yield oxygen and nitrogen. The preparation of anhydrous magnesium perchlorate by dry reaction from ammonium perchlorate was described by Smith and Hardy.[6] Smith, Bernhart and Wiederkehr[7] made a study of its use in laboratory desiccator techniques.

Granular, porous, colourless magnesium perchlorate has been adopted almost universally for use in micro-combustion determination of hydrogen and carbon simultaneously. This desiccant is also employed in purging gases of ammonia. It is employed to determine ethyl alcohol in testing of drunken automobile operators[8] by the "intoximeter." Anhydrous granular and porous magnesium perchlorate is capable of dehydrating gases to a dew-point lower than that for liquid air temperatures[5] at high rates of flow contact, and with absorption capacity higher than any known desiccant. The same is true in its absorption of ammonia gas. It is commercially available under its chemical name and by the trade names "Anhydrone" and "Dehydrite".

An insistent demand has been made that anhydrous magnesium perchlorate be made commercially available with indicator properties added to give visual indication of complete capacity in the absorption of water. This communication describes the solution of this problem.

Potassium permanganate is isomorphous with magnesium perchlorate. When a saturated aqueous solution of magnesium perchlorate is allowed to crystallize by cooling from 110°–120° to room temperature, in the presence of 1–2% of potassium permanganate (based on the magnesium perchlorate content), the $Mg(ClO_4)_2 \cdot 6H_2O$ obtained is purple from co-crystallised permanganate.

Upon dehydration as previously described,[3,5] the anhydrous desiccant thus prepared is lighter purple in colour since dehydration at 200°–220°, with accompanying removal of water and developed porosity, produces a lighter hue. Upon absorption of water the spent reagent becomes dark brown.

This problem was solved particularly as an aid to the micro-analyst for use in filling Pregl tubes, wherein desiccant charges are small and demand indication of the extent to which reagent efficiency is at or near saturation, so as to lessen the frequency of recharging. Otherwise Pregl tube capacity may not be economically employed.

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BOOK REVIEW

Advances in Inorganic Chemistry and Radiochemistry, Volume I. Edited by H. J. EMELEUS and A. G. SHARPE. Academic Press, Inc., New York, 1959. Pp. xi + 449. $12.00.

IN 1938 it was still possible for the senior editor of this book, in collaboration with J. S. Anderson, to present an essentially complete picture of the state of contemporary inorganic chemistry in a single volume of moderate size. The classic *Modern Aspects of Inorganic Chemistry* filled a gap in the literature, and, in its two editions, has for many years satisfied readers seeking a concise and readable account of the most active fields of inorganic chemistry. During the last ten years, however, the pace of new discovery in inorganic chemistry has accelerated enormously. It has become difficult to keep a book of this type reasonably up-to-date with new editions; while for one or two writers to prepare a really adequate and comprehensive new book on current developments would be a forbidding task. In the new circumstances, the best way of satisfying the hunger of chemists for up-to-date information on current work is to publish a continuing series of short, fully documented monographs by specialist contributors, a plan already successfully adopted in other branches of chemistry and physics. This first volume of *Advances in Inorganic Chemistry and Radiochemistry* contains nine chapters by leading research workers on subjects of strong current interest. It has not been unreasonably long in the press; there are many references from 1958 and one or two from 1959.

E. O. Fischer and H. P. Fritz's *Compounds of Aromatic Ring Systems and Metals* is perhaps the most welcome chapter in the book, other reviews of this subject being badly out-of-date. It includes a long section on benzene-metal compounds. The authors' viewpoint on bonding in the aromatic ring-metal compounds is refreshingly different from the Moffitt molecular orbital picture which has for long been rather uncritically accepted in the English language literature. W. N. Lipscombe on *Boron Hydrides* is mostly concerned with structure, especially three-centre bonds, and the topological theory of boron hydride structure. H. Taube's study of the *Mechanism of Redox Reactions* is an excellent piece of criticism in an extremely complex and difficult field. The chapter entitled *The Szilard–Chalmers Reaction in Solids* by G. Harbottle and N. Sutin demonstrates how this subject, not long ago a rag-bag of facts inexplicable except by guesswork, has developed a serious body of theory and shows signs of making useful contributions to our knowledge of solid-state chemistry and physics.

Analytical chemists will be most interested in the chapter by D. H. F. Atkins and A. A. Smales on *Activation Analysis*, which the writers describe as "a powerful addition to the armoury of modern analytical chemistry." They support this contention with a list of eighteen metals which can be detected in amounts of 10^{-9} gram or less by this method. The freedom of the activation method from reagent "blank" and contamination problems ensures that these high sensitivities can be used under practical conditions.

Phosphonitrilic Halides, by N. L. Paddock and H. T. Searle, deals with a group of compounds interesting both as inorganic polymers with possible technical applications, and as one of the starting points of the new inorganic chemistry of homologous series. The other contributions are *Lattice Energies* by T. C. Waddington, *Graphite Intercalation Compounds* by W. Rüdorff, and *The Sulphuric Acid Solvent System* by R. J. Gillespie and E. A. Robinson.

This book is too detailed and too fully documented to make easy reading for the non-specialist, but it and the subsequent volumes of the series will be essential works of reference for anyone whose main interest is in current inorganic chemistry, radiochemistry or analytical chemistry.

H. G. HEAL

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NOTICES

The following meetings have been arranged:

Tuesday 27 *October* 1959: **Society for Analytical Chemistry,** Midlands Section: *The Purity of Analytical Reagents:* Discussion will be opened by Mr. J. T. YARDLEY, B.Sc., F.R.I.C. Nottingham and District Technical College, Burton Street, Nottingham. 7.0 p.m.

Tuesday 27 *October* 1959: **Society for Analytical Chemistry,** North of England Section and Physical Methods Group: **Royal Institute of Chemistry,** North-East Coast Section: *Instrumental Developments in X-Ray Fluorescence Spectroscopy:* Mr. J. R. STANSFIELD, M.A., F. Inst. P. *Some Applications of X-Ray Spectrography:* Mr. H. I. SHALGOLSKY, B.Sc., A.R.I.C. Chemistry Lecture Theatre 2, King's College, Newcastle-upon-Tyne, 1. 6.30 p.m.

Friday 30 *October* 1959: **Society for Analytical Chemistry,** Scottish Section: *The Value of EDTA as an Analytical Reagent:* Dr. H. J. CLULEY, M.Sc., F.R.I.C. Chemistry Department, Queen's College, Dundee. 5.0 p.m.

Friday 30 *October* 1959: **Society for Analtyical Chemistry,** North of England Section: *The Changing Aspects of Chemical Analysis:* Mr. H. N. WILSON, F.R.I.C. Metropole Hotel, Stockton-on-Tees. 7.30 p.m.

Friday 30 *October* 1959: **Society for Anayltical Chemistry,** Western Section: **Royal Institute of Chemistry,** Mid-Southern Counties Section. *Analytical Chemistry and Clinical Diagnosis.* Professor Sir E. CHARLES DODDS, M.V.O., F.R.S. Salisbury.

Thursday 12 *November* 1950: **Society for Analytical Chemistry,** Midlands Section: *The Identification and Determination of Phenols:* Dr. L. BARKER. The University, Birmingham, 3. 6.30 p.m.

Friday 13 *November* 1959: **Society for Analytical Chemistry,** Scottish Section: **Royal Institute of Chemistry:** *Techniques in Radiochemistry for Analysis and Research:* Mr. D. A. LAMBIE, B.Sc., F.R.I.C. Royal College of Science and Technology, Glasgow. 7.15 p.m.

Tuesday 24 *November* 1959: **Society for Analytical Chemistry,** Physical Methods Group. Annual General Meeting. Burlington House, London, W.1. 6.30 p.m.

Saturday 5 *December* 1959: **Society for Analytical Chemistry,** North of England Section: *The Analysis of Cocoa and Chocolate in Relation to Modern Manufacturing Methods:* Mr. B. W. E. MINIFIE, F.R.I.C. and Mr. C. HARRIS, F.R.I.C. City Laboratories, Mount Pleasant, Liverpool. 2.15 p.m.

Wednesday 9 *December* 1959: **Society for Analytical Chemistry,** Midlands Section: *The Determination of Trace Impurities in Metals.* Discussion will be opened by Mr. B. BAGSHAWE, A. Met. and Mr. W. T. ELWELL, F.R.I.C. Wolverhampton and Staffordshire College of Technology, Wolverhampton. 7.0 p.m.

Wednesday 9 *December* 1959: **Society for Analytical Chemistry,** Biological Methods Group. Annual General Meeting. *Biological Methods in Forensic Science.* Dr. H. J. WALLS, B.Sc., Mr. S. S. KIND, B.Sc., and Dr. A. S. CURRY, M.A., A.R.I.C. Burlington House, London, W.1. 7.0 p.m.

Tuesday–Wednesday 3–4 *May* 1960: **Society for Analytical Chemistry: Iron and Steel Institute: Institute of Metals:** Joint Symposium on *Determination of Gases in Metals.* Church House, Westminster, London.

Three sessions are envisaged, occupying the afternoon of the 3rd and the morning and afternoon of the 4th. At the first session invited review papers will be presented covering the determinations of oxygen, hydrogen and nitrogen in a general way; the other two sessions will be devoted to shorter papers and discussions dealing with specialised aspects of the field.

It is intended that preprints of all the papers will be available before the start of the Symposium, and that the proceedings, including discussions, will be published in a single volume at a later date. Further information from the Hon. Secretary, Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1.

Talanta, 1959, Vol. 3, p. 111. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Activation Analysis of Trace Cobalt in Tissue using 10.5m-Cobalt. David G. Kaiser and W. Wayne Meinke. (7 *August* 1959).

Spectrophotometric Determination of Molybdenum in Steel with 3:3′ :4′ :5:7-pentahydroxyflavonone. Frank L. Chan and Ross W. Moshier. (30 *July* 1959).

The Preparation of Iridium Solutions by an Acid Attack of Tin-iridium Alloys. G. H. Faye and W. R. Inman. (30 *July* 1959).

Quantitative Oxidations by Potassium Ferricyanide: Bharat R. Sant and Suseela B. Sant. (7 *August* 1959).

The Precipitation of Zinc Sulphide from Acid Solutions by Thioacetamide. David F. Bowersox, Dwight M. Smith and Ernest H. Swift. (8 *August* 1959).

Potassium Bromate as Volumetric Reagent—I: Determination of Hydrazine and its Organic Derivatives. Balwant Singh and S. S. Sahota. (10 *August* 1959).

Titrimetric Analysis of 3:5-Dinitrobenzoate Derivatives. W. T. Robinson, R. H. Cundiff, A. J. Sensabaugh and P. C. Markunas. (10 *August* 1959).

Anhydrous Magnesium Perchlorate Desiccant with Added Indicator. G. Frederick Smith and Harvey Diehl. (10 *August* 1959).

The Colorimetric Determination of Boron in Nitrate Solutions. W. J. Ross and J. C. White. (10 *August* 1959).

Determination of Deuterium in Organic Compounds by Infrared Spectrophotometry R. Norman Jones and Marjory A. MacKenzie. (14 *August* 1959).

The Spectrophotometric Estimation of Phenol: With Special Reference to Solutions Containing Tyrosine, Tryptophane, Histidine or Chymotrypsin. W. Lee and J. H. Turnbull. (21 *August* 1959).

Solvent Extraction Separations of Platinum Metals—I: Ruthenium and Palladium. J. H. W. Forsythe, R. J. Magee and C. L. Wilson. (22 *August* 1959).

Solvent Extraction Separations of Platinum Metals—II: Rhodium, Palladium and Platinum. J. H. W. Forsythe, R. J. Magee and C. L. Wilson. (22 *August* 1959).

The Effect of Platinum Oxide Films on Reaction Kinetics at Platinum Electrodes. Donald G. Davis, Jr. (24 *August* 1959).

The Determination of Cobalt by Oxidation with Potassium Molybdicyanide. Byron Kratochvil and Harvey Diehl. (1 *September* 1959).

The Spectrophotometric Determination of Copper with Ammonium Pyrophosphate. C. J. Keattch. (2 *September* 1959).

New Redox Systems—I: Oxidation of Bivalent Cobalt with Iron$^{\mathrm{III}}$ Chloride in 1:10-Phenthroline solution F. Vydra and R. Přibil. (12 *September* 1959).

Oxidation-reduction Reactions on Ion-exchange Columns—I: Reduction of Iron$^{\mathrm{III}}$ Ions. L. Erdey, J. Inczédy and I. Markovits. (15 *September* 1959).

A New Micro Method of Studying the Thermal Stability of Easily Volatile Explosives. Vinzenz Anger. (21 *September* 1959).

A Critical Study of the Determination of Platinum with Dimethylphenylbenzylammonium chloride. A. D. Westland and L. Westland. (24 *September* 1959).

Titrimetric Determination of Soluble Silica as Silicomolybdic Acid. Takeo Takahashi and Shingo Miyake. (28 *September* 1959).

Talanta, 1959, Vol. 3, p. 112. Pergamon Press Ltd. Printed in Northern Ireland

BOOKS RECEIVED

Contributi Teorici e Sperimentali di Polarografia, Volume IV. Supplement to La Ricerca Scientifica, 1959. Centro di Polarografia, Via Loredan 4, Padova, Italy. Pp. 361.

The Analysis of Titanium and its Alloys, 3rd Edition. Imperial Chemical Industries Limited, 1959. Pp. 119. 21s.

The following publications have been received and are available from the Office of Technical Service, Department of Commerce, Washington 25, D.C., U.S.A.

An Automatic Recording Titrator. GERALD ROSS UMBREIT and J. S. FRITZ. LSC-1021. *December* 1957. Pp. iv + 50. $1.50.

The Determination of Plutonium in Irradiated Uranium Fuel Solutions by Controlled Potential Coulometry F. A. SCOTT and R. M. PEEKEMA. HW-58491. 10 *December* 1958. Pp. 29. $1.50.

Detection of Nitrite Ion in Plutonium Nitrate Solutions. M. O. FULDA. DP-336. *December* 1958. Pp. 7. $0.50.

An Analytical Method for Neptunium-237 Using Anion Exchange. F. P. ROBERTS. HW-59032. 28 *January* 1959. Pp. 15. $0.50.

Analysis for Neptunium by Controlled Potential Coulometry. R. W. STROMATT. HW-59447. 2 *February* 1959. Pp. 20. $0.75.

Spectrophotometric Study of the Ternary System, Aluminum Nitrate-Nitric Acid-Water: Application to Analysis. ROBERT W. HENRY and GLENN L. BOOMAN. IDO-14460. 31 *March* 1959. Pp. 11.

Remote Analytical Facility Operational Excercises. GEORGE A. HUFF. IDO-14434. 4 *April* 1959. Pp. 13. $0.50.

Extraction of Protoactinium with Diisobutylcarbinol. J. R. OLIVER, J. R. MERIWETHER and R. H. RAINEY. ORNL-2668. 15 *April* 1959. Pp. 13. $0.50.

An In-line Conductivity Meter with Temperature Compensation. D. W. COLVIN. DP-361. *April* 1959. Pp. 12. $0.50.

Van-Slyke Factors for Hydrogen, Oxygen, Carbon Dioxide and Carbon Monoxide. G. E. ADAMS and A. R. ANDERSON. ANL-5991. *April* 1959. Pp. 7.

Preparation of Lithium Isotope Standards—I: Separation of Sodium and Lithium by Dowex 50-X18 DVB Resin. W. C. DIETRICH and R. E. BARRINGER. Y-1254. 14 *May* 1959. Pp. 15. $0.50.

The Determination of Mercury, Copper and Zinc by Derivative Polarography—Application to Solutions of Uranyl Sulfate containing Corrosion Products. R. G. BALL, D. L. MANNING and O. MENIS. ORNL-2717. 25 *May* 1959. Pp. ii + 27. $1.00.

High Temperature Gas Chromatography of Aromatic Hydrocarbons: Instrument Design and Exploratory Studies at Temperatures up to 430°C. ROBERT A. BAXTER and ROBERT T. KEEN. NAA-SR-3154. 1 *June* 1959. Pp. 30. $1.00.

A New Apparatus for Liquid Phase Thermal Diffusion. EDWARD VAN HALLE. K-1420. 24 *June* 1959. Pp. x + 353. $5.00.

The Spectrographic Detection of Trace Impurities in Beryllium Oxide. O. P. KILLEEN. Y-1259. 4 *September* 1959. Pp. 12.

ERRATA

Vol. 2, *page* 226. *Legends to the Figs. should read as follows*:

Fig. 3. Continuous variations of the palladium complex with thiomalic acid.

Fig. 4. Slope ratio of the palladium complex with thiomalic acid. Curve (1), reagent in large excess; curve (2), palladium in large excess.

Note: The first slope in curve (2) is due to the formation of a 1 : 1 complex which absorbs less than the 2 : 1 complex. The second slope in curve (2) was used to establish the 2 : 1 ratio.

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CO-ORDINATION OF THE NO GROUP

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(*Received* 18 *March* 1959, *revised paper received* 17 *July* 1959)

Summary—The evidence indicates that nitric oxide normally co-ordinates as a charged ion. Complexes containing the neutral molecule such as $[Fe^{II}(CN)_5NO]^{3-}$, derived from the compound sodium pentacyanoammine ferrate^{II} which is widely used in analytical chemistry and in which the odd electron is still localised on the ligand, exist as unstable, transient compounds only.

On the basis of its electronic structure, which contains one unpaired electron, we would expect nitric oxide to form co-ordination compounds in three ways. These are:

(1) By loss of the odd electron, followed by co-ordination of the $\overset{+}{NO}$ ion.
(2) By gain of an electron, followed by co-ordination of the $\overset{-}{NO}$ ion.
(3) By co-ordination of the neutral NO group, through a co-ordinate covalency involving two electrons from the N atom.

Examples of both (1) and (2) are well established, particularly the former. Thus the structure of sodium nitroprusside as $Na_2[Fe^{II}(CN)_5\overset{+}{NO}]$ (the N atom having lost an electron) has been deduced from its diamagnetism, from its conversion to $Na_4[Fe^{II}(CN)_5\overset{-}{NO_2}]$ by alkali and from its relation to the compounds $Na_4[Fe^{II}(CN)_6]$ and $Na_3[Fe^{II}(CN)_5 \cdot CO]$. It should, however, be mentioned that recent infra-red studies[1] point to it being a resonance hybrid, with the iron tending to the Fe^{III} and even the Fe^{IV} state. Compounds of the type $Co(NO)(CO)_3$ are also accepted as containing the $\overset{+}{NO}$ ion.

Evidence for the existence of complexes containing the $\overset{-}{NO}$ ion is more scanty, but the diamagnetism of the pink ion $[Co^{III}(NH_3)_5 \cdot \overset{-}{NO}]^{2+}$ is ascribed to its containing tervalent Co and the $\overset{-}{NO}$ ion, this salt being similar to the chloropentammine salts in which the chlorine is bound covalently to tervalent Co. Sidgwick thought the structure of the compound iron tetranitrosyl to be $[Fe(NO)_3]^- \overset{+}{NO}$, but Griffiths, Lewis and Wilkinson[2] consider that its infra-red spectrum points to three of the NO groups co-ordinating as $\overset{+}{NO}$ and the other as $\overset{-}{NO}$.

A number of authors have assumed the existence of compounds in the third class, but it appears that very little experimental evidence can be adduced for their existence. Mattern and Gill[3] state that pentacyano-iron complexes such as $Na_3[Fe^{II}(CN)_5 \cdot NH_3]$ react with nitric oxide to form structures containing the ion $[Fe(CN)_5 \cdot NO]^{3-}$, this being one of the few cases in which NO replaces a neutral group without change of charge, which implies that the iron is in the Fe^{II} state. They say that the complexes are yellow in neutral but violet in acid solution and cite the work of Manchot, Merry and Woringer,[4] and also of Baudisch.[5]

Baudisch[5] explains the reactions into which nitroprusside enters after exposure to light by stating that the NO group has become extremely reactive. This he considers is due to the photo-reaction,

$$[Fe^{III}(CN)_5NO]^{2-} \rightarrow [Fe^{II}(CN)_5\overset{+}{N}O]^{3-}$$

and he states that the unpaired electron is attached to the N of the NO group, although why he should denote this by $\overset{+}{N}O$ is not clear.

Bearing in mind, however, that the accepted structure of nitroprusside is $Na_2 Fe^{II}(CN)_5\overset{+}{N}O$ and that any change in the valency state of the iron would involve an electron gain by the $\overset{+}{N}$ of the $\overset{+}{N}O$ ion, we would expect this activated intermediate to have the structure $Na_2[Fe^{III}(CN)_5{\cdot}NO]$.

This would be paramagnetic, as Baudisch reports, although he appears to associate paramagnetic properties with the Fe^{II} state. Baudisch presents no experimental evidence for the existence of the transitory paramagnetic compound, however, and he never succeeded in isolating it.

Blanchard,[6] also quoting Manchot, states that the tervalent ion $[Fe^{II}(CN)_5{\cdot}NO]^{3-}$ can be prepared but that it is unstable and goes over spontaneously to the nitroprusside anion.

Sidgwick[7] refers to nitroso-prussi compounds with the probable structure $M_3[Fe(CN)_5{\cdot}NO]$ which he considers to contain ferric iron bound covalently to a nitroso group, *i.e.* $>Fe^{III}{-}N{=}O$. He states that these compounds are prepared by the action of nitric oxide on aqueous solutions of pentacyano-aquo or ammine-ferrates^{II}, *i.e.* of the type $Na_3[Fe^{II}(CN)_5{\cdot}H_2O]$, but the papers[8] which he quotes do not mention the isolation of such compounds. He also states that the colour changes which these compounds supposedly undergo ("dark yellow in neutral solution, purple in acid solution") support his postulate of nitroso structure, as the latter can exist in a dimeric colourless state and a blue or green monomeric one.

Hofmann[8] merely suggests that in the reaction between nitric oxide and what he calls "prussid-natrium" (probably the compound $Na_3[Fe^{II}(CN)_5{\cdot}H_2O]$), an intermediate compound "most probably $Na_3[Fe(CN)_5{\cdot}NO]$" is formed, which is then transformed quantitatively into sodium nitroprusside. He also observes that when in the intermediate stage, the yellow neutral solution gives the characteristic violet colour on testing with sulphides, but also becomes violet on acidification. This hypothetical intermediate containing a neutral NO group and the iron presumably in the Fe^{II} state, has never been isolated.

Manchot, Merry and Woringer,[4] who studied the absorption of nitric oxide by the pentacyano-ammine ferrate^{II} $Na_3[Fe^{II}(CN)_5{\cdot}NH_3]$ also postulated the intermediate formation of the same compound. They termed it a ferrous nitroprusside, this being an obvious stage in the formation of a ferric nitroprusside (as sodium nitroprusside was then thought to be) under oxidising conditions.

Krasna and Rittenberg[9] suggest the intermediate formation of the ion $[Fe^{II}(CN)_5{\cdot}NO]^{3-}$ during the reduction of nitroprusside with hydrogen in the presence of the enzyme hydrogenase, but the results on which they base this are somewhat imprecise. They deduce the structure of the products from the reaction of the solution with "neutral iodine" and suggest that the solution of nitroprusside, which turns first blue and then brown, is reduced according to the equation

$$[\mathrm{Fe^{II}(CN)_5\overset{+}{N}O}]^{2-} \rightarrow [\mathrm{Fe^{II}(CN)_5NO}]^{3-} \rightarrow [\mathrm{Fe^{II}(CN)_5NOH}]^{3-}$$

Krasna and Rittenberg state that "2 equivalents of neutral iodine are required to oxidise the N at the oxidation level of NOH to nitrite" and that "oxidation of the blue compound to $[\mathrm{Fe^{II}(CN)_5NO_2}]^{-4}$ would require 2 equivalents of neutral iodine per mole of hydrogen consumed. They do not discuss the chemistry of these novel reactions, however, and in addition, the stoichiometry of the latter is somewhat doubtful. Furthermore, a complex ion containing the nitroxyl radical has never previously been reported.

Koltoff and Toren[10] state that polarographic reduction of the nitroprusside ion gives three waves, the first one of which can be explained in terms of a one electron reduction to the ion $[\mathrm{Fe^{II}(CN)_5{\cdot}NO}]^{3-}$.

The co-ordination compound, sodium pentacyano-ammine ferrate$^{\mathrm{II}}$, is widely used in analytical chemistry, because of the colours which it gives with many organic compounds. Its preparation and use in this connection is described by Fearon[11] and is based on Hoffmann's work. Freshly prepared, it is a pale yellow solid with the formula $\mathrm{Na_3[Fe^{II}(CN)_5{\cdot}NH_3]{\cdot}xH_2O}$, but on exposure of the aqueous solution to light and air, it becomes brown and able to react with compounds ranging from thiourea to phenylhydrazine. During an investigation of its reaction with N-nitroso compounds, the present author found that an intense purple colour was obtained with traces of nitrous acid. This suggested the possible formation of a complex of the type suggested by Sidgwick, in view of the fact that nitrous acid oxidises simple ferrous salts with formation of nitric oxide, which could conceivably enter the complex anion in this case. All attempts to isolate the supposed purple complex failed, however, and it was eventually concluded that the purple colour was due to the formation of the compound $\mathrm{Na_2[Fe^{III}(CN)_5{\cdot}H_2O]}$, the nitrous acid merely oxidising the compound $\mathrm{Na_2[Fe^{II}(CN)_5{\cdot}H_2O]}$, formed by hydrolysis of the original ammine compound.

With regard to other compounds which may contain a neutral NO group, there is again very little concrete evidence. Hückel[13] states that the black paramagnetic ion $[\mathrm{Co(NH_3)_5{\cdot}NO}]^{2+}$ exemplifies the co-ordination of NO as a neutral group, the Co atom being bivalent, but Milward, Wardlaw and Way,[14] in their original paper on the paramagnetic properties of the compound, considered it to be a resonance hybrid of the structure

$$[\mathrm{5NH_3,\ \overset{=}{Co}{-}\overset{+}{N}{\equiv}\overset{+}{O}}]^{2+} \longleftrightarrow [\mathrm{5NH_3,\ \overset{-}{Co}{=}\overset{+}{N}{=}O}]^{2+}$$

Its exact structure is still in doubt.

Cambi and Szego[15] considered that measurements of magnetic susceptibility pointed to the existence of the red Roussin salt $\mathrm{K_2Fe_2S_2(NO)_4}$ as a dimer in which one of the iron atoms is bivalent and the other tervalent, three of the NO groups being in the complex as univalent radicals and the other as a molecule. Ewens,[16] however, considers that these and similar compounds contain a Fe–Fe link and that each NO group contributes three electrons to the corresponding Fe atom.

Moeller,[17] referring to the same compound, also states that Manchot's view that it contains co-ordinated nitrosyl groups is in accord with the general tendency of nitric oxide to transfer an electron and co-ordinate.

The strongest experimental evidence for the co-ordination of NO as a neutral molecule appears in a recent paper by Griffith, Lewis and Wilkinson.[18] Their measurements of the magnetic susceptibility of solutions of sodium pentacyanoammine ferrate^{II} which have absorbed nitric oxide until the ratio Fe : NO is unity, indicate a moment corresponding to somewhat less than one unpaired electron. This corresponds to the co-ordination of the neutral molecule, the odd electron remaining localised on the ligand. They offer no explanation of the moment being less than that corresponding to one unpaired electron, however, (this being unusual for hexa-co-ordinated iron compounds), and also state that the complex cannot be isolated.

These authors also remark that measurements of the magnetic susceptibility of aqueous solutions of the corresponding ferrous sulphate-nitric oxide complex point to the formulation of the penta-aquonitrosyl ferrate ion as

$$[Fe^{I}(H_2O)_5NO]^{2+}$$

Although at first sight this ion would appear to contain iron^{II} co-ordinated with a neutral NO molecule, the nitric oxide has actually donated three electrons to the ferrous iron.

Most of the experimental evidence therefore points to the co-ordination of NO as an ion. The existence of compounds such as $M_3[Fe(CN)_5 \cdot NO]$, containing a neutral NO group, appears to be hypothetical, what evidence there is pointing to their extreme instability and formation as transient intermediates only. This would be in accord with the fact that the odd electron would still be localised on the ligand, and the molecule would therefore be as reactive as that of nitric oxide itself.

Acknowledgements—The author wishes to thank British Nylon Spinners Limited for permission to publish, Dr. D. R. Williams for helpful criticism of the paper, and the translating staff of the Department for translating the original papers referred to in the text.

Zusammenfassung—Aus bisherigen Befunden ist der Schluss zu ziehen, dass das Stickoxyd gewöhnlich in Form des geladenen Ions Koordinierung eingeht. Komplexe welche das neutrale Molekül enthalten und in welchen sich das ungepaarte Elektron noch auf dem Liganden befindet, wie z.B. $[Fe^{II}(CN)_5NO]^{3-}$, werden nur als unbeständige Zwischenprodukte aus dem in der analytischen Chemie vielfach zur Anwendung kommenden Natrium Pentacyanoammineferrat (II) gebildet.

Résumé—Sur la base des données disponibles on déduit que l'oxyde nitrique se coordine généralement sous forme de son ion chargé; des complexes comme, par exemple, le $[Fe^{II}(CN)_5NO]^{3-}$, qui contiennent la molecule neutre et dans lesquels l'éléctron impair se trouve encore sur le ligand, n'ont qu'une existence temporaire sous forme de produits intermediaires, derivés du pentacyano-ammine ferrate (II) de sodium, composé qui a un usage universel dans l'analyse chimique.

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[2] W. P. Griffith, J. Lewis and G. Wilkinson, *ibid.*, 1958, 3993.
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STUDIES ON URONIC ACID MATERIALS—II[1]

THE VARIATION IN COMPOSITION OF GUM NODULES FROM *COMBRETUM LEONENSE*

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Summary—Several gum nodules from the Nigerian tree *Combretum leonense* have been individually investigated. The amount of material present in each nodule has permitted a study of the variation in constitution of both crude and purified forms of the gum. The variations found are much greater than can be explained by analytical error. They are considered to indicate that inter-nodule differences in fine structure exist.

IN certain fields of carbohydrate chemistry, *e.g.* those dealing with starch[2,3,4] and with glycogen,[5] sampling procedures require strict attention when material for investigation of fine structure is being selected. Even if strict control of botanical variety and strain proves possible, variations in growth and maturity caused by seasonal effects are difficult to control, and wide variation in chemical composition can occur.[6] Several extensive studies of such effects, *e.g.* in some varieties of seaweed,[7] barley,[8] grasses and clovers[9,10] have now been reported.

Severe sampling difficulties exist in the study of plant gums. Usually the gum is taken from the tree bark in small nodules which can vary greatly in colour and general appearance. Any guarantee of constancy of originating botanical species is difficult to obtain, particularly when collection overseas is arranged. Furthermore, gum is normally exuded to minimise bacterial attack at localised sites where superficial injury from a variety of possible causes has been sustained at some unknown time. Thus nodules from the barks of a number of trees may possibly vary greatly in maturity and chemical composition, even although each of the trees was authentically of the same botanical species.[11]

Consequently, when a batch of nodules collected in such a way is purified by precipitation in acidified alcohol from aqueous solution, a complex mixture of different polymeric carbohydrate systems may result. Although early studies[12] showed that damson gum from several trees grown in different districts was "essentially a homogeneous chemical entity," recent work has suggested that gum ghatti may be heterogeneous[13] and that sisal pectic acid[14] may contain a series of closely related molecular species.

There have been few investigations of inter-nodule variation. Torto[15] analysed one nodule of gum from *Fagara Xanthoxyloides* for acetyl and methoxyl content, and stated that specimens prepared from nodules from different trees did not show significant variations in optical rotations and equivalent weights; this was claimed to indicate the essential homogeneity of the gum. In a study of the gum from *Brachychiton diversifolium*, three separate nodules were powdered, dried, and analysed for ash, nitrogen, methoxyl and acetyl content: it was deduced that the nodules were "not significantly different in composition".[16]

A sample of the gum from *Combretum leonense** was observed to contain a number of unusually large clean nodules, each approximately the size of a walnut. This appeared to make possible a study of the composition of each nodule.† This paper gives the results of an attempt to investigate the composition of each nodule as fully as the amount of material available permitted.‡

Initially, the six largest, whole nodules, whose weight varied from 8–12 grams, were selected for study. They were alike in appearance, being dark brown in colour with characteristic surface markings, and had a marked odour of acetic acid. The nodules, numbered I–VI, were individually ground to a coarse powder. It was immediately observed that nodules I, III and V gave a pale yellow powder, whilst that from the others was a dark reddish-brown.

EXPERIMENTAL

Analytical methods

(*a*) Moisture contents were found by heating to constant weight at 103°.

(*b*) % ash was found by heating in a muffle at 550°; constant weight was reached in 4 hours.

(*c*) % nitrogen was found by a semi-micro Kjeldahl method.

(*d*) Acetyl contents were determined by the Weisenberger method.[22]

(*e*) Anderson's apparatus[1] was used to determine uronic acid contents.

(*f*) Free titratable acidity was found by direct titration with $0{\cdot}0247N$ sodium hydroxide to phenolphthalein end-point in a stream of CO_2-free nitrogen.

(*g*) Viscosity measurements were made using a suspended-level dilution viscometer (Polymer Consultants Ltd; water = 184 secs) in a thermostat constant to 0·01°; results are expressed using g/ml as concentration units.[23]

Autohydrolysis experiments

The quantity (calculated on an ash-free, dry weight basis) of each nodule to give 100 ml of a 1% (w/v) solution was dissolved in a standard flask. The solutions were transferred to clean, dry flasks which were placed in a boiling water bath after being fitted with short reflux condensers. Aliquots (2 ml) were withdrawn at intervals by pipette (considerably lengthened above the graduation mark) introduced *via* the reflux condenser, which was fitted with an anhydrone guard-tube except when withdrawals were being made.

Paper partition chromatography

This was carried out on Whatman No. 1 paper at 20° with the upper layers of the following systems (v/v): (*A*) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3); (*B*) pyridine/ethyl acetate/acetic acid/water (5 : 5 : 1 : 3).[24] Sugars were located by heating after spraying with either saturated aqueous aniline oxalate solution or with a solution of *p*-anisidine hydrochloride in butan-1-ol. All sugars were identified by comparison with reference sugars run on the same chromatograms.

Quantitative estimation of sugars

This was by the Somogyi method;[25] D-ribose was used as reference sugar after being shown absent in the gum. In the autohydrolysis experiments, total free reducing sugars were calculated as arabinose, which was the main sugar liberated.

Electrophoresis

The electrophoresis of neutralised solutions of purified nodules VII and VIII was attempted (Shandon Universal Filter Electrophoresis Apparatus) using 300 volts for 2–6 hours in $0{\cdot}05M$ borate

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* Collected in Nigeria in 1952, and kindly provided by Dr. R. J. McIlroy.

† Dr. G. O. Aspinall kindly provided several nodules for this purpose, although the total weight of gum available was not large.

‡ The structure of the gum is now being studied in this Department by Dr. Aspinall.

buffer at pH 8 on (*a*) 20 × 5 cm paper strips (Whatman No. 1), (*b*) glass-fibre paper. No movement was observed on the paper strips: small mobilities ($<$0·5 cm after 6 hours) were obtained on the glass-fibre paper, but no separation of components could be detected. Electrophoresis for 6–18 hours on glass-fibre paper in $2M$ alkali[13] resulted in movements of 3–4 cm as a continuous smear, from which no conclusive result could be obtained.

Studies on crude material

Table I shows the results of duplicate determinations of the moisture, ash, nitrogen, methoxyl, acetyl and uronic acid content of the crude powdered material from each nodule. Results of analyses of the ash are also shown.* Chloride, sulphate and phosphate were all absent; carbonate, formed during ashing, was found to account for 55% of the ash from nodule VI.

Table II shows the values for pH, free titratable acidity, total free reducing sugars, and flow-time number obtained from aliquots of aqueous solutions (1% w/v, corrected for moisture and ash content) of each powdered nodule. Each 1% solution was then autohydrolysed at 98°. At intervals, up to a

TABLE I.—DETERMINATIONS ON CRUDE POWDERED MATERIAL

	Nodule					
	I	II	III	IV	V	VI
% Moisture	14·9 14·9	15·3 15·6	14·0 14·0	15·5 15·6	17·1 16·9	14·9 14·9
% nitrogen	0·13 0·14	0·06 0·07	0·16 0·16	0·05 0·05	0·11 0·13	0·12 0·12
% methoxyl	nil	nil	nil	nil	nil	nil
% acetyl	5·1 5·2	6·2 6·2	4·4 4·4	5·9 5·9	6·3 6·2	3·0 3·0 3·1
% Uronic acid anhydride	15·4 15·7	18·7 19·0	15·9 16·0	18·9 19·0	17·7 17·8	15·1 15·4
% Ash	2·56 2·54	4·03 3·96	2·38 2·43	3·79 3·83	3·02 3·12	1·71 1·69
Composition of ash (as parts per million)						
Ca	235,000	235,000	205,000	257,000	257,000	270,000
Na	5,200	5,200	4,700	3,700	3,000	4,400
K	136,000	91,000	180,000	127,000	136,000	37,400
Mg	n.d.	n.d.	n.d.	n.d.	n.d.	84,000
Cu	166	59	538	56	82	272
Mn	25,000	11,400	17,400	17,100	13,400	18,400
Fe	4,800	1,240	2,310	1,200	1,200	1,540
Ba	680	590	620	630	550	540
Sr	1,590	1,290	1,490	1,560	1,170	1,060

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* We are greatly indebted to Dr. R. L. Mitchell, Macauley Institute for Soil Research, Aberdeen, who obtained from the small quantities of ash available the values for Cu, Mn, Fe, Ba and Sr.

TABLE II.—DETERMINATIONS ON 1 % AQ. SOLUTIONS OF CRUDE MATERIAL

	Nodule					
	I	II	III	IV	V	VI
% cold water insoluble	0·3	0·5	0·6	0·2	0·2	0·3
pH	4·25	4·30	4·10	4·25	4·20	4·10
Free titratable acidity	0·378	0·374	0·324	0·426	0·398	0·354
(*ml* 1N NaOH per gram)	0·374	0·384	0·330	0·404		
Hence apparent equiv. wt.	2645	2645	3125	2380	2500	2820
% Free reducing sugars	0·74	1·02	0·72	2·10	0·74	0·90
(Somogyi,[25] as arabinose)		1·02	0·84	2·16		
Flow-time at 26·4°	468	491	425	620	449	366
(water = 184 secs)	466	491	429	618	451	364
Hence $(t - t_0)/t_0$	1·52	1·73	1·32	2·41	1·45	1·00

total of 360 hours, aliquots were withdrawn for determination of total reducing power and total free acidity; the values found are shown in Figs. 1 and 2 respectively. Table III shows the ratios of free sugars present after 70 and 168 hours' autohydrolysis; values of the flow-time number were also found at 70 hours. Hydrolysis with H_2SO_4 (2N) at 100° for 24 hours was incomplete, but formic acid (90 %) in a sealed tube at 100° for 5 hours gave complete hydrolysis. Within the limits of experimental error, the ratios of the sugars found were the same for each of the samples, *viz.* arabinose/galactose/rhamnose = 9/10/1.

Studies on purified material

Preliminary purification experiments were carried out on nodules I and V, which were the largest samples remaining. After dissolution in cold distilled water, the solutions were poured into 3 volumes of acidified ethanol (0·1N with respect to HCl). The white curdy gum precipitate was removed by centrifuge. After one such precipitation, the material from nodule I contained 0·04 %N and 0·11 % ash; two precipitations of the material from nodule V gave purified gum having 0·03 %N and 0·02 % ash. Since re-precipitations and ash determinations at this level consume considerable quantities of material, it was decided to accept this as a reasonable standard of purification. Each of the remaining nodules was therefore precipitated twice, and, to conserve material, it was assumed that their values of %N and % ash would be similar to those found for V.

After removal by centrifugation, the precipitated material was dried by immersion in acetone for 10 days: the acetone was changed daily and the gum was progressively ground to a fine powder. Samples I and V were then placed in a vacuum pistol at 60° over P_2O_5 for 1 hour, then stored in a vacuum desiccator for 14 days. After this treatment, oven drying to constant weight at 103° showed 6·83 % "moisture" in sample I and 4·64 % in V. Purified samples II, III, IV and VI were dried, after acetone dehydration as before, under vacuo at 80° for 48 hours in an attempt to decrease the moisture content; oven drying to constant weight at 103°, however, showed 5·25 %, 4·86 %, 5·73 % and 6·20 % "moisture" for these samples respectively. Since these values were surprisingly high, further drying experiments were carried out on small quantities of each sample. Using an infra-red quantitative technique,[17] it was found that both water and acetone (or any other organic solvent used for precipitation or preliminary dehydration) were retained up to temperatures at which decomposition of the gum began (about 135°) as indicated by slight browning and the start of evolution of CO_2. To augment the material available, a further two nodules (numbers VII and VIII) were obtained; after two

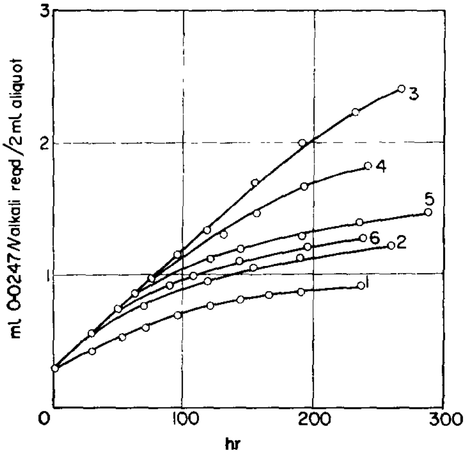

FIG. 1.—Increase in total free acidity on autohydrolysis.

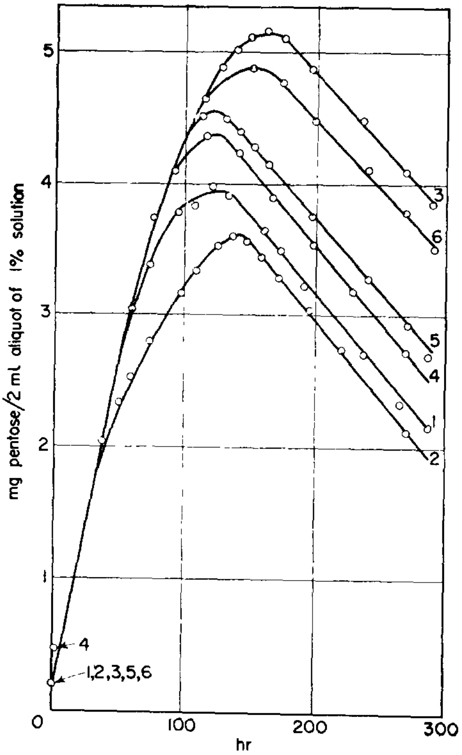

FIG. 2.—Increase in total free reducing power on autohydrolysis.

TABLE III.—DETERMINATIONS ON 1% AQ. SOLUTIONS AFTER AUTOHYDROLYSIS

	Nodule					
	I	II	III	IV	V	VI
After 70 *hours:*						
$(t - t_0)/t_0$	0·04	0·02	0·07	n.d.	0·10	0·06
ratio of sugars: hexose disacch.	1	1	1	n.d.	1	1
pentose disacch.	1	1	1	n.d.	1	1
galactose	1·6	1·2	1·5	n.d.	1·5	1·6
arabinose	12	10	20	n.d.	15	20
rhamnose	1	1	1	n.d.	1	1
After 168 *hours:*						
ratio of sugars: hexose disacch.	1	1	1	1	1	1
pentose disacch.	1	1	1	1	1	1
galactose	2	2	2	2	2	2
arabinose	15	12	14	10	13	13
rhamnose	1	1	1	1	1	1

TABLE IV.—DETERMINATIONS ON PURIFIED MATERIAL

	Nodule							
	I	II	III	IV	V	VI	VII	VIII
% nitrogen	0·04 0·03	n.d.	n.d.	n.d.	0·03 0·03	n.d.	0·04	0·06 0·07
% acetyl	2·9 2·8	3·4 3·3	3·3	2·9 2·9	4·3 4·4	1·7 1·7	3·0 2·9	3·6
% uronic acid anhydride	15·3 15·5	19·2 19·3	15·2 15·4	19·7 19·6	18·1 18·4	14·9 14·9	19·2 19·4	20·1 19·9
Results from 1 % *aq. solutions*:								
% Free reducing sugars	0·21	n.d.	n.d.	n.d.	0·28	n.d.	n.d.	n.d.
Free titratable acidity*	0·882	1·058	0·868	1·106	1·060	0·856	1·072	1·149
Hence equivalent wt.	1133	945	1152	904	943	1168	933	870
Hence % uronic† acid anhydride	15·5	18·6	15·3	19·4	18·6	15·1	18·9	20·2
Limiting flow-time‡ number	0·63	0·76	n.d.	0·98	0·68	n.d.	0·61	0·67

* as mls. 1·0*N* NaOH per gm

† if all acidity due to uronic acid groups

‡ at 25·0° in 1 % NaCl solution.

precipitations in acidic ethanol, the purified material was redissolved, dialysed against distilled water for 3 days, then isolated by freeze drying. The resultant material was found (*a*) to lose 1 % of water on drying to constant weight at 103°, and (*b*) to retain a further 1 % of water up to the temperature at which decomposition began. Robson[18] has reported that freeze drying for 500 hours is required to remove *all* traces of moisture from glucose–gelatine solutions. A full account of the dehydration and solvent retention studies made will be given in a later communication.

Determinations of nitrogen, acetyl, and uronic acid content were made on the purified samples, the results (corrected for the moisture contents reported above) being shown in Table IV, which also gives the results of determinations of free reducing sugars and free titratable acidity made on 1 % (w/v) aqueous solutions. Calculation of the equivalent weight of the gum acid, based on the free titratable acidity value, shows that, in each case, the uronic acid content accounts for the total acidity found.

Before studying the viscosity behaviour of each purified sample, the polyelectrolyte effect was investigated. Fig. 3 shows that 1 % salt solution gives adequate suppression of the polyelectrolyte effect. The limiting flow-time number of the purified samples was subsequently found at 25·0° in 1 % sodium chloride solution; the viscosity curves obtained are shown in Fig. 4. Use of a zero shear viscometer (Polymer Consultants Ltd.) showed that Newtonian behaviour was given by an 0·5 % solution of sample VIII in 1 % sodium chloride.

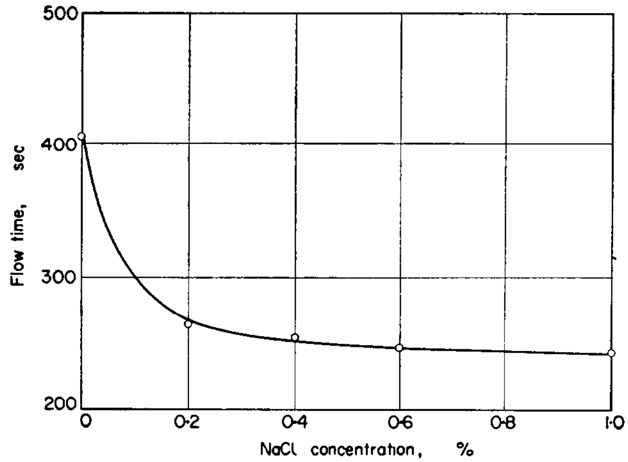

FIG. 3.—Decrease in electroviscous effect.

When a plant gum is purified by acidic ethanol precipitation from aqueous solution (which may, as in this case, have pH = 4) some form of auto-degradation or fractionation could possibly occur. Such an effect would become increasingly serious as the number of re-precipitations—and consequently the percentage of free-acid groups—was increased. To investigate this possibility, the twice precipitated material from nodule VII (curve VII(*a*), Fig. 4) was given two further purifications. During each of these, the possibility for degradation to occur was increased by storing the aqueous solution at 40° for 1 hour before precipitation in ethanol. (In the original precipitations, no heating was employed, and addition to ethanol was made as soon as solution was achieved). Since the material recovered from these treatments gave viscosity curve VII(*b*) in Fig. 4, no degradation of this gum apparently occurs whilst it is in the free acid form during purification processes. The effect of dilute alkali was also tested. An aqueous solution (1 % w/v) of the gum was neutralised to phenolphthalein end-point; a calculated excess of alkali was then added to make the solution 0·1N with respect to

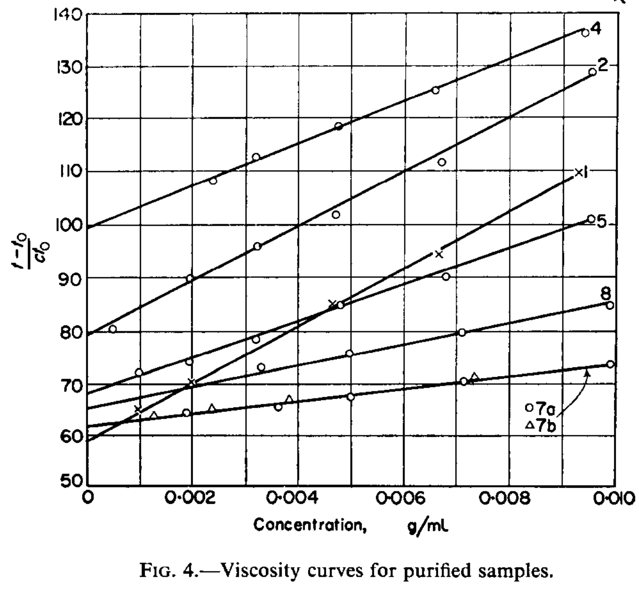

FIG. 4.—Viscosity curves for purified samples.

NaOH. The limiting flow-time number of this solution was determined at 25·0° on portions of the solution (*a*) *immediately*, (*b*) *after storage* at 25·0° for 72 hours. No difference in viscosity behaviour, before and after storage, was detectable.

No tendency for fractionation to occur was observed when the ethanol used in precipitations was varied from 2 to 5 volumes. After centrifugation of the main precipitate, the supernatants were stored at 0° for several days; no further material precipitated. No precipitation of neutral material was given on addition to the supernatants of borate + "cetavlon".[19] Electrophoresis experiments on nodules VII and VIII were inconclusive. (see above).

DISCUSSION

The available material was used to obtain, as far as possible, information supplementary to that which will be obtained in the structural study now in progress on the bulk material. Each of the samples was remarkably homogeneous; good replicates, as shown in the tables, being obtainable without difficulty. Each nodule, however, differed strikingly in composition from each of the others. In view of the reproducibility of results obtained in each of the analytical procedures used, the internodule differences are greater than could be ascribed to any possible experimental error, and are considered to be significant. In only one procedure—determination of the ratio of sugars liberated on complete hydrolysis—was it not possible to distinguish between each nodule; the error involved in such a determination is, however, at best ±5% and is more probably ±10%.

Correlations between the properties of the nodules are difficult. The nodules cannot easily be assigned to sub-groups; a gradation between the maximum and minimum values of each analysis appears to be given. That the nodules are broadly similar in essential detail is not surprising, considering the care with which they were selected for study from a batch. Yet, in the crude material, 100% variation occurred in the nitrogen, ash, and acetyl contents. Calculation shows that, in the crude material, about 50% of the uronic acid carboxyl groups are in the free acid form.

In the purified samples, considerable variations occur in the acetyl and uronic acid anhydride contents, and in the viscosity behaviour. The acetyl contents shown in Table IV are stable in solution under the precipitation conditions used; when stored in the solid state, however, the purified material develops a strong odour of acetic acid, a behaviour reminiscent of the original nodules. The nitrogen content of the crude material was reduced, but not completely eliminated, by the purification process used. Re-precipitations were found to reduce ash contents significantly, but little reduction in residual nitrogen content was achieved. Small residual nitrogen contents persist in other carbohydrate systems[20] despite extensive attempts at purification; their significance remains in doubt.[21]

In only one case (nodule III) is the uronic acid content of the purified sample significantly smaller than that of the crude material. This is difficult to explain since, on a dry weight basis, purification should lead to increased uronic acid content unless some sort of fractionation has occurred. Agreement between the uronic acid values found directly and by calculation from the neutralisation equivalent is good, and strengthens the evidence that the variation from 14·9% to 20·1% is real. Such a variation must reflect fine structural differences; the inter-nodule variation in viscosity and acetyl content, and the kinetic differences found in the autohydrolysis experiments support this indication.

The variations found are sufficiently great to emphasise the need for more careful sampling procedures than have generally been used in the past. It is hoped at an early date to extend the present investigation by securing for study[*] a number of gum nodules obtained (*a*) from the bark of one tree as a result of several injuries made simultaneously and (*b*) from the barks of a number of trees, all of the same species, as the result of one similar injury inflicted simultaneously on each of them.

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Zusammenfassung—Gummitropfen vom Baume Combretum leonense aus Nigeria wurden individuell untersucht. Die Mengen verschiedener Substanzen in einzelnen Tropfen wurden als stark variierend gefunden und gestatteten Rückschlüsse auf Verschiedenheiten in der Zusammensetzung sowohl von Roh- als auch gereinigtem Latex. Verschiedenheiten der Zusammensetzung waren weitaus grösser als dass sie hätten durch Schwankungen der Analysenwerte erklärt werden können. Der Schluss wurde gezogen, dass sie durch Unterschiede in der feineren Stuktur der Tropfen verursacht werden.

Résumé—Les auteurs ont étudié individuellement différents nodules de gomme provenant de l'arbre nigérien, Combretum leonense. La quantité de matière présente dans chaque nodule a permis une étude de la variation de la constitution des deux formes: brute et purifiée de la gomme. On trouve des variations beaucoup plus grandes que ne l'expliquerait l'erreur analytique. On considère que ces variations indiquent qu'il existe des différences internodules dans la structure fine.

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THE APPLICATION OF THE CATHODE RAY POLAROGRAPH TO THE ANALYSIS OF EXPLOSIVES

THE DETERMINATION OF MERCURY FULMINATE*

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Summary—The polarographic behaviour of mercury fulminate has been described, and it is possible to determine this compound polarographically.

THE polarographic behaviour of mercury fulminate has not yet been reported in literature. The simplicity of analytical procedures using the Cathode Ray Polarograph[1,2,3] suggests the value of its application to the determination of this explosive. Consequently, a method has been developed for the rapid determination of mercury fulminate. The method is based on the anodic oxidation and cathodic reduction of mercury fulminate in a pyridine/potassium nitrate basic electrolyte. Mercury fulminate is soluble in pyridine[4] which also acts as as essential part of the base electrolyte in the polarography of fulminic acid.

EXPERIMENTAL

Mercury fulminate was prepared as stated by Davis.[4] It was purified from oxides of mercury by recrystallization from ammonium hydroxide.

The determination was carried out in the following way: 250 mg of sample were placed in a 100-ml flask, dissolved in 50 ml pyridine and made up to the mark with *N* potassium nitrate. 0·04, 0·08, 0·12, 0·16 and 0·20 ml of this solution were transferred to 10-ml flasks and brought up to the mark with a base electrolyte consisting of 10% pyridine and 90% *N* potassium nitrate; thus the concentrations of mercury fulminate in the flasks were 10, 20, 30, 40 and 50 μg/ml. The polarograms were determined using 5 ml of each solution, with starting potentials of −0·5 V for anodic oxidation and −0·05 V for cathodic reduction, and the scale factor was 1·0 in each case. The wave heights, as recorded in Table I, were observed to be directly proportional to the concentration of mercury fulminate. Typical anodic and cathodic waves are shown in Figs. 1 and 2.

TABLE I

Concentration of $Hg(ONC)_2$, μg/ml	Wave height, *divisions*	
	Anodic	Cathodic
10	6·5	9
20	13	18·5
30	19·5	25
40	25·5	36
50	32·5	45

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* Presented at a joint meeting of the Scottish Section of the Society for Analytical Chemistry and the Polarographic Society, held at The Queen's University, Belfast on 26 June 1959.

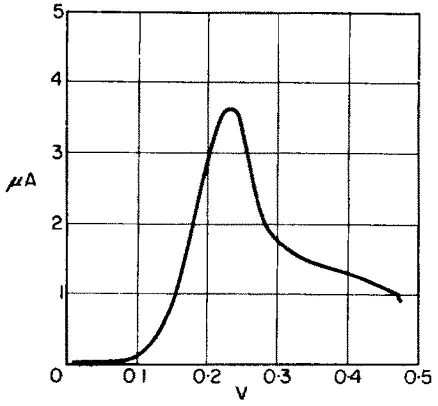

FIG. 1.—Reduction wave of ONC′
40 μg/ml $Hg(ONC)_2$

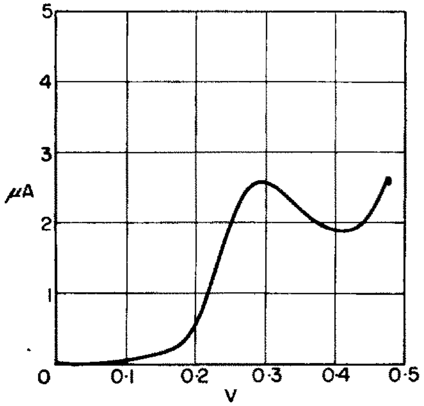

FIG. 2.—Oxidation wave of ONC′
40 μg/ml $Hg(ONC)_2$

Determination of mercury fulminate in explosive primers

To extend this observation for practical application, (to the determination of mercury fulminate in explosive primers), a series of synthetic samples was prepared containing 20, 40, 50, 60 and 80% of mercury fulminate in potassium chlorate, and the percentage of introduced mercury fulminate was determined using the sample containing 50% as "standard" for comparison.

Weights of mercury fulminate, 40, 80, 100, 120, and 160 mg, were introduced into 100-ml flasks, dissolved in 50 ml pyridine, 160, 120, 100, 80 and 40 mg. of potassium chlorate were added respectively, and the solutions were made up to the mark with *N* potassium nitrate; 0·1 ml of each solution was transferred into a 10-ml flask and made up to the mark with base electrolyte (pH 8·8). The polarograms were determined on a 5-ml aliquot of each solution as before, using cathodic reduction, and a scale factor of 1·5. The results are recorded in Table II.

TABLE II

% $KClO_3$ introduced	% $Hg(ONC)_2$ introduced	% $Hg(ONC)_2$ found
80	20	20·6
60	40	38·9
50	50	50·0
40	60	61·1
20	80	79·2

The effect of the addition of lead (as nitrate), sodium azide, mercuric mercury, cyanide, cyanate and copper was next investigated. The addition of lead nitrate, sodium azide or mercuric chloride produce no interference with the formation of red/ox fulminic waves. The addition of cyanide results in the formation of red/ox waves with shapes identical to the waves of fulminic acid, but with peak potentials differing by 100 mV. In consequence the determination of both substances using direct current is not possible; but working with derivative current, the separation of both waves is easily obtained, thus indicating the possibility of the simultaneous determination of both cyanide and fulminate, as indicated by Figs. 3–6. Cyanate is neither oxidisable nor reducible and so has no effect on the determination of fulminate. Copper produces an extremely interesting behaviour. The addition of 1 μg of copper to 100 μg of fulminate depresses the wave height of fulminate by 15%. Further additions of 1 μg of copper decrease the wave height approximately by 15% until the ratio of copper to fulminates is 1 : 5, when the reduction wave of fulminate is completely removed, and the formation of two copper waves is observed with a starting potential of −0·3 V. This indicates that quantitative

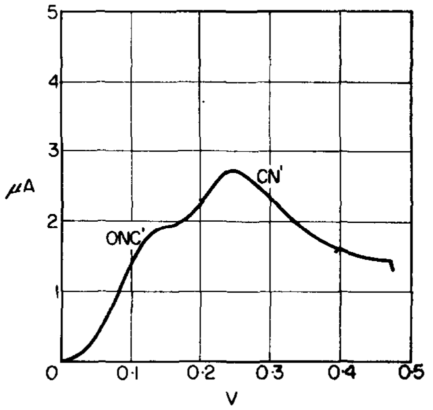

FIG. 3.—Reduction waves of ONC′ and CN′
Direct current
7 μg/ml ONC′ : 3 μg/ml CN′

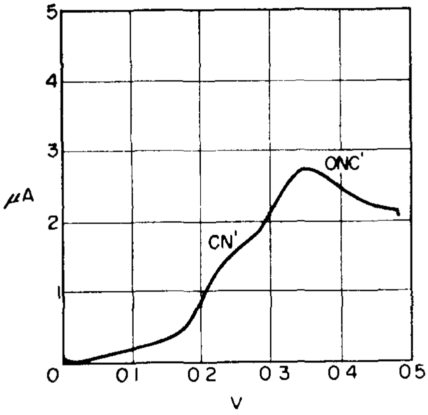

FIG. 4.—Oxidation waves of ONC′ and CN′
Direct current
7 μg/ml ONC′ : 3 μg/ml CN′

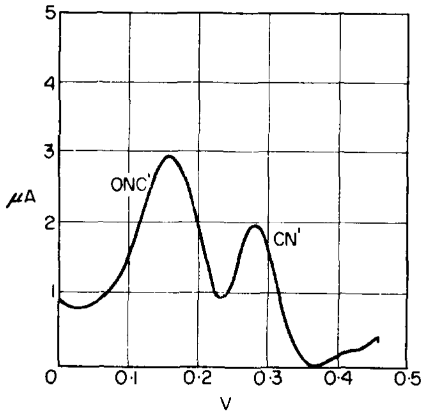

FIG. 5.—Reduction waves of ONC′ and CN′
Derivative current
7 μg/ml ONC′ : 3 μg/ml CN′

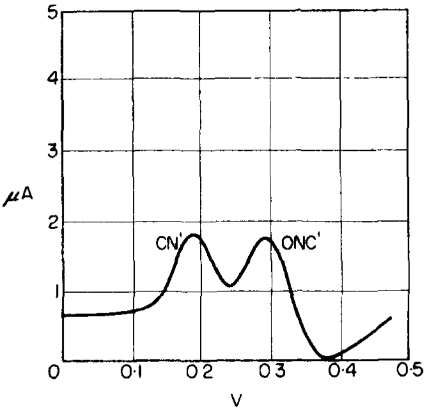

FIG. 6.—Oxidation waves of CN′ and ONC′
Derivative current
7 μg/ml ONC′ : 3 μg/ml CN′

estimation of fulminate cannot be carried out in presence of copper. However, providing the copper content is known, it is possible to determine the fulminate concentration by means of calibration graphs.

DISCUSSION

Fulminic acid is an isomeric form of oxycyanic acid. To the different characteristics, *i.e.* the toxic and explosive property of the one and the non-toxic and non-explosive property of the other, is now added differing polarographic behaviour. The polarographic behaviour of fulminates is similar to that of cyanides. The oxidation of cyanides has been investigated by Kolthoff[5] and the mechanism of the electrode reaction was suggested as being

$$2CN^- + Hg \rightarrow Hg(CN)_2 + 2e^-$$

Similarly the oxidation of fulminates should be

$$2ONC^- + Hg \rightarrow Hg(ONC)_2 + 2e^-.$$

No previous work has been published concerning the reduction of cyanides, but the occurrence of reduction has been proven by the present work. The mechanism of the reduction of cyanides and fulminates remains doubtful.

Acknowledgement—The author wishes to express his thanks to the Directors of Southern Instruments Limited for permission to publish this paper.

Zusammenfassung—Das polarographische Verhalten von Quecksilberfulminaten sowie dessen polarographische Bestimmung werden beschrieben.

Résumé—Le comportement polarographique du fulminate de mercure a été décrit. Il est possible de doser ce composé par polarographie.

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THE SEPARATION AND DETERMINATION OF ALUMINIUM, GALLIUM, INDIUM AND THALLIUM BY PARTITION CHROMATOGRAPHY

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Summary—A method is described for the chromatographic separation and determination of small amounts of aluminium, gallium, indium and thallium. The chlorides of the metals are separated using a solvent-mixture containing phenol : methanol : conc. hydrochloric acid (50 : 30 : 20 W : V : V). Each substance is detected by a single spraying reagent—8-hydroxyquinoline—and the amount of element present estimated semi-quantitatively by visual comparison with standards.

Investigation of the conditions for the removal of the metal oxinates from the paper into an organic solvent has permitted the determination of the elements spectrophotometrically.

A NUMBER of methods have been suggested for the separation of two or more of the elements of Group IIIB of the Mendeleef Periodic Table.[1] Many techniques have been used for separation of elements in this group. In an interesting paper Steinbach and Freiser[2] have examined the extraction of the acetyl acetonates of aluminium, gallium and indium from iron. They suggest a possible separation of these metals by solvent extraction at different pH values. A different approach is that of Klement and Sandmann[3] who separated indium and gallium on cation-exchanger Dowex-50. Gallium has also been separated from aluminium as the thiocyanate by a solvent containing ether and tetrahydrofuran.[4]

One of the most extensive investigations in the separation of this group of elements is that by Arden *et al.*,[5] who separated aluminium, gallium, indium and zinc by partition chromatography using *n*-butanol-hydrochloric acid as the solvent-mixture. Attempts by us to include thallium were found to be unsuccessful.

From the literature survey it appeared that a complete separation of all four elements of the Group had not been successfully achieved. These elements are becoming increasingly important, occurring in small amounts in aluminium alloys and various minerals. Bassett and Tompkins[6] attempted the determination of all four elements in uranium-bearing materials. Aluminium was determined colorimetrically with haemotoxylin or alizarin, but attempts to determine gallium, indium and thallium were wholly unsuccessful.

An important condition in the determination of these elements appears to be the complete separation of one from another. It seemed likely that by careful investigation of solvents or solvent-mixtures, partition chromatography would offer the best and simplest method of separating the elements. This paper, therefore, reports the investigations carried out and the results obtained.

PRELIMINARY INVESTIGATIONS

In 1957, Magee and Headridge[7] reporting results on the chromatographic separation of the alkali metals, suggested that a solvent-mixture containing phenol as complexing agent might give a separation of aluminium, gallium, indium and thallium. A wide range of solvent mixtures were therefore prepared to investigate the action of phenol, in the presence of alcohols and acids. With simple phenol-methanol mixtures, "bearding" occurred. On the addition of acid to these mixtures the bearding disappeared and separation, with good banding, was obtained. The best mixture was found to be one containing phenol-methanol and concentrated hydrochloric acid. Chromatograms with 200 μg of each element were prepared, over a wide range of solvent-mixture components. The Rf values of the most promising are shown in Table I.

TABLE I

No	Phenol	Methanol	Conc. HCl	Rf Values			
				Al	Ga	In	Tl
1	33	33	33	0·18 (±0·04)	0·66 (±0·06)	0·26 (±0·04)	0·43 (±0·03)
2	40	30	30	0·52 (±0·04)	0·80 (±0·05)	0·52 (±0·05)	0·74 (±0·03)
3	25	40	30	0·48 (±0·05)	0·91 (±0·05)	0·53 (±0·04)	0·74 (±0·04)
4	50	30	20	0·10 (±0·03)	0·76 (±0·06)	0·24 (±0·06)	0·50 (±0·06)
5	40	50	10	0·20 (±0·05)	0·68 (±0·05)	0·28 (±0·05)	0·51 (±0·04)
6	20	40	40	0·55 (±0·06)	0·90 (±0·06)	0·50 (±0·04)	0·75 (±0·05)
7	10	50	40	0·70 (±0·05)	0·84 (±0·05)	0·72 (±0·05)	0·77 (±0·05)
8	40	10	50	0·25 (±0·05)	0·55 (±0·06)	0·27 (±0·06)	0·45 (±0·04)

In the solvent-mixtures No. 3–10 each constituent of the phenol-methanol-concentrated hydrochloric acid mixture was varied over the range 20–50%. It can be seen that the separation of gallium, indium and thallium is achieved in every case, but the separation of indium from aluminium is more difficult. This separation was investigated separately and it was found that a large amount of phenol with almost equal quantities of acid and methanol was the most effective. The solvent-mixture used in subsequent work was No. 4 containing phenol : methanol : conc. hydrochloric acid (50 : 30 : 20 : W : V : V).

Development of spraying reagents

Most workers who have investigated these elements by chromatography developed aluminium and gallium with aluminon,[8] indium with dithizone and thallium with an aqueous solution of potassium iodide.[7]

In paper chromatography, however, it is obviously a great asset if a single spraying reagent can be used. Experiments were therefore carried out to find such a reagent. Gallium and indium have been detected by spraying the paper strips with a 5% solution of 8-hydroxyquinoline in methanol : chloroform : water (85 : 10·5% V : V)[7] and then hanging the strips in an atmosphere of ammonia. Under ultra-violet light these elements fluoresce brilliant yellow. Investigations were carried out with this reagent and it was found that, if the chloroform concentration is increased to an amount equal to methanol, the paper sprayed with a 5*N* aqueous solution of ammonia and then with a 8-hydroxyquinoline reagent, aluminium, gallium, indium and thallium may be detected as yellow bands. Aluminium, gallium and indium also give a brilliant fluorescence under ultra-violet light. The composition of the spraying reagent used throughout was a 5% W : V solution of 8-hydroxyquinoline in methanol : chloroform : water (48 : 48 : 4 V : V : V).

Detailed procedure

1. Place the solvent-mixture, phenol-methanol-conc. hydrochloric acid (50 : 30 : 20 W : V : V) in the solvent-trough of the Shandon Chromatank at least one hour before the experiment is started. A beaker containing the solvent-mixture should be placed at the bottom of the tank.
2. Cut sheets of Whatman No. 1 filter paper into 16-cm strips.
3. At distances of 2·5, 4 and 6 cm from the top, rule lines across the strip and bend the paper along the first of these lines.
4. Along the 6-cm line place 0·01 ml of the metal chloride test solution. Three such spots may be accommodated on the paper by placing them 4 cm in from the edge and allowing the same distance between spots. Leave the spots to dry in air and insert the strip into the chromatographic vessel in such a way that all below the 4-cm marks hang vertically.
5. Allow the solvent-mixture to run down the paper to the 40-cm mark. This takes about 16 hours.
6. Remove the strip from the trough and allow it to hang in air for about 30 minutes. Heat in an oven at 80° for 15 minutes. The paper is now ready for spraying.
7. Attach the strip to the strip-holder and spray with the 8-hydroxyquinoline reagent.
8. Hang the strip in an ammonia-saturated atmosphere at 80° for 10 minutes.
9. Wash the strip with hot water to remove excess 8-hydroxyquinoline.
10. Dry in an oven at 120° for about 2 hours.
11. Examine the strips under ultraviolet light. Aluminium, gallium and indium will be observed as brilliant yellow, fluorescing bands with the following Rf values: aluminium 0·10; gallium 0·76; indium 0·24; thallium 0·50.

Notes:

1. Although in the procedure just outlined it is recommended that the strip should be examined under ultraviolet light, it was found, in practice, that aluminium, gallium, indium and thallium, down to the minimum amount, may be detected by the naked eye.
2. For the semi-quantitative estimation of thallium it was found convenient to amend the procedure. If the strip containing thallium is heated to 150° for 10 minutes, the thallium position becomes a vivid purple, due possibly to the formation of a complex of the metal with the phenol on the paper. If desired, a set of standards may be prepared in this way and used for the estimation of thallium.
3. The oxinates of the metals should be kept out of contact with light as much as possible since they tend to be photo-sensitive. Aluminium, gallium and indium show signs of decomposition in 10 hours whereas thallium oxinate breaks down in 5 hours.

Standard and limits of detection

Using the procedure outlined a number of standards were prepared. For all the metals a range of 20 μg up to at least 500 μg may be detected. The minimum amount (20 μg) of any element can be successfully separated and detected in the presence of the maximum amount of any other or combination of the other elements.

As a test of the validity of the proposed scheme synthetic mixtures of "unknown" composition were analysed by one of us (I. A. P. S.). The results are shown in Table II. The estimated amounts are in micrograms.

For estimation purposes, the bands, developed in the recommended manner, were compared with a set of standards. The areas and intensities of the bands increase with increasing amounts of the elements. Where the amounts detected differ from the amount present, the latter are shown in parentheses.

TABLE II

No.	Al	Ga	In	Tl
1	25	30(50)	400	70(50)
2	450(500)	50(25)	—	—
3	50(25)	500	—	—
4	—	—	30(25)	450(500)
5	—	30(25)	470(500)	—
6	25(50)	30(50)	25	25
7	120(150)	125(150)	—	100(150)
8	200(250)	250	50(25)	—
9	—	350(400)	25	70(50)
10	450(400)	—	50(75)	—

The determination of aluminium, gallium, indium and thallium

The success of the separation and the satisfactory manner in which the semi-quantitative estimations were obtained suggested the possibility of quantitative determination of the elements. Since, after detection, all the metals are present as oxinates, it appeared hopeful that the metal oxinates might be extracted quantitatively from the paper.

The metal oxinates are of the form $X(C_9H_6ON)_3$ and show chelate linkages within the molecule which are completely satisfied by co-ordinate number six, normally shown by this group of metals. It therefore appeared highly probable that they would dissolve, under suitable conditions, in a solvent such as chloroform. It would then be possible to carry out a spectrophotometric determination on the solution.

Gallium: Moeller and Cohen[9] have investigated the absorption spectra of chloroform solutions of gallium oxinate and have shown that strong absorption peaks occur at 335, 320 and 392·5 mμ. In this investigation, the authors point out that the precipitation of gallium oxinate in aqueous solution is complete above pH 3·10. It appeared likely that the same conditions of pH would apply to precipitation on the paper and the following procedure was used:

Spray the paper with a 5% solution of 8-hydroxyquinoline in *ethanol*, followed by a 5*N* aqueous ammonia solution. This treatment was found to raise the pH to approximately 6. Dry the strip in the oven for 10 minutes at 75°. Cut a 3-cm square of paper around the metal oxinate band. This keeps the excess of 8-hydroxyquinoline to a uniform minimum. Wash the square of paper with 3 × 10-ml portions of boiling water to remove excess oxine. Dry in an oven for 1½ hours at 120°. To extract the metal complex from the paper place it in a separatory funnel along with 5 ml of hot conc. hydrochloric acid and shake for 5 minutes. After dilution to 25 ml and adjustment of the pH to 4·5, shake the solution containing the gallium oxinate with 2 × 4-ml amounts of chloroform. Dry the combined extracts over sodium sulphate and make the volume up to 10 ml with chloroform.

For the extraction of gallium oxinate completely from aqueous solution into chloroform, careful control of pH conditions is necessary. Sandell[10] states that complete extraction can only take place in the range 2·6–3·0. Lacroix[11] claims that it is complete at pH 2·0, while Moeller and Cohen[9] favour the range 3·0–7·0. Numerous experiments carried out to investigate the extraction showed that pH 4·5 gave the optimum extraction and this pH was used in the subsequent work.

The absorption spectrum of the chloroform solution of the metal complex, prepared as described showed a strong absorption peak at 390 mμ which was used in all subsequent work.

Indium: The precipitation of indium was carried out in the same way as for gallium by spraying with a 5% solution of 8-hydroxyquinoline in ethanol. This method did not, however, give reproducible results and it was found more satisfactory to use a 5% solution of 8-hydroxyquinoline in chloroform. The best method for the development and extraction of indium was devised as follows:

Develop the indium band on the paper by spraying with a 5% solution of 8-hydroxyquinoline in chloroform. Re-spray with 2*N* aqueous ammonia solution. Dry in an oven at 75° for 10 minutes. Cut out the indium oxinate band (keeping the size 3 cm^2 as for gallium). Wash with 3 × 10-ml portions of hot water. Finally, dry in an oven for 1½ hours at 120°. Shake in a separatory funnel with 5 ml of conc. hydrochloric acid to remove the complex from the paper. Dilute the acid extract to about 25 ml and adjust the pH to 4·0 to ensure complete extraction. Shake with 2 × 3-ml portions of chloroform. Dry the combined extracts over sodium sulphate and make up the volume to 10 ml with chloroform.

The absorption spectrum of the chloroform solution of the metal complex prepared in this way showed a strong absorption peak at 395 mμ which was used in all subsequent work.

Thallium: Thallium oxinate was developed and extracted in a very similar manner to gallium, since complete precipitation occurs in the range pH 3·0–8. The following procedure was used:

Spray the strip of paper with a 5% solution of 8-hydroxyquinoline in ethanol and then with 2*N* aqueous ammonia. Dry in an oven at *20° for ½ hour.* Cut out the thallium oxinate band from the paper (keeping the size 3 cm^2 as for gallium), wash with 3 × 10-ml portions of hot water. Dry in an oven for 1½ hours at 120°. Shake in a separatory funnel with 5 ml of hot conc. hydrochloric acid. Adjust the pH, after dilution to 25 ml, to a value between 7 and 8. Extract with 2 × 3-ml portions of chloroform. Dry the combined extracts over sodium sulphate and make the volume up to 10 ml with chloroform.

The absorption spectrum of the chloroform solution of the metal complex prepared in this way showed a strong absorption peak at 400 mμ which was used in all subsequent work.

Note: Photochemical decomposition of thallium oxinate occurs readily in daylight. It should, therefore, be developed and extracted in red light.

Aluminium: The oxinate of aluminium was prepared and extracted in the same way as that of indium:

Spray the strip with a 5% solution of 8-hydroxyquinoline in chloroform, followed by 2*N* ammonia solution. Dry the strip in an oven at 75° for 20 minutes. Cut out the aluminium oxinate band from the paper (keeping the size 3 cm^2 as for gallium) and wash with 3 × 10-ml portions of hot water. Dry at 120° for 1½ hours. Shake in a separatory funnel with 5 ml of conc. hydrochloric acid. Adjust the pH to about 6·0 to give complete extraction into chloroform. Extract with 2 × 3-ml portions of chloroform. Dry the combined extracts over sodium sulphate and make the volume up to 10 ml with chloroform.

The absorption spectrum of the chloroform solution of the metal complex prepared in this way showed a strong absorption peak at 385 mμ which was used in all subsequent work.

The analysis of synthetic mixtures

Using the procedures described calibration curves were prepared for each metal over the range 20–500 μg. In all cases Beer's law was obeyed.

To test the validity of the method a number of "known" mixtures was analysed by one of us (I. A. P. S.). The results expressed in micrograms, are recorded in Table III. Where experimental results differ from the amount actually present, the latter are shown in parentheses.

TABLE III

No.	Al	Ga	In	Th
1	300	—	60(50)	105(100)
2	460(450)	—	50(25)	—
3	250	225(200)	—	65(50)
4	—	40(30)	450	30(20)
5	55(50)	—	245(250)	255(250)
6	—	—	50	480(500)
7	500	—	50(30)	—
8	250	258(250)	25	—
9	—	400	30(25)	60(50)
10	155(150)	140(150)	—	150

Small deviations that occur in the above results are thought to be due most likely, not to the method, but rather to the error inherent in the measuring of small volumes by means of the micro-pipettes and in making up the "unknowns".

For the aluminium the determinations are very good. Gallium and indium also give very satisfactory values. The results for thallium are, perhaps, the least satisfactory. This may be due in part to the fact that thallium oxinate is light-sensitive, and superficial decomposition may occur.

Although the upper limit is given as 500 μg, experiments have shown that this may be increased to 1 mg for gallium, indium and thallium. Aluminium and indium are the bands closest to one another on the chromatogram and, if the ratio of one to the other is increased beyond 25·1, the bands tend to touch.

The behaviour of other elements with the solvent-mixture was investigated. The Rf values of some of them are as follows:

Copper 0·25; iron 0·40; cadmium 0·33; nickel 0·15; chromium 0·15; zinc 0·35.

It will be seen from these figures that many important elements will not interfere with the separation, so that the method may be capable of wider application.

Zusammenfassung—Eine Methode zur papierchromatographischen Trennung und nachfolgenden Bestimmung kleiner Mengen von Aluminium, Gallium, Indium und Thallium wird beschrieben. Die Chloride der Metalle werden getrennt mittels einer Mischung von Phenol: Methanol: conc. Salzsäure (50 : 30 : 20 g/ml/ml). Alle Ionen werden mit einem einzigen Sprühreagens, nämlich Oxin, nachgewiesen. Die Mengen können halbquantitativ durch Vergleich der erhaltenen Flecken mit denen von Standardlösungen erzeugten bestimmt werden.

Die Metalloxinate können mittels organischer Lösemitteln vom Papier gelöst und spectrophotometrisch bestimmt werden.

Résumé—Les auteurs décrivent une méthode de séparation chromatographique et de dosage de faibles quantités d'aluminium, de gallium, d'indium et de thallium. On sépare les chlorures métalliques en utilisant un mélange de solvants contenant du phénol, du méthanol, de l'acide chlorhydrique concentré (50, 30, 20, P.V.V). Chaque substance est décelée par une simple pulvérisation d'oxine, et on dose semi-quantitativement la quantité d'élément présent par comparaison visuelle avec des étalons.

L'étude des conditions pour séparer du papier les oxinates métalliques dans un solvant organique a permis le dosage des éléments par spectrophotométrie.

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A STUDY OF THE CONDITIONS FOR THE DETERMINATION OF BORON WITH DIANTHRIMIDE

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Summary—The reaction between boric acid and dianthrimide in concentrated sulphuric acid has been studied from an analytical point of view using a statistically planned experimental design. Certain interactions between the different factors affecting the reaction that have not previously been taken into account were found to be significant. Thus, the reaction rate is affected by both the acid and the dianthrimide concentrations. The temperature at which the reaction is carried out affects the absorbance less at higher acid concentrations. Suitable analytical conditions are described.

THE analytical laboratory at the Swedish Institute for Metal Research has for a long time used a method for the determination of boron in iron and low-alloy steel based originally on a method given by Rudolph and Flickinger.[1] Boron is determined colorimetrically using quinalizarin without any preliminary separations. It has been found possible to replace the quinalizarin with 1:1′-iminodianthraquinone (dianthrimide) which has a greater sensitivity as well as other favourable properties. A preliminary method has now been in use for two or three years with good results but a systematic investigation of the dianthrimide method seemed desirable. The results of this investigation are described in two papers, this dealing with problems connected with the colorimetric determination of boric acid and a following[2] dealing with the application of the method to the determination of boron in steel.

A. CHOICE OF REAGENT

The determination of boric acid in microgram quantities requires in general the use of colorimetric methods. Curcumin is the best known reagent and probably also the most sensitive. However it requires extensive preliminary separations and the conditions must be standardised very carefully. It was therefore considered less suitable for the present purpose.

Almost all other reagents that have been used for boron are anthraquinone derivatives. The reaction between these and boric acid takes place in strong sulphuric acid solution but with proper precautions this need not cause any great practical difficulties. Many anthraquinone derivatives are very selective and have sufficiently high sensitivity for the concentration range involved. Of these quinalizarin and to a lesser extent carminic acid have been most widely used for the determination of boron in steel. This group of compounds also includes dianthrimide and the substituted hydroxyanthraquinones investigated by Cogbill and Yoe.[3]

A comparison was made of the sensitivities of quinalizarin, carminic acid and dianthrimide. The results are shown in Table I. They are expressed in $\mu g/cm^2$ as suggested by Sandell[4] and it is therefore possible to compare the results directly with those obtained by Cogbill and Yoe.

As shown in the table, dianthrimide is considerably more sensitive than quinalizarin and carminic acid. Comparison with the results obtained by Cogbill and Yoe shows that it is also somewhat more sensitive than the best reagents of the substituted hydroxyanthraquinones.

Like quinalizarin and carminic acid, dianthrimide is strongly coloured in sulphuric acid solution. The absorption maximum is however below 400 mμ and the absorption at the boron complex maximum at 620 mμ is rather small. This is a considerable advantage over quinalizarin which has absorption maxima at wavelengths very close to that of the boron complex maximum. Since a large excess of reagent is usually required for high sensitivity a high reagent absorption at the wavelength of measurement can be very troublesome. Carminic acid and most of the substituted hydroxyanthraquinones have more favourable properties in this respect than quinalizarin.

TABLE I.—SENSITIVITIES OF BORON REAGENTS

Reagent	Method	Sensitivity (μg/cm^2)
Quinalizarin	AOAC[5]	0·003
Carminic acid	Hatcher–Wilcox[6]	0·002
Dianthrimide	Method recommended	0·0006

With boric acid quinalizarin gives calibration curves that show considerable deviations from Beer's law and the useful concentration range is relatively small. Dianthrimide and carminic acid on the other hand give linear calibration curves.

Since preliminary investigations showed also that the colour reaction of boric acid with dianthrimide is relatively free from interference this appeared to be a suitable reagent for further examination. Probably some of the new reagents developed by Yoe and co-workers would also be suitable for this purpose.

B. DIANTHRIMIDE AND ITS BORON COMPLEX

The reaction between boric acid and dianthrimide is very slow at room temperature. For analytical purposes it is therefore essential to heat the reaction solution. Prolonged heating especially at temperatures over 90° gives rise to discoloration of the solutions, probably due to partial degradation of the reagent. A corresponding though less marked change in colour occurs if the reagent solution while in storage is exposed to sunlight. The green colour disappears and the solution becomes yellowish brown. However, although a reagent solution after standing for 5 days in sunlight absorbed strongly in the 400–550 mμ region it showed only a slight increase in the absorption at 620 mμ where the analytical measurements were made. Solutions of the reagent kept in the dark and protected against access of air could be stored for several months.

Attempts were made to determine the empirical formula of the boron dianthrimide complex in solution using the mole ratio method of Yoe and Jones[7] and a modified method of continuous variation.[8]

In the mole ratio method the concentration of dianthrimide was kept constant at $1{\cdot}00 \,.\, 10^{-4}M$ while the concentration of boric acid was varied within the range $1{\cdot}00 \,.\, 10^{-5}M$–$1{\cdot}00 \,.\, 10^{-3}M$. The solutions contained 90·5 % by weight of sulphuric acid and were heated in an oven for 18 hours at 70°. The results obtained indicated a mole ratio of 1 : 1 but are somewhat uncertain since the complex appears to have a low stability constant. The absorption was still increasing at a boron : reagent ratio of 10 : 1.

In the continuous variation method (Job's method) a solution of *a* ml of $2{\cdot}00 \, . \, 10^{-4}$ *M* boric acid was mixed with 30-*a* ml of dianthrimide solution of the same molar concentration. In this experiment *a* was varied between 0 and 30; the solutions contained 90·3% by weight of sulphuric acid and were heated for 48 hours at 70°. The absorbance was measured at 460, 520, 540, 580 and 620 mμ.

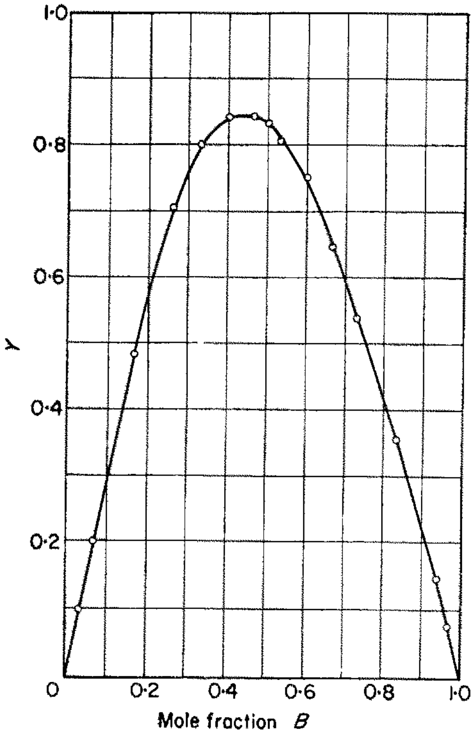

FIG. 1.—Determination of the empirical formula of the boron complex in solution using the method of continuous variation. Wavelength 620 mμ.
Y = absorbance$_{\text{obs}}$—absorbance$_{\text{calc assuming no reaction}}$

Fig. 1 shows the absorbance of the boron complex at 620 mμ plotted as a function of the mole fraction of boric acid. The maximum lies at a mole fraction 0·47 corresponding to a reagent-boron mole ratio of 1·1 : 1. The other wavelengths measured also gave maxima at the same mole fraction. It thus appears probable that there is only one coloured complex and that it is composed of equal numbers of boric acid and dianthrimide molecules.

C. SYSTEMATIC INVESTIGATION OF SUITABLE ANALYTICAL CONDITIONS

Dianthrimide (MW 429·41) is a rather new reagent for boron and the reaction has not yet been examined in full detail. Several modifications of the original method[9] have been described giving different acid and reagent concentrations, heating temperatures and heating times. A detailed study of the effect of these different factors seemed desirable. Since the effects of the individual factors were probably not independent of the other factors it seemed also desirable to use a factorial experiment design. Evaluation of the experimental results would then provide a statistical basis to show which of the effects of the different factors and interactions between the factors were significant and had a real effect on the results.

The levels of the different factors were selected as follows:

Sulphuric acid concentration (% by weight): 95·0, 92·5, 90·0, 87·5, 85·0, 82·5 and 80·0.
Reagent concentration (mg of dianthrimide/ml): 0·100, 0·200 and 0·400.
Boron concentration (μg boron/ml): 0·500, 1·000 and a boron-free blank solution.
Temperature (°C): 60, 80 and 100.

Since the reaction rate is strongly dependent on the temperature a series of different heating times were chosen for the different temperatures as follows:

Temp, °C	Time, *min*
60	120, 240, 480, 960
80	120, 240, 480
100	15, 30, 60, 120

Measurements were made at each temperature using all combinations of the other factors.

Solutions containing 1·000 and 2·000 μg B/ml and with 95·0, 90·0, 85·0 and 80·0% by weight of sulphuric acid were made up using boric acid (H_3BO_3 p.a. Merck). A third solution without boron was made up for each of these acid concentrations.

The reagent solutions were prepared by dissolving 0·200, 0·400 and 0·800 g of dianthrimide (Merck) in sulphuric acid (1000 ml) of the four concentrations given above.

The boron and reagent solutions were stored with protection against atmospheric moisture and the reagent solutions were kept in the dark. The sulphuric acid solutions were prepared by mixing 97% acid with the calculated amount of a diluted acid. The concentrations were determined by acidimetric titration with 0·25*M* NaOH and adjusted to the required level.

The reaction solutions were heated at 60° and 80° in a thermostat-controlled water bath and at 100° in boiling water. The reaction was carried out in Pyrex Erlenmeyer flasks (Jobling) which after repeated treatment by heating in concentrated sulphuric acid did not give off boron in amounts sufficient to interfere with the analyses.

For each determination, boron solution (10 ml) and reagent solution (10 ml) of the same acid concentration were transferred to a 50 ml Erlenmeyer flask with a ground glass stopper. The mixture was heated for a given time at a given temperature in the water bath and then cooled rapidly to 20° in cold water. The absorbance of the solution at 620 mμ was then measured in a 1-cm cell against a boron-free blank with the same reagent and acid concentrations using a Beckman model B spectrophotometer. Acid concentrations of 92·5, 87·5 and 82·5% by weight were obtained by using a reagent solution with the next higher acid concentration and a boron solution with the next lower acid concentration. The amount of heat evolved on mixing and the deviation from the required concentration are very slight.

The results obtained from 396 absorbance measurements were evaluated by analysis of variance. Since no replications were made the highest order interactions were used to estimate the error. The results for the 80% acid concentration were excluded from this calculation, as a complete set of measurements at this level could not be made because it was not possible to dissolve 0·8 g of dianthrimide in 1000 ml of sulphuric acid of this concentration.

Some diagrams have been given to illustrate the results of analytical interest obtained from these factorial experiments. As expected the analysis of variance showed that all the effects of the factors varied were significant and that a number of interactions between the factors were also significant.

Heating time

The reaction rate is of course affected by the heating temperature and it was found that the time required for the reaction to reach equilibrium was four times as long at 80° as at 100°. Of greater interest is the marked influence on the reaction rate of the acid and reagent concentrations.

Fig. 2 shows the absorbance as a function of the heating time for different acid concentrations at 100°. Each point in the diagram represents a mean value for the six combinations of boron and reagent concentrations. It is clearly apparent that an increased acid concentration is accompanied by a strong reduction in the reaction rate. In 85% sulphuric acid equilibrium is reached after only 15 minutes heating while in 95% sulphuric acid the reaction is not complete after 2 hours heating. The results for 60° and 80° were similar.

Fig. 3 shows the absorbance as a function of the heating time for different reagent concentrations at 100°. Each point in the diagram represents a mean value of the absorbances for the twelve combinations of boron and acid concentrations. It is clear that an increase in the reagent concentration increases the rate of reaction.

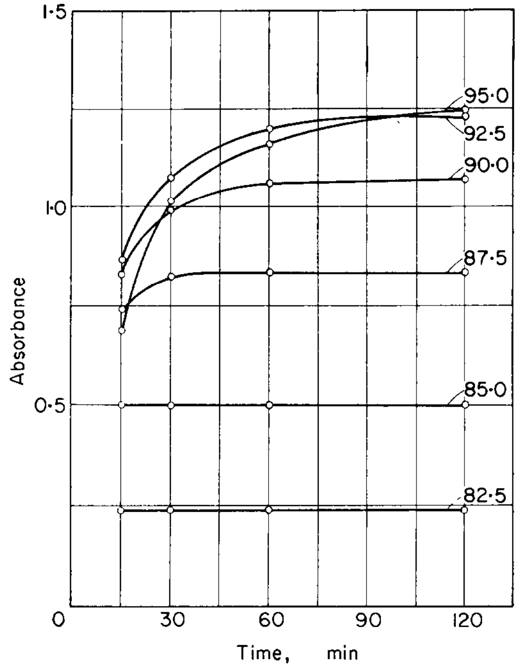

Fig. 2.—Absorbance of the boron complex as a function of the heating time at different acid concentrations (% by weight). Temp. 100°.

The boron concentration on the other hand does not appear to have any effect on the reaction rate. The ratio of the absorbances for the two boron concentrations was the same for different heating times. It should therefore be possible in making a boron determination to interrupt the reaction at any given time before equilibrium was reached but this can hardly be of any great practical interest.

The discussion below of the dependence of the absorbance on other factors will deal only with heating times for which it can be presumed that the reaction will be complete.

Temperature

Baron,[10] in an investigation of the use of dianthrimide for the determination of boron in plant material, found that the same absorbance is obtained when the colour reaction is done at 70°, 85° or at 100° while in a recently published investigation[11] it is stated that temperature variations of only a few degrees can give erroneous results. Our experiments showed that the temperature had a significant effect on the absorbances obtained but that this effect was dependent on the acid concentration. Fig. 4 shows an example of this. At the two highest acid concentrations the absorbance was the same at all three temperatures but if the acid concentration was reduced to 90% or lower the absorbance fell appreciably with the heating temperature. This effect was always greater at lower reagent concentrations. In 90% sulphuric acid at 100° the absorbance was 11% lower than at 80° for the lowest

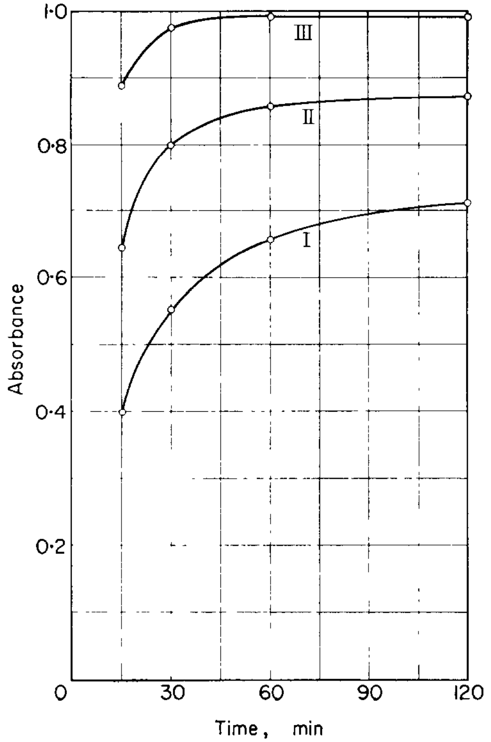

FIG. 3.—Absorbance of the boron complex as a function of the heating time at different dianthrimide concentrations. (I 0.1, II 0.2, III 0.4 mg/ml.) Temp. 100°.

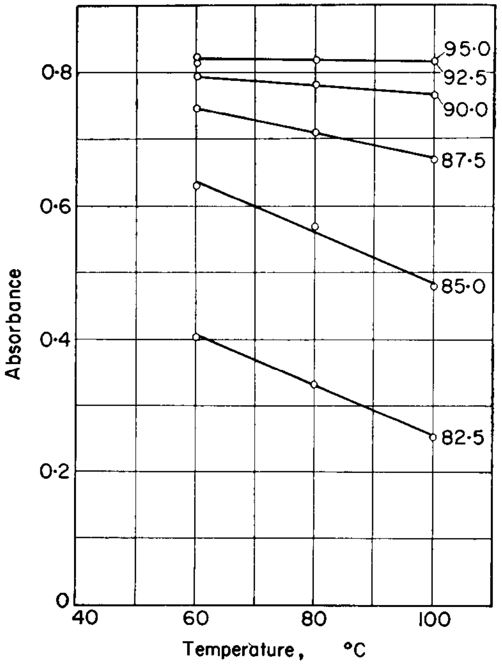

FIG. 4.—Absorbance of the boron complex at different temperatures and acid concentrations (% by weight). Boron 0.5 μg/ml. Dianthrimide 0.4 mg/ml.

reagent concentration but the corresponding value for the highest reagent concentration was 2%. At the lowest reagent concentration the effect of the temperature was already noticeable in 92·5% acid.

It was mentioned earlier that the reagent is discoloured by prolonged heating at higher temperatures, presumably due to degradation. At low acid concentrations such a degradation of the reagent can be expected to reach appreciable values before the reaction between boric acid and dianthrimide is complete.

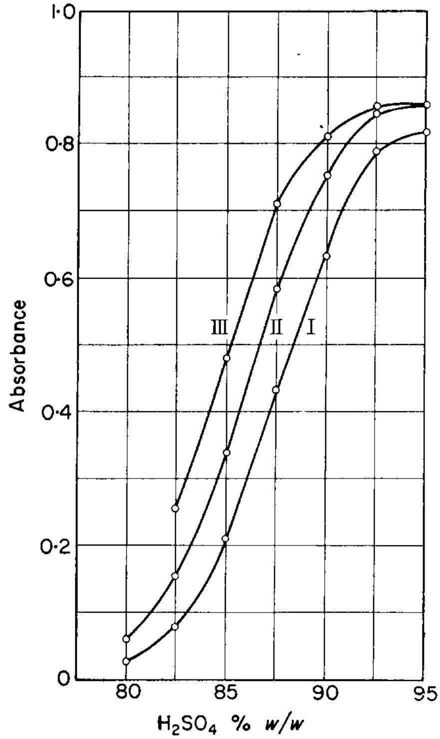

FIG. 5.—Absorbance of the boron complex at different acid and dianthrimide concentrations. I 0.1, II 0.2, III 0.4 mg dianthrimide/ml. Boron 0.5 μg/ml. Temp. 100°. Heating time 120 min.

Sulphuric acid concentration

As in the use of other anthraquinone derivatives it is essential to have a high sulphuric acid concentration. Fig. 5 shows how the absorbance of the boron complex increases with the acid concentration. This increase is rather large at acid concentrations less than 90% and this should therefore be taken as a minimum for analytical use; above this minimum the variations due to any changes in the acid concentration are smaller the higher the reagent concentration. MacDougall and Biggs found the same tendency in the determination of boron with quinalizarin.[12]

If the concentration of the acid is reduced from 92·5 to 90% the heating temperature begins to affect the result, as is shown in Fig. 4. The consequent decrease in the absorbance is only half as great at 60° as at 100°.

Reagent concentration

As discussed above there is reason to suppose that dianthrimide and boric acid react in a ratio of 1 : 1 and that a large excess of reagent is required for Beer's law to apply. In this investigation the molar ratio between reagent and boron has been varied between 2·5 and 20·2. Fig. 5 shows that the absorbance increases with the reagent concentration but that at the highest acid concentrations there is only a very small increase when the reagent concentration is increased from 0·2 to 0·4 mg/ml.

Calculation from the results obtained of the ratio of the absorbances at the lower and the higher boron concentrations for increasing reagent concentrations gives the values 0·532, 0·512 and 0·502. Only the last of these values indicates a direct proportionality to the boron concentrations. This means that the reagent/boron ratio must be of the order of 10 if a linear calibration curve is to be obtained.

D. DISCUSSION OF THE RESULTS

The optimum conditions for an analytical method are not determined by high sensitivity alone. It is also important that moderate variations in the conditions should have as little effect as possible on the results. The factorial experiment showed that both these requirements could be satisfied. Suitable conditions were found to be: Dianthrimide 0·4 mg/ml; sulphuric acid 93–95% by weight; boron 0·3–1·0 μg/ml; heating time at 100°, 1–1·5 h; or, for instance at 80°, 4–5 h.

The choice of reagent concentration is a question of judgement. At 0·2 mg/ml the sensitivity is almost as high as at 0·4 mg/ml. The lower concentration is more advantageous from the point of view of the reagent absorption but at the higher concentration the sulphuric acid concentration can be allowed to vary over a wider range. Although the dianthrimide reagent absorbs comparatively little at 620 mμ the high concentration gives a quite appreciable blank. The reagent absorption is proportional to the concentration but also increases significantly with the acid concentration. It is therefore essential to use high precision in adding the reagent. Particularly at low boron concentrations, however, the disadvantages of a high blank can outweigh the advantage of lower sensitivity to small variations in the conditions that is obtainable at high reagent concentrations. It may then be desirable to reduce the reagent concentration but the mole proportion of dianthrimide to boron should not be much less than 10. The longer heating times this requires can be reduced in certain cases by carrying out the reaction in a small volume and then diluting with sulphuric acid to the desired volume.

The sulphuric acid concentration can be varied within the specified range and a little to either side without affecting the results. Supplementary experiments showed that there was no advantage to be gained by increasing the acid concentration over 95% by weight. The sensitivity slowly decreases and there will also be a further reduction in reaction speed and a greater reagent absorption. Baron reached somewhat different conclusions on the effect of the acid concentration. He obtained an appreciably lower sensitivity in concentrated sulphuric acid (s.g. 1·84) than in solutions with a lower acid concentration. It could however be questioned whether the heating period of 5 hours at 70° used by Baron was sufficient to reach equilibrium at the highest acid concentrations.

The absorbances for the boron concentrations given, when measured against a reagent blank in 1-cm cell, fall within a range of 0·5–1·7 which is suitable for the photometer used (Beckman B). However most photometers work best at lower absorbances and with these it is necessary to use a lower boron concentration.

The heating temperature can be selected arbitrarily within the range investigated, 60–100°, but at 60° the rate of reaction is inconveniently low. The times given must be increased if an oven is used instead of a waterbath since temperature equilibrium is reached more slowly. Unnecessarily long heating at the highest temperatures should be avoided since the reagent gradually decomposes causing a decrease in the accuracy of the determination.

The conditions found most suitable in this investigation can be used for boron determination after separation of the boron by distillation. The alkaline residue must then of course be free from organic material. In other methods of separation such as electrolysis with a mercury cathode and ion-exchange the sample is usually in the form of a solution in weak sulphuric acid. Concentration of this solution by evaporation to fumes of sulphuric acid leads to loss of boron. If however the solution is made $2M$ in sulphuric acid it can be evaporated at 100° without noticeable loss of boron. An example of the use of this method for the determination of boron in steel is given in a following paper.[2]

Acknowledgement—The author wishes to express his thanks to Dr. Axel Johansson, Royal Institute of Technology, Stockholm, for valuable discussions.

Zusammenfassung—Die Reaktion zwischen Borsäure und Dianthrimid in konzentrierter Schwefelsäure wurde vom analytisch-chemischen Standpunkte aus statistisch untersucht. Es wurde gefunden, dass das Zusammenwirken verschiedener, früher nicht berücksichtigter Faktoren die Reaktion in signifikanter Weise beeinflusst. So z.B. wird die Reaktionsgeschwindigkeit sowohl durch die Konzentration der Schwefelsäure als auch die des Dianthrimids beeinflusst. Die Temperatur, bei der die Reaktion abläuft, hat auf die Absorption weniger Einfluss bei hoher Säurekonzentration. Brauchbare analytische Bedingungen werden mitgeteilt.

Résumé—La réaction entre l'acide borique et la dianthrimide dans l'acide sulfurique concentré a été étudiée d'un point de vue analytique en utilisant une méthode expérimentale contrôlée statistiquement. Certaines interactions entre différents facteurs affectant la réaction dont on n'avait pas tenu compte précédemment, se sont révélées significatives. Ainsi, la vitesse de la réaction est influencée par les concentrations et de l'acide et de la dianthrimide. La température à laquelle a lieu la réaction affecte moins l'absorption aux plus hautes concentrations d'acide. On décrit des conditions analytiques appropriées.

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ANALYTICAL APPLICATION OF XYLENOL ORANGE—IV*

A SPECTROPHOTOMETRIC STUDY OF THE FERRIC XYLENOL ORANGE COMPLEX

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Summary—The purplish red ferric Xylenol Orange complex has been studied spectrophotometrically. It offers a reasonably sensitive and selective reaction for determining ferric iron. But it requires a rather narrow acidity (0.04 to 0.05*N*) for maximum colour development. It is a 1 : 1 complex and has a formation constant of 5×10^5 under the conditions studied.

XYLENOL Orange forms a purplish red coloured complex with ferric iron in an acid medium. The coloured complex tends to fade upon standing, however, it offers a very sensitive colour reaction for iron. This paper reports the conditions for the colour formation of the complex, its composition, its formation constant, and the interference.

APPARATUS AND REAGENTS

Standard iron solution

A $1.79 \times 10^{-2}M$ ferric nitrate nonahydrate was prepared in 0.01*N* perchloric acid solution and standardized by EDTA. A solution of $1.79 \times 10^{-4}M$ iron in 0.05*N* perchloric acid was made by appropriate dilution of the stock solution.

Other apparatus and reagents are the same as those reported previously.[1]

EXPERIMENTAL

Calibration curve

Pipette 5 to 50 μg of iron into a 25-ml volumetric flask. Add 4 ml of 0.05% Xylenol Orange in 0.05*N* perchloric acid, dilute to volume with 0.05*N* perchloric acid and mix. Measure the absorbance after 15 minutes at 550 mμ using the reagent blank. Beer's law is followed. The molar absorptivity was found to be 26,600.

RESULTS

Absorption spectra

The spectra for Xylenol Orange and its ferric complex are shown in Fig. 1. The maximum absorption of the complex is at 550 mμ.

Effect of acidity

Fig. 2 shows that the optimum perchloric acid concentration for the colour formation of the ferric Xylenol Orange complex is 0.04 to 0.06*N*. Above 0.075*N*, the absorbance drops sharply. The ferric Xylenol Orange complex requires a low and very narrow acidity range as compared with the Xylenol Orange complexes of zirconium and hafnium. Hydrochloric acid may also be used giving a similar curve to perchloric acid. Sulphate showed somewhat of a masking effect on complex formation. It was noticed that at the higher acidity, the complex faded rather rapidly.

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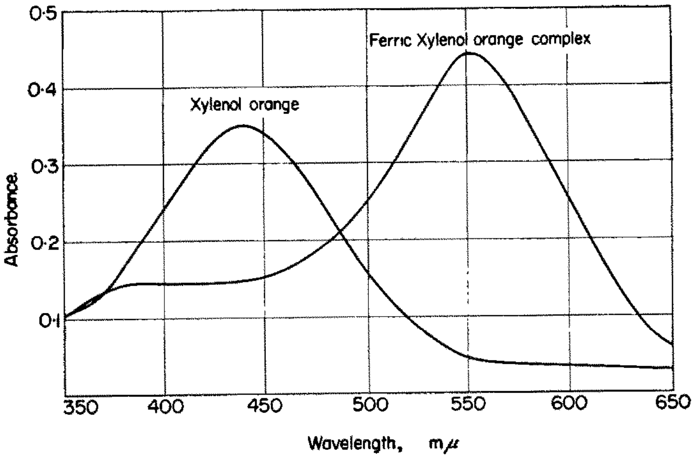

FIG. 1.

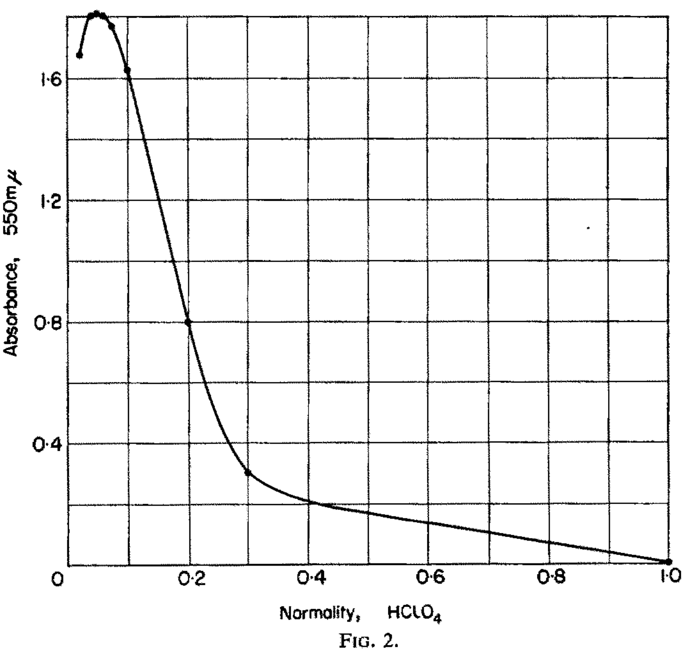

FIG. 2.

The absorbance measurements were made 15 minutes after addition of Xylenol Orange.

Effect of amount of Xylenol Orange

Fig. 3 shows that for 50 μg of iron, 3 to 4 ml of 0.05% Xylenol Orange solution are required. As happened with zirconium and hafnium, large amounts (more than 4 ml of 0.05%) of Xylenol Orange tend to decrease the absorbance.

Interference

Only a few metals in 0.2*N* sulphuric acid medium form a red or purplish colour with Xylenol Orange.[1] Table I indicates the extent of the effect of these interfering

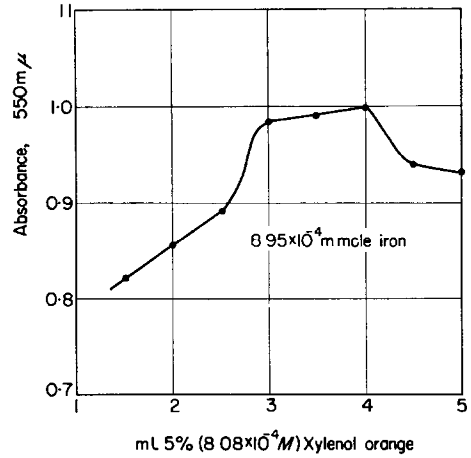

Fig. 3.

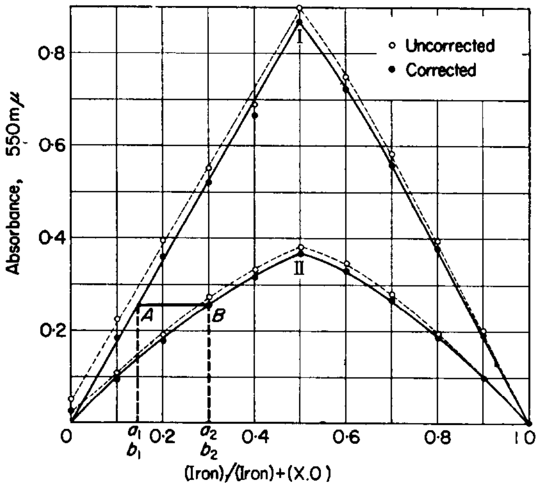

Fig. 4.

metals and of some anions. Some of the interfering metals can be completely or partially masked by the masking agents.

Complex formation

Like zirconium and hafnium, ferric iron also forms a 1 : 1 complex with Xylenol Orange as indicated by Job's method (Fig. 4). The formation constant was calculated from the curves shown in Fig. 4, based on the method used previously.[2] It was found to be 5×10^5 in $0.05N$ perchloric acid.

As compared with the complexes of zirconium and hafnium, the iron Xylenol Orange complex requires a lower and narrower acidity, shows a maximum absorption at longer wave length, and forms a slightly weaker complex (also 1:1). However, this dye ($E_{\max} = 26{,}600$) offers a higher sensitivity for iron than other commonly known iron reagents such as *o*-phenanthroline ($E_{\max} = 11{,}100$) and bathophenanthroline

TABLE I.—EFFECT OF FOREIGN IONS

Taken: 20 μg iron

Ion	Amount added	Iron recovered, %	Remarks
Fluoride	0.1 mmole	64.6	
	0.1 mmole	97.8	0.25 mmole Be^{II} added
	0.1 mmole	99.7	1.0 mmole Be^{II} added
Chloride	10 mmoles	99.0	
Citrate	0.17 mmole	89.3	
	0.1 mmole	98.1	
Orthophosphate	0.15 mmole	97.0	
Sulphate	0.3 mmole	98.4	
	3.1 mmole	85.0	
H_2O_2	1 ml. 30%	108.1	
Bismuth	1×10^{-4} mmole	100.0	10 mmoles chloride added
Molybdenum	0.008 mmole	99.0	1 ml. 30% H_2O_2 added
Zirconium	0.01 mmole	216.5	1 ml. 30% H_2O_2 added
Niobium	0.01 mmole	98.4	
Tin^{II}	0.01 mmole	333.1	
	0.001 mmole	143.6	
	0.0001 mmole	102.9	
Tin^{IV}	0.01 mmole	456.0	1 ml. 30% H_2O_2 added
	0.001 mmole	180.0	1 ml. 30% H_2O_2 added
	0.0001 mmole	112.6	1 ml. 30% H_2O_2 added
	0.001 mmole	205.5	no H_2O_2 added
	0.0001 mmole	105.8	

($E_{\max} = 22{,}400$). It is expected that this dye would find many applications where a highly sensitive reaction for iron is desired. For example this proposed method would be useful in determining traces of iron in nickel-iron thin film (permalloy).

Zusammenfassung—Der purpur rote ferritische Xylenol Orange Komplex ist spektrophotometrisch untersucht worden. Er liefert eine ziemlich empfindliche und selektive Reaktion zur Bestimmung von Eisen. Die Äzidität muss jedoch in engen Grenzen (0.04 bis 0.06*N*) gehalten werden um maximale Farbbildung zu erhalten. Es handelt sich um einen 1 : 1 Komplex mit einer Bildungs-konstante von 5×10^5 unter den untersuchten Bedingungen.

Résumé—Le complexe ferrique rouge-pourpre du Xylenol Orange a été étudié par spectrophotométrie. Il donne une reaction assez sensible et selective pour la détermination du fer. Mais il nécessite une bande d'acidité étroite (0.04 á 0.06*N*) pour obtainer le maximum de coloration. Il a un rapport de complexe 1 : 1 et une constante de formation de 5×10^5 dans les conditions étudiées.

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ORGANIC ANALYSIS—XX*

MICROESTIMATION OF BLOOD SUGAR WITH 5-HYDROXY-1-TETRALONE

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Summary—Blood sugar is estimated with 0·02 ml of blood, measuring the fluorescence produced with 5-hydroxy-1-tetralone in sulphuric acid.

In the previous papers of this series, it was shown that 5-hydroxy-1-tetralone gave, when heated in sulphuric acid,[1] a green fluorescence sensitively and selectively with hexoses, oligosaccharides, and polisaccharides which contained hexose unit in their molecule, and that the fluorescence intensity had a linear correlation with the concentration of glucose in definite conditions.[2] The fluorescent compound produced in this reaction was also isolated in crystalline form, and its probable structure was forwarded as benzonaphthenedione.[3] This paper describes the microestimation of blood sugar with the reagent.

EXPERIMENTAL

Reagents

Trichloroacetic acid solution—5 g of trichloroacetic acid, JIS† 1 st. grade, was dissolved in 100 ml of water.

5-Hydroxy-1-tetralone solution—100 mg of 5-hydroxy-1-tetralone was dissolved in 400 ml of conc. sulphuric acid, JIS 1 st. grade, and stored in a refrigerator.

Standard glucose solution—Stock solution was prepared by dissolving 100 mg of dried glucose in sufficient 0·21% aqueous solution of benzoic acid to measure 100 ml. Glucose solution, 10 μg/ml, was freshly prepared by diluting 1 ml of the stock solution to 100 ml with water.

Fluorescence intensity

This was measured by a Hitachi L-3 fluorometer attached to a Type EPU-2 spectrophotometer with a glass cell of 10-mm optical length. The ultraviolet light, emitted from a high-pressure mercury lamp, was passed through a filter of 365 mμ.

Procedure

0·02 Ml of blood was pipetted with a dried Sahli's pipette for haemoglobin estimation, and the outside of the pipette was wiped with defatted and moistened deerskin. The blood was introduced into 0·5 ml of water placed in a micro centrifuge tube, and the inside of the pipette was rinsed several times with the water. The contents were mixed and haemolysed, 0·5 ml of 5% trichloroacetic acid was added, mixed, and set aside for 5 minutes. The mixture was diluted with 0·98 ml of water to measure 2 ml, and centrifuged. Two aliquots of 0·5 ml of the supernatant clear solution were pipetted into glass-stoppered test-tubes, and 2 ml of 0·025% reagent solution was added to each tube under ice cooling. The mixture was then heated in a boiling water bath for 40 minutes, cooled in ice water, and diluted with 7·5 ml of water before measuring its fluorescence intensity.

At the same time, two aliquots of 0·5 ml of 10 μg/ml glucose solution and two aliquots of 0·5 ml of water were treated in the way described, to act as standard and blank solutions.

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* Part. XIX: *Chem. Pharm. Bull.* (*Tokyo*), 1959, **7**, in press.

† Japanese Industrial Standards.

A large amount of glycerol gave the same fluorescence with the reagent,[1] and in consequence the influence of glyceride in blood was studied. A deproteinised blood solution was divided in two portions. One portion was defatted by extracting for 3 hours with ether, and was then developed with the reagent and compared with the other. The same value for the fluorescence intensity was observed in each solution. Other substances in blood which gave a fluorescence with sulphuric acid, showed no influence upon the intensity. They showed a faint blue fluorescence when a deproteinised blood solution was heated with 80% by volume of sulphuric acid and diluted with water, but the fluorescence intensity was negligible at the wavelength of 532 mμ.

TABLE II.—BLOOD SUGAR VALUES (*mg/100 ml*)

Blood	1	2	3	4	5	6	7	8
Present method	89	88	102	96	81	89	103	75
Hagedorn's method	91	89	100	98	82	92	102	73

TABLE III.—RECOVERY TEST

Blood sugar values,* μg/ml.	Glucose added, μg	Glucose found, μg	Recovery, %
5·3	2·5	7·8	100
5·3	5·0	10·2	98
5·2	2·5	7·6	96
5·2	5·0	9·9	94
2·1	5·0	7·1	100
2·1	10·0	12·3	102
2·9	5·0	7·7	96
2·9	10·0	12·9	100
2·3	4·0	6·6	107
2·3	10·0	12·3	100

* The amount of glucose in 1 ml of deproteinised blood.

The calibration curve was based on the fluorescence intensities of standard and blank solutions. Other intensities of the fluorescence produced by glucose solutions were almost on the line in a range of 0–20 μg/ml. But if the concentration of glucose exceeds this range, the development of fluorescence should be carried out with a diluted solution.

The values of blood sugar found are shown in Table II, and almost agree with those obtained by Hagedorn's method, though the latter gives the amount of reducing sugar, and can not be exactly compared with the present method.

A recovery test was carried out by adding a known amount of glucose to the water, by which the measured blood was haemolysed. The results showed an average rate of 97·3%, and the maximum error of 7%.

Sources of errors

5-Hydroxy-1-tetralone reacts in sulphuric acid with polysaccharides such as cellulose, and therefore contamination with cotton dust may cause a large error. The reagent solution should be stored in a glass-stoppered bottle covered with a small beaker. Pipette and test-tubes should be quite clean before the development of fluorescence. Moistened deerskin is satisfactory for use in the wiping of pipette. The fluorescence intensity increases with rising temperature, and should be read at 15–25°.

Zusammenfassung—Blutzucker wurde in 0·02 ml Blut bestimmt durch Messen der Fluoreszenz, die mit 5-Oxy-I-tetralon in Schwefelsäure entsteht.

Résumé—Le sucre dans le sang a été évalué dans 0,02 ml de sang par mesure de la fluorescence obtenue avec l'hydroxy 5 tetralone 1 dans l'acide sulfurique.

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SPECTROPHOTOMETRIC DETERMINATION OF THORIUM WITH NEOTHORONE

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Summary—In the spectrophotometric method for the determination of thorium with Neothorone, the peak of the absorption spectrum of the thorium-Neothorone solution against a Neothorone blank solution lies between 570 mμ and 580 mμ. A suitable pH for the sample solution in the determination is 2, when the colour of the thorium-Neothorone solution ceases to change about one hour after colour development. Besides several ions reported already, anions such as nitrate and citrate ions also interfere with the colour reaction between thorium and Neothorone.

INTRODUCTION

NEOTHORONE (*o*-arsonophenylazochromotropic acid) (NT) was proposed by Ishibashi and Higashi[1] as a chromogenic reagent for thorium (Th). At the present time, it is increasingly important in the colorimetric determination of Th[1,2] and F (indirect method),[3] because of its excellent sensitivity and selectivity. Furthermore this reagent can be used for the determination of U,[4,5] Be[6] and In,[7] and the behaviour of NT with respect to metallic ions has been studied in the considerable detail.[4,8]

The present authors report here new information regarding the spectrophotometric method for the determination of Th employing NT.

EXPERIMENTAL

Reagents

(1) Standard $ThCl_4$ solution; dissolve commercial $Th(NO_3)_4$ in water and purify the solution by ion-exchange using alginate,[9] precipitate the hydroxide with ammonia and dissolve the hydroxide in hydrochloric acid. Standardise the stock solution thus prepared titrimetrically by EDTA. It contains 5·5 mg of Th per ml. It was diluted to a suitable concentration for each experiment.

(2) 0·1% NT solution; dissolve 0·1 g of guaranteed reagent NT in water and dilute to 100 ml.

(3) Buffer solutions; prepare the following buffer solutions from guaranteed reagents;

pH 1: [KCl 4·7 g + Conc. HCl 10·5 ml] per 250 ml.
pH 2: [KCl 4·7 g + Conc. HCl 1·1 ml] per 250 ml.
pH 4: [1*N* HAc 100 ml + 1*N* NaAc 25 ml] per 250 ml.
pH 6: 125 ml of [1*N* HAc 10 ml + 1*N* NaAc 160 ml] per 250 ml.
pH 8: [NH_4Cl 6·5 g + 1*N* NH_4OH 3·8 ml] per 250 ml.

Apparatus

A Beckman Model DU Spectrophotometer with a self-recording apparatus constructed by the authors[10] was used for the measurement of absorbancy.

General procedure

For the determination of Th in aqueous solution, the following procedure was used. Pipette 1 ml of 0·1% NT solution, 5 ml of buffer solution of pH 2 and an aliquot of the sample solution containing less than 150 μg of Th into a 25 ml measuring flask; make up the volume of the solution to 25 ml with water. Allow the solution to stand for one hour or more, and measure the absorbancy in 1-cm cell at 580 mμ against either water or the blank reference solution.

All measurements were carried out at room temperature which ranged from 10° to 15°, such a temperature range having no appreciable influence on the absorbancy in these experiments.

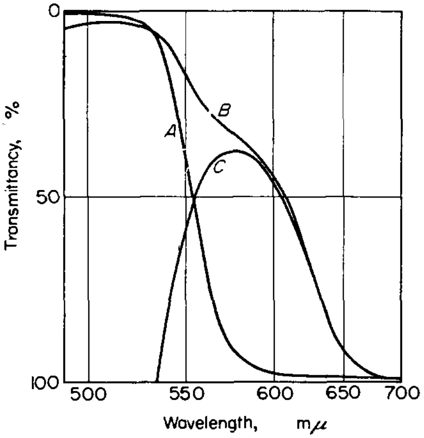

FIG. 1.—Absorption spectra.

A: NT blank solution against water.
B: Th–NT solution against water.
C: Th–NT solution against NT blank solution.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of a NT blank solution and a Th–NT solution against water, and of a Th–NT solution against NT blank solution at pH 2 are shown in Fig. 1 in which the ordinate represents percent transmittancy. The peak of the absorption spectrum of Th–NT solution against a NT blank solution lies between 570 mμ and 580 mμ. The peak has been reported at 600 mμ,[1] 570 mμ[3] and 580 mμ.[5]

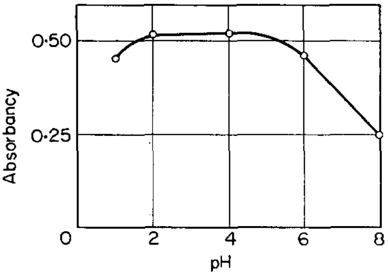

FIG. 2.—Effect of pH upon the absorption of Th–NT solution against a NT blank solution at pH 2, 580 mμ.

Effect of pH

The effect of pH upon the absorbancy of a Th–NT solution at 580 mμ is shown in Fig. 2 in which the ordinate represents the absorbancy of the solution against NT blank solution. The absorbancy has constant maximum intensity over a pH range from 2 to 4, agreeing with the results obtained by Matsuyama *et al.*[5]

Fig. 3 gives the absorption spectra of NT blank solution against water at various values pH; the curves move towards longer wave lengths with increase in pH.

Composition of the TH–NT complex

The absorbancy of Th–NT solution at 600 mμ was measured, the volume of 0·1 % NT solution added to a fixed volume of Th solution being varied. The results are shown in Fig. 4 in which the abscissa represents the mol ratio of NT to Th. The complex is apparently composed of 1 mol Th and 2 mol NT, and 1 ml of 0·1 % NT solution is therefore sufficient for less than 150 μg of Th.

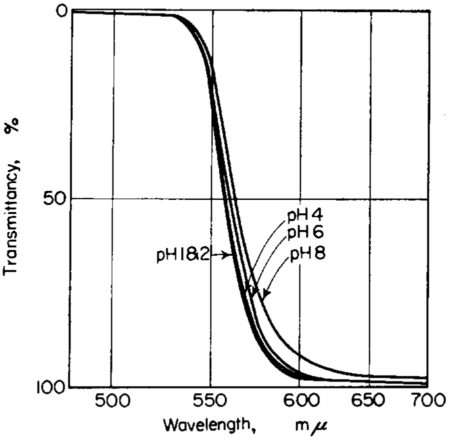

FIG. 3.—Effect of pH upon the absorption spectra of a NT blank solution against water.

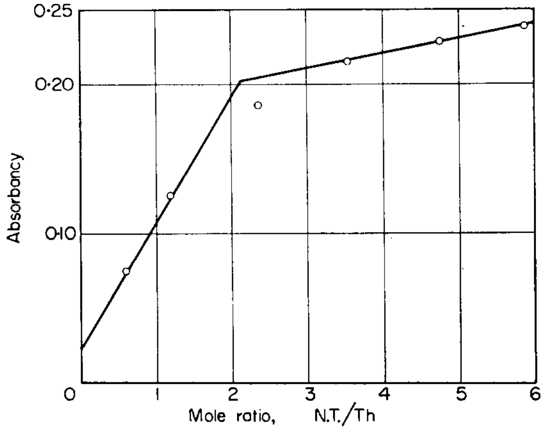

FIG. 4.—Effect of mol ratio of NT to Th upon the absorbance of Th–NT solution at pH 2, 600 mμ.

Stability of colour

It has been reported that the colour of Th–NT solution is lasting and stable. But according to the present results this is doubtful. The relationship between absorbancy at 600 mμ and time at various pH values is shown in Fig. 5. In general, the colour change of the solution is obvious during the initial period of reaction; the absorbancy of a solution of lower pH reaches a constant value after the lapse of about one hour, but at higher pH there is a continuous change of absorbancy over several hours.

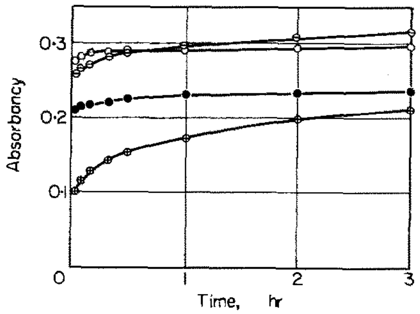

FIG. 5.—Stability of the colour of Th–NT solution at 600 mμ.
⊙ pH 1: ○ pH 2: ⊖ pH 4: ⊕ pH 8.

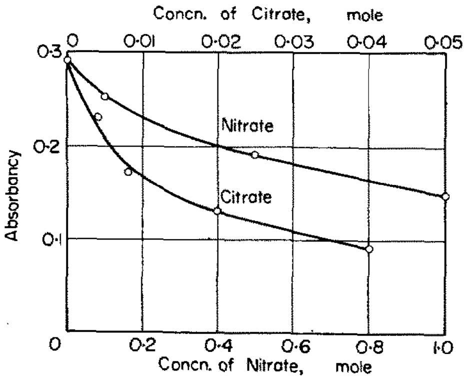

FIG. 6. —Interference of citrate and nitrate with the colour of Th–NT solution at pH 2, 580 mμ.

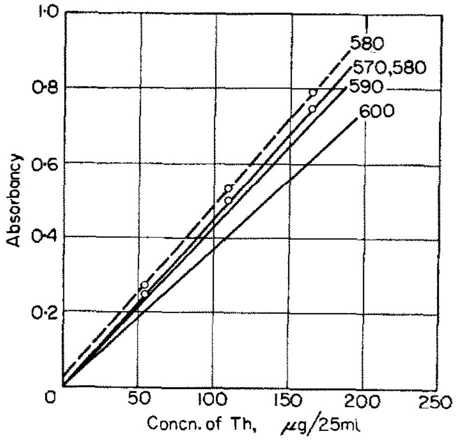

FIG. 7.—*Calibration curves at pH 2.*
- - - - against water.
——— against NT blank solution.

Interfering ions

Ishibashi and Higashi[1] have reported that Zr, Ti, Ce, UO_2, Fe, F, PO_4, SO_4, C_2O_4, etc. interfere with the colour formed by Th. Our experiments also indicate that nitrate and citrate interfere. The magnitude of the interference of varying concentrations of these ions is shown in Fig. 6.

Calibration curve

Calibration curves at pH 2 are shown in Fig. 7. The curve is linear in the concentration range from 0 to 150 μg of Th per 25 ml, at any wave length from 570 mμ to 600 mμ, either against water or NT blank solution. At other values of pH the curve is also linear, but the absorbancy varies with time. Therefore, the measurement of the absorbancy for the determination of Th should be carried out at pH 2 and at 580 mμ.

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Zusammenfassung—Das Absorptionsmaximum bei der spektrophotometrischen Bestimmung von Thorium mit Neothoron liegt zwischen 570 und 580 mμ, wenn gegen eine Neothoron-Blindlösung gemessen. Als geeignet für die Bestimmung wurden Arbeiten in einer Lösung von pH = 2 gefunden. Unter dieser Bedingung wurde Konstanz des Absorptionswertes eine Stunde nach Entwickeln der Färbung erzielt. Neben anderen schon berichteten Ionen wurden auch noch Nitrat- und Zitration für die Farbreaktion als störend gefunden.

Résumé—Dans la méthode spectrophotométrique de dosage du thorium avec la néo-thorone, le maximum du spectre d'absorption de la solution contenant le thorium et la néo-thorone par rapport à la solution témoin de néo-thorone se produit pour une longueur d'onde comprise entre 570 mμ et 580 mμ. On trouve qu'un pH de 2 pour la solution échantillon est convenable pour le dosage; de cette manière la couleur du complexe cesse de se modifier environ une heure après le début du développement de la couleur. De même que différents ions déjà mentionnés, des anions tels que nitrate et citrate perturbent la réaction colorée.

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THE POLAROGRAPHIC DETERMINATION OF NITROGLYCERINE*

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(*Received* 26 *May* 1959)

Summary—The application of the cathode-ray polarograph for the determination of nitroglycerine in certain double base propellant compositions and blasting explosives is described. Employing an alcoholic aqueous solution of tetramethyl ammonium iodide as base solution, only one wave is seen on the conventional polarograph. When the cathode-ray polarograph is used, however, three peaks are clearly seen; these occur at —0·25, —0·45 and —0·75 V (referred to the mecury pool). Nitroglycerine is readily obtained in the ether extract of propellant compositions by measuring the peak height at —0·75 or —0·25 V.

In the case of blasting explosives, in addition to nitroglycerine, dinitroglycol and mononitrotoluene may be present in the ether extract. Dinitroglycol gives two peaks which occur at —0·45 and —0·75 V, thus coinciding with the two later peaks of nitroglycerine. Further, the isomers of mononitrotoluene give peaks which occur very near to nitroglycerine (—0·75 V). In view of this, it is necessary to use the first peak for nitroglycerine, namely that which occurs at —0·25 V. Accuracies of the order of ±2% are obtained.

A METHOD has already been described for the detremination of dibutyl phthalate in propellant compositions, using the cathode-ray polarograph.[1] In this connection it was shown that owing to interference by the large preceding wave of nitroglycerine at the sensitivity required, the orthodox polarograph could not be used for the determination of dibutyl phthalate. Whitnack *et al.*[2] have described a method for the polarographic determination of nitroglycerine in double base powders using a Sargent recording polarograph, presumably based on orthodox polarography. They use a base solution of tetramethyl ammonium chloride in a solution containing 75% alcohol. They refer only to a single wave which is used for quantitative measurement. In an earlier paper,[3] Whitnack studied the polarographic reduction of polynitrate esters; employing alcoholic solutions varying from 60–95% alcohol be obtained only one clearly visible wave. The work described here has confirmed that only one wave is obvious, extending over a very wide voltage range; close examination of the wave does, however, suggest that more than one wave may be present and this has now been shown to be so. The cathode-ray polarograph (Southern Instruments Ltd.) reveals the presence of three clearly defined reduction steps.[1]

Employing the cathode-ray polarograph, in a base solution comprising 0·05M tetramethyl ammonium iodide in 50% aqueous methanol solution, nitroglycerine gives three peaks at —0·25, —0·45 and —0·75 V (vs. mercury pool). Propellant compositions of the type shown in Table I have been analysed for nitroglycerine using the height of the third peak (—0·75 V) as a means of quantitative assessment. Certain propellants (*loc. cit.*) contain substances which reduce around —0·75 V so that in such

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cases the peak at —0·25 V must be used. This peak is not so convenient to use as it is less well defined and more subject to interference by oxygen, but it overcomes the problem of interference by other peaks produced from substances which show peaks in the vicinity of the main peak of nitroglycerine.

It was found that up to a certain level there was enhancement of the nitroglycerine peak height by the dibutyl phthalate in common with that already described for enhancement of the dibutyl phthalate by nitroglycerine,[1] but there was no effect on the blank in the determination of nitroglycerine which was due only to the base solution.

The work has been extended to the determination of nitroglycerine in blasting explosives, for which, compositions are given in Table V. The ether extract from these explosives usually contains in addition to nitroglycerine, also nitroglycol. Glycol is added to glycerine to the extent of about 20% and it is this mixture which is nitrated to give "nitroglycerine 'C'." The only other constituent of the ether extract from some types of explosives which gives a polarographic wave is mononitrotoluene. Nitroglycol gives two well defined waves on the cathode-ray polarograph. These occur at peak potentials of —0·45 V and —0·75 V, namely they are coincident with the two later peaks of nitroglycerine. For this reason it is necessary to use the wave occurring at —0·25 V peak potential for the determination of nitroglycerine. Whitnack *et al.* report only one wave for dinitroglycol;[3] this is most probably because of the difficulty of detection by orthodox polarography. When the value for amount of dinitroglycol present is required, it is a simple matter to use either the —0·45 V or the —0·75 V peaks for further measurement and deduct the height which would be obtained for the nitroglycerine present by multiplying the height of the —0·25 V peak by a predetermined factor. A peak for mononitrotoluene occurs at —0·8 V so that in its presence it is only possible to use the —0·45 V peak in addition to that at —0·25 V.

Comparison with chemical methods has shown excellent agreement for propellants containing between 2 and 35% nitroglycerine in the presence of dibutyl phthalate and, in the case of the lower percentage, also in the presence of a nitro-amine body.

Blasting explosives containing 10–27% "nitroglycerine 'C' " and in some cases about 2% mononitrotoluene have been successfully analysed for nitroglycerine and nitroglycol.

A. PROPELLANTS

Method

1. *Reagents:*

Ether: pure dry ether.

Methanol: pure anhydrous methanol.

Standard nitroglycerine:

(a) *Stock solution:* Dissolve 1 g of *pure* nitroglycerine 'A' in 500 ml methanol in a standard flask.

(b) *Dilute solution:* Dilute 8 ml of the stock solution to 50 ml with methanol in a standard flask. This solution contains 320 μg nitroglycerine per ml.

0·1*M* *tetramethyl ammonium iodide solution:* Dissolve 2 g of tetramethyl ammonium iodide which has been recrystallised 5 times from water in 100 ml of distilled water.

2. *Extraction procedure:* Weigh accurately about 1 g of the sample into a sintered-glass crucible (porosity G. 3) and extract with ether in a suitable extraction unit for six hours (alternatively pure methylene chloride may be used). Evaporate the resulting solution to dryness in a current of dry air, taking the usual precautions for handling materials containing nitroglycerine. Dissolve the residue in methanol and dilute it to 100 ml in a standard flask. Dilute 10 ml of this solution to 100 ml with methanol and use the resulting solution for the polarographic determination of nitroglycerine. When

the amount of nitroglycerine in the sample falls below about 5%, this second dilution should be omitted.

3. *Polarography using the cathode-ray polarograph:* (*a*) For samples which are free from ether soluble substances which may reduce to give peaks near to the third peak of nitroglycerine, the peak occurring at —0·75 V may be used for the estimation of the nitroglycerine. The propellants of composition shown in Table I (A and B) may be examined in this way.

(*a*) Transfer 5 ml of the methanol solution containing the nitroglycerine into a suitable glass stoppered flask, add 5 ml of methanol followed by 10 ml of the tetramethyl ammonium iodide solution. Thoroughly mix the solutions and transfer a suitable amount to a polarographic cell. The concentration of nitroglycerine in the cell should be of the order of 25–150 μg per ml. Place the cell in position in the water bath (at 25°) of the polarograph stand and connect it to a nitrogen bubbler containing equal volumes of methanol and water. Pass a stream of oxygen free nitrogen in the usual manner for a period of 5 minutes in order to remove oxygen. Disconnect the nitrogen and after choosing a suitable sensitivity setting, polarograph the solution using a start potential of —0·40 V. A well defined peak will appear at —0·75 V. Measure the wave height as the vertical height from the base line to the peak (see Fig. 1(*b*)). Repeat the whole procedure, taking 5 ml of the appropriate standard nitroglycerine solution instead of the 5 ml of methanol. Finally, carry out a blank determination on a solution containing equal volumes of methanol and the tetramethyl ammonium iodide solution. In each case take the mean of three determinations.

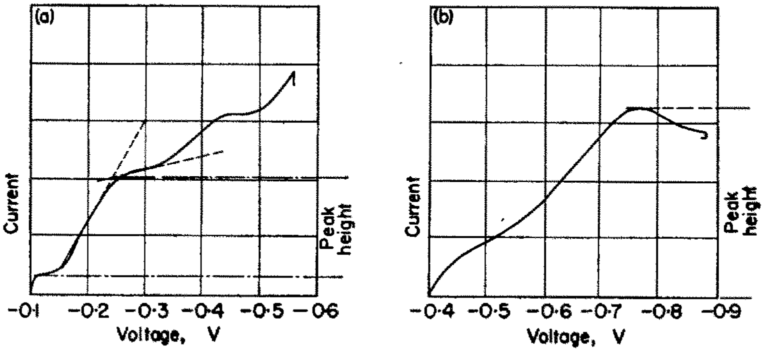

FIG. 1.—Polarograms obtained from nitroglycerine using the cathode ray polarograph and showing methods of measuring peak heights: (a) with start potential —0·1 V, (b) with start potential —0·4 V.

(*b*) If the sample contains substances which reduce near to the third wave of the nitroglycerine it is necessary to choose an earlier wave for measurement. Thus certain nitro-amine bodies which are used as stabilisers may cause interference. Using a start potential of —0·1 V the wave due to nitroglycerine, appearing as a shoulder at a potential of —0·25 V approximately is measured by the procedure shown in Fig. 1(*a*). The determination is completed in the manner described in 3(*a*) above. Since interference by oxygen is very significant at the lower voltage of —0·25 V (Fig. 2) at least 10 minutes are required for de-oxygenation.

(*c*) Calculation of results when the dilute (see 1(*b*) above) standard solution of nitroglycerine is used.

Let a = the peak height of the unknown solution from which the blank has been deducted.

Let b = the peak height of the unknown plus the standard solutions corrected as above.

The concentration C in μg/ml of nitroglycerine in the cell is given by:

$$C = \frac{a \times 80}{b - a}$$

(employing standard solution of nitroglyceine = 320 μg/ml).

From the weight of sample taken and the extent of dilution of the ether extract with methanol and knowing the volume of this methanol solution used, calculate the percentage nitroglycerine in the sample.

EXPERIMENTAL

1. *The examination of nitroglycerine using the conventional polarograph*

Whitnack *et al.* have carried out extensive investigations of the polarography of nitroglycerine and polynitrate esters.[3] In the method described for the determination of nitroglycerine[2] in double base powders they employed a base solution comprising tetramethyl ammonium chloride in 75% alcohol solution and polarographed over the range —0·0 to —1·60 V and measured the height of the wave so obtained. Under the conditions used only a single wave is obtained.

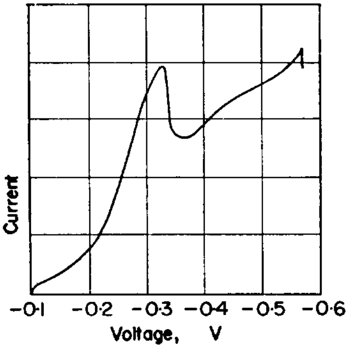

Fig. 2.—Polarogram obtained from nitroglycerine using the cathode ray polarograph showing interference by dissolved oxygen due to insufficient degassing.

Work carried out by us with a similar base solution and using Tinsley model polarograph confirmed that there is one readily distinguishable wave considerably drawn out over the voltage —0·1 to —1·3 (using a base solution of 0·05*M* tetramethyl ammonium iodide in alcohol solution). Gelatine (0·1% solution) was used as maximum suppressor. When Methyl Red (as employed by Whitnack) was used as maximum suppressor it was not possible to obtain a complete wave owing to the presence of a maximum at —0·45 V which was apparently derived from the base solution and could not be readily eliminated. Figs. 3(*a*) and (*b*) show polarograms for the determination of nitroglycerine using (*a*) Methyl Red, (*b*) gelatine as maximum suppressors. Similar results were obtained both for 50% and 75% alcoholic solutions. As already reported in a previous paper[1] this large preceding wave for

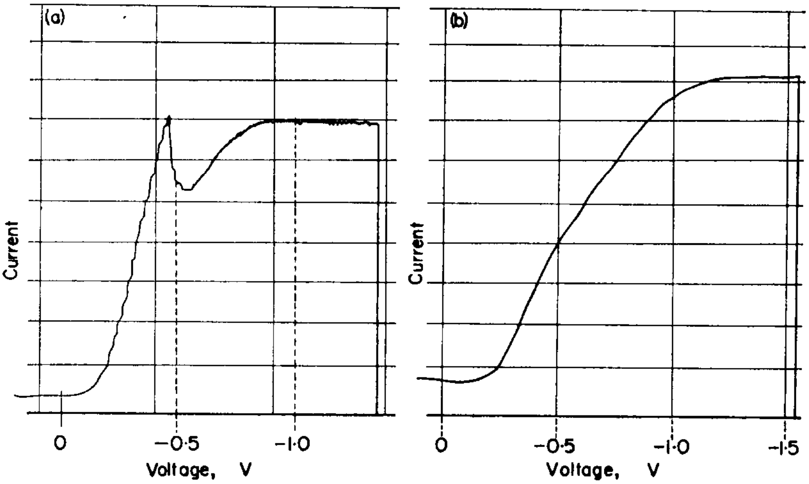

Fig. 3.—Polarograms obtained from nitroglycerine using the Tinsley polarograph.
Sensitivity = 100, damping = 10
Maximum suppressor used: (a) methyl red, (b) gelatine.

nitroglycerine causes marked interference with the reduction of dibutyl phthalate for the determination of which it is not therefore practicable to devise a routine procedure (see Figs. 4 and 5).

Although only one wave is readily discernible on the orthodox polarograph, when the cathode-ray polarograph is used, three waves are obtained with peaks occurring at −0·25, −0·45 and −0·75 V (vs. mercury pool).

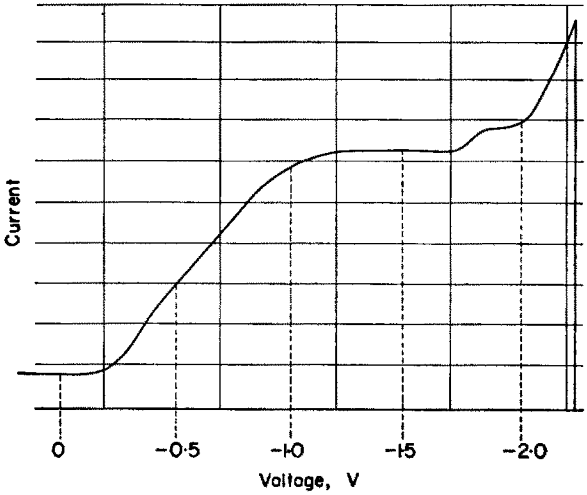

FIG. 4.—Polarogram obtained from a mixture of nitroglycerine and dibutyl phthalate using the Tinsley polarograph. Sensitivity = 150, damping = 10.

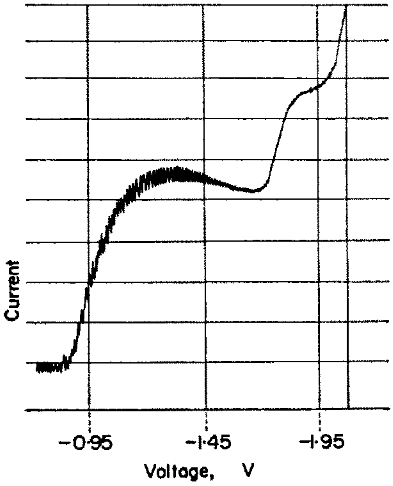

FIG. 5.—Polarogram obtained from a mixture of nitroglycerine and dibutyl phthalate using the Tinsley polarograph. Sensitivity = 30, damping = 10.

2. *Results using the cathode-ray polarograph*

The determination of nitroglycerine in double base propellants: Throughout the work which follows, the cathode-ray polarograph manufactured by Southern Instruments Ltd. was used and the solution employed for polarography consisted of 10 ml methanol containing the nitroglycerine together with an equal volume of 0·1M aqueous tetramethyl ammonium iodide. By choosing a suitable start potential, any one of the three waves with peaks at −0·25, −0·45 and −0·75 V, may be used for measurement of the peak height although the later wave occurring at —0·75 V gives the best defined peak (see Fig. 1(*a*) and (*b*)).

Examples showing the composition of double base propellants are given in Table I. The ether extract from propellants of Type A and B contain dibutyl phthalate, ethyl centralite and mineral jelly as well as the nitroglycerine, but only the dibutyl phthalate in addition to nitroglycerine give polarographic waves.

TABLE I.—APPROXIMATE COMPOSITIONS OF TYPICAL DOUBLE BASE PROPELLANTS

Propellant	A	B	C
Nitrocellulose	49·75	56·5	76·0
Nitroglycerine	34·50	19·5	2·5
Ethyl centralite	6·5	1·0	—
Dibutyl phthalate	8·0	—	—
Mineral jelly	0·25	0·25	—
Potassium nitrate	1·0	1·0	—
Triacetin	—	21·75	—
Other constituents including nitro-amine stabiliser	—	—	21·5

(*a*) *The effect of dibutyl phthalate on the wave and peak potential of nitroglycerine:* It was found that just as the presence of nitroglycerine affected the determination of dibutyl phthalate[1] so dibutyl phthalate caused enhancement of the height of the nitroglycerine peak and a change in peak potential. It was shown that a progressive increase in concentration of dibutyl phthalate from 0 to 250 μg per ml of base solution caused a progressive change in the peak potential of the third step from —0·75 to —0·85 V which remained constant with further increase in concentration of dibutyl phthalate.

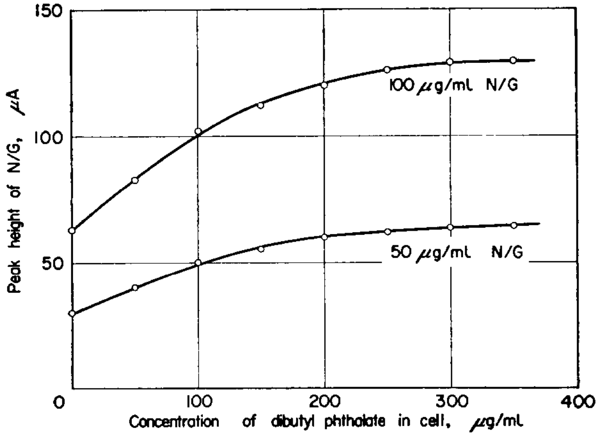

FIG. 6.—The effect of dibutyl phthalate on the peak height of nitroglycerine.

The enhancing effect of dibutyl phthalate on the nitroglycerine peak at —0·75 V reached a maximum at about 250–300 μg per ml of base solution (see Fig. 6). Unlike previous work on the determination of dibutyl phthalate when nitroglycerine had a marked effect on the value of the blank, it was found that dibutyl phthalate had no effect on the value of the "nitroglycerine" blank.

(*b*) *The determination of nitroglycerine in synthetic solutions and propellant samples:* Base solutions were made up in the manner described so that they contained 80 μg of dibutyl phthalate per ml and various concentrations of nitroglycerine. Employing the procedure described under A, the amounts of nitroglycerine were then determined and results are given in Table II. Samples of double base propellants (mechanites) were analysed by the standard routine procedure using reduction by ferrous ammonium sulphate and by the polarographic method; results are shown in Table III and it is seen that a good measure of agreement is obtained.

(*c*) *Special case of propellant containing a "reducible" stabiliser:* It may happen that instead of ethyl centralite a nitro-amine compound may be present as stabiliser (see sample C, Table I) and if this has a reduction peak close to that of the main nitroglycerine peak it is obviously necessary to use either the peak occurring at −0·45 V or −0·25 V. The peak at −0·25 V was taken as it was more clearly defined than the later peak. The measurement of the peak height is clearly demonstrated in Fig. 1(*a*). The low peak potential of −0·25 V makes it essential to ensure that oxygen is thoroughly removed from the solution and therefore a longer period of at least 10 minutes degassing must be given (see Fig. 2). Table IV shows results obtained by the method described in A, 3(*b*) employing samples containing nitroglycerine of the order of 2–3%.

TABLE II.—THE DETERMINATION OF NITROGLYCERINE IN MECHANITE TYPE SYNTHETIC SOLUTIONS

Nitroglycerine added (μg/ml)	Nitroglycerine found (μg/ml)
200	197
240	241
280	275
320	316
360	354
400	398

TABLE III.—THE DETERMINATION OF NITROGLYCERINE IN MECHANITE SAMPLES

Nitroglycerine recovered, %	
(*a*) By polarograph	(*b*) By ferrous-titanous method
34·3	34·4
34·2	34·4
30·0	30·2
29·9	30·2
34·3	34·3
34·3	34·5

B. BLASTING EXPLOSIVES

Method

These methods deal with blasting explosives which normally contain nitroglycerine together with dinitroglycol in contrast to the pure nitroglycerine used in propellants. Thus there is the problem of estimating nitroglycerine in the presence of dinitroglycol. In some cases nitrotoluene may be present. Dinitroglycol gives two peaks which coincide with the last two peaks of nitroglycerine and nitrotoluene gives a peak which is very near to the third peak of nitroglycerine.

1. *Reagents:* The reagents are similar to those given under A but the standard nitroglycerine

solution should be prepared from "nitroglycerine" as used in the manufacture, namely prepared from the nitroglycerine-dinitroglycol mixture.

Standard mononitrotoluene solution: The material used in the actual explosive may be a mixture of the isomers and so the standard solution is best made up from a current plant sample of mononitrotoluene.

Dissolve 0·25 g of the mononitrotoluene in 250 ml of methanol in a standard flask. Dilute 2 ml of this solution to 100 ml in a standard flask. This solution contains 20 μg/ml mononitrotoluene.

2. *Extraction procedure:* Weigh accurately about 1 g of the sample into a sintered-glass crucible, (porosity G.3) and extract in a suitable extraction unit for two hours. Employing suitable precautions evaporate the resulting solution almost to dryness, dissolve the residue in methanol and dilute the resulting solution in such a way as to give a final convenient concentration of nitroglycerine of say about 300 μg/ml. For example, if the explosive contained about 16% nitroglycerine the residue would be dissolved in 100 ml of methanol in a standard flask. 20 ml of this solution would then be diluted to a further 100 ml with methanol and the resulting solution used for the determination of nitroglycerine.

TABLE IV.—THE DETERMINATION OF NITROGLYCERINE IN PROPELLANT POWDERS CONTAINING A NITRO-AMINE STABILISER

Nitroglycerine recovered, %	
(*a*) By polarograph	(*b*) By ferrous-titanous method
2·93	2·84
2·95	2·84
2·30	2·2
2·32	2·2
2·64	2·6
2·59	2·6

3. *Polarography using the cathode-ray polarograph:* (*a*) Samples of the type shown in Table V(Y) which are free from mononitrotoluene:

(i) Assuming that the composition of the nitroglycerine-dinitroglycol mixture incorporated in the explosive is known: Determine the "nitroglycerine" by the method described for propellants under A, but instead of using a standard nitroglycerine solution use a standard solution of the known mixture of nitroglycerine and dinitroglycol.

(ii) If the composition of nitrated glycerine and glycol mixture is not known then it is necessary to use the first peak occurring at −0·25 V. The procedure is as described for propellants (see A). The same method can, of course, be used when the composition of nitroglycerine-dinitroglycol as described above, is known.

(*b*) For samples of blasting explosives which contain mononitrotoluene (see Table V, X and Z).

A peak for mononitrotoluene occurs in the vicinity of the final peak for nitroglycerine and the only reliable method for estimating the nitroglycerine under these conditions is to use its −0·25 V peak. The determination is carried out precisely as described above.

EXPERIMENTAL

The determination of nitroglycerine in blasting explosives

There are two groups of blasting explosives with which this work is concerned, namely those containing mononitrotoluene and dinitroglycol (see Table V) in addition to nitroglycerine and those in which mononitrotoluene is absent (see Table V). Employing the standard base solution comprising 0·05*M* tetramethyl ammonium iodide in 50% methanol, peak potentials as follows were obtained: nitroglycerine: −0·25, −0·45 and −0·75 V; dinitroglycol: −0·45, −0·75 V; mononitrotoluenes: −0·67, −0·80 and −0·82 V. The types of waves obtained are shown in Fig. 1 and Fig. 7 (nitroglycol is similar). The wave due to mononitrotoluene is typical of the type produced by a reversible reduction on the cathode ray polargraph. Adopting the method shown in Fig. 1 for the measurement of peak heights, it was shown that for each substance the peak heights were proportional to the amount of substance present. This applied equally to the three peaks for nitroglycerine and to both peaks of the dinitroglycol.

TABLE V.—APPROXIMATE COMPOSITIONS OF TYPICAL BLASTING EXPLOSIVES

Explosive	X	Y	Z
'C' nitroglycerine*	27·5	10·5	16·0
B.S. nitrocellulose	1·0	—	0·5
Mononitrotoluene	1·5	—	1·0
Ammonium nitrate	31·0	70·7	42·5
Sodium chloride	29·4	10·0	28·0
Oat husk meal	1·1	—	—
China clay	4·0	—	5·0
Diammonium phosphate	0·5	—	—
Alcohol	0·3	—	—
Woodmeal	—	6·7	2·0
Woodflour	—	2·1	—
"Cellofas" B	—	—	0·5
Calcium stearate	—	—	0·5
Barytes	4·0	—	4·0

* Nitroglycerine-nitroglycol mixture prepared from glycerine containing 20% ethylene glycol.

(*a*) *The determination of nitroglycerine in the presence of dinitroglycol:* Blasting explosives differ from propellants in that glycerine containing ethylene glycol is used instead of pure glycerine for nitration and the "nitroglycerine" so prepared is used in the preparation of the explosive. In addition some compositions contain mononitrotoluene as a mixture of the isomers. The only polarographically reducible compounds in the ether extract (see B, 2) of the explosive are nitroglycerine, and dinitroglycol and mononitrotoluene when present. Since the nitroglycerine: dinitroglycol ratio used in the manufacture is usually known, provided mononitrotoluene is absent, it is possible to use the third peak occurring at —0·75 V for the determination of nitroglycerine. Alternatively, by using the early peak occurring at —0·25 V (see Fig. 1) the nitroglycerine can be determined directly in the presence of both dinitroglycol and mononitrotoluene. Results obtained with synthetic mixtures of

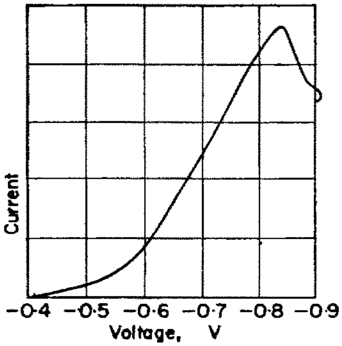

FIG. 7.—Polarogram obtained from mononitrotoluene using the cathode ray polarograph. Peak potentials: ortho = —0·80 V, meta = —0·67 V, para = —0·82 V.

Table VI.—Determination of nitroglycerine in the presence of dinitroglycol

Nitroglycerine added, μg/ml, base solution	Nitroglycerine found, μg/ml	Error %
100	98	−2
200	195	−2·5
300	296	−2
400	410	+2·5
500	492	−1·6

Table VII.—Determination of nitroglycerine in the presence of dinitroglycol and mononitrotoluene

Nitroglycerine added, μg/ml base solution	Nitroglycerine found, μg/ml	Error %
100	97	−3
200	197	−1·5
300	304	+1·3
400	394	−2
500	492	−1·6

Table VIII.—The determination of nitroglycerine in blasting explosives

Nitroglycerine determined by difference method, %		Nitroglycerine determined by polarograph, %	
1	2	1	2
10·5		10·3, 10·4	
	16·1		16·3, 16·4, 16·5
	27·7		27·3, 27·4

1—mononitrotoluene absent
2—nitrotoluene present.

various amounts of nitroglycerine in the presence of 40 μg dinitroglycol per ml of base solution are shown in Table VI.

(*b*) *The determination of nitroglycerine in the presence of dinitroglycol and mononitrotoluene:* The procedure described above, using the peak for nitroglycerine occurring at −0·25 V was used for the determination of nitroglycerine in the presence of both dinitroglycol and mononitrotoluene. Since the mononitrotoluene used in the manufacture consisted of a mixture of the three isomers, the same mixture was used as a standard in the preparation of synthetic solutions used for testing the method

In the actual polarographic determination, the method of standard addition was employed as there was a slight enhancing effect of the nitroglycerine peak by the mononitrotoluene. It was found that the peak potentials for the isomers of mononitrotoluene ranged from −0·67 to −0·82 V.

Table VII shows results obtained for various amounts of nitroglycerine in the presence of 40 μg dinitroglycol and 5 μg mononitrotoluene per ml of base solution. These are the amounts which would be expected in the amount of solution taken from the diluted ether extract of the sample (see B, 2).

(*c*) *The determination of nitroglycerine in blasting explosives:* Table VIII shows results which were obtained for the determination of nitroglycerine in blasting explosives of the types shown in Table V.

Zusammenfassung—Es wird die Anwendung des Kathodenstrahl-Polarographen zur Bestimmung von Nitroglycerin in einigen doppel basischen Treibstoffmischungen und Sprengstoffen beschrieben. Bei Anwendung von einer alkoholisch-wässrigen Lösung von Tetramethyl ammonjodid als Grundlösung kann man nur eine Welle in üblichen Polarographen sehen. Wenn man aber den Kathodstrahl-Polarographen benützt, können deutlich drei Spitzen gesehen werden: diese erscheinen bei −0,25, −0,45 und −0,75V (bezogen auf den Quecksilber-Pool). Nitroglycerin erhält man leicht in Äther-Extrakt von Treibstoffmischungen durch Messung der Wellehöhe bei −0,75 oder −0,25V. Im Falle der Sprengstoffe können sowohl Nitroglycerin als auch Dinitroglykol und Mononitrotoluol in Äther-Extrakt anwesend sein. Die Dinitroglykol gibt zwei Wellen die bei −0,45 und −0,75V erscheinen, und so übereinstimmen mit den zwei späteren Wellen von Nitroglycerin. Weiters, geben die Isomere von Mononitrotoluol Spitzen welche sehr nahe bei den Spitzen von Nitroglycerin erscheinen. In Hinblick dieser Tatsache ist es notwendig für Nitroglycerin die erste Spitze zu benützen, diese die bei −0,25V erscheint.

Die Genauigkeit läuft in der Grössenordnung von ±2%.

Résumé—On décrit l'application du polarographe à rayons cathodiques au dosage de la nitroglycérine dans des mélanges propulsifs à deux constituants de base et dans les explosifs "soufflants". En utilisant une solution hydroalcoolique d'iodure de tétraméthylammonium comme électrolyte support, on observe, sur le polarographe classique, une seule vague. Sur le polarographe à rayons cathodiques on décèle nettement trois pics; ceux-ci se placent à −0,25, −0,45 et −0,75 V (par rapport à la napde de mercure). On dose facilement la nitroglycérine dans l'extrait à l'éther du mélange propulsif(————) en mesurant la hauteur du pic à −0,75 ou à −0,25 V.

Dans le cas des explosifs "soufflants", on trouve dans l'extrait à l'éther, outre la nitroglycérine, du dinitroglycol et du mononitrotoluène. Le dinitroglycol donne deux pics à −0,45 V et −0,75 V, coïncidant ainsi avec les deux derniers pics de la nitroglycérine. De plus, les isomères du mononitrotoluène donnent des pics qui apparaissent très près de celui de la nitroglycérine (−0,75 V). En conséquence, il est nécessaire d'utiliser le premier pic pour la nitroglycérine, c'est-à-dire celui qui apparaît à −0,25 V.

On obtient une précision de ±2 pour cent.

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DISCUSSION

Mr. E. TYRRALL asked whether the reactions corresponding to the three peaks in the nitroglycerine polarogram had been identified. Mr. WILLIAMS replied by indicating that no detailed study had so far been made of the reduction steps involved, but it was possible that each of the three peaks could be due to each of the nitrogroups, although it was possible that they may be reduction steps in any one of the nitrogroups.

Mr. A. O. PEARSON asked whether three peaks are obtained for trinitrotoluene. In his reply, Mr. WILLIAMS referred Mr. PEARSON to the work of J. Pearson (*Trans. Farad. Soc.* 1948 **44**, 683) who had studied that particular reduction and obtained three peaks in both acid and alkaline media.

Mr. E. TYRRALL asked, as an outcome of comments by Mr. HETMAN, whether a suggested cyclic isomer of nitroglycerine was established or was it merely a guess. Mr. WILLIAMS indicated that it could be largely guesswork.

Mr. H. Y. STRAIN wanted to know whether aliphatic nitrates such as those derived from erythritol or mannitol, containing a number of nitrogroups, had been examined to see whether their behaviour was similar. Mr. WILLIAMS replied by pointing out that some work would almost certainly have been carried out on the polarograph but he had no knowledge of this.

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A GAMMA ABSORPTIOMETER FOR LABORATORY ANALYSIS OF THE HEAVY ELEMENTS*

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Summary—Construction of a simple gamma absorptiometer employing a small ^{241}Am source, for the determination of U or Pu in relatively pure solutions, is described. The instrument yields a recorded voltage directly proportional to absorbance.

THE use of low energy radioactive sources in an absorptiometric technique provides a rapid and sensitive means for the determination of the concentration of heavy elments in solution. The liquids to be tested are inserted in a beam of radiation and the attenuation of the beam is a measure of the sample concentration.

This paper describes an instrument constructed at ORNL for the laboratory analysis of uranium or plutonium in relatively pure solutions.

APPARATUS

Radiation source

Americium-241 is a desirable source of photons for this technique[1] because of its low photon energy —approximately 60 keV—and its long half life—470 years. The relatively low intensities available with this source material are offset by the pronounced sensitivity for heavier elements gained by the use of low photon energies. The source is 10 mg of ^{241}Am as the trifluoride, cast in a plastic disc $\frac{9}{16}$ inch in diameter. This casting is sealed in an aluminium container by pouring a low melting alloy (Wood's alloy) over the source after locating it in the well of the container. The source is exposed to the sample through a 0.012-inch aluminium "window". Details of a procedure for source preparation are reported by Milham.[2]

A brass fitting surrounding the source provides biological shielding and serves to define the beam. Only the portion of the beam that passes through the sample is allowed to strike the detector through an orifice in the lead shield (Fig. 1).

Detector

A thallium-activated sodium iodide scintillation crystal coupled to an RCA 5819 multiplier phototube is the sensing unit. The detector crystal is 0.1 inch thick by 1.5 inches in diameter. This thickness was chosen to discriminate against higher energy background radiation. The low energy photons from the source are effectively absorbed in the crystal while higher energy radiation passes through with little interaction. Protection from the sides is afforded by a lead shield surrounding the crystal. Some stray radiation from this direction would otherwise be absorbed, regardless of its energy, since it would traverse the diameter of the crystal.

The multiplier phototube is taped with electrical insulating tape to insure light-tightness, and is magnetically shielded. Fig. 1 shows the construction of the source-detector assembly. The assembly is cylindrical in cross section, with the source and detector located on the axis. Samples are positioned properly in the beam by placing the cylindrical, flat-bottomed absorption cells in a closely fitting

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* Based on a presentation at the ISA Symposium on Instrumental Methods of Analysis, Houston, Texas, 12–14 May 1958.

† Operated by Union Carbide Corp., for the Atomic Energy Commission.

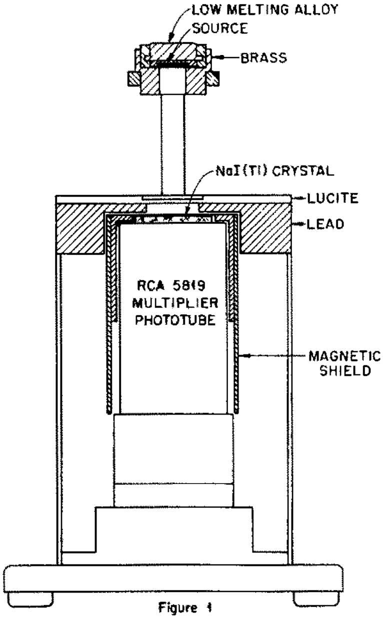

Figure 1
GAMMA ABSORPTIOMETER
SOURCE DETECTOR ASSEMBLY

FIG. 1.

depression in the detector housing cap. These cells are 1 inch internal diameter lucite cylinders having ⅛ inch wall and end thickness.

Photometric circuit

The basic circuit employed in this instrument was originally described by Sweet[3] and has been modified by others[4,5] for various uses. The unique property of the circuit is that the anode current from a multiplier phototube is held essentially constant by a feedback system that controls the dynode supply voltage. Sweet has shown that under this condition the voltage is approximately proportional to optical density over a considerable range. This is explained by reference to Fig. 2. A decrease in the light intensity falling on the photocathode, corresponding to an increase in solution density, causes a tendency for the anode current to decrease. A small decrease in current through the 200-M load resistor causes a relatively large voltage signal—in this instance, positive—and so decreases the bias on the cathode follower tube—12AX7. The cathode follower then passes more current, making the potential of its cathode, and that of the grid of the series regulator tube—6BG6, more positive. The lowered resistance of the 6BG6 permits more current to flow, increasing the voltage applied to the multiplier phototube dynodes and counteracting the tendency of the anode current to decrease.

Measuring circuit

The total voltage applied to the dynodes is divided through a series of resistors from which the "range" switch selects fractions giving full scale recorder deflections for various concentration increments. A zero suppression circuit permits selection of the portion of the total instrument range to be covered by these increments. The 500-ohm potentiometer (Note*, Fig. 2) is intended to allow for possible changes in sensitivity with zero setting or by aging of the detector crystal.

Brown recorder

The recorder is a 50-mV, single point Brown Electronik strip chart recorder (type 153) having a pen speed of 12 sec, a chart speed of ½ inch per minute, and a high gain amplifier modified to accept high impedance negative-going signals. The original low impedance transformer input circuit is

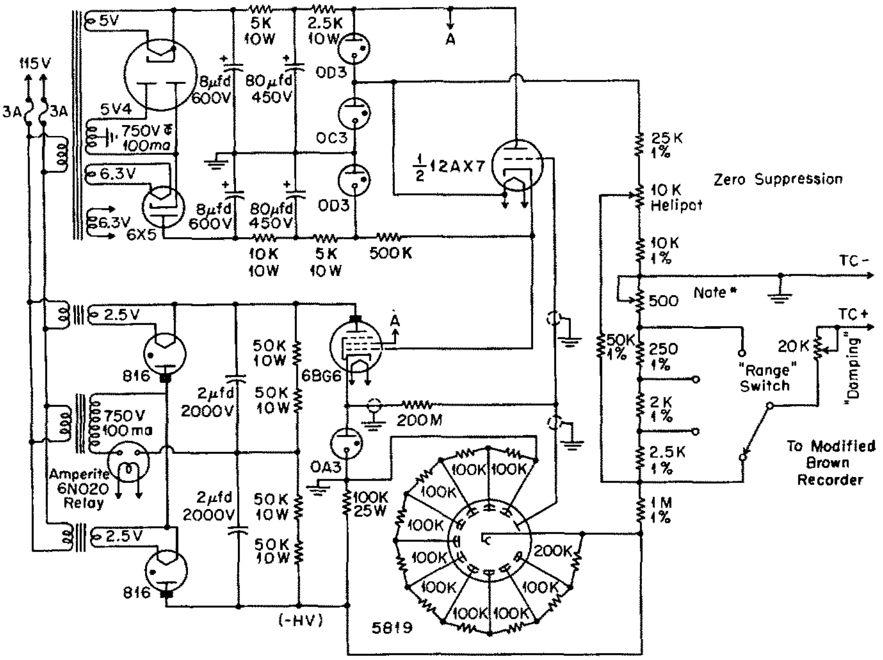

FIG. 2.—Circuit of gamma-absorptiometer, ORNL analytical instrumentation group. Note* Set at 250 Ω

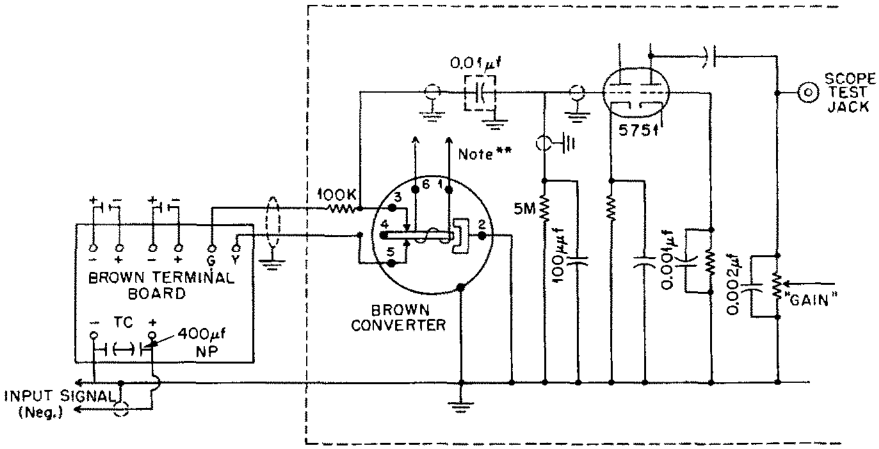

FIG. 3.—Brown recorder modifications for high impedance negative-going signals
Note** Chopper coil polarity is reversed if necessary to get negative feedback. See appendix.

replaced by a high impedance, RC coupling input circuit so that the recorder can be used to record the current through a 5000-ohm resistor. The circuit modifications are shown in Fig. 3. Further information is contained in the appendix.

TEST PROCEDURE

Uranium solutions used in evaluation of the instrument where prepared by dilution of a uranyl nitrate solution that was standardised by potentiometric titration. A sample path length of 4.1 cm was used. A typical series of measurements is shown in Fig. 4.

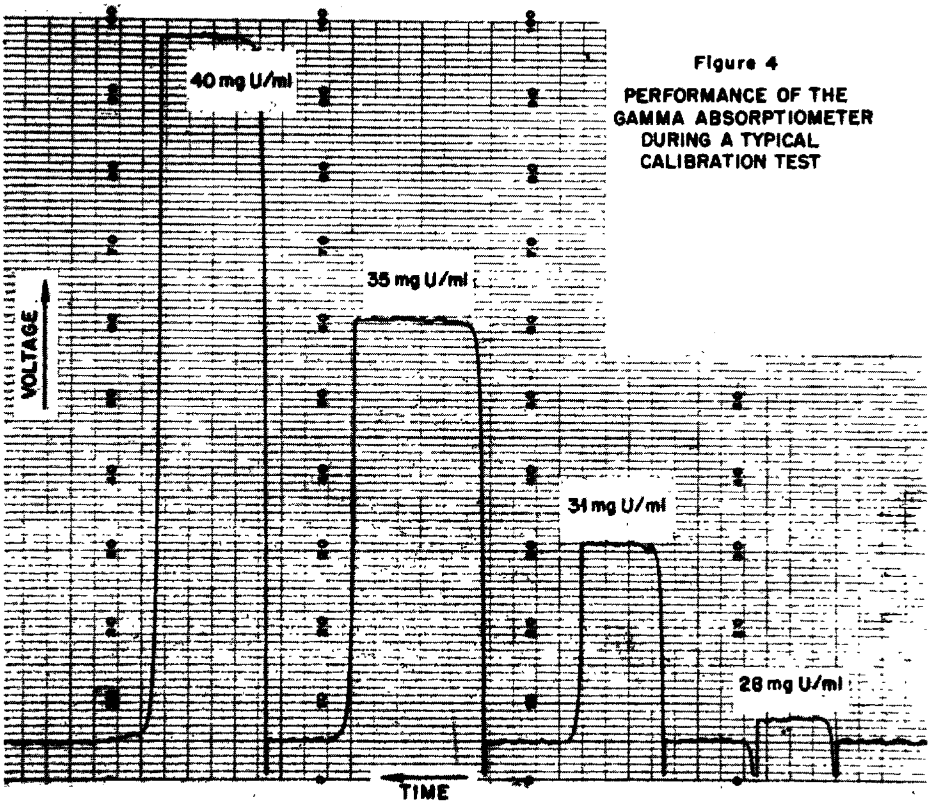

Figure 4

PERFORMANCE OF THE GAMMA ABSORPTIOMETER DURING A TYPICAL CALIBRATION TEST

In order to compensate for both long term drift and short term fluctuations of the dynode voltage, a "background" is obtained by placing a metal absorber of a standard solution in the cell position. This specimen is re-inserted after each sample and the measurement for each material is averaged out over a period of about three minutes. Absorption curves are plotted showing the difference between sample and "background" readings as a function of concentration. These curves are linear and show no change of slope over a period of weeks.

The zero suppression potentiometer is used to set the background absorber reading at a chosen place on the recorder scale each time a given range is used. For example, in Fig. 4, a standard absorber having an absorbance slightly less than that of the 28 g/litre uranium solution was set to 5% on the scale at the beginning of the series.

Contributions to the absorbance by other elements present in the sample can be estimated from a series of measurements made on solutions varying in concentrations of H_2SO_4, HCl, HNO_3, and Fe^{2+} (as sulphate). The relative effects of these materials are illustrated in the curves shown in Fig. 5.

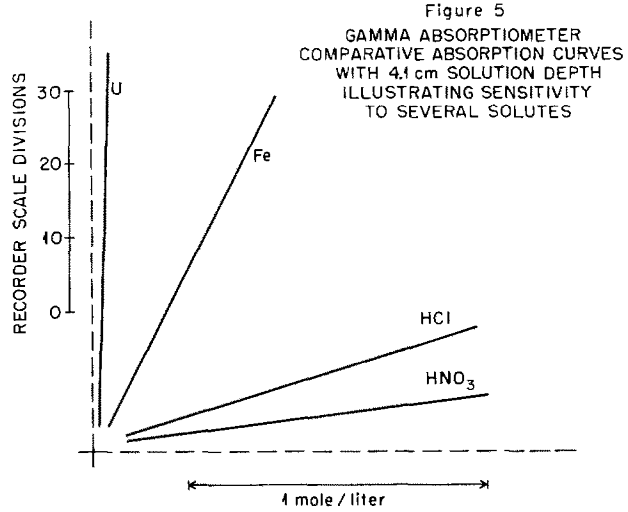
Figure 5
GAMMA ABSORPTIOMETER
COMPARATIVE ABSORPTION CURVES
WITH 4.1 cm SOLUTION DEPTH
ILLUSTRATING SENSITIVITY
TO SEVERAL SOLUTES

From these data it can be shown that an uncertainty of 0.1 mole/litre of HNO_3 would cause an error of 0.06 g U/litre and that Fe, as a typical light element, would contribute an error of 0.2 g U/litre per g Fe/litre.

The solutions for which this instrument is intended will contain Pu in concentrations from 25 to 50 g/litre in various HNO_3 concentrations. In order to analyse such samples, it is planned to analyse two series of standard solutions of different HNO_3 concentrations. The sample concentrations can then be determined by interpolation between the two curves obtained by plotting recorder scale readings vs concentration of Pu.

The reproducibility to be expected from this instrument was obtained from a series of measurements on the absorbance of a 33 g U/litre sample. The standard deviation of 16 observations was 0.55% of recorder scale on the most sensitive range. This corresponds to 0.035 g U/litre in a 4.1-cm absorption cell.

APPENDIX

Brown recorder modifications

1. Remove the two wires leading from the "Run-Standardize" switch to "TC +" and to "G" and replace them with No. 22 shielded Teflon insulated wire. Ground the shields to the recorder chassis.
2. Reverse the polarity of the recorder as follows:
   a. Reverse polarity of standard cell and working cell.
   b. Reverse polarity of chopper coil if required to get negative feedback; wait until the modified amplifier is installed before determining this point.

3. Remove the damping resistor from the terminal board.
4. Remove the input transformer and wire the high impedance circuit as shown.
5. Replace 12AX7 with 5751. Re-label the tube location chart accordingly.
6. Isolate pins 1 and 6 of the Brown converter, by grounded copper shield.
7. Ground the upper, painted shell of the converter to pin 2.
8. Add the scope test jack.
9. Ground all tube socket pin shields.
10. Replace tube shields with Elco low temperature shields.

Acknowledgement—The authors wish to express their appreciation to Dr. D. J. Fisher and Mr. H. C. Jones of the ORNL Analytical Chemistry Division for their advice and assistance.

Zusammenfassung—Die Konstruktion eines einfachen Gammastrahlabsorptiometers unter Verwendung einer kleinen Menge ^{241}Am als Strahlenquelle wird beschrieben. Das Instrument dient zur Bestimmung von Uran oder Plutonium in verhältnismässig reinen Lösungen. Die angezeigte Spannung am Instrument ist der Absorption direkt proportional.

Résumé—On décrit la construction d'un compteur de rayons gamma utilisant une petite source de ^{241}Am, pour le dosage de l'uranium ou du plutonium en solutions relativement pures. L'instrument enregistre une tension directement proportionnelle à l'absorption.

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NUCLEATION IN ANALYTICAL CHEMISTRY—II*

NUCLEATION AND PRECIPITATION OF SILVER CHLORIDE FROM HOMOGENEOUS SOLUTION

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Summary—The nucleation and precipitation of silver chloride from homogeneous solution have been examined. Critical supersaturations of silver chloride were determined; however, they were observed to be qualitatively different from the critical supersaturation of classical nucleation theory, and were interpreted as being dependent on the rates of both nucleation and crystal growth. The precipitation rate is not constant throughout a precipitation from homogeneous solution, but varies considerably during the early portion of the precipitation. Both this early variation in precipitation rate and the number of particles and their size distribution can be controlled to some extent by varying the concentrations of the reactants.

INTRODUCTION

PRECIPITATION is one of the basic and one of the most widely applicable operations of analytical chemistry. Many studies of the precipitation process have shown how the character of a precipitate may be improved by appropriate modifications of the reaction conditions. The purity and crystallinity of the particles are ordinarily improved by decreasing the rate of particle growth. The conditions leading to control of the number and size of the particles, and of their size distribution, are less well known. These properties of the precipitate are determined by the nucleation process, the nature and analytical significance of which have been discussed in a recent review[1]. The present paper describes a study of the nucleation and precipitation of silver chloride from homogeneous solution.

EXPERIMENTAL

Reagents

The chloride-generating reagent selected for the precipitation was allyl chloride, because this compound is easily purified by distillation and it hydrolyzes at a convenient rate in dilute (less than $0.01M$) aqueous solution. Because the suitability of allyl chloride for precipitation depends upon

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hydrolysis, the kinetics of its hydrolysis were examined. The hydrolysis was followed conductimetrically up to only about 0.1 % reaction, because the later stages of the hydrolysis were not of significance in this work. The conductivity versus time line, at 25°, was found to be

$$10^6 L = (0.203 \pm 0.002)ct,$$

where

L = specific conductance of the solution,
c = initial concentration of allyl chloride in grams/litre,
t = time in minutes.

The hydrolysis rate was not affected by the presence of dissolved potassium chloride or silver nitrate, nor of freshly precipitated silver chloride.

Conductivity water was prepared by passing single-distilled water through an ion-exchange column containing a mixture of the analytical grade Amberlite resins IRA-400(OH) and IR-120(H). Although this treatment yielded a product with a specific conductivity of around 2×10^{-7} reciprocal ohms, it appears that there was some contamination of the water by the resin, as will be discussed later.

Silver nitrate stock solutions were prepared from the Mallinckrodt "Analytical Reagent" grade salt which was used without further purification. These solutions were kept in amber bottles and stored in the dark.

Equipment

The hydrolysis and precipitation reactions were followed conductimetrically. The Wheatstone bridge gave resistance readings reproducible to about 0.1 %. A water bath maintained the temperature of the system constant to within ±0.02°.

Although the conductivity cell, shown in Fig. 1, was designed to permit simultaneous conductimetric and turbidimetric observation of the reaction, conductance measurements only were made in the present research. The cell constant was 0.01400 at 25°, and was taken to be constant over the range from 15° to 35°, because the variation of the cell constant with temperature was calculated to be less than 0.02 % per degree. The bright platinum electrodes were 4-cm discs, separated by about 2 mm. Teflon stopcocks were used so as to avoid contamination by stopcock grease. The lower end of the

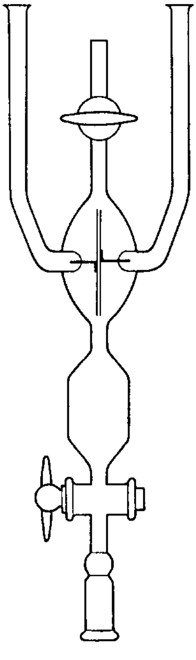

FIG. 1.—Conductivity cell

cell was fitted with a standard taper joint, into which a Teflon filter-support could be set. The arrangement permitted filtration of the reaction mixture immediately before it entered the cell.

Filtration was employed to remove foreign particles which might act as precipitation nuclei. Millipore filters (Millipore Filter Corp., Watertown, Mass.) were used for this purpose. The type HA filters used in this study have a pore size of $0.45\ \mu \pm 0.02\ \mu$.

Procedure

A two-litre resin reaction jar was thoroughly cleaned, placed in the constant temperature bath, swept out with purified nitrogen, and filled with two litres of conductivity water, collected under nitrogen. A suitable amount of stock solution of silver nitrate was added, so as to make the silver concentration about 2.5 to $10 \times 10^{-5}M$, the exact concentration subsequently being determined conductimetrically. An appropriate amount of allyl chloride (about 0.1 to 1 millilitre) was distilled into a hypodermic syringe, and then added to the silver solution with vigorous stirring; a timer was started when the allyl chloride was added. The Millipore filter, in its Teflon support, was connected between the conductivity cell and the mixing jar, and nitrogen pressure applied to the jar to force the reaction mixture through the filter into the cell. After approximately 100 millilitres of solution were rinsed through the cell it was closed off. The conductivity of the mixture was measured at intervals, and the results plotted as conductivity versus time. Upon conclusion of an experiment the cell was rigorously cleaned by consectuive rinsing with concentrated ammonium hydroxide, concentrated nitric acid, alcoholic sodium hydroxide, and then about fifteen times with conductivity water filtered through sintered glass directly into the cell.

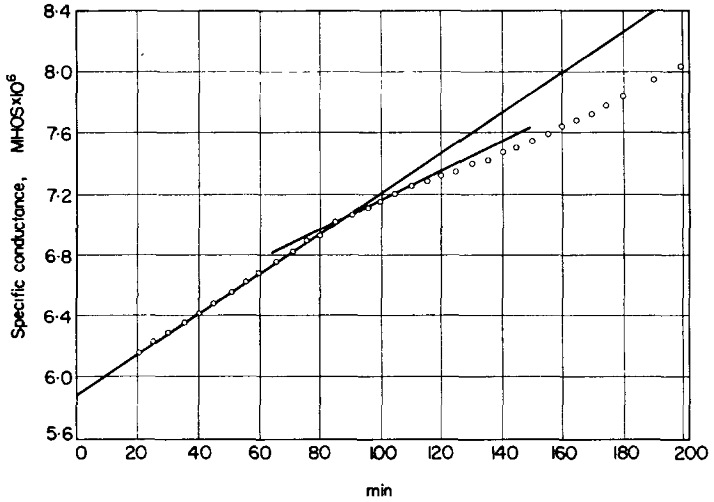

FIG. 2.—Specific conductance of a reacting mixture containing silver nitrate (5.24×10^{-5} M) and allyl chloride (0.28 gram/litre) at 15°.

Kinetic studies had shown that where only hydrolysis of allyl chloride is taking place, the conductivity-time curve was a straight line. This was the case early in an experiment, before nucleation and precipitation began. Precipitation was indicated by a deviation of the observed conductance away from the hydrolysis line, as shown in Fig. 2. The first deviation from the hydrolysis line was taken as the point of "critical supersaturation". Because of the formation of a small amount of the soluble, non-conducting AgCl complex, the conductance of the system at the point of critical supersaturation does not correspond to the concentration of the system. A correction was made for this effect, using the equilibrium constants of Jonte and Martin,[2] and the concentrations of silver and chloride at the point of critical supersaturation were then calculated from the equivalent conductances.[3] In the following discussion, concentrations are expressed either as the ion product, I.P. = $[Ag^+] \times [Cl^-]$, or as the supersaturation ratio, $S = (I.P./K_{sp})^{1/2}$. $[Ag^+]$ and $[Cl^-]$ here refer to the total concentrations, *i.e.* the concentrations of the ions plus the concentration of the complex.

RESULTS

Critical supersaturations of silver chloride

The critical supersaturation, $S_{crit.}$, of silver chloride was examined under various conditions. The first experiments, in which the reacting solution was not filtered, led to a value of $S_{crit.}$ of 2.04, at 25°. When the solution was filtered, using the procedure outlined previously, $S_{crit.}$ dropped to 1.74. This unexpected filtration effect was examined by carrying out the experiments shown in Table I.

TABLE I.—EFFECT OF WATER PURIFICATION AND FILTRATION ON CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE AT 25°

Water	Filtration	mean $S_{crit.}$ ± a.d.
distilled	none	1.44 ± 0.02
de-ionized	none	2.04 ± 0.05
de-ionized	Pyrex, grade M	1.87 ± 0.03
de-ionized	Millipore*	1.74 ± 0.02
distilled	Millipore	1.71 ± 0.04

* In two other experiments, about 500 ml of de-ionized water were passed through the filter before using it. This pre-treatment of the filter did not affect the value of $S_{crit.}$; had there been removable nucleating agents present in the filter, this pre-treatment would have separated at least some of them and thus raised the value of $S_{crit.}$.

TABLE II.—EFFECT OF IMPURITY (EOSIN) ON CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE AT 25°

Water	Filtration	Impurity*	mean $S_{crit.}$ ± a.d.
distilled	none	none	1.44 ± 0.02
distilled	none	25 μg/litre, added in mixing vessell	1.74 ± 0.02
distilled	none	100 μg/litre, added in mixing vessel	1.73 ± 0.03
de-ionized	Millipore	small indeterminate amount of dye added into conductivity cell after cell is filled with solution	1.96 ± 0.05
de-ionized	Millipore	100 μg/litre dye added into mixing vessel before filtration into cell	1.74 ± 0.09

* 0.1% solution of eosin in alcohol, filtered through Pyrex frit.

The results indicate that the de-ionizing column introduced some impurity which inhibited nucleation, or its detection, and which could be removed by passage through the Millipore filter. This possible explanation was further tested using eosin, which is known to be strongly adsorbed on silver chloride. The results of these experiments, which are given in Table II, show (*a*) that a readily adsorbed substance may raise the previously observed value of the critical supersaturation, and (*b*) that such a substance may be removed by passage through the Millipore filter, thus lending support to the proposed explanation of the filtration effect, *i.e.*, an impurity introduced by the resin.

Other soluble impurities were added to the reaction mixture in concentrations of around $10^{-5}M$, the same order of magnitude as the silver and chloride concentrations.

TABLE III.—EFFECT OF TEMPERATURE ON THE CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE

Temp., °C	$10^{10}K_{sp}$[4]	Number of runs	Avg. S	Standard deviation
15	0.700	13	1.51	0.04
25	1.77	14	1.73	0.05
35	4.20	13	1.85	0.08

TABLE IV.—CRITICAL SUPERSATURATION RATIO OF SILVER CHLORIDE AT 25°

$[Ag^+]$, mole/litre × 10^5	$[Cl^-]_{crit.}$, mole/litre × 10^5	$\frac{[Ag^+]}{[Cl^-]}$	$\frac{d[Ag^+][Cl^-]}{dt}$ mole²/litre² minute × 10	$S_{crit.}$
8.14	0.718	11.3	0.436	1.81
3.99	1.43	2.8	0.553	1.79
8.39	0.668	12.5	0.910	1.78
5.26	1.06	5.0	0.769	1.77
5.85	0.936	6.3	0.593	1.76
5.76	0.938	6.2	0.758	1.75
6.74	0.805	8.4	0.900	1.75
8.32	0.653	13.1	0.837	1.73
8.73	0.602	14.5	1.023	1.72
7.66	0.680	11.3	1.820	1.71
5.36	0.928	5.8	0.594	1.68
6.37	0.772	8.3	0.433	1.67
3.97	1.24	3.2	0.359	1.67
4.77	1.01	4.7	0.750	1.65

The presence of ethanol, allyl alcohol, barium nitrate, dextrose, and carbon tetrachloride at these concentrations had no apparent effect upon the critical supersaturation ratio.

The value of the critical supersaturation ratio was then determined at 15°, 25°, and 35°, using de-ionised water, Millipore filtration, and without added impurities. The results are presented in Table III. The temperature effect was in the opposite direction from that observed by LaMer and Dinegar[5] with barium sulphate. The complete data for the runs at 25° are given in Table IV. The observed critical supersaturation ratio appears independent of the $[Ag^+]/[Cl^-]$ ratio; this does not agree with the findings of Davies and Jones.[6] The rate of increase of silver chloride ion product, $d[Ag^+][Cl^-]/dt$, also appears to be without influence upon the critical supersaturation.

Precipitation of silver chloride from homogeneous solution

The technique of precipitation from homogeneous solution has been employed both as an analytical tool and for co-precipitation studies,[7] because it permits precipitation to occur slowly, under controlled conditions. That is, the precipitation rate is kept small throughout most of the course of the reaction. The present results can be treated to elucidate the characteristics of precipitation from homogeneous solution.

The concentrations of silver and chloride in solution at any time can be obtained from a plot of conductance versus time (*cf.* Fig. 2). The conductance of the entire system at any time, if everything were in solution, is obtained by extrapolation of the initial straight line portion of the plot, and from this one can calculate the total chloride in the system at any time. The difference between this extrapolated conductance and the observed conductance corresponds to the amount of silver chloride precipitated. Because the total amounts of silver and chloride in the system at any time are known, their solution concentrations can be easily calculated.

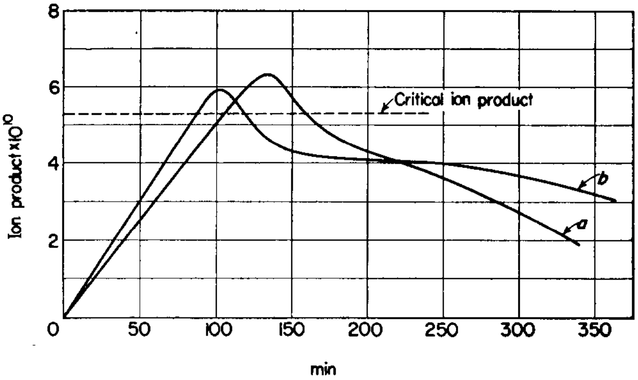

Fig. 3.—Ion product of silver chloride during a precipitation from homogeneous solution.

Fig. 3 represents the ion product, $[Ag^+][Cl^-]$, against time for two of the experiments. In run "*a*", the initial concentrations were: silver nitrate, $10.59 \times 10^{-5}M$, and allyl chloride, 0.10 grams/litre, while in run "*b*" they were: silver nitrate, $5.11 \times 10^{-5}M$, and allyl chloride, 0.25 grams/litre.

Fig. 4 shows a plot of the ion product against the amount of silver chloride precipitated. The ion product initially increased, because chloride ion was being generated and precipitation was not occurring. The curves continued to rise beyond the observed critical ion product. However, as the surface area available for precipitation increased, the ion products decreased. The decrease, rapid at first, became slower as the supersaturation of the system was relieved.

The amount of silver chloride precipitated at any time was known from the calculations for Fig. 3, and thus the rate of precipitation could be computed. Fig. 5 shows the precipitation rates as a function of the amount of silver precipitated. In both cases, the rate rose sharply to a maximum, then decreased, and after the initial supersaturation was relieved somewhat, remained quite constant over the extent of the reaction studied, which was 14% for run "*a*" and 48% for run "*b*". The particular value of precipitation from homogeneous solution as a tool for co-precipitation

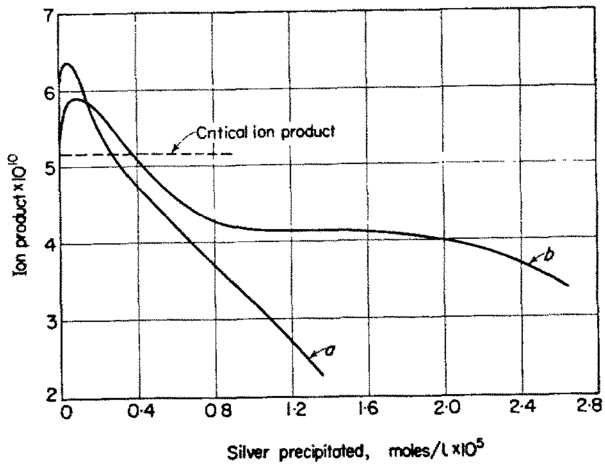

FIG. 4.—Ion product of silver chloride as a function of amount of silver precipitated from homogeneous solution.

studies is dramatically demonstrated by this flat portion of the curve, where precipitation took place at a constant rate.

DISCUSSION

Classical nucleation theory predicts for the formation of relatively large nuclei that the nucleation rate is critically dependent upon concentration; that is, below some well-defined concentration nucleation proceeds so slowly as to be undetectable, while above that concentration the rate becomes so rapid as to be unmeasurable. The critical concentrations of silver chloride observed in the present work are not critical in the sense of the classical theory. This can be seen from Fig. 3, which shows that the ion

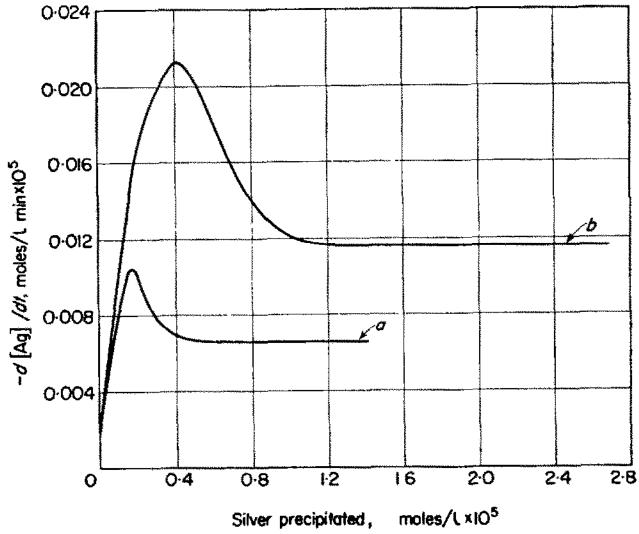

FIG. 5.—Rate of precipitation of silver chloride as a function of amount of silver precipitated from homogeneous solution.

products of the precipitating solutions rise above the observed critical value and remain above it for relatively long periods of time. If the observed critical concentration were truly critical, then concentrations above the critical could exist for only very short times, because the nucleation rate would become extremely large. The relatively long life of the *super-critical* concentrations indicates that nucleation in this system is not drastically concentration dependent. The ability of an impurity (eosin) to increase the value of the critical supersaturation also shows that $S_{crit.}$ cannot be a function of nucleation rate alone. If the nucleation rate were the sole factor determining the value of $S_{crit.}$, then it would not be possible for any additive to raise $S_{crit.}$ above that value required for self-nucleation. The critical supersaturation which is observed must always be that which corresponds to the nucleation process which occurs most readily. Additives which promote nucleation should produce a lower critical supersaturation, while additives which might inhibit nucleation should have no effect on $S_{crit.}$, because the more rapid nucleation process (*i.e.* the eosin-free nucleus) would still be observed before the slower process (the eosin-containing nucleus). Because the presence of eosin leads to a higher observed critical concentration, and because the increase cannot be attributed to nucleation, processes other than nucleation must be significant in fixing the value of the observed critical concentration. Eosin is known to inhibit the growth of silver chloride particles;[8] the effect of eosin in raising the critical concentration can be explained on this basis.

The results of this research also have some significance for co-precipitation studies, as carried out using the technique of precipitation from homogeneous solution. Such studies have shown that when two compounds precipitate together, their distribution between the solid phase and the solution phase may often be described by the following equation:[7]

$$\ln \frac{(\text{A})\ \text{initial}}{(\text{A})\ \text{final}} = \lambda \ln \frac{(\text{B})\ \text{initial}}{(\text{B})\ \text{final}},$$

where the brackets refer to solution concentrations and λ is the distribution coefficient. While λ is ordinarily constant for a fixed set of experimental conditions, Hermann[9] and Feibush, Rowley, and Gordon[10] have presented evidence indicating that λ depends upon the rate of precipitation, approaching unity as the rate increases.

The rate of precipitation of silver chloride from homogeneous solution is shown in Fig. 5. Throughout most of the precipitation, the rate was quite constant showing, however, considerable variation during the early portion of the precipitation. In studying the co-precipitation of manganese on basic stannic sulphate, Gordon, Teicher, and Burtt[11] found that the amount of manganese co-precipitated is large during the initial stages of precipitation, and that further co-precipitation is negligible until the tin has been almost completely removed from solution. Assuming that precipitation of basic stannic sulphate is analogous to that of silver chloride, then the large initial co-precipitation can be attributed to the earlier variable and more rapid precipitation rate.

Unless seeded solutions are used, the first portion of a precipitation process must occur at a greater rate than the subsequent portion, for the supersaturation must be high in order to form sufficient nuclei. The early precipitation rate may be controlled by suitable adjustment of the concentrations in the reacting mixture. Because run "*a*" of Fig. 5 initially contained about twice as much silver as run "*b*", the ion product of "*a*" was much more sensitive to chloride ion concentration, so that precipitation of a small amount of silver decreased the ion product of "*a*" much more than that of "*b*", with the precipitation rate decreasing accordingly. However, the influx of chloride ion from the allyl chloride also had a greater effect on "*a*" than "*b*", tending to raise the ion product more. For silver chloride, therefore, the initial variation of precipitation rate is best controlled by working with more concentrated silver and more dilute allyl chloride. In general, the extent of the early rapid precipitation and its attendant high co-precipitation, will depend upon the initial concentration of the ion to be precipitated, the rate of generation of precipitant, the concentration at which the nucleation rate becomes appreciable, and the kinetics of growth of the precipitate.

By proper adjustment of the concentrations in the reacting solution, it should also be possible to influence the size and the size distribution of the particles of precipitate. Fig. 3 shows that the ion product for run "*a*" was above that of "*b*" for about two hours. Because the nucleation rate depends upon the concentration raised to some low power, many more particles were formed in "*a*" than in "*b*". This can be shown from Davies and Jones[12] expression for the precipitation rate of silver chloride:

$$\frac{-d\,\mathrm{AgCl}}{dt} = kS\Delta^2,$$

where

S = available surface area,

Δ = amount of silver chloride to be precipitated, defined by $[\mathrm{Ag}^+ - \Delta]\,[\mathrm{Cl}^- - \Delta] = K_{\mathrm{sp}}$.

Three hours after the start of the runs, the calculated value of kS for run "*a*" was about three times that for run "*b*", although only about one-eighth as much silver chloride had been precipitated. Therefore, many more particles were present in "*a*" than in "*b*".

At the end of the precipitations, the particles of "*a*" should be more uniform in size than those of "*b*" as is suggested by Fig. 3. After 220 minutes, the ion product of "*a*" dropped below "*b*", meaning that new particles were being formed in "*b*" after nucleation had essentially stopped in "*a*"; that is, nucleation occurred over a longer period of time in "*b*". This distinction is emphasised in Fig. 4, which shows that the ion product of "*b*" was higher than "*a*" at all times after 0.12×10^{-5} moles/litre of silver chloride had precipitated. Therefore, run "*a*" nucleated more rapidly than run "*b*" over about 1% of the total precipitation of "*a*", while run "*b*" nucleated more rapidly over about 98% of its total precipitation.

It appears, therefore, that although many more particles formed in run "*a*", they formed within a shorter time span and their growth rate was smaller, so that the final particles should have been more uniform in size. This aspect of nucleation should be studied by other methods in order to draw more definite and quantitative conclusions.

The results of this research have shown that the rate of nucleation is not drastically dependent upon concentration. This suggests that the process of nucleation may be studied by a kinetic method, such as that of Christiansen and Neilsen[13]. During the course of the present research a kinetic method of determining the size of the nucleus was developed. This method, reported in the following paper[14] indicates a small nucleus consisting of a few ion pairs.

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Zusammenfassung—Keimbildung und Fällung von Silberchlorid aus "homogener Lösung" wurden untersucht. Die kritischen Übersättigungen für Silberchlorid wurden bestimmt. Es wurde gefunden, dass die kritischen Übersättigungen qualitativ von denen nach der klassischen Keimbildungstheorie differieren; dies wurde durch Annahme einer Abhängigkeit von sowohl Keimbildung als auch Wachstum interpretiert. Die Fällungsgeschwindigkeit ist während der Fällung aus homogener Lösung nicht konstant, sondern verändert sich sehr stark in der ersten Phase der Fällung. Sowohl die Änderung der Fällungsgeschwindigkeit am Beginne als auch die Teilchengrösse und die Grössenverteilung der Teilchen können bis zu einem gewissen Grad durch Variieren der Konzentration der Reaktanten beeinflusst werden.

Résumé—Les auteurs ont étudié la formation de germes et la précipitation du chlorure d'argent à partir de solutions homogènes. Ils ont déterminé les sursaturations critiques du chlorure d'argent; cependant, ils ont observé que ces sursaturations étaient différentes qualitativement de la sursaturation critique de la théorie classique de formation de germes et ils les ont interprétées comme dépendant à la fois des vitesses de formation des germes et de croissance des cristaux. La vitesse de précipitation n'est pas constante pendant toute une précipitation à partir d'une solution homogène, mais elle varie considérablement durant la première phase de la précipitation, on peut contrôler jusqu'à un certain point à la fois cette variation initiale de la vitesse de précipitation et le nombre de particules ainsi que leur distribution selon leurs dimensions, en faisant varier les concentrations des corps réagissants.

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NUCLEATION IN ANALYTICAL CHEMISTRY—III*

THE PRECIPITATION NUCLEUS OF SILVER CHLORIDE

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Summary—Precipitation from homogeneous solution has been employed to study the size of the nucleus of silver chloride. The kinetics of particle formation indicate that this nucleus consists of about five ions. This result supports the findings of the Christiansen-Nielsen nucleation theory.

INTRODUCTION

KINETIC methods for studying the nucleation of slightly soluble salts precipitating from solution have been developed by Christiansen and Nielsen,[1] O'Rourke and Johnson,[2] and Duke and Brown.[3] These workers have found that such nuclei are quite small, consisting of less than ten ions. The methods by which these determinations were made have been criticized on the following points: (*a*) the use of methods of precipitation involving direct mixing of the solutions, which might permit nuclei to form during the mixing process rather than after homogenisation of the solution,[4] (*b*) the failure to remove foreign particles from the reacting solution, thus permitting precipitation to take place on such particles rather than on nuclei formed within the solution,[5] and (*c*), the assumption, in the case of Christiansen and Nielsen, that precipitation is first detected when a constant fraction of the solute has precipitated, whereas it seems more likely that their technique would detect a constant absolute amount of precipitate.[2] The present paper describes a determination of the nucleus size of silver chloride, using a kinetic method which avoids the criticisms of the above methods, (except possibly *b*), but which supports their results.

In a study of the precipitation of silver chloride from homogeneous solution,[6] it was observed that the ion product, $[Ag^+][Cl^-]$, initially rose because chloride ion was being generated and nothing was being removed from the solution. Precipitation was always detected at a fairly well defined "critical" ion product. The observed ion product rose above this value of 5.3×10^{-10} and remained above it for an appreciable length of time. If the observed "critical" concentration were really critical in the sense corresponding to classical nucleation theory, then concentrations above the critical could exist for only a very short time, because the nucleation rate would become extremely great. The fact that super-critical concentrations were obtained for

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extended times indicates that nucleation in this system is not drastically concentration dependent, and that kinetic methods may be used to study the nucleus.

Nucleation is generally considered to take place via a step-wise mechanism, as follows:

$$\begin{gathered} Ag^+ + Cl^- = (AgCl) \\ (AgCl) + Ag^+ = (Ag_2Cl)^+ \\ \vdots \\ (Ag_iCl_{j-1})^{(1-j+1)} + Cl^- \rightarrow (Ag_iCl_j)^{(i-j)} \end{gathered}$$

All steps leading to (Ag_iCl_{j-i}) are steady-state equilibria. (Ag_iCl_{j-i}) is the nucleus, here defined as the smallest cluster for which growth is much more likely to occur than is dissociation.

If all nuclei (or constant fraction of them) grow to observable size, then

$$\mathrm{d}N/\mathrm{d}t = k[Ag^+]^i[Cl^-]^j, \qquad (1)$$

where N is the number of particles, t is time, and k is a constant. Assuming for simplicity that $i = j$,

$$\mathrm{d}N/\mathrm{d}t = k\,(\mathrm{I.P.})^n,$$

where I.P. is the ion product, $[Ag^+][Cl^-]$, and n is $\frac{i+j}{2}$. Then

$$N = k \int (\mathrm{I.P.})^n \,\mathrm{d}t.$$

This equation then can be used to determine n, which furnishes an indication of the nucleus size.

In order to apply this equation to the case where chloride ion is being generated continuously, it is necessary to make the additional assumption that at all times the concentrations of the various sub-nucleus clusters are near their steady state concentrations, i.e. the steady state in the formation of these clusters must be attained rapidly with respect to the rate of change of the solution concentration.

EXPERIMENTAL

Silver chloride was precipitated from homogeneous solution, with allyl chloride as the chloride generating reagent. The course of precipitation was followed conductimetrically, the reacting solution having been filtered through Millipore filters (pore size 0.45 $\mu \pm 0.02\ \mu$) immediately before being placed in the conductivity cell. The materials, apparatus, and procedures are discussed in detail elsewhere.[6]

Seven precipitations were carried out at 25°. Aliquots of each precipitate suspension were filtered through Millipore filters (pore size 100 m$\mu \pm 8$ mμ) at a time approximately five hours after the ion product had reached its maximum value. The number of particles retained on the filter was counted microscopically, using dark field illumination and 100×. This technique did not permit detection of extremely small particles formed late in the precipitation. However, errors from this source were felt to be negligible, because in any one experiment the majority of the particles were formed when the supersaturation was near its maximum value. Therefore, the number of particles observed on a given area of the filter was taken to be proportional to N, the total number of silver chloride particles.

RESULTS AND DISCUSSION

Because the nucleation rate is proportional to the concentration raised to a power, the number of nuclei formed at relatively low supersaturations is negligible compared to the number formed at high supersaturations. Therefore, essentially all particles are produced within a fairly well defined concentration internal. The equation

$\mathrm{d}N/\mathrm{d}t = k(\mathrm{I.P.})^n$ may therefore be integrated graphically over a closed concentration interval. The limits for the integration were chosen rather arbitrarily. It is quite likely that nucleation took place, perhaps to a significant extent, below the observed critical ion product. If the nucleation rate is dependent on the ion product to some moderately high power, then the exact location of the limits of integration is not important as long as the limits are not set too high. The integration was carried out above the ion product of 3×10^{-10}; subsequent calculations have shown that the results were unchanged by carrying out the integration above an ion product of 4×10^{-10}.

To determine the number of ions in the nucleus, the area under a plot of the ion product, raised to some power x against time was divided by N to give $1/k$. For each value of x the values of $1/k$ were plotted against the corresponding areas under the curve, and also against N. The best straight lines were fitted to the points, using the method of least squares. When the absolute values of the slopes are a minimum, k is a constant and x equals n.

Table I presents the data used in the determination of the nucleus size. No units

TABLE I.—KINETIC SIZE DETERMINATION OF THE SILVER CHLORIDE PRECIPITATION NUCLEUS

10^5 Ag, *mole/litre*	Allyl chloride *g/litre*	No. of particles, N	$\frac{\int \mathrm{IP}^1\,\mathrm{d}t}{N}$*	$\frac{\int \mathrm{IP}^2\,\mathrm{d}t}{N}$*	$\frac{\int \mathrm{IP}^3\,\mathrm{d}t}{N}$*	$\frac{\int \mathrm{IP}^4\,\mathrm{d}t}{N}$*	$\frac{\int \mathrm{IP}^5\,\mathrm{d}t}{N}$*
4.77	0.32	116.1	0.66	0.80	0.96	1.22	1.53
8.39	0.20	101.7	0.93	0.89	0.87	0.81	0.72
5.26	0.29	85.0	0.76	0.90	0.92	1.01	1.13
6.93	0.16	74.8	1.34	1.28	1.28	1.23	1.13
7.29	0.20	66.5	1.27	1.15	1.07	0.92	0.84
5.36	0.22	52.7	0.93	0.86	0.80	0.67	0.56
8.71	0.14	33.6	1.14	1.11	1.10	1.16	1.11
Slope of plot of $\frac{\int \mathrm{IP}^x\,\mathrm{d}t}{N}$ vs. $\int \mathrm{IP}^x\,\mathrm{d}t$			+0.0027	+0.00041	+0.0011	+0.0031	+0.0052
Slope of plot of $\frac{\int \mathrm{IP}^x\,\mathrm{d}t}{N}$ vs. N			−0.0052	−0.0031	−0.00068	+0.00099	+0.0046

* Expressed in arbitrary units such that the mean value of $\frac{\int \mathrm{IP}^x\,\mathrm{d}t}{N} = 1.00$

are given for $\int (\mathrm{I.P.})^x\,\mathrm{d}t$ and N, because these were determined only relatively. The results indicate that n is 3, corresponding to a nucleus of 5 ions. Too much precision cannot be attributed to the number 5, for the present method would not seem capable of determining the nucleus size exactly. Errors in determining the ion product as a function of time are increased appreciably when the ion product is raised to a power. Also, the precision in determining N is rather poor, being about 15%. Nevertheless, this method does support the results obtained using other kinetic approaches, namely, that nuclei for the precipitation of salts from solution are quite small.

Acknowledgement—The authors wish to acknowledge the partial support of the Atomic Energy Commission under Contract AT(11-1)-582.

Zusammenfassung—Fällung aus "homogener Lösung" wurde angewendet um die Grösse der Keime von Silberchlorid zu ermitteln. Die Kinetik der Teilchenbildung lässt schliessen, dass die Keime aus etwa fünf Ionen bestehen. Dieses Ergebnis stützt die Resultate der Keimbildungstheorie nach Christiansen-Nielsen.

Résumé—Les auteurs ont utilisé la précipitation à partir de solution homogène pour étudier la grosseur des germes de chlorure d'argent. La cinétique de la formation des particules indique que le germe est constitué d'environ cinq ions. Ce résultat est en accord avec les conclusions de la théorie de formation des germes de Christiansen-Nielsen.

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LUMINESCENCE SPECTRA FROM HIGH-FREQUENCY EXCITATION—I

THE SPECTRA OF SOME INORGANIC GASES

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Summary—A high-frequency generator is described which is capable of exciting "Tesla-type" luminescence in inorganic and organic gases and vapours at low pressures. New apparatus and a new method of examining the spectra are described. The results of investigations on air, oxygen, carbon dioxide, sulphur dioxide, nitrogen and argon are presented and discussed.

INTRODUCTION

A HIGH-VOLTAGE discharge in an organic vapour normally decomposes the compound and excites the spectra of carbon and carbon oxides only. Wiedemann and Schmidt[1] were able to produce luminescence, which proved to have continuous emission, in ten particularly stable organic compounds, by passing the electrical discharge from an induction coil through the vapour of the compounds at low pressures. Subsequently Kauffmann[2] produced luminescence in the vapours of a number of carbon compounds, even at ordinary pressures, by applying a high-frequency (Tesla) discharge. He made some attempt, not very successful since it was more or less qualitative, to relate colour of the discharge and constitution of the compound.

In 1923 Stewart and his co-workers[3] published the first results of a series of investigations of the spectra produced by a Tesla discharge in organic vapours, examining the visible and near ultra-violet regions. They examined a fairly complete range of types of organic compound,[4] and to distinguish these spectra from fluorescence spectra and absorption spectra, they coined the name "Tesla-luminescence spectra."

The Tesla discharge used by Stewart and his co-workers was obtained from apparatus of some complexity and massive dimensions. Their first apparatus, for example, consisted of an oil-insulated Tesla transformer having forty coils on the primary and 460 coils on the secondary, and a Leyden jar with a capacity of about 1 litre, in conjunction with a choke-coil off a quarter-kilowatt high-tension transformer. A more powerful apparatus built subsequently contained 330 coils in the secondary and 30 coils in the variable primary of the air insulated high-frequency generator, and four Leyden jars each of about 10-litre capacity; an 18-inch spark coil was employed as source. The lack of detailed information in the literature about their sources, however, makes it impossible to hazard more than a guess about the characteristics of the high-frequency current used by them.

Stewart and his co-workers recorded their spectra photographically using a Hilger Medium Quartz Spectrograph, with no method other than the eye to determine intensities. They found that certain types of compound gave well-defined band spectra, and classified these spectra into the following categories:

1. *Benzene region* spectra, in the range 2500–3150 Å, produced by a phenyl nucleus;

2. *Carbonyl region* spectra in the range 3400–4850 Å, produced by aliphatic aldehydes and ketones;

3. *Blue Band region* spectra in the range 3850–5000 Å, produced by aromatic aldehydes and ketones;

4. *Green Glow region* spectra in the range 4550 Å upwards, produced by a benzene ring substituted by two saturated hydrocarbon radicles or a second non-benzenoid ring;

5. *Condensed Nuclei region* spectra in the range 2900–4900 Å, produced by aromatic condensed ring systems.

They concluded that only compounds containing a benzenoid ring or a carbonyl group were capable of emitting Tesla-luminescence spectra; and Stewart was of the opinion[5] that the diatomic permanent gases, for example, under Tesla excitation, showed only the ordinary spectra which would be produced by high-voltage discharge. Indeed, the original apparatus was used[6] to produce an intense hydrogen continuum in the ultra-violet for the examination of absorption spectra of inorganic crystals, with the advantage that the discharge tube required no internal electrodes and little or no external cooling.

Stewart and his co-workers attempted to calculate relationships between the frequencies of the band heads of the various spectra, and to relate these to structure; but their measurements were too imprecise, with the apparatus then available, to permit of much success. They also recognised the possibility of applying the spectra for analytical purposes, but made no attempt to follow up this line of investigation. A few years ago attention was again drawn[7] to the possibility of applying the spectra analytically, but no work along these lines can be traced in the literature before the present investigations.

In the belief that with modern instrumentation, as applied both to the excitation of the high-frequency discharge and to the recording and measurement of the spectra it should be possible to obtain

1. more precise measurement on which to base an examination of the fundamental nature of the spectra,
2. precise measurements for quantitive analytical purposes as well as for simple identification, and
3. excitation of a greater range of compound types than was obtained by the earlier workers,

we have initiated a series of investigations, both of inorganic and organic compounds, designed to cover these points.

This paper presents the first results obtained in these investigations, and is confined to simple inorganic gases since these have proved more amenable to excitation, and present fewer problems in the recording and measurement of the spectra. Further papers will extend the field to other inorganic compounds and to organic compounds.

EXPERIMENTAL

Apparatus

In developing new apparatus for the production and examination of luminescence spectra excited by high frequency, three separate parts required consideration:

1. The high-frequency or Tesla generator.
2. The sample tube.
3. The instruments for the detection and examination of the spectra.

FIG. 1.

1. *The high-frequency generator:* (Fig. 1): The earlier publications provided little help in the construction of a new high-frequency generator. In none of the papers of Stewart and his co-workers was there to be found a statement of the voltage and frequency attainable, or used in obtaining the various spectra; and none of the contemporaries of these workers could recollect if these values were ever known. From a study of the information available it was deduced that a frequency of some 100 kc/s at, perhaps, 10 kV might possibly have been obtained. Using these figures as a guide the apparatus shown in Fig. 1 was developed. This consists of a simple radio-frequency transformer in a self-oscillating circuit at approximately 200 kc/s with an 807 valve. This generator produces a sinusoidal alternating current in the range 5–15 kV.

Two other electrical arrangements gave inferior results to the above circuit: (*i*) variable direct current, 0–15 kV. (*ii*) a pulsed radio-frequency oscillator. The latter was built using an 807 valve and a television line output-transformer as a self-excited oscillator, producing pulses up to 10 kV, approximately 1 μsec wide, in bursts spaced at about 0·1 msec.

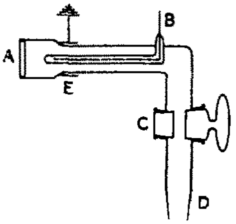

FIG. 2.

2. *The sample tube:* The sample tube in which the vapour or gas was placed for excitation consisted initially of a glass tube 5 cm long and 1 cm in diameter (both dimensions being found by experiment) having at one end a quartz window of diameter 2 cm. Tubes with a body diameter greater than 1 cm did not glow so brightly, presumably because the earth electrode was too remote from the central electrode.

The other end of the sample tube was drawn out, provided with a vacuum tap, and with a ground-glass joint which allowed the tube to be attached to a vacuum train at a convenient point.

The central or inner electrode of the sample tube consisted of a glass-coated tungsten wire, and the external electrode was a piece of metallic foil wrapped round the outside of the tube. The sample tube is shown diagrammatically in Fig. 2.

Notes:

(1) The original sample tubes had straight central electrodes which caused a large portion of the discharge to enter the drawn-out part of the tube, resulting in decreased glow-intensity. The discharge remained opposite the quartz window in sample tubes fitted with the bent central electrode, as shown in Fig. 2.

(2) Some tubes were sealed off before removing them from the vacuum system, but this did not have any advantage. Those with taps fitted retained their low pressures for 3–4 hours, and were very satisfactory.

(3) The quartz window, approximately 1 mm thick, was fixed in position with black wax, and showed no tendency to come away because of heat from the discharge.

(4) The effect of the glass coating on the central electrode was to produce an even discharge without any tendency to sparking, as occurred with uncoated wire.

(5) A sample tube in operation, filled with glowing vapour, is shown in Fig. 3.

3. *Detection of Spectra:* To detect the spectra a Hilger "Uvispek" Spectrophotometer was used. The tube was placed in front of the flame photometer aperture of the spectrophotometer, and the instrument was set as for measurements at this position. The light passing through the spectrophotometer was then examined at different wavelengths in the usual way (see Proceedure below) and the intensities at the different wavelengths recorded on a Honeywell-Brown Pen Recorder.

Notes

(1) Since the intensity of the glow is usually low compared to a normal flame source, it was sometimes necessary to use slit widths of approximately 0·3 mm. If the glow was more intense, the slit was closed to 0·2 mm, thus improving the resolution.

(2) The instrument was set to a high sensitivity, which caused the recorder trace to become slightly erratic at times.

(3) The aperture was screened carefully from external light sources. In addition, it was necessary to wire the hydrogen lamp inside the spectrophotometer in such a way that it could be switched off when not required.

(4) Because of the small size of the high-frequency generator, it was a simple matter, after reducing the pressure in the sample-tube to the required value and admitting the gas or vapour, to arrange the generator and sample-tube in position before the spectrophotometer.

Procedure

A sample-tube was attached to a vacuum train evacuated by a two-stage Hg diffusion pump, backed by a rotary oil pump. The entire system was pumped out to a pressure of less than 10^{-3} mm Hg, as measured by a Pirani gauge, and remained at this pressure for at least half an hour

The filling gas (*i.e.* gas or vapour under examination) was allowed to sweep out the system which was then pumped out again to 10^{-3} mm Hg. The sample-tube was now isolated at 10^{-3} mm pressure and the rest of the system filled with the gas or vapour under examination. On opening the sample-tube to the system the gas or vapour flowed into it.

The pressure in the sample-tube was now reduced. The high-frequency generator was switched on and a note was made of colour changes which occurred at the different pressures. By this means the optimum pressure for the gas or vapour under examination was determined.

The sample-tube was now filled as before, the pressure was reduced to the desired level, and the glow was examined by passing the light through the spectrophotometer. For examination of a spectrum the spectrophotometer was set to "Flame Source" and the recorder was switched on. After allowing approximately 1 hour to warm up, the controls were set to a high sensitivity, keeping the recorder near zero. The slit was set to 0·3 or 0·2 mm, the wavelength drum at 10,000 Å and the generator and sample-tube set up in the recommended way. The generator was now switched on and the optimum glow was obtained by altering the condenser. The slit in the spectrophotometer was opened, the wave-length drum was slowly revolved and the intensity of the glow at each wavelength was recorded on the chart.

A general view of the vacuum train, high-frequency generator, rotary pump and Pirani gauge is shown in Fig. 4.

RESULTS

Air, carbon dioxide, oxygen, sulphur dioxide, nitrogen and argon, have been examined and give reproducible results.

1. *Air*

The spectrum is shown in Fig. 5(*a*). The most intense peak is at 4380 Å. No peaks were observed below 2800 Å or above 6000 Å. Fifteen peaks in all occur in this spectrum.

2. *Oxygen*

The spectrum is shown in Fig. 5(*b*). Nineteen major peaks were present. The spectrum is similar to that of air but is characterised by peaks occurring at 2190 Å and 2300 Å, which were never obtained with air.

3. *Carbon dioxide*

The spectrum, containing seven major peaks, is shown in Fig. 5(*c*). It is completely different from that of air and oxygen. Very slight traces of peaks occur at 5550 Å,

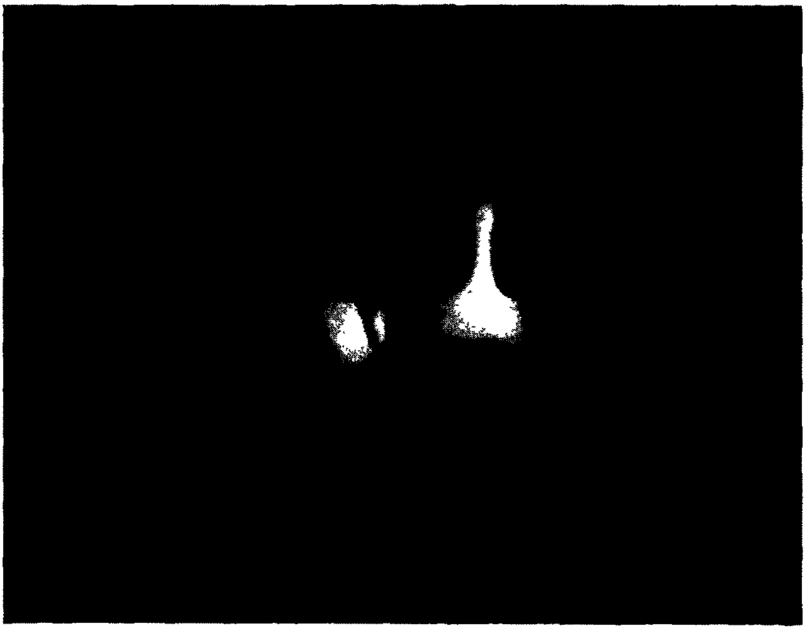

FIG. 3.

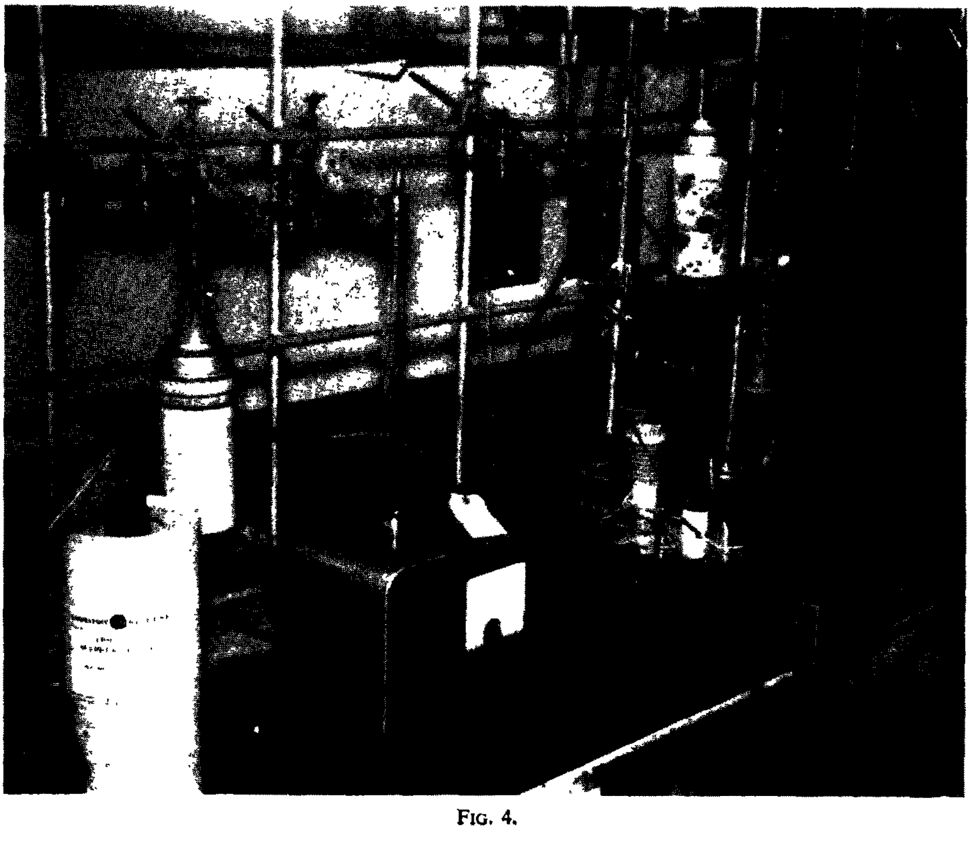

FIG. 4.

5170 Å, 4820 Å etc. These are taken to be due to traces of air or oxygen present in the gas.

4. *Sulphur dioxide*

The spectrum, containing fifteen major peaks, is shown in Fig. 6(*a*). It is similar to that of air or oxygen, but shows a marked difference in having a strong peak at 4270 Å, the strong oxygen peak at 4500 Å being absent.

5. *Nitrogen*

The spectrum, containing ten major peaks, is shown in Fig. 6(*b*). It resembles that of carbon dioxide but shows a difference in the region between 2580 Å and 3900 Å.

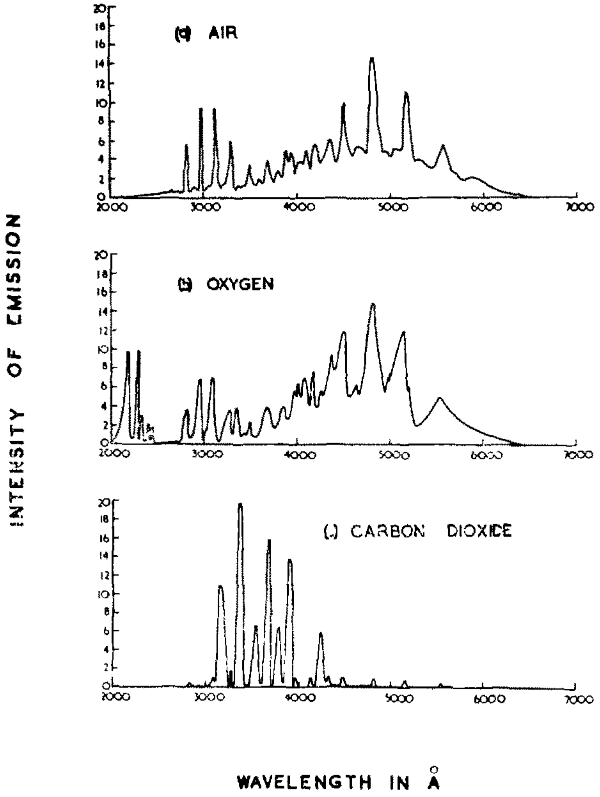

Fig. 5.

6. *Argon*

The spectrum, containing six peaks, is shown in Fig. 6(*c*). It does not resemble any of the others. One characteristic peak occurs at 3085 Å. This did not occur in any other gas examined in the present work.

Detailed results and observations on the above are recorded in the following table.

DISCUSSION

The outstanding characteristic of the results viewed generally is the division of the gases examined into three groups. In one group, comprising air, oxygen and sulphur dioxide, the overall spectra are similar, although distinguishing peaks occur. Nitrogen and carbon dioxide, while showing many common peaks are surprising; bands obtained in spectrographic work associated with high-frequency excitation are generally assumed to be nitrogen bands from air; but in the present work none of the nitrogen bands appear in the air spectrum.

It is believed that the answer to these differences lies in the pressures employed for excitation. The maximum glow of nitrogen was obtained with pressures in the range 1·5–4·0 mm. When operated at pressures below 1·5 mm the luminescence changed to bluish in colour and was then extinguished. For air the maximum glow range was 0·8–1·0 mm Hg, for oxygen, 0·2–2 mm and for sulphur dioxide about 0·1–0·2 mm Hg. In these circumstances, therefore, it would appear that almost all the luminescence spectrum of air is explained by assuming the light emission to result from the oxygen in the air, the nitrogen not showing any luminescence at this pressure.

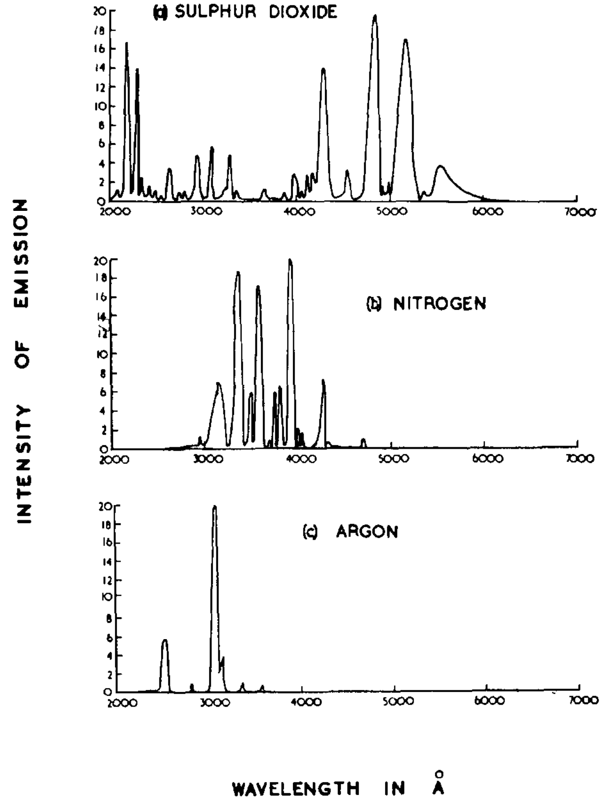

FIG. 6.

It has been pointed out already that sulphur dioxide shows a close similarity to oxygen and air. One portion of the spectrum is common to oxygen and sulphur dioxide but has not been detected in air. This is the portion containing peaks in the far ultra-violet, *viz.* at 2190, 2300, 2325 Å, etc. It may be suggested that the high-frequency excitation of the sulphur dioxide molecule causes dissociation so that the spectrum

TABLE I

Gas	Peaks recorded in spectrum Å	Pressure used, mm Hg	Colour of glow	Remarks
Air	5550 5170 4830 4500 4380 4200 4120 3960 3880 3700 3480 3300 3120 2970 2830	0·8 1·0	Blue-violet	Glow bright and very stable.
Oxygen	5550 5170 4820 4500 4370 4180 4110 4010 3910 3880 3685 3370 3290 3120 2970 2830 2325 2300 2190	0·2 2·0	Blue-pink	Stable glow, maximum at approximately 1 mm.
Carbon dioxide	4260 3910 3780 3580 3540 3370 3160	0·7 1·5	Blue	—
Sulphur dioxide	5550 5170 4840 4680	0·1 0·2	Blue-white	—

TABLE—I (*contd.*)

Gas	Peaks recorded in spectrum Å	Pressure used, mm Hg	Colour of glow	Remarks
	4270 3950 3290 3120 2970 2820 2480 2445 2325 2300 2190			
Nitrogen	4280 4040 4000 3915 3800 3760 3580 3530 3370 3160	1·5 4·0	Deep purple	Stable over a wide range of pressure.
Argon	3580 3370 3150 3085 2820 2535	0·3 3·0	Pink to green	Pinkish at low pressures; greenish at higher pressures.

obtained is largely that of an oxygen fragment and an SO fragment. In this connection it will be observed that of all the gases studied SO_2 shows luminescence at the lowest pressure, starting about 0·05 mm, but this begins to be quenched above 0·5 mm.

In relation to carbon dioxide and nitrogen it is interesting to record that Keller and Smith, in testing a Tesla-coil source[7] for spectrographic analysis, found that nitrogen bands were always present when they used a carbon dioxide atmosphere. They assumed that this may have been due to air not entirely eliminated from the system, a film of nitrogen adhering to the glass wall, or nitrogen impurity in the carbon dioxide. The present authors are strongly of the opinion that the last reason supplies the answer. That this method of excitation brings out distinctive nitrogen peaks in the carbon dioxide suggests considerable sensitivity.

There is independent support of the suggestion that, in the case of sulphur dioxide, the emission of light is due to radicals produced in the dissociation of the SO_2 molecule. Evidence of dissociation of a molecule during the production of luminescence excited by a high-frequency discharge has already been obtained by the authors in connection with work on organic vapours.[8] It is thought that the emission of the light by the other molecular gases examined may be due not so much to the dissociation of the molecule concerned but to the production of excited states.

The apparatus outlined above is not costly to construct and is capable of wide adaptability. It offers possibilities in the field of analysis and in investigations of inorganic and organic material which, up to the moment, appear to have been overlooked.

Acknowledgement—We would like to express our thanks to Mr. K. Quigg of the Electronics Division of this Department for his assistance and advice in connection with the construction of the Tesla-generator.

Zusammenfassung—Ein Hochfrequenzgenerator wird beschrieben, der imstande ist Teslaluminiscenz in anorganischen und organischen Gasen und Dämpfen, bei niederem Druck zu erregen. Ein neuer Apparat sowie eine neue Methode die Spectren zu untersuchen wird beschrieben. Die Ergebnisse der Untersuchungen an Luft, Sauerstoff, Kohlendioxyd, Schwefeldioxyd, Stickstoff und Argon sind dargelegt und werden diskutiert.

Résumé—Les auteurs décrivent un générateur à haute fréquence qui est capable d'exciter la luminescence "Tesla" dans les vapeurs et les gaz minéraux et organiques à faibles pressions. Ils décrivent un nouvel appareil et une nouvelle méthode d'examen des spectres. Ils présentent et discutent les résultats de recherches sur l'air, l'oxygène, l'anhydride carbonique, l'anhydride sulfureux, l'azote et l'argon.

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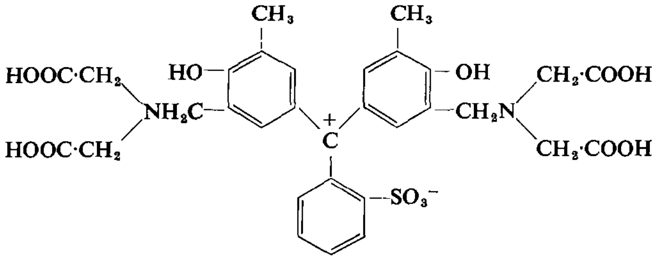
PRELIMINARY COMMUNICATIONS

Contributions to the basic problems of complexometry—II

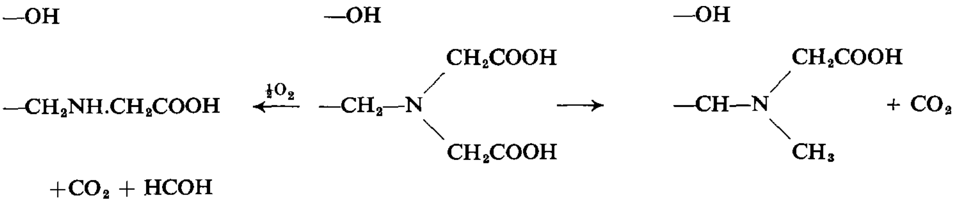
Decomposition of Xylenol Orange in aqueous solutions

(*Received* 3 *October* 1959)

One of the more promising metallochromic indicators of the "complexone type" suggested in recent times[1,2] is Xylenol Orange (I). It has already been utilized by a number of authors in various practical applications.



However, the stability of aqueous solutions of Xylenol Orange is limited. Its decomposition is accompanied by slow loss or complete disappearance of its metallochromic properties. This can be well observed in its colour reactions, for example with thorium, bismuth, lead or zinc. In solutions of these cations at suitable pH,[1] one drop of 0·1% to 0·5% Xylenol Orange solution produces an intensely red, eventually red-violet coloration. Aqueous solutions of the indicator more than one month old either do not give these reactions at all or give them only very weakly. Only the reaction with copper—the development of an intense violet-red coloration—is fully maintained. Indeed it is possible, though this is very surprising, to use such "aged solutions" as an excellent indicator for copper, in spite of the fact that fresh Xylenol Orange alone produces with copper robust complexes which react only slowly with EDTA solution. Xylenol Orange thus becomes effectively a specific indicator for copper. The most probable explanation of this is that in aqueous solutions slow decarboxylation of two symmetrically placed carboxyl groups takes place. In this manner a substance with a new complex-forming grouping (III) is developed, which is very similar to the complex-forming grouping of Glycinethymol Blue (IV).[3]



IV Glycinethymol Blue grouping

II Xylenol Orange

III

It is very difficult to achieve artificial aging of Xylenol Orange solutions. Freshly prepared aqueous solutions tolerate boiling without decomposition, and may be evaporated to dryness or heated at 60° for several days. Solutions acidified with glacial acetic acid or hydrochloric acid can also be boiled for a longer time without decomposition. Xylenol Orange decomposes rapidly on boiling with nitric acid or sodium hydroxide. The aqueous solutions are stable to oxidation by atmospheric oxygen. Stronger oxidizing agents (hydrogen peroxide, cerium^{IV} sulphate) decompose the indicator immediately. In the decomposition in this manner all the metallochromic properties disappear, and only the original acid-base properties of the parent indicator—cresol red—are maintained.*

The behaviour of Xylenol Orange with lead dioxide is very interesting as illustrated by the following experiments. Solid lead dioxide was added to an aqueous solution of Xylenol Orange which was slightly acidified with acetic or sulphuric acid and the solution was thoroughly stirred with an electromagnetic stirrer. As in the case of our earlier experiments on the oxidation of EDTA,[4] carbon dioxide and a large quantity of formaldehyde were detected. According to the experimental conditions (quantity and quality of PbO_2, time and intensity of stirring, etc.) the Xylenol Orange solutions lost their metallochromic properties for heavy metals in a short time with the exception of copper, which could still be titrated using the indicator treated in this manner. The quality of the colour changes in the titration of copper (pH 5·5 to 6, hexamethylenetetramine) is, however, not so distinct as in the case of "naturally aged" solutions of Xylenol Orange. With the "artificially aged" indicator the colour change is from red-violet to clear yellow as in the first case. Only solutions carefully buffered to pH 5·2 to 5·4 give a sharp colour change.

This difference in behaviour can be easily explained. In the case of the "natural aging" of solutions only the decarboxylation takes place while the sarcosine derivative (III) develops (formaldehyde was not detected), whereas in the oxidation with lead dioxide the glycine derivative (IV) is produced, which is less suitable for the titration of copper. It would, of course, be necessary to prove this assumption by a chromatographic examination of the two decomposition products of Xylenol Orange, followed by their isolation. The experiments are being continued.

Methylthymol Blue[5] behaves in a similar way. Because of its slight stability in aqueous solutions, it is easily converted to Glycinethymol Blue.[3] This decomposition reaction is also being studied further.

CONCLUSION

On storage aqueous Xylenol Orange solutions are subject to slow decomposition and lose their metallochromic indicator properties. It is probable that during the decomposition a sarcosine derivative is formed, which is a reasonably suitable indicator for the complexometric determination of copper in weakly acidic medium.

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Isomeric complexans:† The dl and meso forms of 2:3-butanediamine-N:N:N′:N′-tetra-acetic acid

(*Received* 19 *October* 1959)

In recent studies on complexans[1] we have isolated two isomers of 2:3 butanediamine-N:N:N′:N′-tetra-acetic acid—2:3 BDTA$^{\alpha}$ and 2:3 BDTA$^{\beta}$, m.ps. 211–2° (decomp.) and 138–151° (decomp.) respectively.

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* Xylenol Orange is prepared by condensation of Cresol Red with formaldehyde and iminodiacetic acid.

† The term "complexan" has been recommended by the Analytical Chemistry Section of the IUPAC to describe polyamino-poly-carboxylic acids.

heated at 60° for several days. Solutions acidified with glacial acetic acid or hydrochloric acid can also be boiled for a longer time without decomposition. Xylenol Orange decomposes rapidly on boiling with nitric acid or sodium hydroxide. The aqueous solutions are stable to oxidation by atmospheric oxygen. Stronger oxidizing agents (hydrogen peroxide, cerium^{IV} sulphate) decompose the indicator immediately. In the decomposition in this manner all the metallochromic properties disappear, and only the original acid-base properties of the parent indicator—cresol red—are maintained.[*]

The behaviour of Xylenol Orange with lead dioxide is very interesting as illustrated by the following experiments. Solid lead dioxide was added to an aqueous solution of Xylenol Orange which was slightly acidified with acetic or sulphuric acid and the solution was thoroughly stirred with an electromagnetic stirrer. As in the case of our earlier experiments on the oxidation of EDTA,[4] carbon dioxide and a large quantity of formaldehyde were detected. According to the experimental conditions (quantity and quality of PbO_2, time and intensity of stirring, etc.) the Xylenol Orange solutions lost their metallochromic properties for heavy metals in a short time with the exception of copper, which could still be titrated using the indicator treated in this manner. The quality of the colour changes in the titration of copper (pH 5·5 to 6, hexamethylenetetramine) is, however, not so distinct as in the case of "naturally aged" solutions of Xylenol Orange. With the "artificially aged" indicator the colour change is from red-violet to clear yellow as in the first case. Only solutions carefully buffered to pH 5·2 to 5·4 give a sharp colour change.

This difference in behaviour can be easily explained. In the case of the "natural aging" of solutions only the decarboxylation takes place while the sarcosine derivative (III) develops (formaldehyde was not detected), whereas in the oxidation with lead dioxide the glycine derivative (IV) is produced, which is less suitable for the titration of copper. It would, of course, be necessary to prove this assumption by a chromatographic examination of the two decomposition products of Xylenol Orange, followed by their isolation. The experiments are being continued.

Methylthymol Blue[5] behaves in a similar way. Because of its slight stability in aqueous solutions, it is easily converted to Glycinethymol Blue.[3] This decomposition reaction is also being studied further.

CONCLUSION

On storage aqueous Xylenol Orange solutions are subject to slow decomposition and lose their metallochromic indicator properties. It is probable that during the decomposition a sarcosine derivative is formed, which is a reasonably suitable indicator for the complexometric determination of copper in weakly acidic medium.

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Isomeric complexans:[†] The dl and meso forms of 2:3-butanediamine-N:N:N′:N′-tetra-acetic acid

(*Received* 19 *October* 1959)

In recent studies on complexans[1] we have isolated two isomers of 2:3 butanediamine-N:N:N′:N′-tetra-acetic acid—2:3 BDTA$^{\alpha}$ and 2:3 BDTA$^{\beta}$, m.ps. 211–2° (decomp.) and 138–151° (decomp.) respectively.

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There were obtained by successive crystallisation from a chloroacetic acid condensation of the unresolved amine, and it is not therefore yet known which is the *meso* and which the *dl* form

By use of the polarographic technique described in a previous communication[2] it has been possible to show that there is a marked difference in the chelating properties of the two isomers. Thus 2:3 BDTA$^{\alpha}$ has virtually the same chelating power as CDTA for copper^{II} and cadmium, whereas that of 2:3 BDTA$^{\beta}$ is considerably weaker and is intermediate between those of CDTA and EDTA.

Values for one of these isomers have already been recorded.[2,3] The purpose of this preliminary communication is to amend the migration rate previously reported for 2:3 BDTA$^{\alpha}$ and to give more complete information on both isomers.

Complexan	M.p.° C	M_{I_1}	$E_{1/2}$ value for Cu chelate, *Volts S.C.E.*	$E_{1/2}$ value for Cu chelate from pherogram, *Volts S.C.E.*	$E_{1/2}$ value of Cd chelate, *Volts S.C.E.*
2:3 BDTA$^{\alpha}$	211–2	4·1	−0·41	−0·33	−0·97
2:3 BDTA$^{\beta}$	138–151	3·8	−0·32	−0·28	−0·87

To the best of our knowledge, this is the first occasion on which isomeric complexans have been reported.

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SHORT COMMUNICATIONS

The determination of boron in iron and low-alloy steels with dianthrimide: A colorimetric method that does not require preliminary separations

(*Received* 23 *May* 1959)

IN recent years boron has been used increasingly in certain types of steel for constructional purposes. It gives improved hardenability and allows economies in the use of other alloying elements. Since the amounts of boron present are usually very low, about 0·001–0·005%, chemical determination has presented some difficulties. There has therefore been a need for a method that is simple but still accurate.

The first stage in the determination of boron in steel is to convert it from the different forms in which it may be present into boric acid. In general this is done by dissolving the steel sample in sulphuric acid and oxidising with hydrogen peroxide. Any boron compounds in the insoluble residue are brought into solution by fusion with sodium carbonate.

Usually the colorimetric determination of boric acid is preceded by some separation process, the extent of which depends on the colour reagent used. The most commonly used reagent, quinalizarin, is highly selective and does not react with any other element normally present in low-alloy steels. Nevertheless the quinalizarin method is often combined with a separation by electrolysis with a mercury cathode. This removes iron, chromium and other elements which would interfere with the determination, the iron by precipitation as the sulphate in the strong sulphuric acid solution in which the determination is made and the chromium by absorption of light at the wavelength of measurement.

A. *Experiments on keeping* Fe^{II} *in solution*

The principal source of interference in the determination of boron in steels low in chromium is the precipitation of iron as sulphate. For boron determinations in steels of this type, Rudolph and Flickinger[1] therefore developed a procedure using quinalizarin without preceding separations in which the ferrous sulphate is allowed to precipitate and settle out before a visual comparison is made. This method was taken as a starting point for the present investigation.

A prerequisite of increased accuracy is the replacement of the visual comparison with standard solutions by a photometric measurement. For this it is necessary to separate the precipitated ferrous sulphate but some difficulty was encountered. The precipitation and the sedimentation are both very slow. Even centrifuging was not sufficiently effective and the strong sulphuric acid solution could not be filtered in a practical way.

It seemed that it might be possible to dilute the solution and thereby keep Fe^{II} in solution at least for the time required to carry out the determination. The acid concentration cannot however be allowed to fall below 90% by weight since this would appreciably impair the sensitivity of the boron determination. These conditions are satisfied by the addition of 25 ml of 96% sulphuric acid to 3 ml of a solution of iron in approximately $2M$ sulphuric acid. It was found that this solution could hold up to 100 mg of Fe^{II} without any risk of the iron being precipitated. The resultant solution was colourless and had no absorption in the 600–650 mμ region.

A method for the determination of boron in low-alloy steels and cast iron based on these results has been in use in this laboratory for several years with satisfactory results. This method offered several advantages, especially in simplicity and speed, over methods used previously. The necessary limitation of the size of the sample and the reduction in the concentration of the acid has however an adverse effect on the determination of the lowest boron concentrations. A considerable improvement was afforded by replacement of quinalizarin by dianthrimide which has a higher sensitivity and more favourable spectral properties.

It was found that up to 100 mg of Fe^{II} could be retained in solution under the same conditions as before, even during the heating necessary for the reaction between boric acid and dianthrimide. No precipitate formed when the reaction solution was heated in a water bath for 2 hours at 100° or for 15 hours in an oven at 80°.

B. *Interferences*

Earlier investigations have shown that there are very few substances that interfere with the reaction between boric acid and dianthrimide. Among them are oxidants such as chromate and nitrate which destroy the reagent. Interference has also been reported due to fluoride, to large amounts of phosphate, and to titanium.

When steel is dissolved in sulphuric acid no oxidising compounds are formed that can interfere with the reaction; they may however be formed when the insoluble residue is fused with carbonate. It is therefore necessary after dissolving the melt to reduce such compounds; sulphurous acid is suitable for this purpose and a slight excess does not interfere with the reaction.

An investigation of possible sources of interference was carried out using solutions, with and without added boron, containing 100 mg of Fe^{II} and varying amounts of the alloying elements that may be present in steel. Tests were made with 10 mg of Ni, 2 mg of Mn, Cu, Cr, Co, 1 mg of Al, V, Ti, Mo, Zr, P and 0·1 mg of Sn and As. No interference from these substances was found provided that corrections were made for the absorption of coloured ions. The quantity of sodium carbonate used for fusion was also without any interfering effect on the determination. The high chromium contents that occur in stainless steels give blank values so large that they reduce the precision of the determination.

Several alloying elements are not completely soluble in diluted sulphuric acid and a considerable amount is then found in the acid-insoluble fraction as well as in the acid-soluble fraction. In some cases the same element may be present with different valency in the two solutions; this is possible with molybdenum and titanium. Analyses of low-alloy steels containing molybdenum showed that this element did not interfere with the determination in either the acid-soluble or the acid-insoluble fractions when the method recommended in section E was used. Unfortunately no corresponding Ti-containing steels were available. Titanium in the acid-soluble part might be present as Ti^{III} but it should be possible to oxidise such a solution with a stream of air followed by sulphurous acid reduction back to Fe^{II} of the iron oxidised at the same time.

C. *Dissolving the sample*

Steel samples for the determination of boron are usually dissolved in sulphuric acid in a flask fitted with a reflux condenser. Experiments on the use of a mixture of sulphuric acid and phosphoric acid showed that the presence of large amounts of phosphoric acid caused a strong decrease in the colour of the boron complex. It was found that it is not necessary to use a reflux condenser. If strong boiling is avoided while the sample is being dissolved a simple pear-shaped glass bulb in the neck of the vessel is just as effective. A series of analyses of a steel sample gave, in both cases, 0·0195% of boron as the mean of four determinations.

When the sample is dissolved in sulphuric acid in a vessel of boron-containing glass there is a risk of dissolving boron out of the glass. It is of course advantageous to use a flask of quartz or boron-free glass but after repeated and prolonged boiling with sulphuric acid even flasks of boron-containing glass can be used. These flasks should be reserved for boron determinations and should only be washed in dilute acid without any added oxidising agent.

The acid-insoluble residue is fused with anhydrous sodium carbonate after ignition in a platinum crucible at a dull red heat. The same results are obtained in this way as when the sodium carbonate is added before ignition, as usually recommended, but it avoids the occasional incomplete ashing of carbonaceous material which may cause the subsequent sulphuric acid solution to be discoloured.

It has long been customary in boron analyses on steel to report the boron contents of the acid-soluble and of the acid-insoluble fractions separately. This presupposes that some boron compounds are always soluble in acid and that others are always insoluble. Analyses of steel samples as described in section F showed large variations in the acid-insoluble fractions from different steels but in every steel there was a certain amount of boron that was insoluble in dilute sulphuric acid. The spread of these values was however greater than that for the total boron content. If the sample was oxidised when it was dissolved a little more of the boron usually went into solution. Kelly[2] made analyses on the same steel samples after solution in hydrochloric acid and oxidation with hydrogen peroxide and in some cases obtained rather large variations in the proportion of acid-soluble to acid-insoluble boron in the same steel. In another investigation,[3] however, treatment with different acids gave roughly the same amount of boron from the same steel.

D. *Modification of the dianthrimide method*

The optimum conditions for the determination of boric acid with dianthrimide as described in an earlier paper[4] were found to be:

Dianthrimide 0·4 mg/ml; *sulphuric acid* 93–95% by weight; *boron* 0·3–1·0 μg/ml; *heating time* at 100°, 1–1·5 h; or at 80°, 4–5 h. In the determination of small amounts of boron in steel without separations, some consideration must be paid to the presence of the iron and the smallness of the boron concentrations. To get the maximum accuracy it is necessary to use the largest amount of sample possible even if the acid concentration has to be reduced to 90% by weight. If the acid concentration is kept in the range 93–95% the weight of sample must be reduced to less than half, thus reducing the possibility of determining the lowest boron contents. It is also advisable to reduce the reagent concentration to less than half. This will of course reduce the sensitivity by 1 or 2 per cent but it will also reduce the reagent absorption by more than a half.

With these modifications it is essential to pay particular attention to certain of the results of the investigation described in the earlier paper.[4] A change in the strength of the concentrated sulphuric acid will affect the analytical result. It is therefore essential to check and if necessary to correct the calibration curve when a new stock solution is taken into use. The small variations in the acid concentration that are produced by varying consumptions of acid when dissolving the acid-soluble and the acid-insoluble parts can be neglected. In the method recommended, two different heating temperatures are suggested. With the modifications suggested here the calibration curves for these two methods will not be identical.

E. *Recommended method*

Solutions required. Dianthrimide reagent solution: Dissolve 150 mg of dianthrimide in 1000 ml of sulphuric acid (approx 96% w/w).

Diluted sulphuric acid (1 + 3).

Sulphurous acid (approx 6%).

Procedure: Take 3 g of sample in an Erlenmeyer flask (100–150 ml) and add 40 ml of diluted sulphuric acid (see note 1). Use a reflux condenser or a simpler corresponding arrangement. Heat to dissolve. Filter through a dense filter paper into a 100-ml volumetric flask. Wash with hot water. Cool to room temperature, dilute to the mark with water and mix. This flask (A) contains the acid-soluble boron. Ignite the filter in a platinum crucible at low temperature. Fuse with 2 g of anhydrous sodium carbonate. Dissolve the melt in 40 ml of diluted sulphuric acid. Add 1 ml of sulphurous acid for the reduction. Filter if necessary. Transfer the solution to a 100-ml volumetric flask, dilute to the mark and mix. This flask (B) contains the acid-insoluble boron.

Transfer 3 ml of solutions A and B to two dry 50-ml Erlenmeyer flasks. Add 25 ml of dianthrimide reagent solution with shaking, then close the flasks with glass stoppers (note 2). For the blanks, transfer 3 ml of solutions A and B to two Erlenmeyer flasks and add 25 ml of sulphuric acid (approx 96% w/w). Heat all four flasks in a boiling water bath for 60 minutes (note 3). Cool to room temperature and measure the absorbance of the solutions against pure concentrated sulphuric acid at 620 mμ in 1 cm or 2 cm cells. Correct for the blanks.

Calibration: Dissolve 0·7621 g boric acid (H_3BO_3 p.a.) in water and dilute to 1000 ml. Take 50 ml of this standard solution and dilute to 1000 ml. This working solution contains 6.667 μg B/ml. Transfer 5–50 ml of this solution by means of a burette to 100-ml volumetric flasks, add 30 ml of diluted sulphuric acid and make up to the marks. These solutions contain 1–10 μg B/3 ml. Take 3 ml from each solution and from a boron-free comparison solution and then proceed according to the description above. Plot a calibration curve or calculate the factor relating the absorbance with the amount of boron present. It is advisable to include with every series of boron determinations a boron-free solution and a standard solution containing, for example, 5 μg boron.

Notes: 1. Alternatively for instance, 50 ml of solution could be prepared from a 1·5-g sample by dissolving in acid and diluting or 10 ml of solution could be prepared from an 0·3-g sample. The quantity of acid should be reduced in proportion to the volume. For occasional boron contents of more than 0·010% of either acid-soluble or acid-insoluble boron a smaller sample can be weighed out. If the boron content is regularly appreciably higher a smaller aliquot should be taken and a higher reagent concentration used. The calibration curve will of course be different in this case.

2. The dianthrimide reagent should be kept in the dark and protected from moisture. The reagent can suitably be dispensed from an all-glass automatic pipette protected from atmospheric moisture by a drying tube.

3. When the Erlenmeyer flasks are immersed in the water bath the stoppers should be lifted for a moment to release the pressure and allowed to fall back again of their own weight. The colour reaction can also be carried out at a temperature lower than 100°. Heating in an oven at 70° overnight was found quite suitable. The calibration curve will be somewhat steeper the lower the temperature chosen.

4. If only the total boron content is required, dissolve the melt in flask A and then add a few ml of sulphurous acid for reduction. In some cases it may be advisable to add sulphurous acid to the acid-soluble part also. This will counteract any tendency for the iron to oxidise if the solution is kept for a longer time.

5. Check that no boron contamination is introduced from reagent, filter paper or glass vessel. This can be done by making a parallel determination on boron-free carbon steel.

F. *Applications*

This method of analysis has been tested on standard samples from the National Bureau of Standards, USA, the acid-soluble and the acid-insoluble fractions being determined separately. The results are shown in Table I.

TABLE I.—BORON DETERMINATIONS ON NBS STANDARD STEELS

Number and steel type	Certificate value	No. of analyses	Boron sol. in dil. H_2SO_4	Boron insol. in dil. H_2SO_4	Boron total	Stand dev.	Coeff. of variation %
825 Mn–Ni–Cr	0·0006	5	0·0002	0·0005	0·0007	0·00007	10
826 Cr–Mo	0·0011	5	0·0010	<0·0001	0·0010	0·00006	6
151 Cr–Mo	0·0027	11	0·0017	0·0010	0·0027	0·00008	3
828 Mn–Cr	0·0059	6	0·0033	0·0026	0·0059	0·00009	1·5
829 Ni–Cr–B	0·0091	9	0·0041	0·0053	0·0094	0·00016	1·7
830 Ni–Cr–B	0·019	9	0·0103	0·0092	0·0195	0·00017	0·9

Boron values in per cent.

The results show good agreement with the certificate values. The coefficients of variation are relatively low considering the low boron contents. These results compare well with the results of the much more involved procedures that have been reported previously. It should be pointed out that the spread in the values for soluble and insoluble boron is considerably larger than for the total boron.

The results shown here apply to low-alloy steels. The method has also been found to give good precision in analyses on malleable iron but no standard samples with known boron contents were available. In analyses on stainless steel it must be expected that the accuracy will be impaired by the large correction that must be made for chromium. Only a single standard sample of this type was available for testing the method. NBS No. 444 gave by the present method 0·0034% B; certified value 0·0033%; this sample contains 20% Cr, 10% Ni, 0·2% Mo, Nb and W and 0·1% V.

The sensitivity of the method is insufficient for the determination of boron contents below a few ten thousandths of one per cent. In such cases the iron must first be removed, for instance by electrolysis with a mercury cathode, and the solution concentrated. Experiments showed that this could be done without loss of boron by evaporation of a solution in 2*M* sulphuric acid at 100° in a water bath. Analyses of NBS No. 825 in this way gave a value of 0·00062% B as the mean of 6 determinations with a coefficient of variation of 3%. Samples containing vanadium could not be analysed in this way since the vanadium is not removed on electrolysis. Even when the solution is reduced with excess sulphurous acid before the evaporation it may subsequently be oxidised to V^V. Vanadate, like chromate, destroys the dianthrimide reagent. The vanadium can however be removed by ion-exchange.[3]

Acknowledgement—The author wishes to express his thanks to Nils Lange for technical help with the analyses on steels.

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Quantitative spectrochemical determination of minor elements in silicates

(*Revised paper received* 1 *September* 1959)

In general, quantitative spectrochemical determination of minor elements in silicates has been based upon separate arcings for the volatile and involatile groups of elements with or without an internal standard.[1,2] The proper selection of suitable internal standard and spectroscopic buffer may eliminate the necessity for the tedious separate arcings. An attempt was made to provide a spectrochemical method for minor elements in silicates, which differ greatly in their volatilization rates from the electrode cavity, (i.e. Pb, Ga, Sn, Cr, V, Co, Ni, and Sc) with a single arcing procedure, by using two internal standards (Sb_2O_3 and metallic Pd).

One part (by weight) of the powdered silicate sample was thoroughly mixed with one part of carbon powder containing 0.8% Sb_2O_3 and 0·04% metallic palladium as the internal standards. The mixture was packed into the crater of the lower graphite electrode and excited for 60 sec by an 8-amp, 210-volt continuous a.c. arc supplied from a Pheilsticker-type intermittent a.c. arc source unit with radio-frequency spark. The spectrum was photographed on a process-type plate. For the purpose of plate calibration a self-calibrating method was used with a five-step sector (1 : 2 step ratio). A large Littrow-type spectrograph, Shimadzu QL-170, was used. Natural silicate rocks or minerals were

TABLE I.—ANALYSIS PAIRS AND RANGES OF ANALYSIS

Pair	Range, *ppm*
Ga 2943·637 (4·3)/Sb 2877·915 (5·3)	10 ~ 300
Pb 2833·069 (4·4)/Sb 2877·915 (5·3)	10 ~ 1000
Sn 3175·019 (4·3)/Sb 2877·915 (5·3)	10 ~ 3900
Co 3453·505 (4·0)/Pd 3481·152 (4·8)	5 ~ 300
V 3183·982 (3·9)/Pd 3242·703 (4·6)	10 ~ 1000
Cr 3593·488 (3·4)/Pd 3481·152 (4·8)	5 ~ 500
Ni 3414·765 (3·6)/Pd 3481·152 (4·8)	5 ~ 500
Sc 3613·836 (10·1)/Pd 3242·703 (4·6)	—

The values in parentheses are excitation potentials (eV).

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selected as the basis for standards. If necessary, a correction for residual impurity was made. Analysis pairs and analysis ranges are indicated in Table I together with the excitation potentials for the analysis and the internal standard lines.

Following the statistical method of Shaw and Bankier,[3] the precision of the procedure (expressed as a 68% confidence limit and shown in Table II) was evaluated from working curve data and from repeated analyses of arbitrary samples or of the well-known standard rock W1 prepared by the U.S. Geological Survey.

TABLE II.—PRECISION OF THE PROCEDURE

Element	Sample	Values obtained, *ppm*	Values previously reported, *ppm*	Values given by Ahrens, *ppm*
Ga	W 1	$13{\cdot}6^{+1{\cdot}2}_{-1{\cdot}1}$	11 ~ 20	14·5
Pb	Feldspar	177^{+17}_{-16}	—	—
Sn	Gneiss	48^{+11}_{-9}	—	—
Co	W 1	55^{+10}_{-9}	20 ~ 55	36
V	W 1	236^{+27}_{-24}	170 ~ 340	240
Cr	W 1	139^{+20}_{-18}	100 ~ 150	130
Ni	W 1	59^{+6}_{-5}	47 ~ 150	90
Sc	W 1	280^{+88}_{-67}	15 ~ 51	37

If suitable standards are available, the present method may be extended to cover further species of elements including copper. However, the results in Table II indicate that the method failed for scandium. For its successful determination the quantity of carbon buffer should be made at least three times as much as the amount used in the proposed procedure, in order to eliminate a matrix effect.[4] With some modification the logarithmic sector method can be successfully applied without appreciable loss of precision.

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Variamine Blue sulphate as redox indicator

(*Received* 9 *October* 1959)

VARIAMINE Blue (4-amino-4′-methoxy-diphenylamine), a redox indicator well established in practice, is usually employed in the form of the hydrochloride,* from which is prepared a 1 % aqueous solution or a 1 : 100 solid indicator mixture with sodium chloride or with anhydrous sodium sulphate.[1,2] In such titrations, where the chloride content of the indicator gives some trouble (*e.g.* argentometric titration), chloride-free Variamine Blue acetate solution may be prepared from the hydrochloride by shaking it with benzene and alkali and then with aqueous acetic acid.[3] The preparation of the pure base, soluble in alcohol, is a rather long and expensive operation.[4] Both the hydrochloride and the base are light-sensitive, preparations originally white quickly becoming blue. The indicator solutions are unstable, become blue on standing and a precipitate separates from them. The sulphate provides a chloride-free and stable form of the indicator.

Preparation of sulphate

Dissolve 50 g of technical Variamine Blue B base in 1·5 litre of warm distilled water. Bleach the solution with 5 g of sodium dithionite and 10 g of animal charcoal, then boil the suspension and filter it quickly. Add to the slightly yellow or blue (depending on the pH of the solution), clear, hot filtrate 0·5 litre of sodium sulphate solution, upon which the separation of the sulphate begins immediately. The sodium sulphate solution contains 200 g $Na_2SO_4 . 10\,H_2O$ per litre. Cool the solution to room temperature, filter the separated white needle-like crystalline material, wash it with cold water and dry it in vacuum, in a desiccator at room temperature.

The sulphur content (determined by the Grote-Krekeler method) indicates half a molecule of sulphuric acid. Its composition is therefore: 4-amino-4′-methoxy-diphenylamine,$\frac{1}{2}H_2SO_4$. Polarographic examination shows it to be chloride free. Its ash-content is practically zero.

It is very stable, and kept in dark glass it keeps its white colour for months.

Preparations of the indicator

The most stable form of Variamine Blue sulphate for use is the solid indicator mixture made with anhydrous sodium sulphate in a ratio of 1 : 400, using about 200 mg in a titration. This amount dissolves quickly and without residue in the solution to be titrated. For colorimetric use it is naturally

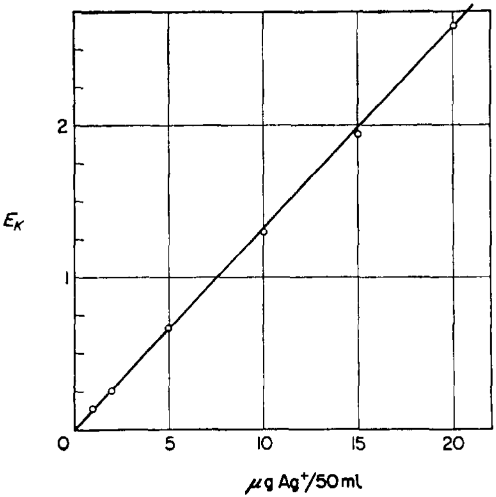

FIG. 1.—Colorimetric determination of silver ion with Variamine Blue sulphate.

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* In the textile industry it is known under the name Variamine Blue B base.

better to use an indicator solution; this may be 0·2% aqueous or 0·4% in 10% acetic acid. The freshly made solution is at the very most pale blue, so that its blank value can be neglected. On standing, this solution, also, naturally becomes blue, and in 4–5 days precipitation takes place.

Some practical applications

The applicability of the indicator was tested for the determination of the ascorbic acid factor and in argentometric chloride determination. The factor of an ascorbic acid solution against potassium iodate was found to be 1·010 with Variamine Blue hydrochloride and 1·009 with Variamine Blue sulphate. The results of argentometric chloride determinations are shown in Table I.

In the colorimetric determination of silver ion, where chloride content would cause some trouble[5], about 0·2% aqueous Variamine Blue sulphate indicator in acetate–acetic acid buffer at pH 3·6 was tested. Fig. 1 shows the extinction curve given.

TABLE I.—ARGENTOMETRIC DETERMINATION OF CHLORIDE WITH VARIAMINE BLUE SULPHATE

0·01*N* NaCl added, *ml*	0·01*N* $AgNO_3$ used, *ml*	Δ %
5·00	5·02	+0·40
10·00	10·03	+0·30
15·00	14·98	−0·13
20·06	19·94	−0·60
25·00	24·94	−0·24

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[5] L. Erdey and F. Szabadváry, *Z. analyt. Chem.*, 1957, **155**, 90.

A new micro method of studying the thermal stability of easily volatile explosives*

(*Received* 21 *September* 1959)

WHEN studying highly brisant explosives, which were very insensitive to shock and impact, and consisted of a solution of chloronitrobenzene (equilibrium mixture of the isomers) in nitric acid, in the molar ratio of chloronitrobenzene : nitric acid : water 1 : 4.6 : 1, it was not found possible to determine the detonation temperature by the usual procedures;[1] on heating, the water and nitric acid volatilized and the isomeric chloronitrobenzenes distilled unchanged at 243°. It therefore became necessary to develop a method for solving the problem, and one which could be used with tiny amounts of the specimen in view of the danger of explosion.

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* Translated by Ralph E. Oesper, University of Cincinnati, U.S.A.

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Method

The test was conducted in an aluminium block designed for the heating of micro crucibles[2] and provided with a well for a thermometer. Channels were cut into the under side; these were 1.8 mm wide and 2 mm deep. The aluminium block was heated by means of a Teklu burner, and the temperature was read from the thermometer.

The explosive under test was placed in glass capillaries (melting point tubes) whose external diameter ranged from 1 to 1.5 mm. The amounts taken were sufficient to occupy one-fifth of the length of the tube, which was then sealed. The charged tubes were placed in the channels of the block, and heated slowly or rapidly, according to the conditions of the test. Alternatively, the tubes were placed in the channels of a block which had been preheated to the chosen temperature. In this way it became possible to remove tubes at any selected temperature and examine them for changes after they had cooled. In all cases, direct observations were made through a glass shield to avoid injury in case the tubes exploded.

The strength of the tubes was tested by charging the capillaries with nitric acid and heating. It was found that they withstood the vapour pressure of nitric acid up to 330°.

Experimental findings

The mixture described above was tested first. It represents an explosive with an equalized oxygen balance. It explodes violently when detonated with a primer cap.

When heated in the capillary, there resulted above 120° a brown gas (NO_2) as in the case of nitric acid, whose colour deepened with rising temperature. Tubes heated to 200° showed no visible change when cooled; the reactions, such as the formation of nitrogen dioxide, were accordingly reversible. In tubes heated to 210° there was an irrevesible change, in that the contents after cooling consisted of two liquid phases. The heavier (isolated by centrifuging) was green to blue-green. The same behaviour was found also on heating up to 300°. Between 300 and 320° there was a change even in the hot material in that the initial almost black colour (NO_2) gradually faded. After cooling, the contents of the tube consisted entirely of a colourless liquid, which proved to be aqueous hydrochloric acid. When the capillaries were placed in the channels of a block preheated to 330°, no detonation or deflagration was observed. Accordingly, the explosive must have decomposed without detonation:

$$5C_6H_4NO_2Cl + 23HNO_3 \rightarrow 30CO_2 + 19H_2O + 14N_2 + 5HCl$$

For comparison purposes, a study was made of the behaviour of other organic compounds dissolved in highly concentrated nitric nitric acid. A solution of *m*-dinitrobenzene in nitric acid (molar ratio 1 : 4) behaved initially like the chloronitrobenzene-nitric acid studied. Here again, two liquid phases were produced, starting at 210°; however detonation occurred around 290°. Nitric acid solutions of xylene, *p*-dichlorobenzene, pyridine, paraffin, and petroleum were tested at 220 and 300°. The findings are summarized in the following table.

Compound dissolved in or mixed with HNO_3	Behaviour after heating to 220°	Behaviour at temperaures to 300°
Monotrochlorobenzene	2 phases, blue-green	no detonation
m-Dinitrobenzene	2 phase, blue-green	detonation
Xylene*	1 phase, green	detonation
p-Dichlorobenzene	2 phases, blue-green	no detonation
Pyridine	1 phase, light yellow	detonation
Paraffin oil	2 phases, yellow	detonation
Petroleum	combustion	detonation

* Two phases likewise appear in the case of xylene on cooling below 10°.

Discussion

The composition of the green product is not clear as yet; it is noteworthy that it is stable only in closed tubes, *i.e.* under pressure. Possibly, addition compounds of N_2O_3 with organic aromatic nitro compounds are formed.

Of more interest perhaps is the finding that, against all expectation, the system chloronitrobenzene–nitric acid cannot be made to detonate or deflagrate by heating. Since this stability appears only in the instances (see the Table) in which chlorine-containing aromatic compounds were used, it seems logical to assume that the presence of the chlorine atom is essential to this stability. In contrast to all other solutions of organic compounds in highly concentrated nitric acid used for explosive,[3] the mixture monochloronitrobenzene-nitric acid is extraordinarily resistant to shock, impact or bombardment, with no impairment of its ability to be set off by a primer cap.

The following assumption may be advanced to explain the thermal stability and the insensitivity against shock and impact. The reasoning is analogous to the action of anti-knock materials in motor fuels. The relatively heavy and sluggish chlorine atom stops or interrupts some of the reaction chains initiated by temperature or shock. The result is that a continuous reaction is possible only through the initiation of an adequate number of reaction chains, such as is provided by the initial ignition. Consequently, the thermal decomposition, which leads to the same results as the detonation, proceeds slowly and apparently is in accord with the van't Hoff law.

This latter view gives interesting glimpses into the possible use of such solutions as monopropellants.

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Talanta, 1959, Vol. 3, pp. 213 to 215. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Gaschromatographie. A. I. M. Keulemans; übersetzt und bearbeitet von E. Cremer. Verlag Chemie, Weinheim, 1959. DM 24.—xvi + 288 Seiten, 103 Abbildungen und 26 Tabellen.

Dieses 1957 bei der Reinhold Publishing Corporation, New York erschienene Buch liegt nun in ausgezeichneter Ergänzung und Übersetzung in deutscher Sprache vor. Es ist durchaus kein Wagnis, das der Verfasser unternimmt, da er über eine im rasanten Kommen befindliche Methode in buchmässiger Zusammenstellung berichtet. Wohl sind die Methoden der Gaschromatographie noch sehr jung,—über die Gasflüssigkeitschromatographie wurde ja erst von A. J. P. Martin 1952 berichtet—, demnach aber sind die Ergebnisse und der mit dieser Methode erzielte Zeitgewinn so bestechend, dass die Herausgabe einer eingehenden Einführung in dieses Gebiet voll gerechtfertigt erscheint. Das vorliegende Buch ist in acht Hauptkapitel und zwei Anhangskapitel unterteilt.

Kapitel eins erläutert neben einer geschichtlichen Übersicht die allgemeinen Grundlagen der gaschromatographischen Methodik; die von einem Spezialkommitee, welches anlässlich eines vom Institute of Petroleum in London im Juni 1956 veranstalteten Symposiums über Gaschromatographie zusammentrat, vorgeschlagene Nomenklatur wird auch hier benutzt und in diesem Kapitel näher erörtert. Im zweiten Kapitel wird die praktische Anwendungsmöglichkeit der Gasflüssigkeitschromatographie aufgezeigt, im dritten Kapitel die Einzelheiten der möglichen Apparaturen besprochen und auf die verschiedenen Detektoren und ihre Charakteristiken eingegangen. In den Kapiteln vier, fünf und sechs werden die der Gasflüssigkeitschromatographie zu Grunde liegenden Theorien so weit sie heute vertretbar erscheinen, sehr klar und übersichtlich dargelegt. Ein Verzeichnis der verwendeten Symbole (162!) mit ihren genauen Definitionen sind auf den Seiten IX–XII angeführt. Das siebente Kapitel interpretiert die Anwendung dieser Prinzipien bei sehr schwierigen Trennungen und bei ihrer nicht analytischen Verwendung. Das letzte Hauptkapitel (acht) ist endlich der bereits scheinbar überholten Gasfestkörperchromatographie gewidmet, die in letzter Zeit wieder zu gutem Rufe gekommen ist. Im ersten Anhangskapitel wird eine Auswahl von stationären Flüssigkeiten für die Gasflüssigkeitschromatographie angegeben und deren Verwendbarkeit besprochen, das zweite Anhangskapitel, von E. Cremer verfasst, bringt eine vorzügliche Betrachtung über die Gaschromatographie an Adsorptionsschichten unter besonderer Berücksichtigung der auftretenden Grenzschichtphänomene.

Alles in allem liegt hier eine ganz ausgezeichnete, gut ausgefeilte Darstellung über die Gaschromatographie mit instruktiven Abbildungen, sehr brauchbaren Tabellen, ausführlichem Literaturverzeichnis und übersichtlichem Autoren- und Sachverzeichnis vor, die allen Interessenten für dieses Gebiet bestens empfohlen werden kann.

G. Wagner

Analytical Chemistry in Nuclear Reactor Technology, 1st Conference 1957. U.S. Atomic Energy Commission, Office of Technical Services. Department of Commerce, Washington 25, D.C. Pp. vi + 256. $3.50.

This thick paper-bound volume contains 17 of the 21 papers presented at the first conference on analytical chemistry in nuclear reactor technology held at Gatlinburg, Tennessee, U.S.A. in November, 1957. This conference, the first of a projected series, had as theme the analysis of reactor materials; the second conference, which took place in September, 1958, considered analysis in the commissioning and operation of reactors and the third may deal with post-operational analytical problems.

The papers presented aim to describe recent advances in methods for the analysis of some materials of construction of nuclear reactors and for reactor fuels, moderators, coolants and blanket materials.

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As is unavoidable in conferences of this sort, there is a marked variation in the standards of the papers as now presented; some, for example, are admirably referenced (*e.g.* "Recent Developments in the Analytical Chemistry of Thorium and its Compounds" by C. V. Banks, with 152 references mostly for the years 1955-7 and "The Analytical Chemistry of Beryllium" by E. S. Melick with 78 references) whilst some others have few or no references (*e.g.* "Recent Developments in the Analytical Chemistry of Titanium" by A. L. Gahler where the references are embodied in the text and are for the most part inadequate from the point of view of ready procurement).

C. E. Larson in his reminiscent and sometimes light-hearted introductory paper dealing with the role of analytical chemistry in atomic energy, rightly stresses the importance of the increased participation of the analyst in the discussion and solution of the problems arising both in development and production; this theme is given practical expression by the inclusion in the conference of several papers discussing problems involving both process chemistry and analysis and their frequent interdependence. Whilst appropriately stressing the remarkable developments in instrumental techniques in the course of the war-time atomic energy programme it may be questioned whether "quantitative spectrographic analysis was carried to its present stage of perfection through the development of apparatus for the Manhattan Project"—this does less than justice to the important and independent advances made in the ferrous and non-ferrous metals industries.

The book is clearly printed and well illustrated with nearly 100 diagrams and reproductions from photographs and is undoubtedly a useful reference volume for the increasing numbers of analysts engaged in the expanding field of reactor technology, particularly if one anticipates setting beside it the forthcoming companion volumes covering the second and third conferences.

F. J. WOODMAN

Chemistry of the Co-ordinate Compounds. Vol. I, International Se^ies of Monographs on Inorganic Chemistry. (Papers presented at the Rome Symposium of the International Union of Pure and Applied Chemistry, September, 1957.) Edited by H. TAUBE and A. G. MADDOCK. Pergamon Press, London and New York, Symposium Publications Division, 1958. Pp. 638. £5.

IN the reviewer's opinion it is a mistake to publish volumes of papers presented at symposia. The author who has to write up research work for one of these books is thereby delayed or prevented from publishing it in the proper place, namely one of the standard journals; and it makes the work inaccessible to the many readers whose local libraries cannot afford to buy the (usually expensive) symposium volume. There is, perhaps, a better case for publishing in collected form the review lectures given at symposia, leaving the research communications to appear in due course in the journals. The present volume is a typical symposium publication, containing thirteen reviews and sixty-five research communications. Many papers of both kinds are excellent and interesting, but the result of putting so many diverse items between one pair of covers is a rather indigestible whole, which will probably collect dust on the library shelf at a faster rate than the average for recent books. Most of the papers are in English, with a sprinkling in French, German, and Italian. The book is elegantly turned out but replete with minor errors in the spelling and usages of English.

The book is divided into five sections, each consisting of one or more review papers followed by a number of research communications. There is not space in this review to discuss all the papers individually, but the following selection (which has been made at random without any implication as to merit) will indicate the general character of the book.

Section I, on bonding in complexes, opens with a review by L. E. Sutton of recent developments in the ligand field theory, and is mainly devoted to the spectroscopy of complexes. There is a paper on the vibrational frequencies of water in aquocomplexes. Section II, on stereochemistry, stability constants and reactivity, is distinguished by an amusing account from L. G. Sillén on the problems he

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In spite of the excellence of many of the individual contributions, this volume is too incoherent, too expensive and of too little lasting interest to justify private purchase. Larger scientific libraries should have it.

HENRY HEAL

Talanta, 1959, Vol. 3, p. 216. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Contributions to the basic problems of complexometry—II: Decomposition of Xylenol Orange in aqueous solutions. R. Přibil. (3 *October* 1959)

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The determination of silver and thallium in rocks by neutron-activation analysis. D. F. C. Morris and R. A. Killick. (5 *October* 1959).

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The determination of small amounts of organic sulphur in small samples. Jean P. Dixon. (11 *November* 1959).

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International Union of Pure and Applied Chemistry

Analytical Chemistry Section

DURING the XXth Conference of the I.U.P.A.C., which was held in Munich in August, 1959, the Committee of the above Section discussed certain points of confusion in the literature. Recommendations* were made as follows:

1. *Terminology of complexing agents*

Because of the existing confusion regarding terminology in the use of complexing agents as titrants, the committee tentatively recommends the use of the following terms until such time as further action is taken.

(*a*) The group of *polyamino-polycarboxylic acids* which form *anionic* complexes shall be termed **complexans.**

(*b*) Titration processes in which any type of complexing titrant is used shall be termed **complexometric titrations.**

(*c*) Those complexometric titrations which involve titration with a chelating agent shall be termed **chelatometric titrations** and represent a special type of complexometric titration.

2. *Notation of indicators in titrimetric analysis*

Many dyestuffs have been recommended as indicators in chelatometric and redox titrations and a host of trivial names often exists for the same compound. Examples can be found in the literature of a compound having been recommended as a new indicator because it has a different name, when the compound has in fact been in use for years under a different name.

To avoid future confusion, and embarrassment of authors and editors, the Committee recommends that when a dyestuff is proposed as an indicator in any type of titration, *and particularly when it is claimed as new*, the **British Colour Index** or **Schultz Number** be quoted along with the trivial name.

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A CRITICAL STUDY OF THE PRECIPITATION OF AMMONIUM PHOSPHO-12-MOLYBDATE

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Summary—The precipitation of yellow ammonium phospho-12-molybdate is used as a quantitative measure as well as a separative procedure for phosphorus. The procedure is subject to a number of errors. This paper describes the history of the recognition of some of them, and reports critical experiments involving some chemical variables not previously investigated. The precipitation is discussed with respect to the physico-chemical properties of molybdic oxide and phosphomolybdic acid, and a set of best conditions for the determination of phosphorus are described. The precipitation is not regarded as suitable for the most precise work, but may be used as a preliminary separation before weighing a substance of greater chemical integrity.

INTRODUCTION

AMMONIUM phosphomolybdate is a material which has been of considerable interest to chemists since the time of Berzelius. It, its parent acid, and its related arsenic derivative have possessed importance in analytical chemistry for over a century, with regard to the precipitation of phosphates and arsenates. Although the precipitation and weighing of phosphorus as magnesium pyrophosphate is widely regarded as the best procedure available, it is not always thought attractive, and precipitation of phosphate in the form of phosphomolybdate is used in the interest of greater speed. This latter method is fraught with error: this paper attempts to review sources of such error, and to describe experimental evidence for conditions under which many of them may be eliminated.

When solutions containing alkali molybdates or alkali tungstates are mixed with solutions containing alkali phosphates or alkali arsenates, and the solutions are acidified, numerous substances may be crystallised out which have the general composition $wR_2O{\cdot}xP_2O_5{\cdot}yXO_3{\cdot}zH_2O$, where R represents an equivalent of a base and X is either a molybdenum or a tungsten atom. A large number of such substances has been reported, and it is noteworthy that the ratio of *e.g.* P : Mo in these materials never falls below 1 : 12.[1] However, the stability of many of these materials in solution has not been investigated; indeed, some are incapable of recrystallisation. Since such substances have frequently been formed by the mixing of the components in the right quantities and crystallising, it seems unlikely that the great majority of these reported substances represent compounds. On the other hand, those salts and acids in which the ratio P : Mo is 1 : 9 or 1 : 12 are capable of recrystallisation, and of repeated extraction with organic solvents without change in composition, and here there is definite evidence for complex formation.[2] Further, even when the actual ratio of P : Mo in solution is less than 1 : 12, the substances which separate after the addition of acid contain phosphorus and molybdenum in the ratio 1 : 12 or greater.

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The well-known yellow precipitate which is formed when phosphate is tested for with ammonium molybdate solution has, according to Hundeshagen,[3] the composition $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$, but this has recently been disputed by Thistlethwaite,[4] who described conditions under which yellow precipitates of like appearance but of varying composition may be obtained. The composition of this precipitate has been studied by a number of workers, but the remarkable fact remains that only Hundeshagen[3] and Thistlethwaite[4] have attempted a fully systematic study of the effect of varying the conditions of formation upon the composition. The other workers have concerned themselves with individual facets of the problem, particularly from the standpoint of the quantitative removal of phosphorus from solution, as an analytical method. The above formula represents the composition of the precipitate obtained under certain rigorously controlled conditions; this has been confirmed by Riegler[5] and also by Clarens,[6] both of whom also noted that although the ratio P : Mo in the solid remains constant at 1 : 12, the content of the base may vary, depending upon the conditions, from zero to three equivalents per phosphorus atom. On the other hand, Lagers[7] and Hissinck and van der Wearden[8] quoted formulae which contained a little more molybdic oxide, namely $(NH_4)_3PO_4{\cdot}12{\cdot}65MoO_3$. Richardson[9] supported Hundeshagen's original formula, with miscellaneous errors up to 1·2%, as also did Thistlethwaite.[4] Recently Stockdale[10] has given the formula of the fresh precipitate as $(NH_4)_2PO_4{\cdot}12MoO_3{\cdot}H_2O$. The results obtained by workers in earlier days before the 1 : 12 ratio for the P : Mo ratio in the compound was accepted are shown in Table I.

From the above reports, it can be seen that a number of variables affect the composition. If the temperature at which precipitation is carried out is too high, it will cause some precipitation of molybdic oxide with the yellow precipitate, creating a higher ratio of P : Mo than is required by the Hundeshagen formula. This, incidentally, would destroy the efficiency of the use of the titrimetric method for the determination of phosphorus, which depends on a constancy of the composition of the yellow precipitate. The temperature range 40°–60° for the precipitation is recommended in order to avoid this error by Baxter,[11] Kilgore,[12] Baxter and Griffin,[13] Chesneau,[14] Hissinck and van der Waerden,[8] Artman,[15] Lagers[7] and Taylor and Miller.[16]

Frey[17] states that if precipitation is carried out below 65°, an ammonium phospho-9-molybdate is precipitated, whereas if the temperature is higher than 65°, ammonium phospho-12-molybdate is formed. He suggested dissolution and reprecipitation to obtain more consistent results. Thistlethwaite[4] has studied the effect of changing the temperature at which precipitation is effected, and the influence of the concentrations of the reactants upon the composition of the precipitate. Unfortunately, he did not always analyse weighed portions of the precipitate, apparently because of the hygroscopic nature of his preparation. His analyses are therefore restricted to the determination of the molar ratios of the components; the mean value of the ratios he obtained for NH_4 : P : Mo was 1 : 1 : 12, and he therefore gave ammonium phosphomolybdate the formula $(NH_4)H_2PO_4{\cdot}12MoO_3$. It is particularly evident from his work that physical variables such as time and the rate of stirring have an important effect on the composition of the precipitate; other workers have noted this type of effect, and many have given specific times for stirring.

It is also evident that the chemical conditions laid down for the precipitation of ammonium phosphomolybdate are very largely empirical. Thus, if a considerable excess of molybdenum and strong mineral acid is present in the reaction mixture, substances of approximate composition "1 : 12" are always obtained, but if weak acids such as acetic acid are used, then substances with a higher ratio of phosphorus to molybdenum are formed, which have a different colour. These may be other heteropoly acids, and may also have suffered some reduction. It is almost certainly true that the 1 : 12 compound cannot be formed under these conditions, since its precursors are not present at the high pH due to acetic acid.[2] Sulphuric acid is rarely used in this preparation, since it has a peculiar action on molybdic acid, alleged by Falk and Suguira[18] to be due to the formation of a sulphomolybdate. This is supposed by them to be precipitated with the yellow precipitate, thus leading to large positive errors in analysis, as noted by Gregersen,[19] Wardlaw,[20] Neumann,[21] Hissinck and van der Waerden,[8] Richardson[9] and Artman.[15] Stockdale[10] notes the same error, but ascribes it to co-precipitated MoO_3. However, a reagent containing sulphate has been recommended[22] and has enjoyed some popularity. Hydrochloric acid may be used, but there is the danger of dissolution of the molybdic oxide[23] as well as the slight chance of

TABLE I.—THE DEVELOPMENT OF THE PRESENT ACCEPTED FORMULA FOR AMMONIUM PHOSPHOMOLYBDATE

Author	Reference	Formula and analytical data					
			%MoO_3	%P_2O_5	%NH_4	%H_2O	Notes
Sonnenschein	*J. prakt Chem.*, **53**, 342		85·42	3·12	11·40		(dried at 120°C)
			86·70	3·20	11·23		
			86·11	2·93	10·91		
Seligsohn	*J. prakt. Chem.*, **67**, 470		90·74	3·14	3·57	2·55	(dried at 100°C)
Eggertz	*J. prakt. Chem.*, **79**, 496		91·28	3·74	3·31	1·32	
Debray	*Compt. Rend.* **66**, 704		Formula given as $20MoO_3{\cdot}P_2O_5{\cdot}3(NH_4)_2O{\cdot}3H_2O$; no figures				
Rammelsberg	*Monatsber. der Akad.* 1877, 573		$22MoO_3{\cdot}P_2O_5{\cdot}3(NH_4)_2O{\cdot}12H_2O$				
		(calc.)	86·04	3·86	4·24	5·86	
		(obs.)	86·70	3·91		5·63	(dried at room temperature)
			86·21	3·86	4·25	5·91	
			86·68	3·92		5·77	
Finkener	*Ber.*, 1883, **11**, 1638		Gives ratio of Mo : P as 12 : 1, with 2–3 molecules of NH_3 per "$PO_4{\cdot}12MoO_3$" radical				
Gibbs	*Amer. Chem. J.*, **3**, 317, 402		89·00	3·75	3·39	3·86	
			87·21	3·86	8·93		
			89·21	4·25	4·12	2·54	
Hundeshagen	*Z. analyt. Chem.*, 1883, **28**, 141		Formula given as $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3{\cdot}H_2O$ or as $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3{\cdot}2HCl{\cdot}H_2O$; no figures				

Where suitable data were recorded in these papers, the original results were recomputed using modern atomic weights.

reduction of the oxide. For these reasons, nitric acid is generally used for the acidification, but too great an excess must not be present, since, as Hundeshagen[3] observed, it will prevent the complete precipitation. With regard to the question of mineral acid-molybdic oxide interactions, Cannon[23] has recently shown that the solubility of molybdic oxide in nitric acid first increases with nitric acid concentration, and then drops to zero. This effect is very important in the present case, where a small excess of nitric acid (greater than 0·1*N*) will upset the quantitative nature of the precipitation unless a neutral salt be present. Ammonium nitrate is used for this purpose, and in order to promote the formation of an easily filtrable precipitate, but if too much be present, the precipitate dissolves in the solution of the salt and molybdic oxide is precipitated from the reagent solution. Stockdale[10] has minimized this effect in his commentary, with respect to added ammonium nitrate, but it is evident from his data that an increase of free acid in the mixture must be accompanied by an increase in the amount of precipitant (which contains free ammonia) in order to maintain complete precipitation.

The order of mixing the reagents is important, since if the molybdate solution be added to the acidified phosphate solution, the precipitate is (in the present work) formed as very small particles, and is rather hygroscopic after heating in the oven. This effect, which may be due to the occlusion of phosphate ions within the precipitate, or to a simple surface-area effect, may largely be avoided by adding the phosphate solution to the molybdate.

In addition to the highly critical conditions of formation, the manipulation and analysis of the solid obtained are also likely to introduce errors into the empirical formula. Firstly, the precipitate must be freed of its mother liquor. This cannot be accomplished using either water or dilute nitric acid solution alone, since the substance has a small but definite solubility,[14] and is in addition hydrolytically unstable.

A slightly acid, dilute solution of ammonium nitrate (0·8 % NH_4NO_3 in 0·8 % HNO_3 according to Thistlethwaite[4]) is preferred for this washing; if this solution is used, then the last traces of ammonium nitrate must be removed by heating. In this heating the water and nitric acid which were alleged by Hundeshagen[3] to be present in the air-dried substances are lost, producing a more or less hygroscopic body which is difficult to weigh. Stockdale[10] has proposed the use of a 2% nitric acid solution saturated with ammonium phosphomolybdate. Von Endredy[24] avoided this difficulty by washing the precipitate with anhydrous acetone, and then drying it in an air stream. Under these conditions, however, he found that the composition was not expressed by the formula $(NH_4)_3PO_4{\cdot}12MoO_3$, but that the solid still contained a little water. Drying under vacuum appears to have the same effect as heating, but it does not remove the water as quickly.[3]

For the determination of phosphorus, as a complete alternative to weighing the precipitate, the precipitate may be dissolved in a known amount of sodium hydroxide solution and the excess back-titrated with hydrochloric acid. This technique was used by a number of workers, among them Thilo,[25] and Pemberton Jr.,[26] all of whom standardised the method with a sample containing a known quantity of phosphorus. There is a complication here in that if phenolphthalein be used to indicate the end-point of the titration, the quantity of ammonia present (which has previously been noted to be variable) effects the end-point. Workers who subsequently recognised this difficulty and attempted to remove the ammonia, were Neumann,[21] who evaporated the alkaline solution, and Bang,[27] who used formaldehyde to form hexamine with the ammonia. Stockdale[10] has suggested a similar technique with a parallel titration of paramolybdate, but he did not consider the complicating effect of the phosphorus, which causes a "delay"[2] in the titration curve due to re-formation of the complex phosphomolybdate.

In spite of the established use of the formation of the yellow precipitate in the determination of phosphorus, there exist unresolved differences in individual reports. The differences in the formulae ascribed to the substance from time to time are most certainly partly due to improvements in analytical technique (compare the earlier results in Table I) but there is the need for systematic investigation of the formation of ammonium phosphomolybdate under various conditions, leading to the possible establishment of analytical methods which are exact and rapid, and which are based on a technique of some chemical integrity. Accordingly, an attempt has been made here to ascertain the conditions under which a precipitate of constant composition might be obtained. The principal conditions studied were:

(*a*) the effect of the concentration of nitric acid.

(*b*) the effect of temperature.

(*c*) the effect of the concentration of ammonium nitrate.

(*d*) the effect of the time for which the precipitate was allowed to stand before being removed from the solution.

(*e*) the relative values of various methods for drying the substance.

The effect of the time and rate of stirring was eliminated in this work, by not stirring the solution at all, and relying on convection currents in the mixture to effect mixing. This was thought justifiable in view of the great difficulties in defining what is meant by stirring *e.g.* with an unspecified glass rod for a given period of time.

EXPERIMENTAL

(*i*) *Chemicals and apparatus*

All chemicals used were of analytical reagent quality, particular care and attention being paid to procuring reagents which were free of arsenic and spurious phosphorus.

It was found necessary to use new hard glass apparatus for all the precipitations. This was pretreated by steaming out for several hours. Attempts to perform successive precipitations in the same glassware led to erroneous results, apparently due to the formation of sites of easy attack on the glass by the acid molybdate reagent.

Weighings were performed on a specially adjusted undamped Stanton Instruments balance with a seventy-second period, using weights calibrated against a National Physical Laboratory Class A master set.

(*ii*) *The quantitative precipitation*

In the introduction it was seen that although the precipitation of ammonium phosphomolybdate might be used for the determination of phosphorus, the results were not always consistent, the variations in them being due either to incomplete precipitation or to the formation of a precipitate of inconstant composition, depending on the conditions under which the precipitation was carried out.

In order to gain first-hand knowledge of the accuracy of the determination, precipitations were carried out in accordance with the conditions set out by Hillebrand and Lundell,[28] by Scott and Furman[29] and by Mellor.[30] The cited method of preparation of the molybdate reagent solution was in each case examined to determine the excess hydrogen ion and neutral salt concentrations. It was thus determined that the condition of the reagent was essentially that of a supersaturated solution of molybdic oxide in nitric acid.[31] The concentrations of the various components of the precipitating systems are set out in Table II, together with the weights of precipitate obtained from the same quantity of phosphorus. The variations in the weight of precipitate obtained made it necessary to analyze the prepared samples for their various components. When this was done, and the precise contents of Mo, P and NH_3 known, it was apparent that all three techniques resulted in the formation of precipitates of so nearly equivalent a composition that the difference in weights could not be accounted for on the basis of differences in composition (the analysis for Mo was done gravimetrically using oxine,[4] for phosphorus using the magnesium pyrophosphate technique, and for ammonia by a conductometric titration).

TABLE II.—RESULTS OBTAINED IN THE PRECIPITATION OF AMMONIUM PHOSPHOMOLYBDATE, BY THE PROCEDURES OUTLINED BELOW

(The solution from which the precipitate was obtained was in each case 200 ml in volume.)

Source	Procedures	Concentrations (*g.mols./l.*)				Weight of ppt., *g*
		KH_2PO_4	MoO_3	HNO_3	NH_4NO_3	
Hillebrand and Lundell[28]	1. Molybdic acid soln, added to phosphate soln. at 45°. 2. Maintained at 45° for 1 hr., then 12 hrs. at 20°. 3. Washed with: a. 0·1M NH_4NO_3 + 0·13M HNO_3 b. 0·15M HNO_3 4. Dried for 2 hrs. at 110°, with additional drying to constant weight for this work	·007348	1·4 —2·3	·50 1·1	1·0	2·6604 2·7139 2·7134 2·7115 2·6810 mean 2·6960 99·4% of calc. wt.
Scott and Furman[29]	1. Molybdic acid soln. added to phosphate soln. at 45° 2. Maintained at 45° for 1 hr. 3. as 3. above 4. Dried for 2 hrs. at 100°.	·007348	·23	0·8	0·4	2·3640 2·3834 2·3952 2·5364 2·3652 2·3672 mean 2·3734 87·5% of calc. wt.
Mellor[30] ("alternative procedure")	1. Molybdic acid soln. added to phosphate soln. at 20°. 2. Mixture brought to 60° and allowed to cool for 12 hrs. 3. as 3. above 4. as 4., Hillebrand and Lundell.	·007348	·05	0·8	0·2	2·5230 2·3036 2·4876 2·6013 mean 2·4789 91·4% of calc. wt.

The weight of yellow precipitate which would be obtained from 200 ml 0·007348M KH_2PO_4 solution were the formula of the yellow precipitate, $(NH_4)_3 \cdot PO_4 \cdot 12MoO_3$, is 2·713 gms.

(iii) *The precipitation of ammonium phosphomolybdate under various conditions*

The method used for the preparation of ammonium phosphomolybdate samples under various conditions was as follows: 50 ml of a molybdate solution were placed in a beaker, and the required amount of excess nitric acid added. The volume was made up to 100 ml, the required amount of excess ammonium nitrate solid added, and the mixture brought to the required temperature on a water-bath. Fifty ml of a solution of potassium dihydrogen phosphate of known concentration were then added from a burette over a period of fifteen minutes. The mixture was maintained at the required temperature for a definite time (usually one hour) and allowed to cool before filtering the suspension through a weighed sintered glass crucible, porosity no. 4 ("fine"). The residue was washed on the filter with an acid ammonium nitrate solution, 0·15M NH_4NO_3 and 0·10M HNO_3, and finally with 0·13M ammonium nitrate solution at 0°. The crucible and its contents were then dried at 130° to constant weight. The stock molybdate reagent solution was an acid solution of ammonium heptamolybdate in nitric acid, 35 g of ammonium heptamolybdate being dissolved in a mixture of 50 ml of water and 50 ml of ammonia solution, S.G.O. 880, this solution then being poured into 350 ml of a solution containing 168 ml of nitric acid, S.G. 1·42. The mixture was made up to 800 ml and filtered before use.

TABLE III.

Conditions	Final wt. as a percentage of that calculated for the formula $(NH_4)_3PO_4 \cdot 12MoO_3$.
At room temperature in a desiccator containing $CaCl_2$ and KOH, for one month	101·2 102·1
130° for 15 hrs.	99·8 100·8

Ammonium phosphomolybdate samples prepared at 60°, from such a solution 1·8M with respect to nitric acid and 0·1M with respect to ammonium nitrate were dried under different conditions. Twenty-four hours were allowed for the solution to cool and the precipitation to complete itself. The results are presented in Table III.

The general influence of temperature upon the extent of precipitation was studied with a set of solutions containing the following concentrations of reactants: 0·083M MoO_3, 0·15M NH_4NO_3, 1·54M HNO_3, ·001471M KH_2PO_4. The precipitate weights and the molybdenum content of the various preparations are shown in Fig. 1 as a function of temperature. The results show a trend which agrees with that observed by Thistlethwaite,[4] but the effect of temperature on precipitate weight was much more marked in the present case.

It was found in this work that there was a strong correlation between the ratio Mo : P in solution and the final weight of the precipitate, even when the ratio Mo : P was very large (in excess of 30 : 1). Since this is one of the major results of Thistlethwaite's study,[4] there is little point in recording the present experimental observations. It is however worthwhile to note that the extreme effect of changing the ratio Mo : P from 56 : 1 (as above) to 63 : 1, and maintaining all other conditions constant, leads to a statistically significant (eight replicates) decrease in precipitate weight, from 102·3% of theoretical to 100·6%, at 60°.

The effects of changes in the nitric acid and ammonium nitrate concentration upon the precipitation are shown on Figs. 2 and 3. In these experiments, the solution was brought to 40° for one hour and allowed to stand 24 hr before filtering. The concentration of nitric acid present in the precipitating solutions had a profound effect on the observed weight of the precipitate. It was found that precipitation was not nearly quantitative with respect to the phosphate present if the concentration of the nitric acid was greater than 2·7M. However, when the filtrates from these latter experiments were diluted with neutral ammonium nitrate to bring the nitric acid concentration to 1M, and heated for one hour at 45°, a further precipitate of ammonium phosphomolybdate appeared, the weights of the combined precipitates being within 1% of that calculated on the basis of the formula $(NH_4)_3PO_4 \cdot 12MoO_3$.

The effect of length of time of standing on precipitate weight is shown in Table IV.

(iv) *Analysis of the precipitate for its components*

The molybdenum contents of the preparations were determined by the oxine method,[4] which proved to be entirely satisfactory. It was found to be possible to determine ammonia by the hypobromite reagent, but it is necessary to distil the ammonia from the precipitate before its determination,

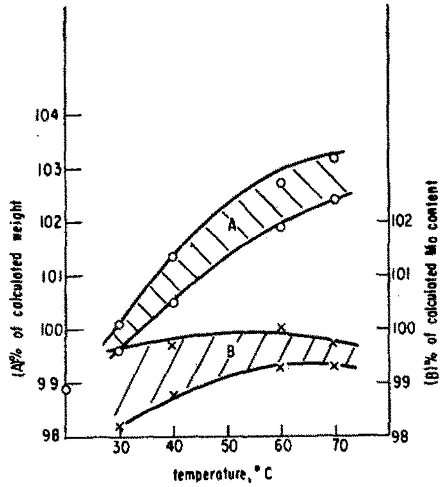

FIG. 1.—Effect of temperature upon the weight of precipitate recovered from a mixture of solutions 0·083*M* MoO_3 0·15*M* NH_4NO_3, 1·54*M* HNO_3 and 0·001471*M* KH_2PO_4.

The precipitating medium was held at a temperature of x° for one hour, and then set aside for 24 hours at room temperature (*ca* 16°). The calculated weight is 100% for a quantitative yield of $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with respect to the phosphorus in the system. The Mo content according to this formula is 61·36%.

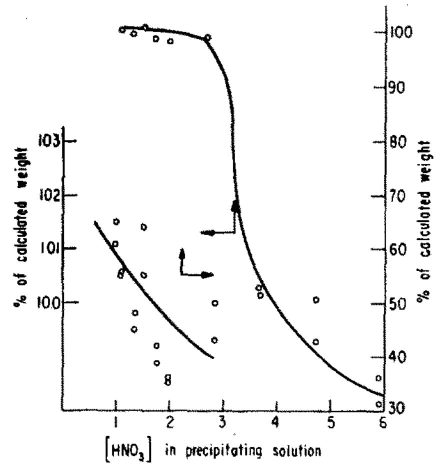

FIG. 2.—Effect of nitric acid concentration upon the weight of precipitate recovered from a mixture of solutions 0·083*M* MoO_3, 0·12*M* NM_4NO_3, ·001471*M* KH_2PO_4 and x*M* HNO_3.

Precipitation conditions: 40° for one hour, then set aside for 24 hours at room temperature (*ca.* 16°). The calculated weight is 100% for quantitative yield of $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with respect to the phosphorus in the system.

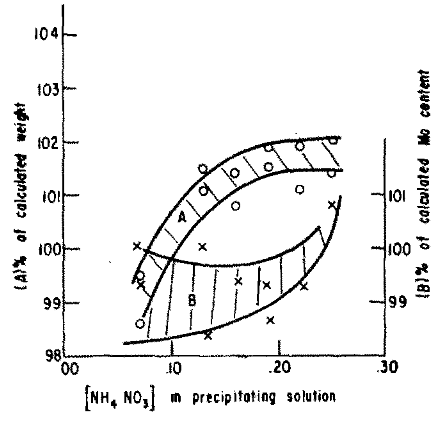

FIG. 3.—Effect of ammonium nitrate concentration upon the weight of precipitate recovered from a mixture of solutions 0·083*M* MoO_3, 1·00*M* HNO_3, ·001471*M* KH_2PO_4 and x*M* NH_4NO_3.

Precipitation conditions: 40° for one hour, then set aside for 24 hours at room temperature (*ca.* 16°). The calculated weight is 100% for a quantitative yield of $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with respect to the phosphorus in the system. The Mo content according to this formula is 61·36%.

in order to use this technique, and consequently a direct conductometric titration method was developed. This was accomplished by back titration with acid of a solution of the precipitate in CO_2-free alkali. No exact systematic variation in the ammonia content of the precipitate was discovered, though smaller values were more frequently detected in the precipitates formed from highly acid media. The range of values found was between 0·03% and 3·73%: the most frequently occurring values were between 1·80% and 2·00%, corresponding approximately with the formula $(NH_4)_2HPO_4 \cdot 12MoO_3$, in agreement with Stockdale.[10] The average value was 2·42%.

In all the experiments, save those performed in solutions containing a large concentration of nitric acid, there was found to be no phosphate remaining in solution, after precipitation had taken place. The precise amount of phosphate present in the precipitate was in most cases in these experiments therefore taken to be the amount initially introduced into the precipitating solution.

TABLE IV.—THE VARIATION IN THE WEIGHT OF THE PRECIPITATE AND THE MOLYBDENUM CONTENT OF THE PRECIPITATE WITH THE LENGTH OF TIME THE MIXTURE WAS ALLOWED TO STAND BEFORE FILTRATION.

Time, *hrs.*	% calculated wt.	%Mo
1	92·4 96·1	59·8
24	98·9 99·5	59·8
72	99·2 100·0	60·5

(These precipitations were performed at 50°. The percentage of molybdenum according to the formula $(NH_4)_3 \cdot PO_4 \cdot 12MoO_3$, is 61·36. The per cent calculated weight is based on a quantitative recovery of precipitate of the above composition with respect to the phosphorus present).

(*v*) *Back titration of solutions of ammonium phosphomolybdate in alkali*

This technique is fairly commonly employed as an alternative to weighing the precipitate. It is subject to errors introduced by varying the concentration of molybdenum in the system, and by the loss of ammonia to the atmosphere.

In this investigation, care was taken to reduce ammonia loss to a minimum by avoiding procedures such as boiling with alkali to effect dissolution of the precipitate, and the solutions which were prepared contained only small concentrations of ammonia (of the order 0·01*M*). The precipitate itself was dissolved in sodium hydroxide solution in such a manner that the pH of the solution was never higher than 11·4. Stirring was effected by a stream of purified nitrogen, and the precipitate was completely dissolved in ten minutes. In a blank experiment in which nitrogen was passed through a solution of 0·015*M* ammonium chloride, to which had been added sufficient sodium hydroxide to bring the pH of the solution to 11·4, it was found that a loss of 1·5% of the ammonia initially present occurred in ten minutes. By using a lower concentration of ammonium salt, a still lower loss would be observed. In spite of these precautions, and even when the back titrations were done potentiometrically and the results plotted differentially, it was found that the inflexions in the curves were so indistinct, at the low concentrations necessary to avoid the confusing effects due to neutral salt formation,[31] that the technique gave results which were useless for determining phosphorus to within ±10%. It is thus unlikely that this technique is of any great utility for precise work unless an arbitrary conversion factor is used.

DISCUSSION

(*i*) *Standard methods*

The somewhat elaborate directions cited in the literature and in texts for the preparation of the molybdate reagent appear to be designed to avoid spurious precipitation of molybdic oxide during the precipitation process. Depending on the molarity of the solution with respect to nitric acid, the molybdenum is present either as a polymolybdate[31] or a basic molybdenyl nitrate.[23] Whichever of these cases obtains in the present situation, the reagent is such that it is supersaturated with respect to molybdic oxide, since it will on standing spontaneously deposit the yellow dihydrate of molybdic oxide. Bearing this in mind and remembering the importance of the neutral salt and free acid concentrations to the precipitation, it might be quite reasonable to regard the precipitation basically as a salting-out process. It certainly is not directly comparable with any normal metathetical reaction.

The cited standard procedures give rather different results, but a trend towards a more reproducible, quantitative precipitation is seen with an increase in the Mo : P ratio in the initial system. The presence of a large excess of ammonium nitrate appears to aid the reproducibility of the precipitation, as measured by the weight of the dried precipitate. It appears that the best method is that which combines the longest time of heating, the longest time of standing, the largest excess of molybdate and ammonium nitrate in solution.

(*ii*) *Experiments under deliberately varied conditions*

The effect of high nitric acid concentration in inhibiting complete precipitation appears to be due to the solubility of the precipitate in that acid. Thus, it was shown that on diluting the filtrate from highly acid precipitation media, more precipitation occurred, proceeding quantitatively to the limit of the earlier observed deficiency. The fact that the precipitate from highly acid systems is of a slightly variable composition with respect to molybdic oxide is explicable on the basis of a certain enhancement of the basic function of molybdic oxide in nitric acid.

The overall effect of an increase in the concentration of ammonium nitrate was to cause an increase in the total quantity of molybdenum associated with the precipitate, although the actual molybdenum content did not increase all the time. The precipitate was found to contain traces of nitrate when precipitated from solution containing $0{\cdot}25M$ NH_4NO_3.

If the precipitation functions by some salting-out mechanism, it is not surprising that the length of time which the precipitate is allowed to stand in contact with its mother liquor has an effect on the observed weight of the precipitate. In Table IV, it was shown that there is a certain minimum time for which the precipitate must be allowed to stand, if the precipitation is to be quantitative with respect to the phosphate present; if, however, the mixture is allowed to stand indefinitely, the molybdate reagent itself deposits molybdic oxide, and thereby upsets the accuracy of any analysis based on the precipitation. The general effect of temperature also involves the question of the stability of the reagent, which is also subject to ageing. However, the temperature must be maintained at least at 40°, since the precipitation will not be quantitative with respect to the phosphate present within a reasonable length of time at lower temperatures. Increase in the temperature appears to produce a slightly greater quantity of the precipitate under otherwise constant conditions, and associated with this increase, there is an increase in the molybdenum content of the precipitate, which may be due to the presence of molybdic oxide.

(*iii*) *The properties of phospho-*12*-molybdic acid and the precipitation of ammonium phosphomolybdate*

Phosphomolybdates are formed when solutions containing phosphates and molybdates are acidified, or via the direct reaction between phosphoric acid and molybdic acid. By both methods, solutions are obtained which will furnish crystals of phospho-12-molybdic acid. This substance is readily extracted from cold, acidified solutions, by the use of ether, and this in itself demonstrates that the ratio 1 : 12 for phosphate : molybdate in this material marks a definite extent of combination.

It might be expected that since this substance contains a large proportion of molybdic oxide, the basic function of molybdic oxide would be manifested in strongly acid solutions of phospho-12-molybdic acid. This is not quite the case, since phospho-12-molybdic acid is not completely soluble, even in the most concentrated hydrochloric acid. It was also found that the addition of a quantity of similarly concentrated nitric acid to a saturated aqueous solution of phospho-12-molybdic acid produced a small precipitate, which analysed as the hydrated phospho-12-molybdic acid. This is important, since the conditions under which ammonium phospho-12-molybdate is formed are such that molybdic oxide is at its greatest solubility in nitric acid, whereas the solubility of phospho-12-molybdic acid has been substantially reduced. The addition of ammonium nitrate to such a solution of phospho-12-molybdic acid in nitric acid may then be expected to cause the salting-out of the sparingly soluble ammonium phospho-12-molybdate, as is indeed the case. The quantitative formation of ammonium phospho-12-molybdate then depends on the behaviour of phospho-12-molybdic acid itself, but is complicated by the presence of a necessary excess of molybdic oxide which may separate spontaneously.

The variation of the ammonia content of the precipitate may be due to either of two causes; the co-precipitation of phospho-12-molybdic acid with ammonium phospho-12-molybdate may occur (providing the hydrogen ion concentration of the solution is sufficient to prevent the degradation of the complex, but not sufficiently great to favor the formation of basic molybdenyl salts), or the base-exchange properties if the precipitate, mentioned by Thistlethwaite,[4] may be in evidence.

(*iv*) *A recommended procedure*

From the results, it appears that the best conditions that can be observed for the quantitative precipitation of phosphate are that the solution should be about $0{\cdot}0015M$ with respect of phosphate, and also contain the following concentrations of reagents: $0{\cdot}08M$ MoO_3, $0{\cdot}1M$ NH_4NO_3, and $1{\cdot}5M$ HNO_3. The stabilized molybdate reagent should be prepared as described in the present experimental section. Precipitation should be performed in hard glass vessels at 40° for one hour, and the mixture allowed to stand 24 hours before filtering. Washing should be performed using acid ammonium nitrate ($0{\cdot}15M$ NH_4NO_3 $0{\cdot}1M$ HNO_3, followed by $0{\cdot}1M$ HNO_3 at 0°). In order to avoid difficulties with the hygroscopic nature of the oven-dried material, it has been found experimentally that if the phosphate solution is added to the molybdate solution, the precipitate is much less hygroscopic than if the reagents had been mixed in the reverse order. The precipitate should be dried at 130° for at least two hours, and preferably longer. The procedure should always be checked with a phosphate sample of known concentration, in order to make any allowance necessary for the deposition of molybdic oxide from the reagent. If no such allowance is thought necessary, the precipitate formed under the above conditions may be weighed as $(NH_4)_3{\cdot}PO_4{\cdot}12MoO_3$ with a standard deviation of less than $0{\cdot}3\%$.

This recommended procedure involves an elapsed time in excess of one day to obtain only semi-exact results, judging from the standard deviation observed. It is appreciated that this prolongs what is normally used as a rapid method, but it could be confined to occasions where the more exact result is required. For the most precise work, it is apparent that this precipitation should only be used as a separative procedure before weighing phosphorus as pyrophosphate.

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Zusammenfassung—Die Fällung des gelben Ammoniumphosphomolybdates wird sowohl zur Abtrennung als auch zur Bestimmung von Phosphor verwendet, Die Methode hat einige Fehlerquellen. Die vorliegende Arbeit teilt Geschichte der Entdeckung dieser Fehlermöglichkeiten mit und beschreibt einige kritische Experimente welche Abänderungen betreffen, die bisher nicht in Betracht gezogen wurden. Die Fällung selbst wird von physikalisch-chemischem Standpunkte aus diskutiert soweit es die Eigenschaften der Molybdän- und Phosphomolybdän-säure betrifft. Die bestmöglichen Bedingungen werden beschrieben. Die Fällung wird nicht als bestgeignet erachtet, wenn es sich um höchste Genauigkeit handelt, kann jedoch als Abtrennungsschritt verwendet werden bevor die endgültige Wägung einer günstigeren Wägeform erfolgt.

Résumé—La précipitation du phospho-12-molybdate d'ammonium jaune est utilisée comme mesure quantitative aussi bien que comme méthode de séparation pour le phosphore. La méthode est sujette à un grand nombre d'erreurs. Ce papier décrit l'historique de la mise en évidence de certaines d'entre elles et rend compte d'expériences critiques relatives à certaines variables chimiques qui n'avaient pas été étudiées jusqu'à présent. On discute les conditions de précipitation compte tenu des propriétés physico-chimiques de l'acide molybdique et phospho-molybdique et on décrit les conditions les meilleures pour le dosage du phosphore. On ne considère pas la précipitation comme adaptée à un travail très précis, mais elle peut convenir comme séparation préliminaire avant la pesée d'une substance de composition chimique mieux définie.

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DOSAGE COLORIMETRIQUE DU SOUFRE EN FAIBLES TENEURS DANS LES ACIERS, LES FERS ET COBALTS PURS*

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Résumé—La méthode proposée consiste à dégager le soufre sous forme d'acide sulfhydrique et à le faire entrer alors dans la synthèse du bleu de méthylène à partir de diméthyl-para-amino-phénylène-diamine. Le bleu de méthylène possède une coloration très intense et relativement stable. Différents modes d'attaque sont proposés suivant la nature du métal. Dans le cas des fers et aciers, on forme d'abord de l'acide sulfhydrique à partir des sulfures par attaque chlorhydrique. On peut alors réduire les formes oxydées du soufre par l'emploi du mélange réducteur des acides iodhydrique et hypophosphoreux. Dans le cas du cobalt, on met en solution dans l'acide nitrique concentré de façon à oxyder en sulfate tout le soufre présent. On en dégage alors H_2S au moyen du mélange réducteur signalé.

INTRODUCTION

AUCUNE des méthodes classiques de dosage du soufre dans les métaux (combustion et dosage iodométrique, gravimétrie, évolution classique) ne s'est révélée bien adéquate pour la détermination de teneurs de l'ordre de 0,010% dans le cobalt métallique.

C'est dans le cas de ce matériau que la méthode que nous proposons a été mise au point. Sa sensibilité la rend particulièrement intéressante pour le dosage de teneurs de 0,001 à 0,010% S.

Son applicabilité aux aciers et fers purs a été établie par quelques modifications de mode opératoire qui la rendent plus simple et plus rapide encore.

Cette méthode est basée sur la formation de bleu de méthylène à partir de diméthyl p-aminophénylène diamine et d'hydrogène sulfuré, ainsi que l'avaient proposé divers auteurs.[1,2,3]

Ceux-ci préconisent divers milieux absorbants de l'hydrogène sulfuré: soit l'acétate de zinc en milieu acide[1]—soit un mélange d'acétates de zinc et de sodium[2] soit une solution d'hydroxyde de cadmium[3]. Nous avons constaté que les résultats étaient plus exacts lorsqu'on utilise une solution alcaline d'acétate de zinc.

Précisons que le principe de l'attaque réductrice par le mélange $HI + H_3PO_2$ aux fins de libérer H_2S après une mise en solution oxydante rapide a été proposé par Sands[8] et par Heineman et Rahn[9].

I. DANS LES ACIERS ET FERS PURS

A. *Principe de la méthode*

Le métal est attaqué par l'acide chlorhydrique concentré et le soufre est ainsi dégagé des sulfures sous forme d'acide sulfhydrique. Celui-ci est fixé dans une solution d'acétate de zinc en milieu sodique.

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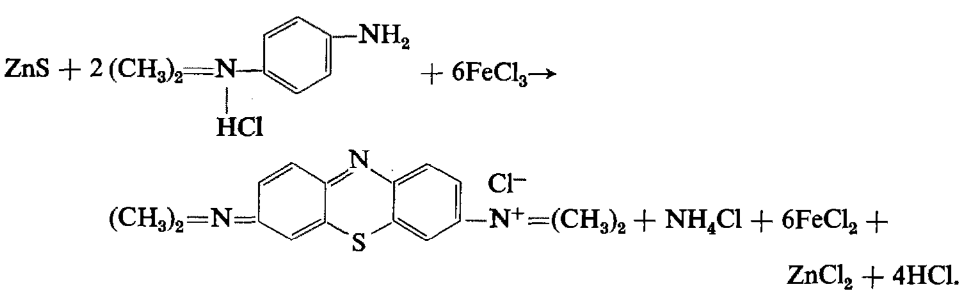
Le soufre ainsi fixé entre dans la synthèse du bleu de méthylène à partir de diméthyl para-aminophénylène diamine.[1–3]

On effectue la colorimétrie du bleu de méthylène en milieu acide, à la longueur d'onde de 650 mμ.

Après la fin de la dissolution chlorhydrique, on traite la liqueur d'attaque par un mélange réducteur d'acide iodhydrique et d'acide hypophosphoreux qui libère l'acide sulfhydrique à partir des combinaisons oxydées du soufre.[8,9] Cet acide sulfhydrique peut être recueilli séparément dans une solution absorbante identique à celle citée ci-dessus et entrer à son tour dans la formation de bleu de méthylène.

Le principe de la détermination répond aux équations suivantes:

$$MeS + 2HCl \rightarrow MeCl_2 + H_2S \nearrow$$
$$H_2S + Zn(C_2H_3O_2)_2 \rightarrow ZnS + 2C_2H_4O_2$$
$$MeSO_4 + 10HI \rightarrow MeI_2 + 4I_2 + 4H_2O + H_2S \nearrow$$
$$2I_2 + H_3PO_2 + 2H_2O \rightarrow 4HI + H_3PO_4$$



B. *Echantillon*

La sensibilité de la méthode étant telle que la prise d'essai, pour des teneurs habituelles, est de l'ordre de quelques décigrammes, seulement certaines précautions particulières sont à prendre pour l'échantillonnage.

Il est notamment requis de réduire les copaux à une granulométrie telle que la prise d'essai soit représentative du métal analysé. (Nos échantillons passaient entièrement au tarnis No. 35.)

C. *Appareillage*

Les différentes parties de l'appareil sont reliées entre elles par des rôdages normalisés, soit côniques, soit hémisphériques.

L'appareil comprend:

(1) un débitmètre à niveau
(2) un dispositif d'épuration du courant gazeux entraîneur. Celui-ci est composé de deux flacons laveurs, à plaque frittée, munis de 40 cc d'une solution de NaOH à 15%.
(3) un ballon d'attaque (fond plat) à deux tubulures
(4) un dispositif d'introduction sous pression des solutions d'attaque
(5) un réfrigérant à reflux
(6) un flacon laveur rempli de la solution (4); celle-ci est remplacée après chaque utilisation.

Nous avons préféré utiliser comme laveur une solution acide afin d'y réduire la solubilité de H_2S. L'acide iodhydrique y maintient un caractère réducteur car on sait que H_2S s'oxyde facilement.

Ces deux dernières parties sont destinées à empêcher la distillation des acides iodhydrique et chlorhydrique jusqu'à l'absorbeur. Sinon, des colorations parasites se produiraient lors de l'addition du réactif organique.

(7) un absorbeur original à grande surface de contact.

La figure 1 représente schématiquement l'appareil.

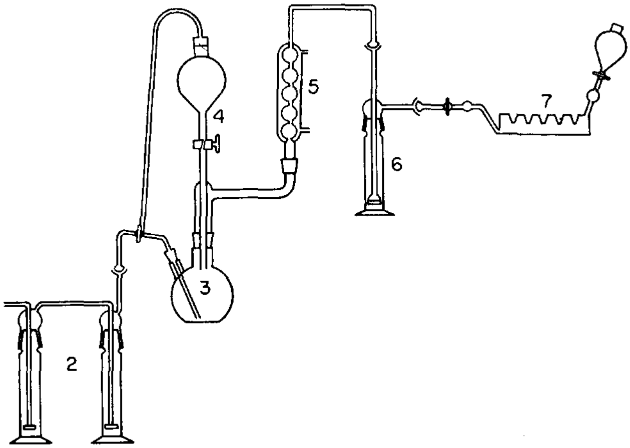


Fig. 1.—Schéma de l'appareil de distillation d'H_2S.

D. *Réactifs*

(1) *HCl* densité: 1,19

(2) *Acide formique* (*HCOOH*) 98 %

(3) *Mélange réducteur:* HI densité: 1,70 (56–57 %); H_3PO_2 densité: 1,274 (50 %); On mélange 100 cc HI et 25 cc H_3PO_2; on fait bouillir ce mélange pendant trois minutes et on garde en flacon bouché, à l'abri de la lumière.

(4) *Solution de lavage:* HCl 0,2 N et HI 0,1 %

(5) *Diméthyl para amino phénylène diamine. 2 HCl:* Dissoudre 0,5 gr dans de l'eau distillée. Ajouter 230 cc d'HCl concentré et amener à 500 cc par de l'eau distillée.

(6) *Solution de chlorure ferrique:* 0,6 à 0,7 gr de $FeCl_3 \cdot 6H_2O$ sont dissous dans 10 cc d'HCl concentré et cette solution est complétée au volume de 100 cc par de l'eau distillée.

(7) *Acétate de zinc* à 1 %: $Zn(C_2H_3O_2)_2$, $2H_2O$: Aciduler par 2 à 3 gouttes d'acide acétique par litre de solution afin d'empêcher le dépôt d'hydroxyde au cours de la conservation

(8) *NaOH:* solution aqueuse à 12 %

(9) *Sulfate de potassium* pour l'étalonnage: dissoudre 271,75 mgr dans 100 cc; reprendre 10 cc et amener à 500 cc par de l'eau distillée (1 cc = 10 μg S).

Remarque: Du fait de la grande sensibilité de la méthode, la pureté des réactifs a une grande influence sur la valeur de l'essai à blanc.

E. *Essai à blanc*

Les mêmes volumes de solution d'attaque et de solution absorbante sont mis en jeu en suivant exactement le même mode opératoire que celui décrit ci-après.

F. *Mode opératoire*

La prise d'essai est choisie de manière à mettre en jeu moins de 120 μg de S.* Cette prise d'essai est introduite dans le ballon d'attaque. Celui-ci est adapté sur l'appareil de distillation que l'on a préparé de la manière suivante:

Le laveur est rempli de 15 cm³ de la solution (4). L'absorbeur reçoit 2 cm³ de la solution (8) et 50 cm³ de la solution d'absorption (7). On sèche la tubulure d'entrée à l'aide d'une bandelette de papier filtre. Tous les rôdages sont graissés légèrement au moyen de graisse silicone Edwards. On balaye tout l'appareillage par un courant d'azote ou d'hydrogène pendant deux minutes environ. On introduit alors 15 cm³ d'HCl concentré dans l'entonnoir supérieur. On tourne le robinet à trois voies de façon à dériver le courant gazeux par la voie supérieure et on ouvre le robinet mettant en communication l'entonnoir et le ballon d'attaque.

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* Il est naturellement possible, en utilisant des cuvettes plus minces ou en opérant par dilution, de prolonger l'échelle de mesure dans le domaine des quantités de soufre plus importantes. Cependant, la loi de Beer n'étant pas respectée, il serait alors nécessaire de refaire un étalonnage dans les conditions choisies.

Dès que l'acide est complètement écoulé dans le ballon, on rétablit le courant d'azote par la voie normale* et on commence à chauffer le ballon de distillation. Le chauffage est réglé de façon à obtenir une ébullition douce après cinq minutes. Après une demi-heure, on observe, en général, une dissolution complète lorsque la prise d'essai n'est pas supérieure à 0,5 gr et que la granulométrie est suffisamment fine.

On isole alors le barbotteur au moyen de ses deux robinets et on le déconnecte. On y crée une légère dépression au moyen d'une trompe à eau en prenant garde de ne pas laisser aspirer de solution absorbante. Grâce au vide ainsi créé, les diverses solutions de rinçage et d'addition peuvent être introduites très rapidement dans l'absorbeur et sans risque de laisser échapper de l'hydrogène sulfuré.

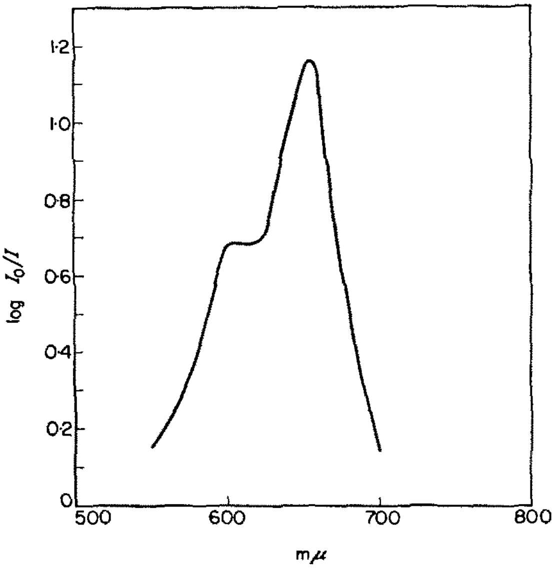

FIG. 2.—Courbe d'absorption du bleu de méthylène de 500 à 700 mμ: Concentration correspondant à 120 μg de soufre/100 cc. 50 cm³ acétate de zinc à 1 %—2 cm³ NaOH à 12 %—10 cm³ du réactif (5)—2 cm³ de la solution (6).

On introduit, par l'ampoule, 10 cm³ du réactif (5), puis on rince à l'eau distillée la tubulure d'entrée de l'absorbeur. On agite l'absorbeur bien fermé pendant environ une minute puis on y ajoute, par l'ampoule, 2 cm³ de chlorure ferrique, réactif (6). La coloration bleue apparaît assez rapidement et on continue à agiter vigoureusement pendant quelques minutes. L'addition du réactif (5) en solution chlorhydrique a, en effet, redégagé de l'acide sulfhydrique et il faut favoriser par l'agitation le contact entre la solution et la phase gazeuse.

Après une dizaine de minutes, le contenu de l'absorbeur est transféré dans un ballon jaugé de 100 cm³. Les eaux de rinçage de l'absorbeur sont ajoutées et l'ensemble est complété au volume par de l'eau distillée. Il est recommandé de mesurer la densité optique de cette solution dans un délai d'un quart d'heure à une heure après sa formation.

Nous avons effectué la colorimétrie en cuvettes de 2 cm d'épaisseur en utilisant un photomètre Spekker avec le filtre 608 ou en cuvettes d'un cm d'épaisseur avec un spectrophotomètre Beckman B.

La longueur d'onde du maximum d'absorption est assez controversée. G. Patterson Jr.[4] donne ce maximum à 745 mμ tandis que Roth[6] ainsi que Pomeroy[5] indiquent 670 mμ. La courbe d'absorption que nous avons relevée de 500 à 700 mμ est donnée dans la figure 2 (120 μg S/100 cc).

Après la fin de la dissolution chlorhydrique, lorsqu'on enlève l'absorbeur, on peut le remplacer par un second dispositif d'absorption contenant une solution identique.

On ajoute alors, par petites portions, 15 cm³ du mélange réducteur (3) à la liqueur d'attaque tout

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* Le courant entraîneur doit être suffisamment rapide pour obtenir un bon balayage de l'acide sulfhydrique, mais assez lent pour n'occasionner aucun entraînement mécanique important vers l'absorbeur. Pour l'appareil que nous avons utilisé (volume intérieur: environ 300 cm³), un débit de 7 litres/heure s'est révélé satisfaisant.

en maintenant le courant gazeux et le chauffage. On distille pendant 25 à 30 minutes l'acide sulfhydrique formé par réduction des formes oxydées du soufre[8,9] puis on isole le second absorbeur et on y développe la coloration du bleu de méthylène comme plus haut.

REMARQUES

(a) Lorsque l'appareil est resté quelques heures sans fonctionner, on apercoit, dans le réfrigérant et dans le tube qui le relie au laveur intermédiaire, des gouttelettes brunes provenant de l'oxydation de l'acide iodhydrique condensé sur les parois. Il est nécessaire d'éliminer ces gouttelettes, soit par un rinçage à l'eau, ou mieux en faisant distiller de l'acide iodhydrique pendant quelques minutes, réfrigérant coupé.

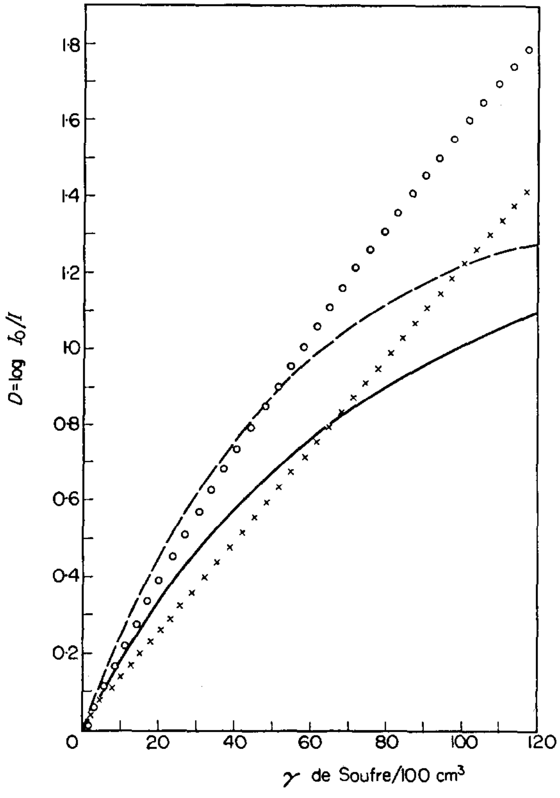

Fig. 3.—Densité optique des solutions de bleu de méthylène en fonction des quantités de soufre mises en oeuvre (en μg de S/100 cc).

—— bleu de méthylène produit à partir de H_2S distillé
- - - bleu de méthylène pesé et dissous dans l'acétate de zinc et HCl
} courbes d'étalonnage obtenues à l'absorptiomètre Spekker

+ + bleu de méthylène produit à partir de H_2S distillé
○ ○ bleu de méthylène pesé et dissous dans dans l'acétate de zinc et HCl
} courbes d'étalonnage obtenues au spectrophotomètre Beckman B ($\lambda = 655$ mμ)

En effet, le résultat de la première distillation d'une série s'est toujours révélé trop bas et ceci est dû très probablement à l'oxydation de H_2S par l'iode.

(b) Il est signalé dans la littérature[7] que le bleu de méthylène n'obéit pas à la loi de Beer Lambert. La courbe dans la Fig. 3 représente la variation de la densité optique mesurée au spectrophotomètre en utilisant des fentes très étroites ($\simeq$ 2 mμ). La loi de Beer est respectée jusqu'à des concentrations d'environ 100 μg de soufre/100 cc. Au-delà de cette concentration on observe des écarts relativement importants qui sont dus à des réactions secondaires avec le solvant, réactions qui varient donc avec la dilution.

Cependant, la Fig. 3 montre également que la densité optique des solutions de bleu de méthylène produit à partir de H_2S distillé est inférieure à celle des solutions de bleu de méthylène pesé et dissous dans le même milieu. Ceci provient de ce que la réaction de production du bleu de méthylène à partir de H_2S est limitée à un équilibre. (Après un quart d'heure d'agitation, lorsqu'on ouvre l'absorbeur, on sent encore l'odeur de H_2S, si les teneurs en S se situent dans la partie supérieure de l'échelle de mesure.) Il est d'autre part intéressant de noter l'influence vraiment importante du polychromatisme sur l'obéissance à la loi de Beer.

Pour le cas du Spekker, on se trouve ici dans des conditions peu favorables. Le filtre 608 présente une bande passante très large (350 mμ à D = 2; 80 mμ à D = 0,1) alors que le pic d'absorption du bleu de méthylène est relativement étroit. Au fur et à mesure que la concentration croît, les radiations peu absorbées prennent la prépondérance et il en résulte une densité optique apparente inférieure à la densité optique réelle en lumière monochromatique et qui s'en écarte de plus en plus.

G. *Etalonnage*

Les solutions de sulfures étant très instables et que les prises d'essai étaient trop faibles pour pouvoir utiliser directement des quantités pesées, nous avons préféré recourir à des solutions de sulfate potassique, (9).

Des quantités comprises entre 0 et 12 cm³ de la solution à 10 μg/cm³ ont été traitées dans le ballon d'attaque par 15 cm³ du mélange réducteur (3) pendant 25 à 30 minutes. Toutes les opérations ont été réalisées en respectant exactement le mode opératoire décrit ci-dessus et la courbe d'étalonnage est reprise a la Fig. 3.

H. *Résultats*

	Méthode proposée		S total dosé par gravimétrie %	S total dosé par combustion et iodométrie %	S évolution (sans coeff. de correction par échant. type) %
	S à l'état de sulfures %	S oxydé %			
Fer pur VN12	0,0047	0,0003		0,004 (Woestoff)	
	0,0046 0,0040	0,0004 0,0004		0,012	
Acier 4	0,0106 0,012	0,0014 0,0007	0,018	0,015–0,015	0,014–0,0145
Acier 5	0,014	0,0022	0,018	0,016–0,016	0,016–0,016
Acier 6	0,025	0,0022	0,029	0,032–0,032	0,027–0,027

II. DANS LE COBALT

Mode opératoire

Le cobalt s'attaquant beaucoup plus lentement dans l'acide chlorhydrique que les alliages ferreux, nous avons trouvé préférable de procéder de la façon suivante: 10 gr de cobalt sont attaqués par 40 cc d'acide nitrique concentré (d : 1,40). Celui-ci doit être ajouté par petites portions afin d'empêcher que la réaction ne s'emballe. Il est parfois nécessaire de refroidir le récipient d'attaque. Vers la fin de l'attaque, on commence à chauffer et on laisse bouillir 1 ou 2 minutes après la fin de la dissolution. On amène alors cette liqueur au volume de 200 cc et on l'homogénéise vigoureusement. On en prélève à la pipette 10–15 ou 20 cc que l'on introduit dans le ballon de l'appareil de distillation. On évapore cette solution jusqu'à ce que le volume soit réduit à environ 2 cc puis on ajoute 5 cc HCl. Une grande partie de l'acide nitrique s'élimine puis on ajoute 20 cc HCl et trois fois 0,5 cc d'acide formique au cours de l'évaporation qui suit.

On va jusqu'à un peu plus près de la siccité que la première fois, puis on ajoute à nouveau 10 cc HCl et 0,5 cc d'acide formique. On réédite exactement cette opération encore une fois, puis on évapore de nouveau jusqu'au même stade de siccité avant d'ajouter les dix derniers cc de HCl.

On évapore cette solution finale jusqu'à un volume d'environ 3–4 cc et on transfère le ballon sur l'appareil à distiller.

On procède alors à la distillation telle qu'elle est décrite pour le dosage du soufre oxydé dans les fers et les aciers.

L'étalonnage et l'essai à blanc sont réalisés conformément à ce dernier mode d'attaque.*

Résultats

Le tableau suivant montre la reproductibilité obtenue dans le cas de divers echantillons de cobalt métalliques de qualité commerciale.

Repères	Teneurs
N° 1	0,013—0,009
2	0,011—0,013
3	0,0115—0,0105—0,012—0,010
4	0,013—0,0125—0,0135
5	0,008—0,009
6	0,0085—0,009—0,009
7	0,010—0,011
8	0,016—0,013
9	0,018—0,0145—0,015
10	0,016—0,020—0,016
11	0,015—0,0135
12	0,012—0,0145
13	0,0135—0,0125
14	0,010—0,0105—0,011—0,0115
15	0,0095—0,010
16	0,0085—0,0095
17	0,008—0,0095
18	0,006—0,006—0,006—0,0065—0,006—0,006
19	0,010—0,0085
20	0,0125—0,015

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* Pour réduire la valeur de l'essai à blanc, il est recommandé de faire bouillir tous les acides avant leur utilisation. (Essai à blanc moins de 10 μg S.)

CONCLUSIONS GÉNÉRALES

La méthode proposée présente une grande sensibilité et est vraiment adaptée aux teneurs inférieures à 0,020%. En utilisant des prises d'essai d'environ un gramme, elle permet de doser des traces de l'ordre du millième de %.

Par ailleurs cette méthode ne requiert pas les précautions très sévères qui sont habituelles dans ces gammes de teneurs mais peut occasionnellement fournir des résultats erratiques. D'après Pomeroy, ceux-ci seraient dus à une élimination incomplète des nitrates.[5]

Dans le cas d'une attaque oxydante suivie de la réduction du soufre total, le dosage complèt dans une série dure 45 à 50 minutes. Dans le cas du dosage séparé du soufre "sulfures" et du soufre oxydé, la durée des deux analyses est d'environ 70 à 75 minutes. Dans le cas des aciers, nous pensons, de plus, que le dosage séparé du soufre "sulfures" et du soufre oxydé fournit au métallurgiste une donnée supplémentaire perfois très intéressante.

Summary—A method is proposed for the determination of small amounts of sulphur in steels, and in iron and cobalt, which involves conversion of the sulphur to hydrogen sulphide, and then conversion of this to methylene blue, using dimethyl-*p*-aminophenylenediamine. The methylene blue has an intense and relatively stable colour.

Various procedures have been proposed depending on the nature of the metal. For irons and steels sulphides are converted hydrochloric acid attack, and any oxidized forms of sulphur are reduced by a mixture of hydriodic and hypophosphorus acids. Cobalt is dissolved in nitric acid, thus converting all the sulphur to sulphate, which is subsequently converted by means of the same reducing mixture to hydrogen sulphide.

Zusammenfassung—Die zur Bestimmung von Schwefel in Metallen vorgeschlagene Methode beruht auf der Überführung des Schwefels in Schwefelwasserstoff und dessen Reaktion mit Dimethyl-*p*-aminophenylendiamin unter Bildung von Methylenblau, Die Farbe des Methylenblaus ist intensiv und relativ stabil.

Verschiedene Methoden wurden vorgeschlagen, abhängig vom Metall in dem der Schwefelgehalt bestimmt werden soll. Für Eisen und Stähle wird Salzsäure als Lösungsmittel verwendet und Oxyde des Schwefels werden mit einer Mischung von Jodwasserstoff und hypophosphoriger Säure reduziert. Cobalt wird in Salpetersäure gelöst wobei der gesamte Schwefel in Sulfat übergeführt wird, welch letzteres durch die obige Mischung zu Sulfid reduziert wird.

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A COMPARISON OF THE ALKALI METHOXIDES IN THE HIGH-FREQUENCY TITRATION OF ACIDS IN DIMETHYLFORMAMIDE*

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Summary—The five alkali-methoxides were prepared and standardized in 9 : 1 benzene-methanol solution. The strengths of these bases were compared by means of *HF* response and conductance curves and by means of the titration of a selected series of acids dissolved in dimethylformamide. The caesium and rubidium methoxides were the strongest bases. However the difference in basicity of these two methoxides as compared to potassium and sodium methoxide does not warrant their preferred use. Lithium methoxide acted as a very weak base in the 9 : 1 benzene-methanol solvent but became more dissociated as the concentration of the methanol was increased.

There was a small but definite drift of the Oscillometer as the concentration of the methoxide ion was increased. This was shown to be due to the slight reaction of the methoxide ion with the dimethylformamide.

Traces of acidic impurities in the dimethylformamide caused salicylic acid to behave as a weak acid while in very pure dimethylformamide it acted as a medium strong acid.

INTRODUCTION

MOST of the high-frequency titrations recorded by the early workers were in aqueous solutions. Since then a few investigators have studied certain titrations in a few non-aqueous solvents. The solvents used chiefly for weak bases have been glacial acetic acid and benzene-methanol solutions.

Ishidate and Masui[4] titrated some weak organic acids with sodium methoxide using a benzene-methanol solution as the solvent. Phenols and phenolic mixtures dissolved in benzene-methanol solutions were titrated with potassium methoxide by Karrman and Johansson.[5] Young[10] titrated some alkali halides in pyridine. Dean and Cain[1] titrated a number of organic acids in dimethylformamide with sodium methoxide.

The purpose of this investigation was to study the response and titration curves of a series of acids in dimethylformamide with the five alkali methoxides obtained by the high-frequency and conductance methods.

EQUIPMENT AND REAGENTS

Sargent Chemical Oscillometer Model V equipped with cell compensator, standard condenser type cell, and a Sola voltage transformer. Protect the instrument from drafts to avoid thermal drift.

Leeds and Northrup Campbell-Shackelton Shielded Ratio Box with accessories and No. 4920 dip cell. Store this cell in dimethylformamide when not in use.

Perkin-Elmer Model 154-C Vapor Fractometer with column K at 80°, flow rate of helium 55 mm/min and column pressure 15 psi.

Dimethylformamide: Brothers Chemical Co. No. 1943 and Du Pont technical grade. To purify further and to reclaim solvent, distil over solid potassium hydroxide and calcium hydride. Store the purified solvent as well as solutions under dry nitrogen.

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* Supported by the United States Atomic Energy Commission.

Benzene: A.C.S. grade. Shake with Drierite and distil over phosphorous pentoxide.

Methanol: A.C.S. grade. Reflux with magnesium turnings and distil.

Lithium, sodium, and potassium methoxides: Dissolve approximately 0.025 gram equivalents of the metal in 25 ml of cold methanol then dilute to 200–250 ml with 9 : 1 benzene-methanol solution. Standardize against benzoic acid, using thymol blue indicator according to the procedure described by Fritz.[8] Then prepare the standard 0.01*N* alkali methoxides by the proper dilution of a portion of the above known solutions.

Rubidium and caesium methoxides: In contrast to the rather elaborate apparatus used by Thomas[9] to prepare caesium methoxide, a simple procedure was used. Partly immerse a 50 mm × 400 mm Pyrex test tube containing 25 ml of dry methanol in a large Dewar flask containing an acetone-dry ice slush. Pass argon into the test tube throughout the procedure. Scratch the glass vial containing the metal, then break into the opening of the tube under the argon and immediately drop. At the temperature of the acetone-dry ice mixture the reaction proceeds quite slowly.

Store all methoxides under nitrogen for additional protection from carbon dioxide and moisture.

Dissolve the acids in dimethylformamide then dilute to 0.01*N*. Standardize the dichloroacetic acid against standard sodium methoxide.

All the methoxides dissolved readily in the 9 : 1 benzene-methanol solution at approximately 0.1*N* concentration. This 9 : 1 ratio was greater than was expected to be possible for sodium methoxide[3] and appeared to be about the upper limit for lithium methoxide.

EXPERIMENTAL PROCEDURE

Since dimethylformamide and other basic solvents absorb carbon dioxide rather rapidly the dry oscillometer and conductance cells were flooded with dry nitrogen before adding the solvent. Also nitrogen covered the solution during the titration and response curve procedures. The titration vessels were fitted with special Lucite covers.

All volumetric ware was dried and the air expelled with dry nitrogen. The burette was protected with drying tubes containing a desiccant and Ascarite. The flasks containing solutions were also kept in large desiccators charged with soda lime and phosphorous pentoxide or Ascarite.

As a special precaution all transfers of solutions were made with no or only minute contact with air or any moisture.

For the high-frequency measurements, after the instrument had been balanced to resonance, 100 ml of dimethylformamide and 5 ml (about 0.05 milliequivalent) of the sample were adedd to the cell. The titrant was added in 0.5-ml increments. Owing to the considerable drift of the Oscillometer after 8–10 ml of the titrant had been added, instrument readings were made precisely one half minute after the addition of each increment of titrant. The high-frequency response curves were obtained by adding 10 ml of 0.01*N* solution to 100 ml of dimethylformamide in 0.5-ml increments.

For the conductance vs. concentration curves and the conductometric titrations 170 ml of dimethylformamide were used in a 250-ml electrolytic beaker. Twenty ml of 0.01*N* methoxide and about 0.1 milliequivalent of acid were used.

DISCUSSION

The instrument response curves for acids represent the concentration of the protonated dimethylformamide ion which has large capacitance effect and also represent the degree of dissociation of the acidic substances. The response curves for the acidic substances (Fig. 1), and the similar slopes obtained by conductance, indicate that the NH_4^+ ion is quite acidic in dimethylformamide and that benzoic acid has a very low degree ionization.

The slopes of the response curves (Fig. 2), as well as the similar slopes obtained by conductance, for the alkali methoxides indicate that these methoxides, except lithium methoxide, appear as strong bases in the 9 : 1 benzene-methanol solution. The slopes obtained by conductance were similar. These slopes decrease as $CsOCH_3 > RbOCH_3 > KOCH_3 > NaOCH_3 > LiOCH_3$ which is parallel with the decrease in ionic size of the alkali metals. This is according to Fajan's rule[8] that covalent linkage is favoured by the small cation; the lithium methoxide is the most covalent compound while the caesium methoxide is the most ionic compound and is the strongest base of the alkali methoxides.

The instrument response curves (Fig. 3) indicate that the degree of ionization of the lithium methoxide increases as the ratio of the methanol is increased. Methanol is more polar and its concentration apparently controls the degree of dissociation of the lithium methoxide. Since the response curve for the 9 : 1 benzene-methanol solution is very near to that for the lithium methoxide in this solvent the degree of dissociation is very low. In solvents with relatively low dielectric constants, as that of dimethylformamide or below,[6,7] the lithium methoxide due to ion association may be in the form of ion-pairs which will not contribute to the capacitance or conductance of the solution. Then as the solution becomes more concentrated, triple ions may form which bear a charge and can contribute to the capacitance or conductance of the solution. An increase in the conductance of the lithium methoxide in the 9 : 1 benzene-methanol ratio was not observed in the very dilute solutions but was detected when the solution became about 7 × $10^{-4}M$.

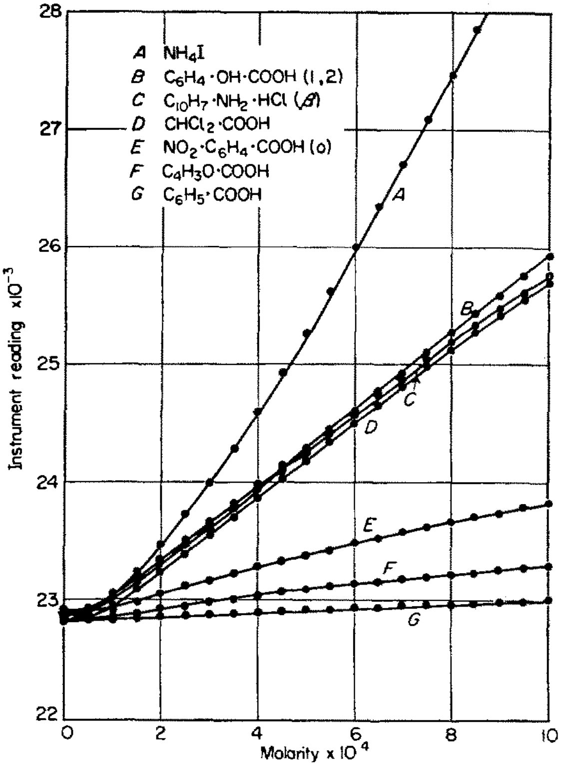


FIG. 1.—H-F response curves for acids and salts.

Increasing the ratio of methanol in the benzene-methanol solution had little effect on the other alkali methoxides. Thus the larger cations are more likely to be present in ionic form even though they are in a solvent of low dielectric value.[6]

When determining the response curves (Fig. 2), after a few millilitres of the alkali methoxide had been added to the dimethylformamide the drift of the Oscillometer became noticeable, as well as after the end-points during the titrations. It was observed that the magnitude of this drift increased with an increase in concentration of methoxide ion. The drift of the Oscillometer was negligible when operating under optimum conditions, *e.g.*, constant temperature, no draughts, and adequate warm up time. As expected, with an atmosphere of nitrogen or argon over the dimethylformamide there was no drift and the addition of pure benzene or methanol to the dimethylformamide produced no drift.

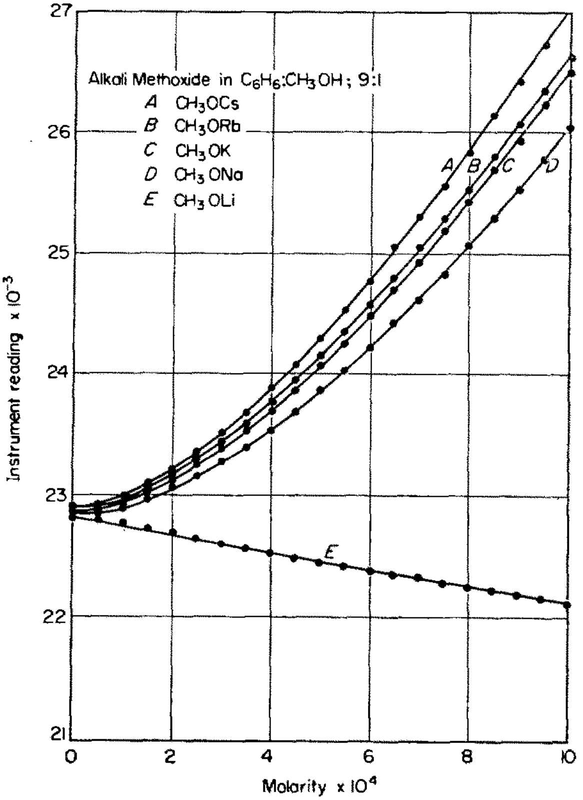
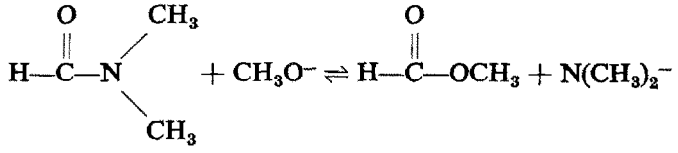


FIG. 2.—H-F response curves for the alkali methoxides.

With lithium methoxide in the 9 : 1 benzene-methanol solution there was a very small drift which increased greatly when potassium methoxide in 9 : 1 benzene-methanol solution or lithium methoxide in methanol was added. An increase in concentration of the methoxide ion also produced an increase in the magnitude of the drift, Fig. 4. Readings were recorded starting one minute after the addition of the initial quantity of the substance. The change in drift with respect to time indicates that the following equilibrium



$$H\text{—}\overset{O}{\overset{\|}{C}}\text{—}N(CH_3)_2 + CH_3O^- \rightleftharpoons H\text{—}\overset{O}{\overset{\|}{C}}\text{—}OCH_3 + N(CH_3)_2^- \qquad (1)$$

is being shifted slightly to the right due to the mass action effect of the methoxide ion though the dimethylamide ion is the much stronger base. The dimethylamide ion will protonate according to

$$H_3COH + N(CH_3)_2^- \rightleftharpoons H_3CO^- + HN(CH_3)_2 \qquad (2)$$

By the use of vapour phase chromotography the dimethylaminde and methylformate were both identified as being present. Due to the very small quantities present, the reaction mixture was swept with dry nitrogen and the vapours condensed in a cold trap immersed in an acetone-dry ice slush.

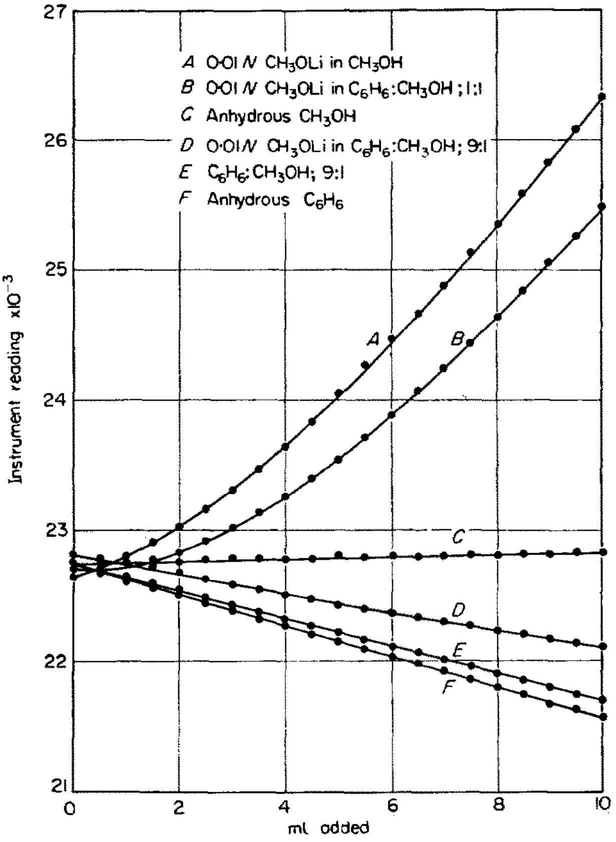
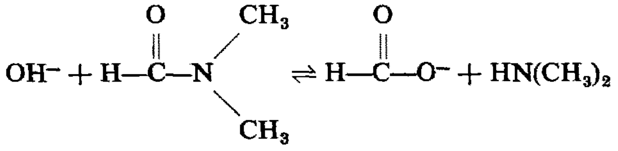


FIG. 3.—H-F response curves for $LiOCH_3$ and solvents.

The presence of water caused a rapid drift with an increase in capacitance (Fig. 4) due to the following:

$$CH_3O^- + H_2O \rightleftharpoons CH_3OH + OH^- \qquad (3)$$



$$OH^- + H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \rightleftharpoons H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- + HN(CH_3)_2 \qquad (4)$$

The effect of 0.2% water added to the dimethylformamide before the methoxide is shown by curve C. For curve D, Fig. 4, the dimethylformamide had been exposed to air for some time.

The dimethylformamide acts as a "non-levelling solvent" in the presence of the alkali methoxides. The dimethylamide ion, in Eq. 1, is a much stronger base than the methoxide ion consequently there is no levelling effect. If the concentration of the methoxide ion is increased by the use of caesium methoxide instead of lithium methoxide the equilibrium will shift slightly to the right and caesium methoxide acts as the stronger base.

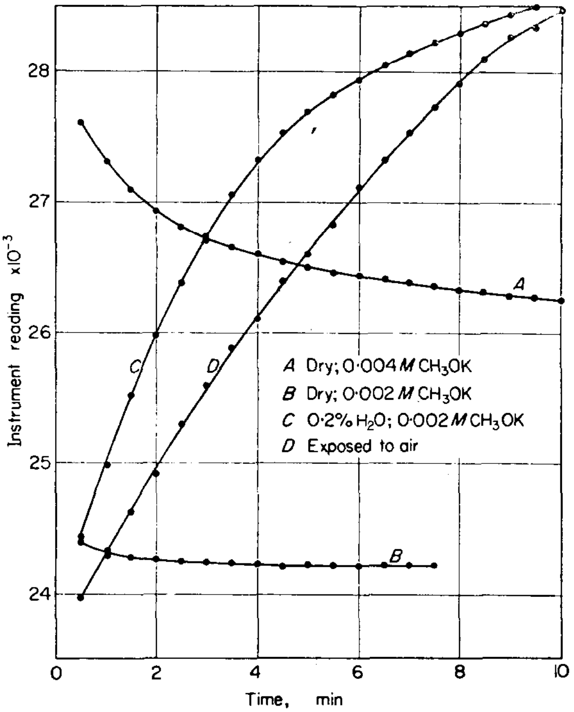


FIG. 4.—Drift of oscillometer; potassium methoxide in dimethylformamide.

The purity of the dimethylformamide may affect the shape of the response and titration curves. In this work using distilled dimethylformamide the response curves for the alkali methoxide and salicylic acid did not pass through a minimum, and salicylic acid did not behave as a slightly dissociated acid in concentrations above 0.0005M as reported by Dean and Cain.[1] In distilled dimethylformamide the titration curve for salicylic acid was characteristic of a medium strong acid (Fig. 5A) but in technical grade dimethylformamide (acid impurities neutralized to the thymol blue end-point with sodium methoxide) the titration curve was characteristic of a weak acid (Fig. 5B) and was similar in shape to the titration curve shown by Dean and Cain.[1] When the technical grade dimethylformamide was distilled as described for this work, salicylic acid reproduced the response and titration curves as observed with other distilled or redistilled solvent. This effect was not observed for any of the other acids reported in this work (Fig. 5) or for *p*-hydroxybenzoic acid. This behaviour of a solution of salicylic acid may be due to a tautomeric equilibrium between the classical and the chelate structures[2] and the impurities in the solvent shift the equilibrium to make the weak acid the predominant form.

The titration of the acids in dimethylformamide with the alkali methoxides is represented in Fig. 6. The differences in the angles at the end-point for the NH_4^+ ion and the different alkali methoxides are shown in Fig. 7. The high-frequency and conductance titration curves were very similar in shape.

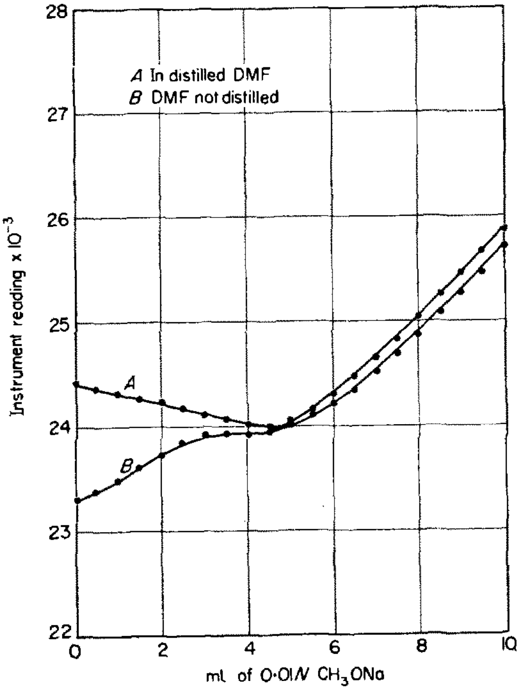


FIG. 5.—Titration of salicylic acid in distilled and non-distilled dimethylformamide.

Caesium methoxide and rubidium methoxide are the strongest bases of the alkali methoxides while lithium methoxide is the weakest in the 9 : 1 benzene-methanol solution. The strongest bases do produce slightly more acute end point angles as shown in Fig. 7; however the difference in basicity as compared to the potassium or sodium methoxide was not great enough to titrate successfully such very weak acids as phenol and do not justify their use due to the extra cost and care in handling, for ordinary use.

The end-points of the instrumental titration curves were in good agreement with the theoretical amount of acid when the strong methoxides were used as the titrant and in good agreement with the thymol blue end-points for those acids with a pK_a of 3 or less. The high-frequency method was more convenient to use than the conductometric method due to the greater ease of handling the cells in an inert atmosphere, since no solution was in contact with the electrodes. Also, the high-frequency method is useful for titrations if a coloured impurity is present and if the compound is coloured or changes colour during the titration. However this method offers no advantage when the proper indicators are available.

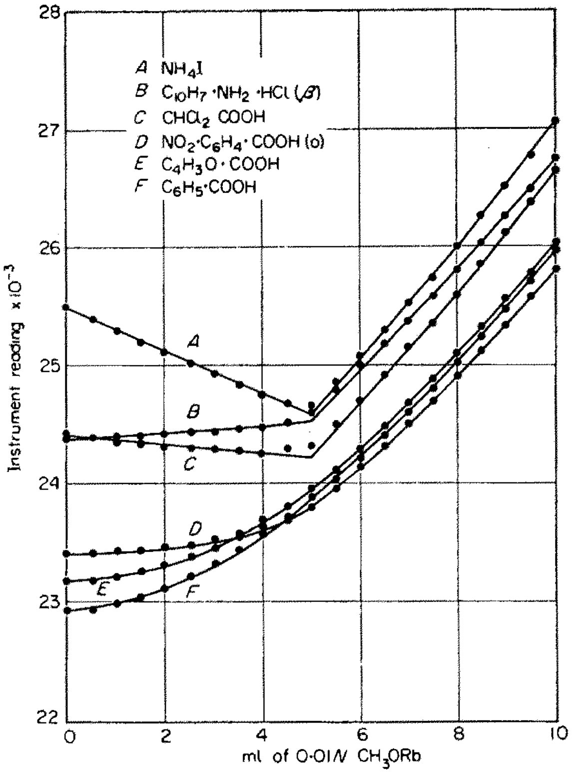


Fig. 6.—H-F titration curves of acids with rubidium methoxide.

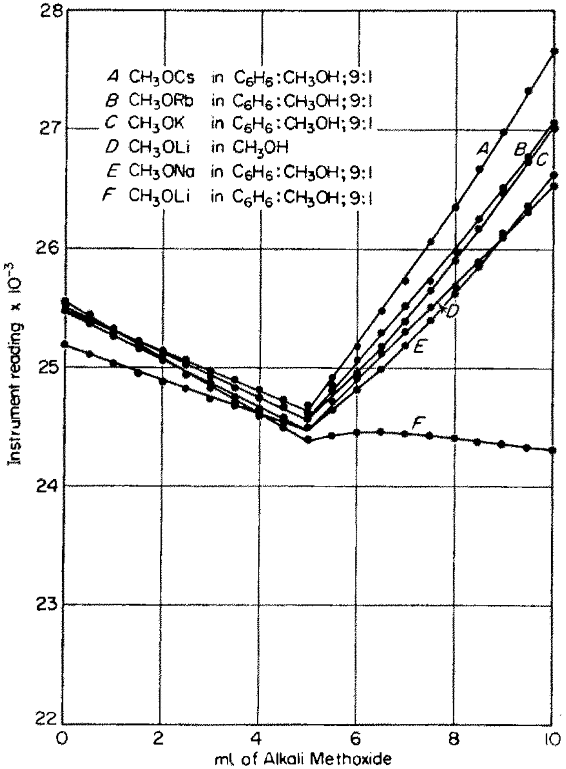


Fig. 7.—Comparison of the H-F titration curves for ammonium iodide with the alkali methoxides.

The high-frequency titration of the weak acids with lithium methoxide in the 9 : 1 benzene-methanol solution produced only a very small change of slope. This change in slope was after the stoichiometric end-point to the extent of about 10%. In the conductometric titrations this break appeared about 10% late or not at all.

Acknowledgement—The authors wish to express their appreciation to Dr. Ernest Grunwald, Florida State University; Dr. Jack Hine, Georgia Institute of Technology; and Dr. R. B. Scott, University of Alabama, for their advice concerning the instrument drift and the equilibria discussed in this paper. Also to Frank Unietis and Reichold Chemicals Inc. for their help and use of the vapor phase chromotography equipment. The financial support was from the U.S. Atomic Energy Commission contract No. AT-(40-1)-1354.

Zusammenfassung—Die fünf Alkalimethoxyde wurden hergestellt und in Benzol-Methanol (9 : 1) Lösung titriert. Die Stärke der Basen wurde durch Hochfrequenz- und Leitfähigkeitstitration ermittelt wobei verschiedene Säuren in Dimethylformamid gelöst als Titrationsmittel dienten. Caesium und Rubidum-methoxyd waren die stärksten Basen. Die Stärke ist jedoch keineswegs so beträchtlich höher, dass diese beiden Methoxyde denen des Natriums und Kaliums vorgezogen werden sollten. Litheummethoxyd war in 9 : 1 Benzol-Methanolmischung nur schwach basisch, doch nahm die Basizität zu, wenn der Methanolgehalt der Mischung gesteigert wurde.

Ein geringfügiges aber merkliches Wandern der Oscillometernadel konnte festgestellt werden, wenn die Konzentration des Methoxydions gesteigert wurde. Es konnte gezeigt werden, dass dies auf einer geringfügigen Reaktion des Methoxydions mit Diemthylformamid zurückzuführen ist. Spuren von sauren Verunreinigungen im Dimethylformamide bewirkten dass Salizylsäure als schwache Säure reagierte, während ihr Verhalten in völlig reinem Dimethylformamid das einer mittelstarken Säure war.

Résumé—Les cinq sels alcalins du methanol ont été préparés et étalonnés en solution benzène-méthanol (9 : 1). La force de ces bases a été comparée par des déterminations en haute fréquence et des courbes de conductivité et également par titrage d'une série sélectionnée d'acide dissous dans la dimethylformamide. Les méthanolates de cesium et de rubidium sont les bases les plus fortes. Cependant la différence entre la basicité de ces deux bases, et celle des méthanolates de sodium et de potassium, ne justifie pas leur emploi préférentiel. Le méthanolate de lithium se comporte comme une base très faible dans le mélange benzène-methanol (9 : 1) utilisé comme solvant, mais se dissocie davantage lorsque la concentration du méthanol augmente.

On observe sur l'oscillateur une faible mais nette dérive lorsque la concentration du méthanolate augmente. On montre que celà est produit par une légère action du méthanolate sur la diméthylformamide.

En présence d'impuretés acides dans la dimethylformamide, l'acide salicylique se comporte comme un acide faible alors qu'il réagit dans la dimethylformamide très pure comme un acide fort.

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TITRATION OF METAL OXINATES IN ETHYLENEDIAMINE WITH POTASSIUM METHOXIDE

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Summary—Several metal oxinates can be titrated with potassium methoxide in ethylenediamine solution, using conductometric end-point detection. The reliability of the method has been established using aluminium oxinate samples representing about 2–13 mg of aluminium. Errors are generally under 1%. Evidence is presented for a simple interpretation of the behaviour of the oxinates as weak acids in ethylenediamine solution.

BECAUSE important analytical chelate compounds such as the metal 8-quinolinolates (oxinates) would be expected to exhibit weak acidic and basic properties, it was of interest to investigate whether they could be determined by nonaqueous titrimetry. One could then combine the selectivity of such reagents to effect separations, with the advantage of direct titrimetry to conclude the determinations. Titrations of certain oxinates, notably aluminium, with perchloric acid in glacial acetic acid solution were described recently,[1,2,3] but it was found that most of the oxinates could not feasibly be titrated in this way. It was reasonable then to see whether their acidic properties could be utilized in titrations with a very strong base like potassium methoxide. Such titrations in solvents like ethylenediamine and dimethylformamide have been reported many times and are now commonplace,[4] but their application to important analytical precipitates appears to be new.

For an oxinate like that of aluminium in an ethylenediamine system, one might formulate the following equilibria using the simple Bronsted ideas but substituting an aluminium ion for a proton:

$$\begin{array}{c} \mathrm{Al(Ox)_3} + 3\mathrm{en} = (\mathrm{Alen_3})^{3+} + 3\mathrm{Ox^-} \\ (\mathrm{Alen_3})^{3+} + 3\mathrm{CH_3O^-} = \mathrm{Al(CH_3O)_3} + 3\mathrm{en} \\ \hline \mathrm{Al(Ox)_3} + 3\mathrm{CH_3O^-} = \mathrm{Al(CH_3O)_3} + 3\mathrm{Ox^-} \end{array}$$

where $\mathrm{Ox^-}$ represents an oxinate anion and en represents ethylenediamine. The titration process is then seen as a competition of three bases, oxinate, ethylenediamine, and methoxide, for the acidic aluminium ion. One might predict that the titration reaction would go well to completion because methoxide ion is obviously the strongest base, although it must be remembered that we are comparing bases with regard to their reaction with aluminium ion and not with the usual standard, namely hydrogen ion. In any case, the results show that the titration is feasible, not only for aluminium but for a number of other metal oxinates. Ultraviolet absorption spectra, mentioned below, support the above formulation.

Oxinate solutions in ethylenediamine are highly coloured, and it is not possible to perform the titrations visually. Conductometric end-point detection is emphasized in this paper, although potentiometric titrations with platinum or glass indicator electrodes and a calomel reference electrode can be performed as noted below. Conductivity measurements give stable and reproducible values, while electrode potentials in the systems studied are much more erratic. Photometric end-point detection would be possible in some cases, but precipitates which would interfere with the measurements form during the titrations with other oxinates.

The oxinates studied may be grouped into three classes: (1) Oxinates which give good to excellent end-points are those of aluminium, zinc, scandium, thorium, molybdenum, tungsten, vanadium, and magnesium. (2) Oxinates which give end-points that are fair to poor include uranium, copper, and manganese. (3) Oxinates of nickel, lanthanum, iron, and thallium yield no useful end-points at all. This grouping is naturally very rough; manganese, for example, is nearly as good as magnesium. Oxine itself gives a very good end-point.

Dimethylformamide was investigated briefly because in many ways it is a more convenient solvent with which to work than ethylenediamine, but the end-points were found to be much sharper in the latter solvent.

EXPERIMENTAL

Apparatus and reagents

The conductometric titration cell was a 150-ml beaker fitted with a rubber stopper which has holes for the electrodes, the burette, and the nitrogen inlet tube. Nitrogen simply escaped through the opening for the burette. The electrodes were platinized platinum foil, each 1 cm^2, tap-welded to short lengths of platinum wire which were sealed into soft glass tubing. The cell constant for the set-up used for most of the titrations was 0.28 cm^{-1}, as determined by measuring the resistance of a 0.100M aqueous potassium chloride solution at 25°. Measurements were performed with a Model RC-1B conductivity bridge from Industrial Instruments Inc. The burette was a 10-ml microburette graduated at intervals of 0.02-ml. A magnetic stirrer with a Teflon-coated stirring bar was employed. The titration cell was placed in a large pan of water at room temperature to minimize the effect of temperature changes upon the conductance values during the titrations. Potentiometric titrations were performed in a similar cell with Beckman glass-calomel or platinum-calomel electrode systems, using a Beckman "Zeromatic" pH meter. Ultraviolet absorption spectra were measured in 1-cm quartz cells with a Beckman Model DU spectrophotometer equipped with a hydrogen discharge tube.

The nitrogen used to blanket the solution in the titration cell was passed through a tube packed with Ascarite and silica gel. Ethylenediamine solvent was Eastman "white label", 98%. In the beginning, this was distilled from sodium and activated alumina, and collected under nitrogen, but later it was found to be suitable for use directly, provided a blank titration was run. The blank, generally less than 0.1-ml of 0.1N titrant for a 75-ml portion of the solvent, could be determined conductometrically or visually using azo violet indicator. Fresh bottles of ethylenediamine were transferred under nitrogen to all-glass siphon bottles protected by silica gel and Ascarite and provided with stopcocks for easy dispensing. Of a number of greases tested for these stopcocks, the best was Sisco 300 (from the Swedish Iron and Steel Co., Westfield, N.J.) as Katz and Glenn had found previously.[5] This grease was also more resistant than most to the titrant solution, although it was necessary to regrease the burette stopcock each day.

The titrant was 0.1N potassium methoxide in benzene-methanol, prepared according to the directions of Fritz and Keen.[6] It was stored in a siphon bottle protected from the air, and was delivered to the burette through a Teflon stopcock. This solution was standardized against aluminium oxinate by conductometric titration as described below. Sodium methoxide can be used as the titrant, but the end-points are slightly sharper with potassium.

The metal oxinates were prepared by various methods which are summarized in Hollingshead's monograph.[7] It is realized that there are doubts regarding the exact compositions of some of these compounds. In particular, there is often disagreement about the effect of drying temperature upon composition. Most of the quantitative work reported here was done with aluminium oxinate, about whose composition there seems to be no controversy. Actually, the titration method suggested here might be useful in studying the compositions of some of the uncertain oxinates.

Titration procedure

A weighed quantity of the metal oxinate was placed in a 150-ml beaker, and the stopper bearing the electrodes and nitrogen inlet tube was inserted. 75-ml of ethylenediamine was then introduced through the hole for the burette; nitrogen flow over the solution was started as soon as sufficient ethylenediamine had been added to prevent dry particles of oxinate from blowing away. The solution was then placed in the pan of water over the magnetic stirrer, the burette was inserted with its tip in the liquid, and the titration was begun. After each addition of desired increments of titrant, the stirrer was stopped, and the resistance of the solution was measured. Because the titration curves are generally not strictly linear except fairly near the end-point (within, say, 1 to 2-ml), it was best to get a number of points near the end-point and not rely upon too extreme an extrapolation. Conductance values were corrected for dilution, and then the results were plotted for graphical determination of the end-point. The scale was blown up considerably so that the graphical process itself did not limit the obtainable accuracy.

So long as the numbers are consistent, the conductance units chosen for the plotting are obviously unimportant. In the figures in this paper, the conductances are in arbitrary units, but the units are the same for all the curves shown. To give an idea of the actual conductance values, it is mentioned that the number 100 on the figure ordinates represents an actual specific conductance of about 2.8×10^{-6} ohm^{-1}cm^{-1}.

The benzene-methanol titrant, compared with water, has a fairly large coefficient of thermal expansion. Thus all volumes of titrant read from the graphs were corrected to a standard temperature of 22° using the equation

$$V_{22} = V_t\left(\frac{1 + 22\alpha}{1 + t\alpha}\right)$$

which is obtained from the usual equation

$$V_t = V_0(1 + \alpha t + \beta t^2 + \alpha t^3)$$

by dropping the negligible higher-order terms and eliminating V_0 between the two temperatures involved. A weighted mol fraction mean value, based upon the ratio of methanol to benzene in the titrant solution, was used for α.

Aluminium oxinate dissolves rather slowly in ethylenediamine at room temperature. Rather than warming to effect complete solution, it was convenient to start the titration even though some suspended material remained. The solution cleared early during the titration, and the important points near the end-point were not jeopardized.

RESULTS

Titrations of various oxinates

Fig. 1 shows potentiometric titration curves for zinc oxinate using glass-calomel and platinum-calomel electrode systems. Successful potentiometric titrations of aluminium oxinate have also been carried out. But such titrations were generally frustrating. The electrodes equilibrated very slowly with the solutions, as much as an hour sometimes being required to complete a titration. Occasionally no electrode response whatsoever was obtained during a titration. And sometimes sudden emf changes of several hundred millivolts occurred for no apparent reason. These problems might have been overcome with experience, but the potentiometric titrations were abandoned when it was found that conductometric titrations worked very well.

Fig. 2–5 show conductometric titration curves for a number of oxinates. Most of these resemble typical weak acid-strong base titration curves as seen in the more familiar aqueous system. Aluminium oxinate was chosen for a more detailed study because it is probably the best known, most thoroughly studied, and most widely used of the metal oxinates.

Titrations of aluminium oxinate

Table I shows the results of a number of titrations of aluminium oxinate samples ranging from about 29 to 228 mg. The table is formulated on the basis of the corresponding quantities of aluminium (about 1.7 to 13.4 mg), which are perhaps of more interest. The average absolute error is 0.062 mg, which represents an average relative error of 0.9 %. If one omits the 5 worst results (numbers 1, 6, 7, 9, and 10), the relative error drops to 0.6 %, but all the results are retained in the table to indicate what may be expected in practice. Four of the worst 5 results are too high, suggesting that inadvertent admission of carbon dioxide (which is a strong acid in this system) to either the titrant or the ethylenediamine solution may have been the source of most of the occasional large errors, despite the exercise of reasonable care. It is felt that the results reported here are the best obtainable consistent with speed and convenience; unusual precautions could probably increase the accuracy slightly.

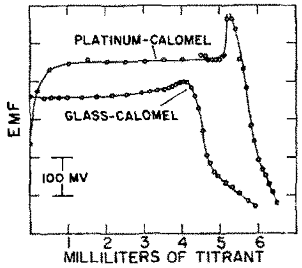

FIG. 1.—Potentiometric titration curves for zinc oxinate.

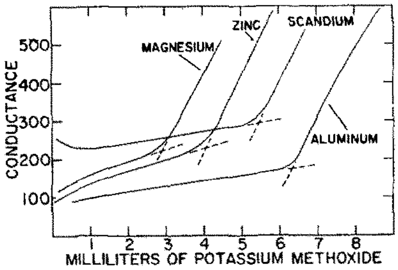

FIG. 2.—Conductometric titration curves for metal oxinates

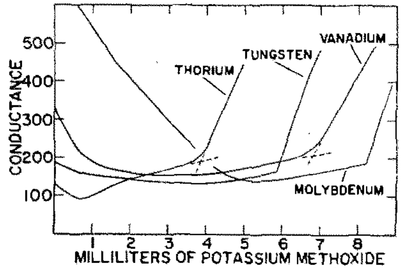

FIG. 3.—Conductometric titration curves for metal oxinates

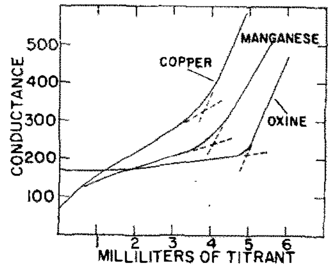

FIG. 4.—Conductometric titration curves for metal oxinates.

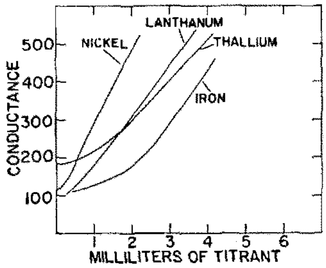

FIG. 5.—Conductometric titration curves for metal oxinates.

TABLE I.—RESULTS OF CONDUCTOMETRIC TITRATIONS OF ALUMINIUM OXINATE

No.	Al taken, *mg*	Al found, *mg*	error, *mg*	relative error, %
1	1.721	1.750	0.029	1.7
2	3.095	3.082	0.013	0.4
3	3.494	3.485	0.009	0.3
4	5.010	4.975	0.035	0.7
5	6.037	5.969	0.068	1.1
6	6.096	6.224	0.128	2.1
7	6.120	5.991	0.129	2.1
8	6.272	6.335	0.063	1.0
9	6.372	6.521	0.149	2.3
10	6.595	6.725	0.130	2.0
11	6.813	6.825	0.012	0.2
12	6.960	6.917	0.043	0.6
13	7.018	7.050	0.032	0.5
14	7.165	7.145	0.020	0.3
15	7.294	7.320	0.020	0.3
16	7.899	7.927	0.028	0.4
17	9.403	9.399	0.004	0.0
18	11.206	11.072	0.134	1.2
19	13.437	13.313	0.124	0.9
			average: 0.062	0.9

Effect of water on the titration of aluminium oxinate

Because in practice one might wish to titrate aluminium oxinate precipitated from aqueous solution, it was desirable to study the effect of water on the titration to see if it would be necessary to dry the precipitate. Fig. 6 shows that up to only

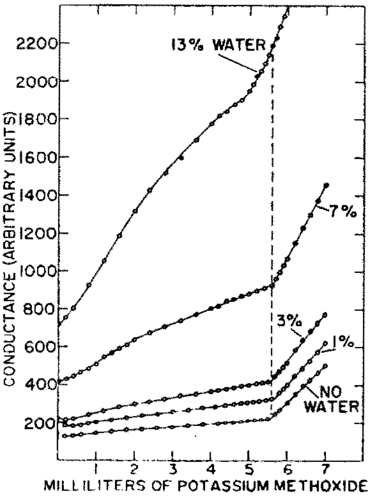

FIG. 6.—Effect of water on the titration of 100 mg of aluminium oxinate.

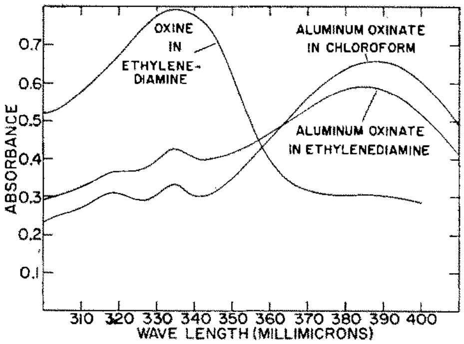

FIG. 7.—Ultraviolet absorption spectra of oxine and aluminium oxinate: all solutions $3 \times 10^{-4}M$ in chromophore.

slightly more than 7% of water in the ethylenediamine solvent is well tolerated. (Percentages of water shown in the figure are approximate volume percentages based upon volumes taken and neglecting the slight volume change which occurs when water and ethylenediamine are mixed.) It is apparent that in handling fresh aluminium oxinate precipitates, suction filtrations or centrifugations would remove enough of the water to permit titration, and special drying would be unnecessary.

Absorption spectra

Fig. 7 shows ultraviolet absorption spectra which are pertinent to the consideration of the dissociation of aluminium oxinate in ethylenediamine solution. Oxine itself exhibits an absorption maximum at about 335 mμ in ethylenediamine (in carbon tetrachloride, an inert solvent, the peak occurs at about 320 mμ). Aluminium oxinate in chloroform exhibits a small peak in this same region, and a larger one at about 385 mμ which is not shown by oxine itself. But when aluminium oxinate is dissolved in ethylenediamine, the absorbance at the peak near 335 mμ increases, while that at 385 mμ decreases. As the figure shows, this shift in the aluminium oxinate spectrum toward that of oxine itself in ethylenediamine solution is far from complete, but it is appreciable, and it supports the dissociation picture presented earlier in this paper. Because copper ions generally have a much stronger affinity for nitrogen ligands than do aluminium ions, one might predict a much more pronounced spectral shift for copper oxinate in ethylenediamine, indicating greater dissociation than in the aluminium case. This is found to be true, although to save space the spectra are not shown here. The poorer titration curve for copper oxinate as compared with the less dissociated aluminium oxinate might then be interpreted as indicating that the titrant was not sufficiently more basic than the solvent to give equally good results, the term "basic" referring here to the tendency to accept copper ions.

Zusammenfassung—Mehrere Metalloxinate wurden in Äthylendiaminlösung mit Kaliummethoxyd konduktometrisch titriert. Die Zuverlässigkeit der Methode wurde an Hand von Analysen von Aluminiumoxinatproben (entsprechend 2–13 mg Al) gezeigt. Der Fehler ist im allgemeinen kleiner als 1%. Eine einfache Deutung des Verhaltens des Oxinates als schwache Säure in Äthylendiaminlosungen wird mitgeteilt.

Résumé—Plusieurs oxinates métalliques ont pu être titrés par le méthanolate de potassium en solution dans l'éthylène-diamine le point équivalent étant déterminé par conductimétrie. La méthode a été testée sur des échantillons d'oxinate d'aluminium correspondant à 2 à 13 mg d'aluminium. Les erreurs sont en général inférieures à 1%. Il est présenté une interprétation simple montrant que les oxinates se comportent comme des acides faibles dans des solutions d'éthylénediamine.

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ACTIVATION-ANALYSIS OF TRACE COBALT IN TISSUE USING 10.5-MINUTE 60m-COBALT

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Summary—Microgram amounts of cobalt from vitamin B_{12} have been analyzed by rapid activation-analysis in rat kidney tissue as well as in vitamin preparations. A 15-minute radiochemical separation procedure coupled with gamma-ray spectrometry permitted utilization of the 10.5-min ^{60m}Co radioisotope. With this procedure the lower limit of detection at a thermal neutron flux of 10^{12} n/cm^2 sec was about 5×10^{-8} grams of cobalt.

INTRODUCTION

SINCE the advent of vitamin B_{12} as a medicinal for the treatment of certain hæmatological disorders, considerable attention has been focused on the determination of cobalt in biological systems. Saltzman and Keenan[1] have presented a review of the methods used for the microdetermination of cobalt in biological materials. Determination of this element by conventional wet chemical procedures coupled with spectroscopy or sensitive colour reactions frequently lacks sensitivity or is complicated by trace contamination from the reagents. In many cases, however, the use of radioisotopes can offer a rapid and sensitive procedure to assist in this analysis.

Until now much effort has gone into using radioactive tracers of cobalt, or labelled vitamin B_{12}, in exploring the distribution of this element in biological systems. Several procedures have been described for the production of vitamin B_{12} labelled with ^{60}Co either by a biosynthetic route[2,3] or by direct slow neutron irradiation.[4] This labelled vitamin is available routinely[5] for tracer studies of pernicious anæmia in humans and is used in an isotope-dilution method for the assay of vitamin B_{12} as described in the U.S. Pharmacopoeia.[6]

Published studies of tracer distributions include work with injected ^{60}Co in polycythemic rats,[7] metabolism of ^{60}Co-labelled vitamin B_{12} by the rat,[8] and the distribution of orally administered ^{56}Co-labelled vitamin B_{12}.[9]

Another method for determining the distribution of trace amounts of cobalt in a system is to analyse directly for this element but for many systems the sensitivities required eliminate most standard analytical techniques. Activation-analyses for trace amounts of cobalt have, however, been made on many types of samples using the long-lived ^{60}Co. Smales, Mapper and Wood[10] have given an excellent discussion of the procedures used in the analysis of rocks and marine sediments by this technique. They checked the accuracy of their methods by analysing standard steel samples and report working sensitivities for cobalt of about 10^{-8} grams. The disadvantage of this method is that the 5.2-year ^{60}Co formed requires a long activation to attain these sensitivities and many days may elapse between the time that an analysis is started (the beginning of the irradiation) and the time that the results can be obtained.

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We have been using the facilities of the Ford Nuclear Reactor at the University of Michigan to explore the use of short-lived radio-isotopes in activation-analysis. These rapid activation and measurement facilities have been coupled with a fast radiochemical separation to determine cobalt (by the 10.5-min ^{60m}Co) in the kidneys of rats that had been given unlabelled vitamin B_{12}.

EXPERIMENTAL

Apparatus

Samples were irradiated in polyethylene snap-type "rabbits" in the pneumatic tube system of the Ford Nuclear Reactor of the University of Michigan. This system permits irradiations at thermal neutron fluxes of about 10^{12} n/cm^2 sec (when the reactor is operating at full power of 1 megawatt) and delivery to a hood in the neighbouring Michigan Memorial Phoenix Laboratory within 3 seconds after the end of irradiation. Samples were then worked up chemically and were measured by a 3" × 3" NaI(Tl) crystal coupled with a special 100-channel pulse-height analyzer with duplicate memories. This equipment has been described in detail elsewhere.[11-13]

Preparation of animals and tissue

Holtzman* albino male rats weighing between 275 and 350 g were used in this study. They were maintained on Rockland Rat Diet† and had free access to drinking water. With the exception of animals No. 1 and 2, intraperitoneal injections of vitamin B_{12}‡ containing 45 micrograms§ of Co were administered 10 to 12 hours before sacrificing. Animal No. 1 received three 45 microgram doses 24 hours apart while animal No. 2 received two doses 24 hours apart. Both the kidneys and the liver tissue were surgically removed for analysis; however, the kidneys were found to be more readily adaptable to the chemical procedure.

The weighed tissues were allowed to air dry at room temperature for 24 hours and then re-weighed. They were placed in envelopes prepared from 4 mil thick polyethylene film, which were closed by heat sealing. The sealed sample was then irradiated in the "rabbit" along with suitable monitoring foils for a period of 30 minutes at full power.

Radiochemical separation

While the sample was being irradiated a nickel crucible was prepared containing 10 mg of Co carrier solution plus a known amount of 5.2-year ^{60}Co tracer. Three sodium hydroxide pellets were added and the solution heated almost to dryness. Two minutes before the end of the irradiation 10 g of sodium peroxide were added to the crucible and melted.

The irradiated sample was then fused in this melt for 1 minute. (CAUTION: A cover must be used on the crucible since the reaction may be quite violent.) The outside of the crucible was then cooled by dipping it into a beaker of cold water and the melt made to solidify in a thin, readily dissolved coating by manipulation of the crucible. The melt was then dissolved by immersion in 50 ml of distilled water, and 50–70 ml of liquid nitrogen were added to cool the solution to room temperature. Fifteen to twenty ml of glacial acetic acid were then added slowly and the solution was again cooled with liquid nitrogen.

This mixture at a pH of 5–6 was then transferred to a 150-ml separatory funnel containing 25 ml of 8-hydroxyquinoline solution (3% solution in chloroform) and shaken for 1 minute. Ten ml of 9*M* HCl were used to re-extract the cobalt from the organic layer. Co was then precipitated as the oxide from the HCl solution by addition of Na_2O_2. This precipitate was collected on a filter chimney,¶ was washed with water, and mounted for measurement on the spectrometer. The entire procedure could be completed in about 15 minutes with an average recovery of about 40% of the cobalt.

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* Holtzman Company, Madison 4, Wisconsin.

† A product of Rockland Farms, New City, N.Y.; Manufactured by A. E. Staley Mfg. Co., Chicago 27, Illinois.

‡ Injection Vitamin B_{12}, (1000 micrograms/ml.), University Hospital Control No. 1104580, Ann Arbor, Michigan.

§ Based on the value of 4.5% as the amount of Co in Vitamin B_{12} N. G. Brink, *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 1854.

¶ If foaming occurs add 10–15 ml of 0.1*M* HCl.

Activity determination

Linearity of the measurement system was established by the use of ^{137}Cs, ^{60}Co, ^{203}Hg, ^{75}Se, and ^{113}Sn standards. Spectra were obtained in the energy ranges of about 0–0.25 and 0–2.0 MeV as shown in Fig. 1. The amount of ^{60m}Co was determined from the area under the 0.059 MeV photopeak while correction for chemical yield was made by measuring the recovery of the long lived tracer ^{60}Co utilizing the 1.17 and 1.33 MeV photopeaks.

Monitoring procedures

Gold foils weighing between 0.5 and 1.0 mg were wrapped in plastic envelopes and scotch taped to the inside of the cap of the "rabbit." Following irradiation the foils were dissolved in 4 ml of *aqua regia* and diluted to 10 ml with distilled water. An aliquot of this solution was placed on a filter paper and mounted for measurement of the 411 keV gamma ray of ^{198}Au on the spectrometer. Comparison with other measurements made with calibrated gold foils permitted normalization of all irradiations to a neutron flux of 1×10^{12}.

RESULTS AND DISCUSSION

Preliminary experiments were carried out using this procedure without the chemical separation on pure materials. Aliquots of the Vitamin B_{12} injection were sealed in polyethylene tubing and irradiated in the same manner as described for the kidney samples. Spectral determinations in the 0–0.25 MeV range permitted the measurement of peak areas for the 0.059 MeV gamma ray emitted during the decay of the ^{60m}Co. Successive spectra, taken at several-minute intervals, showed that the peak decayed with the 10.5-minute half life of this isomer. Analysis of decreasing concentrations of Vitamin B_{12} showed the lower practical limit of detection to be about 5×10^{-8} g of cobalt. The same procedure was performed on cobalt nitrate solutions with similar results.

Preliminary studies to determine the level of naturally occurring Co in normal rat kidney tissues indicated that it was less than 10^{-8} g, or below the limits of detection for this method at a flux of 10^{12}. Thus experiments were conducted to determine the tissue level of Co after administration to the rat of a Co-containing pharmaceutical (Vitamin B_{12}).

Determinations made on tissues from ten different rats show that this method is readily applicable to μg amounts of Co in biological systems. The results, summarized in Table I, indicate that under the conditions of these experiments 1–3 μg of Co are found in rat kidney tissue 10–12 hours after the intraperitoneal administration of 45 μg of Co as Vitamin B_{12}. This does not indicate that the Co is present as Vitamin B_{12} in the kidney but rather that the Co portion of the molecule is excreted via the kidney.

The chemical procedure went smoothly although Cu and Mn were found to be interfering elements. These elements are present in considerably greater quantities than Co in the kidney and this particular rapid procedure did not separate them completely. Half-life studies and energy determinations with the gamma spectrometer indicated that the 12.8-hour ^{64}Cu and 2.6-hour ^{56}Mn were responsible for the contamination. Attempts to reduce this contamination by extractions with EDTA, dithizone, and NH_4CNS resulted in a significant decrease in the per cent recovery of the Co. Since for our work we were able to separate and determine the Co radiations by gamma spectrometry in the presence of the Cu and Mn, no further refinement of the chemical procedure was attempted at this time.

It should be pointed out that somewhat higher sensitivities can be obtained in

TABLE I.—ACTIVATION ANALYSIS FOR COBALT IN RAT KIDNEY TISSUE USING ^{60m}Co

Animal number	Live weight (gms.)	Co administered as vitamin B_{12} (μg)	Fresh kidney weight (gms.)	Yield of separation procedure (%)	Co found in kidneys (μg)*
1	335.7	135	2.47	39.4	8.85
2	323.4	90	2.02	40.3	6.60
3	315.3	45	2.38	23.8	3.02
4	268.1	45	1.87	38.8	1.80
5	287.2	45	2.12	49.5	3.37
6	363.0	45	2.19	50.4	2.18
7	374.0	45	2.28	44.3	1.60
8	349.3	45	2.27	53.8	2.56
9	259.2	45	1.98	35.7	1.25
10	363.5	45	2.10	36.9	1.94

* Corrected to neutron flux of 1 × 10^{12} n/cm^2 sec.

activation-analysis when gross gamma counting is used instead of spectrometry. Thus an improvement in the specificity of the Co separation to reduce the Cu and Mn to a point where the ^{60m}Co activity is the primary activity present would permit

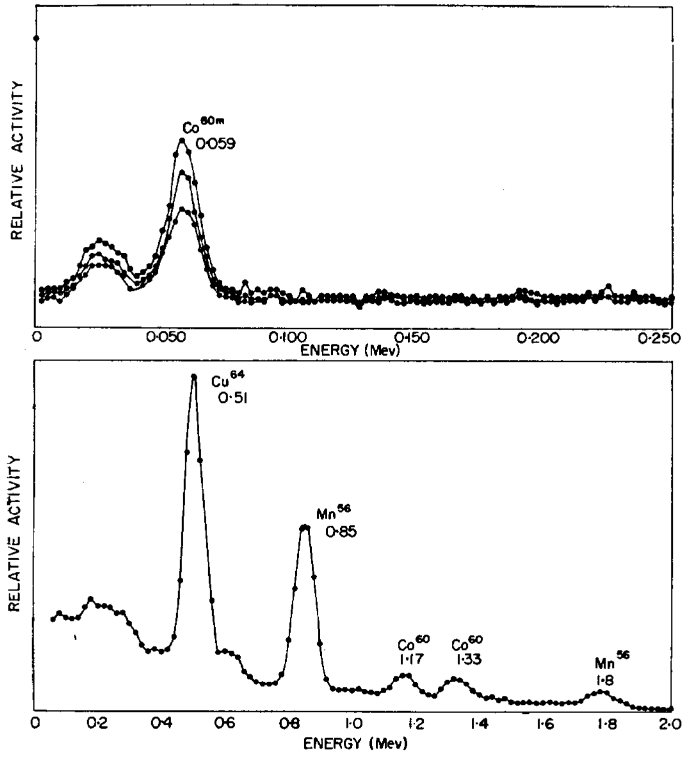

FIG. 1.—Gamma-ray spectra of cobalt fraction separated from rat kidney tissue. Spectra in top curve taken at four-minute intervals. Bottom curve taken after short-lived ^{60m}Co has decayed out.

utilization of this method without elaborate spectrometry equipment and in addition would probably increase the sensitivity by a factor of 2–5.

The variability of individual rats does not permit an exact evaluation of this method such as is possible using standard samples of alloys, etc. The results of Table I do, however, show the right order of magnitude for the relative values. The overall reproducibility of the method for tissue samples was shown to be around 10% at these microgram levels by several runs in which known amounts of cobalt were added to rat liver before the analysis.

Preliminary investigations have also shown that this procedure may be readily adapted to the analysis of Co-containing vitamin capsules such as Myadec.* Single gelatin capsules were irradiated and subjected to the previously described chemical separation. Since Cu and Mn were also separated with this procedure a simultaneous determination of these elements could be performed using gamma spectrometry. The spectra obtained for this type of sample are quite similar to those shown in Fig. 1.

CONCLUSION

Thermal neutron activation analysis has definite advantages over tracer studies for the determination of pharmaceutical localization. For medicinals amenable to this type of procedure the advantages are (1) the biological system is not exposed to radiation during the course of the experiment, (2) utilization of short-lived radioisotopes reduces the possibility of prolonged contamination, and (3) there is no problem of disposal of contaminated animal wastes such as carcasses or excreta. In addition, analysis by activation eliminates the problem of reagent blanks, so common to other analytical techniques.

Furthermore, the use of 10.5-min ^{60m}Co in activation-analysis has been shown to be feasible and permits completion of analyses of this sort within a period of an hour or so rather than of days or weeks.

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Zusammenfassung—Microgrammengen von Cobalt aus Vitamin B_{12} wurden im Gewebe von Rattennieren und auch in Vitaminpräparaten bestimmt. Es wurde eine Schnellaktivierungsmethode verwendet. Eine 15-Minuten radiochemische Trennungsmethode in Verbindung mit Gammstrahlenspectrometrie gestattete die Verwendung des 10.5 Min. ^{60m}Co-Isotopes. Bei der Methode lag die untere Grenze der Bestimmbarkeit bei einem von einem Thermal-Neutronen Strom von 10^{12} n/cm^2 sec bei etwa 5×10^{-8} gram Cobalt.

Résumé—On dose quelques microgrammes de cobalt provenant de vitamine B_{12}, issue de tissus de rein de rat aussi bien que de préparations de vitamine, par une analyse par activation rapide. Une méthode de séparation radio-chimique de 15 minutes associée à une spectrometrie gamma permet l'utilisation de radioisotope 10,5 min ^{60m}Co. Par ce procédé la limite inférieure de détection pour un flux de neutrons thermiques de 10^{12} n/cm^2 sec. est d'environ 5×10^{-8} gramme de cobalt.

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QUANTITATIVE OXIDATIONS BY POTASSIUM FERRICYANIDE

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Summary—Titrimetric methods using potassium ferricyanide as an oxidant for the estimation of various inorganic and organic substances are reviewed. An attempt has been made to evaluate the importance of these methods. Although the emphasis is on the literature that appeared in the past five years, some older procedures are included because of their significance.

In contrast to commonly employed oxidants such as permanganate, cerate, halogens and several others, the use of potassium ferricyanide is relatively limited. Much of the work reported in this field is fragmentary and no extensive review or summary is available on potassium ferricyanide as an oxidizing agent in quantitative analysis. Thyagarajan[1] reviewed oxidations by ferricyanide from the standpoint of synthesis and reaction kinetics of organic compounds. Kolthoff and Belcher[2] in their third volume on *Volumetric Analysis* have devoted a small section to potassium ferricyanide. As the literature on potassium ferricyanide has built up considerably, especially in the last few years, it was thought useful to compile systematically the applications of potassium ferricyanide as an oxidizing agent. In the present review, methods of practical significance are described in some detail while relatively unimportant methods are either not included or cited only by references. Although the emphasis is on the literature that appeared in the last five years, some classical procedures are described because of their significance.

Potassium ferricyanide belongs to the class of oxidizing agents in which the oxidizing species is a complex-abstracting ion.

$$\mathrm{Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}} \qquad E_0 = +0.3560\ \mathrm{V} \quad \text{at} \quad 25^\circ\mathrm{C}^{3}$$

The change of potential in a very dilute solution with increasing ionic strength is greater than that calculated on the basis of simple Debye–Hückel expression because of the incomplete dissociation of the alkali and the alkaline earth metal ferrocyanides. The value of E_0' at pH 7 and at 30° is +0.43 volt, while the rH value is + 28.4.[4] The ferricyanide/ferrocyanide is one of the unique systems, the redox potential of which is

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unaffected by pH (except in strongly acidic solutions). The redox potentials in different acid media are given here:

	Acid concentration, molar			
	0.01	0.1	1	3
HCl	+0.48*v*	+0.56*v*	+0.71*v*	— (5)
H_2SO_4	—	+0.57*v*	+0.72*v*	+0.77*v* (5)
			+0.69*v*	(6)
$HClO_4$	—	—	+0.72*v*	— (5)

From the redox potential and rH values it is clear that ferricyanide ion is rather a weak oxidizing agent. This, and the fact that the reactions in many cases proceed slowly, precluded the extensive use of potassium ferricyanide as an oxidimetric reagent. In a few cases where oxidation did proceed reasonably rapidly, lack of suitable indicators for end-point detection in a titration naturally restricted its use. A few indicators have been suggested in specific instances: diphenylamine ($E_0 = 0.75$ volt)[7], ferrous dimethylglyoxime (E_0' at pH 9.4 = 1.25 volts)[8], methylene blue ($E_0 = 0.53$ volt)[4], and thionine ($E_0 = 0.56$ volt)[4]. In certain instances, zinc sulphate is added initially, which helps in end-point detection through the formation of a white precipitate of zinc potassium ferrocyanide.[9] Potentiometric indication is possible in practically every case. Many reactions employing ferricyanide as an oxidant take place at elevated or boiling temperatures. Because of the inconvenience accompanied with the use of salt bridges at higher temperature, the potentiometric method is not very attractive. The derivative polarographic titration technique should be preferred for this purpose.[10,11]

In spite of the above demerits, potassium ferricyanide possesses distinct features as a titrimetric oxidant. The compound is obtainable in a high state of purity, is non-hygroscopic, has a large equivalent weight (329.26) and can serve as its own standard. Aqueous solutions of potassium ferricyanide are stable on long storage if properly protected from light.* The oxidizing capacity of ferricyanide is more particularly superior in alkaline than in acidic medium. Oxidations which are incomplete or slow under ordinary experimental conditions can be made to proceed quantitatively and rapidly by effecting them in presence of a catalyst and/or at elevated temperatures. Osmic acid is generally used as a catalyst in ferricyanide oxidations.[12] Alkaline solutions of ferricyanide are stable at elevated temperatures. The oxidizing capacity of potassium ferricyanide can also be enhanced by removing the ferrocyanide formed for instance, as the sparingly soluble zinc potassium ferrocyanide.

METHODS USING FERRICYANIDE

The titrimetric approaches that have been made in determining reducing substances are: I. Oxidation of the substance using an excess of ferricyanide, and II. Direct titration. These procedures are discussed here with their applications.

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* 0.1*N* solution of potassium ferricyanide did not alter in strength for a period of 5 weeks.

I. *Oxidation by Excess Ferricyanide*

Generally, two methods are practised in the estimation of a reducing substance by excess ferricyanide: (*i*) titration of the ferrocyanide formed against standard ceric sulphate and (*ii*) determination of the excess ferricyanide. The cerimetric titration of ferrocyanide can be performed either potentiometrically[13] or by using ferroïn or ferric chloride as indicator.[14]

$$Fe(CN)_6^{3-} + Ce^{4+} \rightarrow Fe(CN)_6^{4-} + Ce^{3+}$$

The stability of ceric sulphate solutions and its large equivalent weight are the chief advantages in this titration.[15] In addition, this approach eliminates the necessity of standardizing ferricyanide. In the latter method, the excess of ferricyanide is usually determined iodometrically.[2] The recommended procedure for this is the addition of 2 ml of $4N$ hydrochloric or sulphuric acid, 10 ml of N potassium iodide and 10 ml of 25% zinc sulphate solution to 25 ml of ferricyanide and after a minute, titrating the liberated iodine with standard thiosulphate adding starch towards the end. At the end-point the solution is colourless and a pure white precipitate is formed if all the reagents used are iron free.

$$2\,Fe(CN)_6^{3-} + 2I^- \rightleftarrows 2\,Fe(CN)_6^{4-} + I_2$$

Zinc sulphate is added to shift the equilibrium from left to right.

Determination of metals having variable valency

Quantitative oxidation of such metals as arsenic^{III},[16] antimony^{III},[16,17] cerium^{III},[18] chromium^{III},[16,19] manganese^{II},[19] thallium^{I},[18] tin^{II},[16] and uranium^{IV},[20] has been reported from time to time, but in view of existing superior and simpler methods, the ferricyanide oxidation for these metals is of little importance.

In contrast to other methods, the ferricyanide procedure for vanadyl ion appears more dependable.[21] The oxidation of vanadyl ion is effected by ferricyanide in $1N$–$2N$ alkali and after 0.5 hr the ferrocyanide formed is titrated with standard ceric sulphate in presence of sulphuric or hydrochloric acid using ferroïn or ferric chloride as indicator.

Hydrazine and hydroxylamine

The reaction between hydrazine and ferricyanide has been a subject of numerous investigations.[22] Ray and Sen[23] were the first to employ this reaction for a gasometric analysis wherein the nitrogen evolved was measured.

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

Later, titrimetric methods were described based upon the estimation of either the resulting ferrocyanide[24] or the excess of ferricyanide.[25] The addition of too large an excess of ferricyanide obscures observation of the end-point in the ferrocyanide-cerimetric titration. Direct-titration methods for hydrazine estimation by ferricyanide have also been reported and these are described in a later section.

Sant[26] in a study of the reaction between hydroxylamine and ferricyanide showed that although in a strongly alkaline medium hydroxylamine is oxidized to various products, it is converted quantitatively to nitrogen if the pH of the medium is maintained at 8–10.

$$2NH_2OH + [O] \rightarrow N_2 + 3H_2O$$

Sulphur compounds

In a short communication, Solymosi[27] has shown that inorganic sulphur compounds such as sulphite, bisulphite, pyrosulphite, sulphide, dithionate, thiosulphate and tetrathionate are all oxidized to sulphate by ferricyanide in $4N$–$5N$ alkali, at 50°–60° and in presence of osmium tetroxide as catalyst. At room temperature and in $0.2N$–$1N$ alkali, dithionate is oxidized only to sulphite. It is not clear if the above sulphur compounds can be analyzed when present together.

Thiourea: Joshi[28] outlined a method for the quantitative oxidation of thiourea to sulphate and urea by alkaline ferricyanide:

$$CS(NH_2)_2 + 8Fe(CN)_6^{3-} + 10OH^- \rightarrow CO(NH_2)_2 + 8Fe(CN)_6^{4-} + SO_4^{2-} + 5H_2O$$

The experimental conditions are so restricted that a slight deviation from them tends to give erroneous results owing to the nonstoichiometric conversion of thiourea to products other than sulphate and urea.

Thiocyanate: The complete oxidation of thiocyanate to sulphate and cyanate by alkaline ferricyanide in presence of osmic acid to initiate and catalyze the reaction appears to be an excellent method for the determination of thiocyanate.[29]

$$SCN^- + 8Fe(CN)_6^{3-} + 10OH^- \rightarrow SO_4^{2-} + CNO^- + 8Fe(CN)_6^{4-} + 5H_2O$$

Besides the cerimetric and the iodometric finish, it has been shown that the excess ferricyanide can also be titrated conveniently with standard arsenite solution employing a potentiometric end-point.[30] The large equivalent is the chief advantage in analyzing very small quantities of thiocyanate. As this oxidation of thiocyanate takes place only in presence of osmic acid as catalyst, it should be useful in determining thiocyanate in presence of other readily oxidizable substances.

Reducing sugars

Potassium ferricyanide as an oxidant for aldoses and ketoses was reported by Gentele[31] a hundred years ago. The method, since then, has undergone several modifications. In concluding their critical study on methods of estimating reducing sugars, Blom and Rosted[32] consider that the cupric method is superior to the ferricyanide, because the latter oxidizes many non-sugar substances which copper does not attack at all. The ferricyanide method, although it lacks specificity and is empirical, has been immensely useful in biochemistry and is by far the most reliable method for evaluating true glucose, rather than total reducing substances, in blood.[33] Hagedorn and Jensen[34] laid down optimum conditions for such an analysis. In principle, a known excess of alkaline ferricyanide is added and the excess oxidant is determined iodometrically with standard thiosulphate. The Association of Official Agricultural Chemists[35] recommend the ferricyanide method for the determination of reducing and nonreducing sugars in flour and of the diastatic power of beverages, etc.

Milton[36] proposed a sensitive colorimetric analysis based upon the spectrophotometric determination of the ferrocyanide formed as brown uranyl ferrocyanide. Great precautions have to be taken to avoid interferences due to other reducing substances. According to Pinxteren[37] the ferrocyanide formed by the reduction of ferricyanide can be titrated potentiometrically with standard zinc sulphate solution.

Certain quaternary compounds

Quaternary ammonium salts, such as, alkyldimethylbenzylammonium chloride, can be oxidized by ferricyanide in a sodium acetate-acetic acid buffered medium.[35] The excess ferricyanide is determined iodometrically. The method is applicable to commercial preservatives. Tomíček and Šimon[38] found that direct titration of ferricyanide with quaternary salt (obtained from quina alkaloids) is also possible. The titration is performed in 2–3 % potassium hydroxide and at 50°–60°, potentiometrically or visual. One mole of the salt requires 2 moles of ferricyanide. As the salt is slightly soluble in water, it is dissolved in a mixture of alcohol and water.

II. *Direct Titration Methods*

In the majority of the cases, the reducing substance is used as the titrant. An electrometric end-point, in general, is possible in almost every instance. Indicators are suggested in a few cases. Titrations in the presence of zinc sulphate, where no indicator is needed, are also reported. Ferricyanide may be used as the titrant in a few instances.

Ascorbic acid (vitamin C)

Erdey and Svehle[39] reported the titration of ferricyanide with ascorbic acid at pH 5–6.

$$C_6H_8O_6 + 4Fe(CN)_6^{3-} + 4OH^- \rightarrow C_6H_6O_6 + 4Fe(CN)_6^{4-} + 2H_2O$$

2:6-Dichlorophenolindophenol was suggested as an indicator. Near the end-point the greenish color changes to an azure-blue which disappears suddenly at the end-point. A potentiometric end-point is also possible. Sant[40] developed a simple method for the determination of ascorbic acid based upon its oxidation to dehydroascorbic acid by ferricyanide in presence of zinc acetate. The latter maintained the necessary pH and at the same time removed the ferrocyanide ion by precipitation. Potassium iodide-starch served as an internal indicator. This method was successfully applied for the determination of ascorbic acid in fruit juices.

Vanadyl sulphate

Fresno and Mairlot[41] carried out potentiometric titrations, and Willard and Manalo[42] studied several diphenylamine derivatives as indicators in the titration of alkaline ferricyanide with vanadyl sulphate and found 2-carboxy-2-methoxy diphenylamine to be the most suitable. The method served as an indirect means for estimating arsenic^{III}, antimony^{III}, chromium^{III}, hydrazine and hydrogen peroxide. The procedure is only of academic interest.

Thallium^{I}

Fresno and Valdes[43] first studied the potentiometric titration of thallium^{I} with potassium ferricyanide in alkaline solution but obtained results which were 1 % low. Miura[44] claimed accurate results when the titration was performed in a strongly alkaline solution and at 60°. Recently Hartley and Lingane[45] studied this reaction coulometrically using electrogenerated ferricyanide, obtained through the anodic oxidation of ferrocyanide, as a source for the oxidation of univalent thallium. The equivalence point was located potentiometrically or amperometrically. These titrations could be performed in comparatively low alkali concentrations and at room temperature. The interference due to light and dissolved oxygen was easily avoided. Milligram quantities of thallium can be determined by the above procedure within an error of $\pm 0.2\%$.

The ferricyanide-ferrocyanide couple possesses very favourable characteristics and is applicable to both redox reactions and precipitation titration of various metal ions. Because of the intermediate formal potential (ranging from *ca.* +0.4 to +0.7 V *vs* N.H.E. depending upon acidity and other conditions) of this reversible couple, it is relatively easy to generate either ferricyanide or ferrocyanide ion at a platinum electrode with 100% efficiency over a wide range of solution conditions.

Mercury$^{\mathrm{I}}$

In the presence of iodide[46] or thiocyanate,[47] ferricyanide can be titrated in controlled pH conditions (3–7) at about 15° with mercury$^{\mathrm{I}}$ perchlorate. The end-point is determined potentiometrically or by using diphenylamine sulphonate as indicator. The stability of mercurous perchlorate reagent on storage is noteworthy.

Cerium$^{\mathrm{III}}$

The potentiometric method for the determination of cerium$^{\mathrm{III}}$ by ferricyanide in concentrated solution of potassium carbonate, though reliable and precise, gives poor inflection points when the ceric/cerous ratio is large. Leonard *et al.*[49] overcame this difficulty by adopting an amperometric end-point. The titrations were carried out using a rotating platinum electrode at an applied potential of 0.0 V *vs* the S.C.E. Good results were obtained in the presence of a 100-fold excess of ceric ion. In order to avoid air oxidation of cerium$^{\mathrm{III}}$, it is necessary to perform the titration in an atmosphere of nitrogen. Cerous impurity in solid ceric salts could be determined by the above method.

Cobalt

The general principle involved in this method is the oxidation of cobalt$^{\mathrm{II}}$ in ammonium hydroxide-ammonium citrate medium by ferricyanide.[50] Cobalt sulphate is used as the titrant. The method is extensively applied in the determination of cobalt present in non-ferrous mining and metallurgical products,[51] irons and steels,[52] and cemented carbides.[53,54] The only common interfering element is manganese but this can be removed by a nitrochlorate separation. The following elements do not interfere: Hg$^{\mathrm{II}}$, Pb,Fe, Ni, Cu, Bi, Cd, As$^{\mathrm{V}}$, Sb, Sn$^{\mathrm{IV}}$, Se, Te, Mo, Be, Al, Zn, Ti, W, U, Zr, vanadate and chromate. By using ethylenediamine instead of ammonium hydroxide Diehl and Butler[55] obtained sharper end-points and carried out the successive determination of cobalt and manganese. The cobalt$^{\mathrm{II}}$-ethylenediamine complex is a stronger reducing agent than the corresponding ammonia complex by about 0.5 volt. However, dissolved oxygen now becomes an interfering factor and must be removed. Recently Kopanica and Doležal[56] described a direct titration of cobalt with standard potassium ferricyanide in presence of glycine. The latter forms a more stable complex with cobalt than either ammonia or ethylenediamine and no inert atmosphere is needed during the titration.

Arsenic^{III}

Fresno and Valdes[43] studied the potentiometric titration of arsenic^{III} with potassium ferricyanide as a titrant. These titrations were carried out at 70° in presence of 40 ml of 50% potassium hydroxide per 10 ml of the solution.

$$AsO_2^- + 2Fe(CN)_6^{3-} + 4OH^- \rightarrow AsO_4^{3-} + 2Fe(CN)_6^{4-} + 2H_2O$$

Solymosi[57] performed reverse titrations but with little advantage. Sant[58] worked out a simpler and more rapid method in which titrations were carried out in the presence of osmic acid as catalyst, in as low an alkalinity as 1*N* and at room temperature. An indirect method for the estimation of thiocyanate was developed, based on the back-titration of excess ferricyanide with a standard solution of sodium arsenite. The chief advantage, besides accuracy, of this method is that the two oxidation processes, *viz.*, of thiocyanate and arsenite take place under identical experimental conditions.

Glucose

Britton and Phillips[59] studied the direct titration of ferricyanide with glucose in sodium carbonate medium and at 90° employing a potentiometric end-point. They also suggested methylene blue as a suitable internal indicator. The course and velocity of the glucose-ferricyanide reaction are dependent upon pH, the length of the oxidation period, temperature and the ionic strength of the medium. Adams *et al.*[11] re-investigated this reaction and recommended the derivative polarographic end-point. If a pair of platinum electrodes are polarized by a small constant current (*ca.* 2 μA), the electrode will give continuous e.m.f. readings corresponding to the slope of a polarographic curve at the zero current axis. The derivative voltage is measured with a Beckman Model G pH meter. The apparatus assembly is simple and the readings rapidly become steady. The end-points, which are sharper than in potentiometry, can be detected easily without plotting. As the reference half-cell and hence the salt bridge is eliminated, this method is ideally suited at high temperatures. As little as 20 μg of glucose could be estimated in a titration volume of 5 ml with an accuracy of $\pm 5\%$. A slight manipulation of ionic strength of the system is needed when analyzing unknown samples because of the dependence of the reduction equivalent of ferricyanide on the ionic strength.

Sulphide and hydrosulphite

Charlot[60] found that in an ammonium chloride–ammonia buffer (pH = 9.4) sulphide is oxidized to sulphur by ferricyanide.

$$S^{2-} + 2Fe(CN)_6^{3-} \rightarrow S + 2Fe(CN)_6^{4-}$$

Ferrous dimethylglyoxime is used as an internal indicator. At the end-point the red colour of the ferrous complex disappears. As oxygen interferes in this method a hydrogen atmosphere has to be maintained. Sulphite, if present, is first removed by precipitation with barium chloride. The same procedure can be applied to the determination of hydrosulphite.[61]

$$S_2O_4^{2-} + 2Fe(CN)_6^{3-} + 4OH^- \rightarrow 2SO_3^{2-} + 2Fe(CN)_6^{4+} + 2H_2O$$

Scagliarini[62] suggested a potentiometric end-point in the titration of sulphide with ferricyanide. Recently, Kiboku[63] described the use of sodium nitroprusside as an indicator in the sulphide-ferricyanide titration. It is claimed that sulphite and thiosulphate will not interfere. No mention is made of interference due to atmospheric oxidation.

Hydrazine

Vulterin and Zýka[64] reported that hydrazine, hydroxylamine and *iso*nicotinoyl hydrazide can be determined by direct potentiometric titration with potassium ferricyanide in 10–25% potassium hydroxide solution. In the presence of alkali the above compounds will exist as free bases, which are susceptible to air-oxidation and decomposition, and therefore the above method cannot be recommended. The same authors later reported reverse titration at an alkali concentration of 2.5–5% and at 70–80°. Sant[58] developed a simple procedure for the determination of hydrazine depending upon the potentiometric titration of alkaline ferricyanide with hydrazine sulphate at room temperature using osmic acid as a catalyst. In the presence of this catalyst the reduction of ferricyanide by hydrazine takes place very rapidly and therefore during the titration there is little chance for hydrazine to undergo atmospheric oxidation.

Cysteine

Recently Waddill and Gorin[65] described an amperometric method for the determination of semimicro amounts of cysteine with standard potassium ferricyanide in a phosphate buffer of pH 7.

$$\begin{aligned} &2HSCH_2CH(NH_3^+)COO^- + 2Fe(CN)_6^{3-} \rightarrow \\ &\qquad [-SCH_2CH(NH_3^+)COO^-]_2 + 2Fe(CN)_6^{4-} + 2H^+ \end{aligned}$$

Copper sulphate is used to catalyze the reaction. The precision is within 1% and common amino-acids do not interfere. This method appears superior to other methods investigated heretofore.[66–69]

Titration of ferricyanide in presence of zinc sulphate

The oxidation potential of the ferricyanide ion can be increased by removing the ferrocyanide formed as sparingly soluble zinc potassium ferrocyanide. Based on this principle, ferricyanide can be titrated with a reducing substance. The titrations are usually performed in boiling solution in a suitable pH environment, using the reducing substance in question as the titrant. The principal advantage of this titrimetric method is that no indicator is needed. During the titration there is a distinct yellow-orange precipitate of zinc ferricyanide. At the end-point a pure white precipitate of zinc potassium ferrocyanide is formed and the supernatant liquid is colourless. The first application of this titration was made by Bhukarov and Podlubnya[9] for the estimation of glucose.

Recently Sant studied the determination of hydrazine,[70] hydroxylamine[71] and nitrite[72] by the above method. In the hydrazine reaction, titration was performed in an almost neutral or slightly acidic solution. Beyond $0.8N$ alkali concentration the results were faulty and the end-point was difficult to discern. The corresponding nitrite-ferricyanide reaction, where nitrate is the oxidation product, takes place in an almost neutral medium (pH = 6–7). The oxidation of nitrite does not proceed rapidly at alkali concentrations beyond $0.3N$. Large excess of nitrate has no adverse effect on the determination of nitrite. An important application of ferricyanide titration in the presence of zinc sulphate is in the analysis of a mixture of hydrazine and hydroxylamine. Very few rapid and accurate methods are available for such an analysis. In the presence of zinc sulphate, hydrazine and hydroxylamine are oxidized to nitrogen and nitric acid respectively, but in a weakly alkaline medium excess of ferricyanide oxidizes both to nitrogen. Oxidation of a mixture of hydrazine and hydroxylamine under two sets of conditions would give a measure of the individual components. The determination of hydroxylamine by the ferricyanide-zinc sulphate method is particularly useful for small quantities of hydroxylamine.

Miscellaneous

Methods have also been described for the direct titration of the following with potassium ferricyanide: antimony^{III},[43] hydrogen peroxide[73,74], quinol,[75] selenite,[76] titanium^{III},[77–79] tin^{II},[7,80,81] uranium^{IV},[82] chromium^{III},[83] chromium^{II},[84] molybdenum,[84] tungsten^{IV},[84] tungsten^{V},[85] and iron^{II}.[86]

Zusammenfassung—Es wird eine Übersicht übert itrische Methoden unter Verwendung von Kaliumferricyanid als Oxydens gegeben. Es wurde versucht die Wichtigkeit der Methoden zu bewerten. Wenn auch in der Hauptsache die Literatur der letzten fünf Jahre besprochen wurde, so sind doch einige ältere Methoden wegen ihrer grossen Bedeutung mit einbezogen.

Résumé—On présente une mise au point des méthodes titrimétriques utilisant le ferricyanure de potassium comme oxydant pour le dosage de nombreuses substances inorganiques et organiques. Les auteurs ont tenté d'évaluer l'importance de ces méthodes. Bien que l'accent soit mis sur ce qui a paru durant ces cinq dernières années dans la littérature, quelques méthodes plus anciennes sont introduites en égard à leur importance.

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SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN STEEL WITH 3:3′:4′:5:7-PENTAHYDROXYFLAVANONE

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Summary—Studies on the organic reagent 3:3′:4′:5:7-pentahydroxyflavanone (dihydroquercetin) have led to the development of a colorimetric method for molybdenum in steel. By an extraction process all interfering metals are removed except tungsten. The method is applicable to the determination of molybdenum in all substances which do not contain tungsten. Known methods of separating molybdenum from tungsten will permit its use when tungsten is present.

INTRODUCTION

THE colorimetric or spectrophotometric method of analysis is a rapid and accurate means of determining low concentrations and traces of metals in alloys, ores and biological materials. In our study of the development of superior procedures for the accurate analysis of the special alloying metals used in high-temperature-resistant and high-strength alloys, colorimetry was found applicable in certain instances.

In our continuous screening of possible reagents for application to the solution to our problem, the naturally occurring material 3:3′:4′:5:7-pentahydroxyflavanone showed promise of being a suitable reagent for certain metals, one of these being molybdenum, which, under suitable conditions gave a yellow-coloured solution with this reagent. This reagent has the common name of dihydroquercetin and the symbol DHQ will be used hereafter in designating it in this report.

The history of DHQ and its preparation from the cork of Douglas fir bark[8] have been reported elsewhere[1,3,4,7,10,11]. Reagent quality DHQ, necessary for this study, was prepared by passing a diethyl ether solution of DHQ through a column of 1 : 3 activated carbon and celite. The colorless eluate, which appears first, was heated gently to remove the ether and obtain the pure product. The yellowish eluate was discarded. Recrystallize once from water which yields long colorless needles with 2–1/2 moles of water; m.p. 241–2°; solubility in boiling water 9.3 g/100 ml; optical rotation $[\alpha]_D^{25} + 39°$ (4 g in 100 ml of equal volumes of acetone and water).

APPARATUS AND REAGENTS

Beckman DU Spectrophotometer.

Benzoin-α-oxime: 0.1% weight/volume in chloroform.

DHQ: 0.300 g dissolved in 100 ml absolute ethanol.

Molybdenum solution: appropriate quantities of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Merck, were dissolved in water to give stock solutions containing 0.1, 0.2, 0.5 and 1.0 mg molybdenum per millilitre.

Acetate buffer, pH5: 0.67 mole sodium acetate plus 1.33 moles acetic acid per litre.

Other chemicals used were of reagent quality.

PROCEDURE

Dissolution of the sample

The steel sample of suitable size (containing approximately 1 to 2 mg molybdenum) was placed in 15 ml of 50% hydrochloric acid in a 30- or 50-ml beaker with a cover glass on a low temperature hot plate. When hydrogen evolution had ceased the mixture was cooled, sufficient concentrated nitric acid (1 ml or less) was added, and the beaker was returned to the hot plate. This dissolves any carbides and oxidizes, free carbon and the iron to Fe^{III}. A little more hydrochloric acid was added to insure that an excess was present and then the solution was evaporated to a small volume. If chromium or vanadium are present they will remain as Cr^{III} and V^{IV}. Tungsten will be oxidized to W^{VI} and will precipitate, carrying with it some of the molybdenum.

Extraction

The extraction procedure of Goldstein[2] was used as follows: The steel sample solution was rinsed into an 125-ml separatory funnel with 5% hydrochloric acid to a final volume of about 50 ml. If the sample of steel taken contained more than 2 mg of molybdenum, it was transferred to a 50-ml volumetric flask and made up to volume with 5% hydrochloric acid, and an aliquot was taken for the extraction. The molybdenum was then extracted with 0.1% benzoin-α-oxime in reagent-grade chloroform using 10-,10-,10-,10-,5-ml portions. The combined extracts in another 125-ml separatory funnel were washed with 20 ml of 5% hydrochloric acid, and the chloroform layer was transferred to a 100-ml volumetric flask. The aqueous layer was washed with 5 ml of chloroform, which collects any droplets of extract clinging to the glass, and this chloroform was added to the main extract. A liberal portion of absolute ethanol was added, and then 1 ml of 5% sodium hydroxide in methanol. This mixture was agitated for a minute or two which caused the flocculent material in the extract to dissolve, forming a clear solution. The solution was then made up to volume with absolute ethanol.

Preparation of the solution for the spectrophotometric determination

To a 10-ml volumetric flask, using analytical pipettes, was added 0.5 ml of pH 5 acetate buffer and 3 ml of 0.3% DHQ ethanol solution. To this was added with agitation 5 ml of the extract solution and 0.5 ml of water. The solution was then diluted to volume with absolute ethanol and thoroughly mixed. The maximum colour intensity is reached in 10 minutes and is stable for at least 24 hours.

Preparation of the spectrophotometric reference curve for molybdenum

To conserve reagents, 10-ml volumetric flasks were used for preparation of all solutions for spectrophotometric observations. Place in the flask 0.5 ml of pH 5 sodium acetate-acetic acid buffer solution, 3 ml of 0.3% DHQ reagent solution and 3 ml of chloroform, and mix; add the aqueous molybdenum solution; add sufficient water to bring the total water present to 1 ml, and mix; dilute to volume with ethanol and mix. The order of addition of the reagents is important. A series of solutions containing 10 to 100 micrograms of molybdenum was prepared, and a reference solution containing all of the reagents, but no molybdenum. The colour intensity was read against the reference solution after 10 minutes at 410 millimicrons on the Beckman DU spectrophotometer. The absorption intensity follows Beer's law.

DISCUSSION

Development of the procedure

Preliminary studies on the colour reactions of DHQ with aqueous solutions of metals revealed that molybdenum gave a characteristic yellow colour. A spectrophotometric study showed that maximum absorption occurred at a wave length of 410 millimicrons. The colour reaches a maximum intensity at pH 5 and is appreciably less intense at 3.5 and 7.0. In aqueous solution buffered at pH 5 with sodium acetate-acetic acid buffer the absorbance follows Beer's law provided sufficient excess DHQ is present with 5 to 100 micrograms of molybdenum in 10 ml of solution. By use of the Slope Ratio Method of Harvey[5] the complex was found to contain two moles of DHQ to one gram atom of molybdenum. The molar extinction coefficient at 410 millimicrons is about 5000.

Removal of molybdenum from steel for colorimetric determination

It was early learned that DHQ forms an appreciable colour with iron, which yields a bluish-black precipitate upon standing. This interferes with the molybdenum determination and requires prior separation of the molybdenum from iron.

At first, removal of molybdenum from the steel solution was accomplished by precipitating with the specific reagent benzoin-α-oxime from hydrochloric acid solution.[6] Ashing this precipitate, dissolving the resulting molybdic oxide in ammonium hydroxide, evaporating gently to dryness, and taking the residue up with water yielded a solution of pH 5, free from iron, which with DHQ gave the characteristic colour. However, no matter how carefully the procedure was carried out, recovery of molybdenum in amounts of the order of a milligram or less was not quantitative.

The recovery of molybdenum from steel solutions was much more satisfactory with this same reagent, benzoin-α-oxime, by an extraction method.[2] Recovery of 99% of the molybdenum by this method (see procedure) was routine.

In order to obtain the molybdenum in a form to put into aqueous solution, an aliquot of the chloroform extract was very gently evaporated. The residue was ashed with sulphuric, sulphuric plus nitric or perchloric acid, and the acid removed on the hot plate. The carbonaceous ash was ignited in an electric muffle at 350°. Owing to the spreading of the residue by wet ashing and low-temperature of ignition over the inside of the small beaker used in this process, it was difficult to obtain quantitative results repeatedly for the molybdenum content of steel samples.

The chloroform extract of the molybdenum-benzoin-α-oxime is a suspension. Aliquoting this suspension leaves reason for doubt, and it was believed that variations in replicate assays were due at least in part to this inadequate aliquoting.

Upon addition of a secondary amine to the extract, the mixture became a homogeneous solution. Sometimes, however, too much water had been brought over in the extraction process and this water remained as a droplet which could very readily contain appreciable amine and molybdenum.

A dilute solution of sodium hydroxide in methanol was substituted for the amine, and the extract was made up to volume with ethanol giving a clear solution, which could then be aliquoted without error.

To avoid bringing the molybdenum into aqueous solution for the colorimetric determination, studies were made on the use of non-aqueous solvents for the colour development. By use of an ethanol solution of DHQ and an aliquot of the chloroform-ethanol-sodium hydroxide extract, a very faint yellow colour was obtained. On occasion this solution was alkaline and required to be brought to pH 5.

The addition of water alone greatly intensifies the colour, and by the addition of the aqueous pH 5 acetate buffer uniformity was obtained in colour development.

The colours of reference standards are stable for at least 24 hours. Steel solutions tend to drop in intensity by 1–2% in 24 hours.

RESULTS

By the procedure developed, satisfactory results were obtained on synthetic steel samples, and on Bureau of Standards steel samples. Table I shows the results obtained.

TABLE I.—DETERMINATION OF MOLYBDENUM IN BUREAU OF STANDARDS STEEL SAMPLES

Sample	Weight sample	Aliquot extracted	Molybdenum Present %	Molybdenum Found %	Molybdenum Error %
30d	0.8005	all	0.035	0.0340	−0.0010
				0.0341	−0.0009
				0.0341	−0.0009
	1.2522	all		0.0333	−0.0017
				0.0332	−0.0018
	1.1658	all		0.0337	−0.0013
36	0.3960	0.20	1.01	1.042	+0.032
				1.026	+0.016
				1.016	+0.006
				1.030	+0.020
	0.3960	0.20		1.018	+0.008
				1.015	+0.005
	0.3095	0.40		0.986	−0.024
				0.986	−0.024
	0.2249	0.40		1.013	+0.003
				1.002	−0.008

Note: 5 ml of the 100-ml extract was used in each of these determinations.

Interferences

Tungstate, chromate and vanadate ions are partially extracted by the benzoin-α-oxime chloroform solution. No method of preventing the extraction of some tungsten could be found. However, the procedure for preparation of the steel sample solution for extraction purposes kept the vanadium as the vanadyl ion and the chromium in the tervalent state and these caused no interference.

Tungsten also forms a complex with DHQ which is colourless unless considerable tungsten is present, when the solution is tinged with yellow. A spectrophotometric study revealed that the maximum absorption peak of the tungsten complex is at wave length 365 millimicrons whereas the peak for the molybdenum complex is at 410 millimicrons.

It is theoretically possible to determine both molybdenum and tungsten in the same solution by taking measurements at these two wave lengths. Of course there is some absorption of the one metal complex at the absorption peak of the other metal complex. Considerable effort was expended to obtain the conditions for additiveness at these two wave lengths with these two metals, but without success.

The problem is further complicated by the fact that in the extraction process benzoin-α-oxime chloroform solution extracts up to 80% of any tungsten in the acid steel solution by the multiple extraction procedure. Since most of the tungsten in a steel sample, *e.g.*, Bureau of Standards No. 134, is precipitated by the solution procedure, both tungsten and molybdenum are lost in this process. By digesting the steel solution with sodium hydroxide, pH 10–11, acidifying and extracting, up to 80%

of the tungsten is recovered in the extract. If now the residual acid solution is again made alkaline, acidified and extracted, more tungsten is removed. A third treatment permits recovery of 98% of the tungsten as determined by use of radioactive tracer tungsten. Even though this procedure was followed, spectrophotometric analyses were low for both tungsten and molybdenum. Therefore this method is not applicable in its present form for the determination of molybdenum in steel samples containing tungsten.

By use of the hydrogen sulphide method of precipitating molybdenum free from tungsten, the method could be applied to steels which also contain tungsten.

Zusammenfassung—Studien am organischen Reagenz 3,3′,4′,5,7-Pentaoxyflavanon, (Dihydroquercetin) führten zu einer photometrischen Bestimmung von Molybdän in Stahl. Mittels eines Extraktionsprozesses werden alle störenden Metalle ausser Wolfram entfernt. Die Methode ist anwendbar zur Bestimmung von Molybdän in allen Substanzen die frei von Wolfram sind. Bekannte Verfahren zur Trennung von Molybdän und Wolfram sollten die Anwendung auch auf wolframhältige Materialien erweitern.

Résumé—Une étude sur le réactif organique 3,3′,4′,5,7 pentahydroxyflavanone, "dihydroquercetine", a conduit au développement d'une méthode colorimétrique de dosage du molybdène dans l'acier. Par un procédé d'extraction on sépare tous les métaux gênants sauf le tungstène. La méthode est applicable au dosage du molybdène dans toutes les substances qui ne contiennent pas de tungstène. Des méthodes connues de séparation du molybdène et du tungstène permettront son utilisation quand le tungstène est présent.

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THE PREPARATION OF IRIDIUM SOLUTIONS BY AN ACID ATTACK OF TIN–IRIDIUM ALLOYS*

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Summary—Iridium metal is alloyed with a large excess of tin, and the alloy is dissolved in a mixture of hydrochloric acid and hydrogen peroxide. The bulk of the tin is distilled from the solution as a mixed halide after the addition of a mixture of hydrochloric and hydrobromic acids. Residual tin is then separated from the iridium solution by precipitation with ammonium hydroxide.

INTRODUCTION

A PROGRAMME has been undertaken at the Mines Branch laboratories to determine the suitability of tin as a collector for the platinum metals in fire assaying. During the course of this work radiochemical experiments involving the use of ^{192}iridium were performed to study the behaviour of iridium during the crucible fusion process in which tin is used as the collector.

The radioactive iridium was obtained in the form of compact metal pellets weighing approximately 20 mg each. Because it was desired to add the ^{192}iridium to the test samples in the form of a solution, a suitable method for dissolving the pellets had to be selected. The published methods for converting iridium metal or its native alloys to soluble forms[1,2] are time-consuming, and require special apparatus and rather exacting techniques; therefore, a simpler method was desired.

It is known that tin forms intermetallic compounds with all the precious metals with the possible exception of osmium;[3,4] however, little use of tin has been made as a collecting or working medium for the platinum metals. Pollard[4] developed a micro-titrimetric method for determining the iridium content of solutions prepared by dissolving tin–iridium alloys in a mixture of concentrated sulphuric acid and an alkali sulphate at temperatures over 300° C. The method is not, however, suitable for the preparation of pure solutions of iridium because the iridium is still associated with large quantities of tin and alkali sulphate in the final solution.

The present report describes a new and simple method for preparing iridium solutions from the metal.

APPARATUS AND REAGENTS

Preset time scaler: Model SC15CST, Electronic Associates Ltd., Toronto, Canada.

Glass envelope immersion-type Geiger–Müller tube, Type B6, manufactured by 20th Century Electronics, Croydon, Surrey, England. The tube was fitted with a glass collar and a cell capable of holding a 5 ml sample when fitted around the tube.

Vycor melting tube, internal diameter 2·2 cm, height 10 cm.

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GENERAL EXPERIMENTAL PROCEDURE

Preparation of alloys

(a) *Tin-iridium master alloy* (0·1 ± 0·005% iridium): was prepared by alloying a 20 mg pellet of iridium containing approximately 2 mc of ^{192}iridium with 20 grams of pure tin according to the procedure given below. To determine the homogeneity of the alloy, weighed portions were dissolved and the resulting solutions were assayed radiometrically for iridium as described below.

(b) *Test alloys:* Each test sample was prepared by placing a weighed quantity of the master tin-^{192}iridium alloy (0·5–1·0 gram), pure tin (3·0–3·5 grams), and in certain cases, iridium sponge, into the Vycor melting tube. Air was purged from the tube by nitrogen gas delivered through a 1 × 15-cm Vycor tube placed directly over the materials to be alloyed. The melting tube was then held in an open flame until the tin had melted. While a stream of nitrogen was played over the melt, the tube was vigorously swirled until the bed of iridium sponge at the bottom of the tube was taken up and alloyed with the molten tin. The nitrogen delivery tube was then removed from the melting vessel and the molten alloy was quickly poured into approximately 1 litre of cold water contained in a 2-litre beaker.

After decanting the water, the beaker was placed on the cool part of the hot-plate until the spongy tin-iridium alloy was thoroughly dry. Any alloy which had frozen on the upper walls of the melting tube during pouring was scraped off with a steel spatula, and combined with the main portion of the alloy in the beaker.

In each test the dried alloy particles were thoroughly mixed and two separate weighed samples (each representing approximately 10–15% of the total alloy) were removed for use as radiochemical standards as described below. The remainder of the test sample was brushed out of the beaker, weighed and transferred to a 300-ml tall-form beaker.

Dissolution of alloys

Approximately 40 ml of concentrated hydrochloric acid was added, followed immediately and cautiously by 30% hydrogen peroxide. Further additions of hydrogen peroxide were made during the vigorous dissolution of the alloy, until an excess was present (as judged by the persistence of the colour of chloroiridate ion). The mixture was then heated and from time to time further dropwise additions of hydrogen peroxide were made until the alloy appeared to be completely dissolved and the solution was clear. (In several tests a few shiny metallic flakes remained at this stage but were dissolved in subsequent steps.) The solution was then evaporated to approximately 5 ml.

Volatilization of tin

Next 10–20 mg of sodium chloride and 10 ml of a 7 : 2 mixture of hydrochloric and hydrobromic acids were added and the beaker was swirled over an open flame to volatilize tin. After evaporating to approximately 1 ml, a further addition of the mixed acids was made and the evaporation was repeated as before. To remove as much tin as possible, the volatilization step was repeated six times. The solution was then treated with 10 ml of a 1 : 1 mixture of hydrochloric acid and hydrogen peroxide to re-dissolve any iridium which might have separated out by thermal decomposition of the chloro-iridate. The solution was then evaporated to approximately 2 ml, diluted with water and filtered through a No. 42 Whatman filter paper into a 100 ml volumetric flask, and was finally diluted to the mark with water.

The ^{192}iridium content of an aliquot of the solution was then determined radiometrically with the immersion Geiger–Müller tube and scaler.

Radiochemical standards were prepared by dissolving each of the portions removed from the main alloy sample in a mixture of hydrochloric acid and hydrogen peroxide as described above. The resulting solutions were each diluted to 100 ml in volumetric flasks without filtration and their ^{192}iridium activities were determined radiometrically.

The amount of iridium present in the test solutions was calculated by comparing their activities with those of the standard reference solutions prepared in each test.

Self-absorption corrections were not needed for the activity figures of the test and standard solutions.

RESULTS AND DISCUSSION

Effectiveness of acid attack on tin–iridium alloys

A series of tests was done to determine the effectiveness of the acid attack on tin–iridium alloys. In each test 3·0–3·5 grams of tin, 0·5–1·0 gram of the master tin–^{192}iridium alloy and a weighed quantity of iridium sponge were alloyed and treated according to the procedure given above. Table I gives the results of these tests.

TABLE I.—EFFECTIVENESS OF ACID ATTACK IN PREPARING SOLUTIONS OF IRIDIUM TIN–IRIDIUM ALLOYS

Test No.	Wt Ir in alloy, *mg*	Wt Sn in alloy, *grams*	Percent Ir in alloy	Percent of added Ir found in solution
1	0·3*	2·75	0·01	100·1
2	1·2	3·16	0·04	100·2
3	3·6	3·06	0·1	98·0
4	7·2	2·63	0·3	99·5
5	11·7	2·68	0·4	98·9
6	20·8	2·78	0·7	97·2
7	40·0	2·80	1·4	Only partial dissolution of intermetallics
				Average 98·9

* Iridium sponge not used in Test 1.

The results in Table I show that iridium in a tin–iridium alloy containing less than 0·7% iridium can be quantitatively dissolved in a mixture of hydrochloric acid and 30% hydrogen peroxide. With alloys containing more than 0·7% iridium, there is a tendency for large flakes of tin–iridium intermetallics to separate out. Although these particles can be dissolved in the hydrochloric–peroxide mixture, the time required is excessive.

Removal of residual tin by precipitation with ammonium hydroxide

Because the presence of milligram quantities of tin in the iridium solutions would be undesirable in many cases, it was necessary to determine the effectiveness of the tin volatilization step described in the experimental procedure. After determining their ^{192}iridium contents, certain of the test solutions were split into two 50-ml portions and the tin content of one portion from each test solution was determined polarographically[5] (Table II). Iridium did not interfere with this determination. Because the residual tin content of these solutions was found to be appreciable, the second 50-ml portion of each test solution was treated with an excess of ammonium hydroxide to precipitate the tin. After the stannic hydroxide had coagulated, it was filtered off on a No. 42 Whatman filter paper with the aid of pulp, and washed well with a dilute ammonium chloride–ammonium hydroxide solution. The stannic hydroxide was then dissolved from the paper with warm dilute hydrochloric acid and diluted to 50 ml in a volumetric flask. The ^{192}iridium content of the tin solution was then measured radiometrically to determine the extent of co-precipitation and/or occlusion of iridium. The results of these experiments are given in Table II.

TABLE II.—EFFECTIVENESS OF SEPARATION OF IRIDIUM FROM RESIDUAL TIN

Test No.	Weight Sn remaining in test solution (100 ml) after volatilization step, *mg*	Percent of added Ir retained by $Sn(OH)_4$ precipitate
1	11·6	0·03
3	9·6	0·25
4	5·4	0·12
5	9·4	0·21

The results in Table II show that even after repeated evaporations with the hydrochloric–hydrobromic acid mixture, milligram quantities of tin remain in the iridium solution. However, the residual tin can be conveniently removed by precipitation with ammonium hydroxide, negligible quantities of iridium being retained in the stannic hydroxide precipitate. During the treatment of microgram quantities of iridium, it is probable that the degree of co-precipitation or occlusion would be significantly greater.

On addition of excess ammonium hydroxide, the iridium solutions gradually become decolorized, probably due to the formation of an ammine complex. This complex was destroyed when the solutions were evaporated to a small volume and then treated with a few millilitres of concentrated nitric acid. This also served to destroy the ammonium salts which were present in the solution. The iridium was converted back to chloro-iridate by repeated evaporations of the nitric acid solution with hydrochloric acid.

Chemical determination of effectiveness of acid attack on tin–iridium alloys

Although visual observation indicated that the inactive iridium sponge used in the above tests was completely alloyed with the tin and behaved chemically in an identical fashion to the ^{192}iridium derived from the master alloy, the radiometric results alone could not substantiate this observation. Therefore, a series of tests was performed in which weighed quantities of iridium sponge and pure tin were alloyed, dissolved, and the resultant solution freed of tin according to the procedures described

TABLE III.—CHEMICAL DETERMINATION OF COMPLETENESS OF SOLUTION OF IRIDIUM SPONGE

Weight Ir taken, *mg*	Weight Sn in alloy, *grams*	Weight Ir found in final solution, *mg*
6·18	3·73	6·16
9·27	3·84	9·10
8·76	3·90	8·90

above. The quantity of iridium present in each of the final solutions was determined by the Gilchrist method of bromate hydrolysis.[6] The results of these tests are given in Table III.

From the results given in Table III it can be concluded that the radiometric results of the tests described above are valid for the inactive iridium sponge as well as for the ^{192}iridium added as the master alloy.

CONCLUSIONS

It is considered that the method presented in this paper offers a new approach to the problem of converting iridium metal into a soluble form. It is more rapid than existing methods, it does not require special equipment and it is suitable for treating any quantity of iridium metal in either sponge or compact form. The method also makes it possible to prepare solutions of iridium which do not contain foreign cations.

Zusammenfassung—Iridiummetall wird mit grossem Überschuss von Zinn legiert und die Legierung in einer Mischung von Salzsäure und Wasserstoffperoxyd gelöst. Die Hauptmenge des Zinns wird als gemischtes Halogensalz nach Zugabe einer Mischung von Salz und Bromwasserstoffsäure abdestilliert. Das restliche Zinn wird vom Iridium durch Fällung mit Ammoniumhydroxyd abgetrennt.

Résumé—On fait un alliage avec l'irridium métal et un grand excès d'étain. L'alliage est alors dissous dans un mélange d'acide chlorhydrique et d'eau oxygénée. La majeure partie de l'étain est distillée à partir de la solution à l'état d'halogénures mixtes après addition d'acide chlorhydrique et bromhydrique. L'étain restant est alors séparé de l'iridium en solution par précipitation par l'ammoniaque.

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THE PRECIPITATION OF ZINC SULPHIDE FROM ACID SOLUTIONS BY THIOACETAMIDE

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Summary—The rate of precipitation of zinc sulphide by thioacetamide from solutions having pH values less than 2.5 is controlled by the rate of hydrolysis of thioacetamide to give hydrogen sulphide; significant supersaturation may occur initially. This reaction is first order with respect to the hydrogen ion and the thioacetamide concentrations. In solutions having pH values between 4.5 and 6.3 the precipitation occurs by a direct reaction which conforms to the expression

$$-\frac{d\,[\mathrm{Zn(II)}]}{dt} = k_d\frac{[\mathrm{Zn(II)}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

The rate constant, k_d, is 4.2×10^{-4} litre$^{1/2}$ mole$^{1/2}$ min^{-1} at 90° and the energy of activation 19 ± 2 kcal per mole in the 70°–90° region.

Precipitation conforming to this rate expression occurred at hydrogen ion concentrations higher than those at which precipitation by hydrogen sulphide could be obtained. Studies of the relative effectiveness of thioacetamide and hydrogen sulphide for the separation of lead as sulphide from zinc by precipitation from solutions approximately 0.3 *VF* in hydrochloric acid showed that more zinc was precipitated by thioacetamide than by hydrogen sulphide; this precipitation is attributed to the above direct reaction. By modification of procedure and proper control of time and hydrogen ion concentration an effective separation can be made with thioacetamide.

Similarly, more nickel was precipitated with zinc sulphide from solutions of approximately pH 2 when thioacetamide was the precipitant.

Spectral studies have given no evidence of the formation of zinc thioacetamide complexes in neutral solutions.

INTRODUCTION

This investigation was undertaken as part of the general study of the precipitation of metal sulphides by thioacetamide being carried out in these laboratories. The hydrolysis of thioacetamide in acid[4,18] and in alkaline solutions[4] and its reactions in certain buffer systems[14] have been the subjects of previous studies; the reactions involved in the precipitation of lead$^{\mathrm{II}}$,[18] arsenic$^{\mathrm{III}}$ and $^{\mathrm{V}}$,[3] cadmium,[1] and nickel[2] have also been investigated.

These investigations have shown that in solutions of hydrogen ion concentration greater than about $10^{-3}M$, the rates of precipitation of lead$^{\mathrm{II}}$ [18] and cadmium[1] are hydrolysis-controlled, that is they quantitatively follow the rate of hydrolysis of thioacetamide, which is first order with respect to both the thioacetamide and hydrogen ion concentrations. At hydrogen ion concentrations between about $10^{-3}M$ and $10^{-6}M$, lead$^{\mathrm{II}}$ and cadmium sulphides precipitate by what appears to be a direct reaction between the metal ion and thioacetamide. The rate of this precipitation is first order with respect to both the thioacetamide and metal ion concentrations and inversely half order with respect to the hydrogen ion concentration.

The precipitation of nickel sulphide by the hydrolysis-controlled reaction was not observed in solutions having pH values of 2 or less.[2] This is in accordance with the observations[2,7] that nickel sulphide does not precipitate in solutions saturated with hydrogen sulphide under similar conditions. However, precipitation of nickel sulphide by the direct reaction was observed in solutions 0.3–$10^{-7}M$ in hydrogen ion[2].

Equal contributions of the hydrolysis-controlled and direct reactions to the overall rate of precipitation have been shown to occur at approximately pH 3 in solutions 0.01 *V F* (volume formal) in lead^{II} or cadmium and 0.10*V F* in thioacetamide at 90°. That is, under these conditions, in solutions more acid than $10^{-3}M$ the hydrolysis reaction is predominant, and in solutions having hydrogen ion concentrations lower than $10^{-3}M$ the direct reaction is predominant.

Since the pH range of 2 to 3 has been reported to be most favourable for the quantitative precipitation of zinc sulphide by hydrogen sulphide there seems justification for a study of the mechanisms by which zinc sulphide is precipitated in acid solutions by thioacetamide and of the application of this reagent to the quantitative precipitation and separation of zinc from other elements.

EXPERIMENTAL

Reagents

Reagent grade chemicals were used throughout the investigation.

Arapahoe thioacetamide (Lots No. 1402 and 1651) was used to prepare 1.00*VF* stock solutions by weight. These solutions were clear, colourless, and had approximately the pH of the distilled water that was used in their preparation.

Stock solutions of 0.10*VF* zinc nitrate, 0.10*VF* lead nitrate, and 3.0*VF* ammonium chloride were prepared by weight, as were solutions of zinc, lead, and nickel nitrates containing 20 milligrams of metal per millilitre.

Hydrochloric acid solutions, 3.0*VF* and 6*VF*, and perchloric acid solutions, 1.0*VF* and 0.10*VF*, were prepared from the commercial acids.

Standard 0.05*VF* potassium iodate solution was prepared by weight. Sodium thiosulphate solutions, approximately 0.05*VF*, were standardized against the potassium iodate solution.

Stock carbon tetrachloride dithizone solutions, 3.9×10^{-4}*VF*, were prepared as needed; 3.9×10^{-5}*VF* solutions were prepared by dilution.

A 0.5*VF* sodium acetate solution was prepared by weight and heavy metal traces removed by extraction with small portions of 2×10^{-4}*VF* dithizone solution.

An acetic acid-acetate buffer solution of pH 4·8 was made by mixing appropriate volumes of 2*VF* sodium acetate and 2*VF* acetic acid.

A 1 *VF* sodium thiosulphate solution was prepared by weight.

Standard zinc solutions, 2.5 micrograms per ml., were prepared by dilution of previously standardized stock 0.10*VF* zinc nitrate.

A sulphate-hydrogen sulphate buffer solution having a $HSO_4^-/SO_3^=$ ratio of 1 : 3 was prepared from the sodium salts; the total formal concentration of sulphate was 1.5. This solution was diluted by a ratio of 9 : 40 in the reaction solutions and under these conditions gave a pH of 1.7 at 25°.

A 0·1 *VF* solution of dimethylglyoxime in ethanol was used.

For the study of the rate of precipitation of zinc sulphide in the pH range 3–7, sodium formate-formic acid buffer solutions were prepared from sodium hydroxide and 90% formic acid solutions. These buffer solutions, which contained a constant sodium formate concentration, were prepared by mixing various quantities of formic acid with constant volumes of a 6*VF* sodium hydroxide solution and then diluting each solution to the same final volume.

Apparatus

The apparatus used for the rate studies was essentially that described by Swift and Butler[18]. In the separation study 50-ml centrifuge tubes were used as the reaction vessels.

Procedures

The rate measurements and the separation studies were made by separate procedures as described below.

Rate measurements. In the measurements of the rate of precipitation of zinc sulphide, measured volumes of the stock zinc nitrate solution and either hydrochloric, perchloric, or sodium formate-formic acid buffer solutions were mixed in the reaction vessel, thioacetamide solution was added, and the solution was diluted to 100 ml. The solutions were heated to approximately 90° before mixing. The tube was then placed in the constant temperature bath.

At timed intervals, and after temperature equilibration, 12 ml of solution were removed from the reaction tube, immediately cooled to quench the reaction, and the zinc sulphide centrifuged. The precipitate was granular and easily separated. Duplicate 5.00-ml portions of the centrifugate were pipetted into 15 × 125-mm test tubes.

An excess of ammonium hydroxide was added to each test tube, and the solutions were placed in a bath of hot water in order to obtain rapid precipitation of the zinc sulphide. The mixtures were cooled, centrifuged and the centrifugate drawn off and discarded. The precipitate was washed with 2-ml portions of a formate-formic acid buffer having a pH of 5.4 until the wash solution was free of sulphide. The precipitate was washed into a 100-ml conical flask; then potassium iodide, standard potassium iodate solution, and 6 *VF* hydrochloric acid were added in the order listed. The solution was titrated with standard sodium thiosulphate solution. The average deviation in confirmatory analyses by this procedure was less than one part per hundred.

Separation studies. A colorimetric method was used to determine the quantity of zinc that precipitated with the lead sulphide when either thioacetamide or hydrogen sulphide was used to separate lead^{II} from zinc. Reaction solutions were prepared by mixing measured quantities of zinc, lead^{II}, hydrochloric acid, and ammonium chloride solutions in 50-ml centrifuge tubes. Either distilled water and hydrogen sulphide gas or thioacetamide solution was added to each solution. In all cases, the solutions were heated quickly to about 90° over a flame and immediately placed in a bath at 90° ± 1°. The reaction solutions and thioacetamide were heated separately and mixed in the constant temperature bath. When hydrogen sulphide was used as the precipitating agent, the gas was slowly bubbled through the solution to insure saturation. The precipitations were carried out for timed intervals and then the vessels were cooled in a bath of ice-water. After centrifugation, the precipitates were washed with 10-ml portions of the formic acid-formate buffer until the washed solutions gave no dithizone test for zinc. To the precipitates were added 1 ml of 9 *VF* perchloric acid and 5 drops of 6 *VF* nitric, the tubes placed first in boiling water, then finally heated over a flame until all of the precipitate had dissolved and oxides of nitrogen were expelled. The solutions were neutralized to a pH of about 4.8 by the addition of purified 0.5 *VF* sodium acetate solution, diluted to 100.0 ml in a volumetric flask and aliquots of 1.00 ml or 5.00 ml taken for the colorimetric analysis.[16] The aliquot was diluted to 20 ml in a separatory funnel; 10 ml of acetate buffer, 2.00 ml of sodium thiosulphate solution, and 10.0 ml of dithizone reagent were added. The solutions were shaken for 2 minutes, portions of the carbon tetrachloride phases delivered into matched 1-cm Corex cells and the absorbancies of the solutions at 535 mμ determined by means of a Beckman Model DU Quartz Spectrophotometer. A calibration curve for this instrument was prepared with solutions containing known quantities of zinc and lead^{II}.

The effectiveness of the separation of zinc and nickel was studied by a similar procedure. Reaction solutions were prepared by mixing measured quantities of nickel, zinc, and sulphate-hydrogen sulphate buffer solution in 50-ml centrifuge tubes. The subsequent procedure for precipitation, washing, and dissolving of precipitates was exactly that described above for the separation study of zinc and lead^{II}.

The quantities of nickel precipitated were determined by the precipitation of nickel dimethylglyoxime and a comparison of the volume of the precipitate with precipitates from standard solutions of nickel. The procedure followed was essentially that described by Bowersox, Smith, and Swift[2], the only difference being the neutralization with, and addition of, excess ammonium hydroxide before the precipitation of nickel with dimethylglyoxime. Under the conditions employed here, the limit of detection of nickel was found to be 0.02 mg.

RESULTS AND DISCUSSION

Flaschka[5] observed that only a small amount of zinc sulphide precipitated when neutral or slightly acidic solutions of thioacetamide and zinc salts were boiled, but that zinc sulphide was precipitated from ammoniacal solutions.

Preliminary qualitative experiments showed that the initial rate of formation of zinc sulphide from acid thioacetamide solutions having pH values less than 6 increased with increasing pH. However, in solutions at pH 1 and 2 the rate of zinc sulphide formation at 90° increased rapidly after six to eight minutes, indicating that supersaturation effects were involved.

Quantitative rate measurements were then made in solutions having pH values ranging from 2–6.3. The reactions were carried out at 90° in order to obtain a rate of precipitation which could be easily measured.

Precipitation by the direct reaction

Qualitative experiments indicated that a direct reaction similar to that observed with lead^{II},[18] cadmium,[1] and nickel^{II}[2] occurred between zinc and thioacetamide. Therefore formic acid-sodium formate buffer solutions were used to control the hydrogen ion concentration in the pH range 6.3–4.5 and measurements were made to determine the effects of the hydrogen ion, zinc ion, and thioacetamide concentrations on the rate of the precipitation.

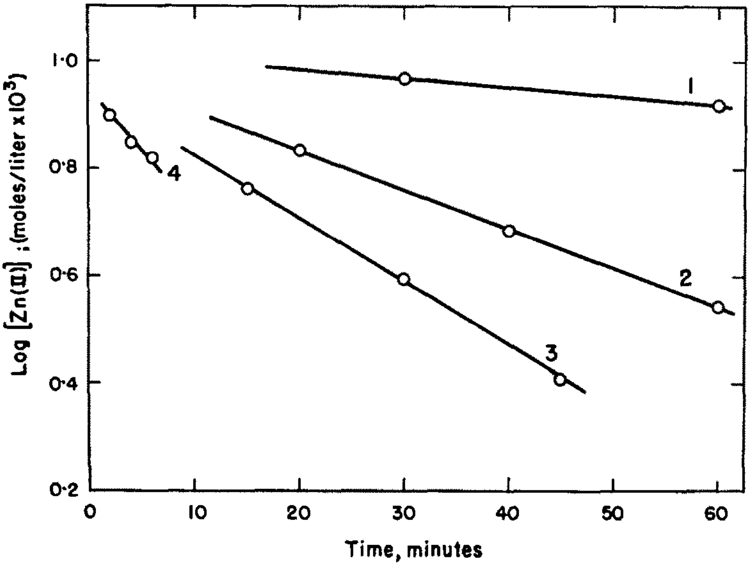

FIG. 1.—The effect of zinc and hydrogen ion concentrations on the rate of precipitation of zinc sulphide by thioacetamide.
Initial zinc, 0·04*VF*; thioacetamide, 0.10*VF*; 90°. 1, pH 4.56; 2, pH 5.40; 3, pH 5.70; 4, pH 6·31 .

Effect of zinc concentration

As is shown by Fig. 1, plots of the logarithms of the zinc concentrations versus times for the pH region 6.3–4.5 are essentially linear; therefore one concludes that the reaction is first order with respect to the zinc concentration. The plots do not extrapolate back to exactly the same initial zinc concentration because of the method used in this rate study. Since temperature equilibration at the outset of the reaction was difficult, an initial point was taken when the reaction mixture achieved a constant 90° and after some reaction had taken place.

Effect of thioacetamide concentration

At a pH of 5.7 the effect of the thioacetamide concentration was investigated over the range 0.05–0.3 *VF*. Rate constants calculated from the data are presented in Table I and show that the rate of precipitation is dependent upon the first power of the thioacetamide concentration.

Table I.—Effect of thioacetamide concentration upon the rate of precipitation of zinc sulphide

Initial zinc, 0.011 *VF*; hydrogen ion, 2.0 × 10^{-6} M; 90°

(CH_3CSNH_2) *Moles/liter*	$k_1 \times 10^8$ [a]	$k_2 \times 10^7$ [b]
0.050	2.9	5.8
0.100	5.9	5.8
0.200	11.8	5.8
0.300	18.4	6.1

[a] Calculated from the expression $-\frac{d[Zn(II)]}{dt} = k_1[Zn(II)]$

[b] Calculated from the expression $-\frac{d[Zn(II)]}{dt} = k_2[Zn(II)][CH_3CSNH_2]$

Table II.—Effect of hydrogen ion concentration upon the rate of precipitation of zinc sulphide

Initial zinc, 0.011 *VF*; thioacetamide, 0.10 *VF*; 90°

$[H^+]$	$k_1 \times 10^9$ [a]	$k_2 \times 10^4$ [b]
2.8×10^{-5}	21	4.0
4.0×10^{-6}	8	4.3
2.0×10^{-6}	6	4.2
5.0×10^{-7}	3	4.2
		Average $(4.2 \pm 0.1) \times 10^{-4}$

[a] Calculated from the expression $-\frac{d[Zn(II)]}{dt} = k_1\frac{[Zn(II)][CH_3CSNH_2]}{[H^+]}$

[b] Calculated from the expression $-\frac{d[Zn(II)]}{dt} = k_2\frac{[Zn(II)][CH_3CSNH_2]}{[H^+]^{1/2}}$

Effect of hydrogen ion concentration

Rate measurements were made in which the hydrogen ion concentration was varied from 2.8 × 10^{-5}–5 × 10^{-7} *VM*; the initial thioacetamide and zinc ion concentrations were held constant. The rate constants calculated from these data are shown in Table II and show that the rate of precipitation is dependent on the inverse half power of the hydrogen ion concentration. This dependency upon hydrogen ion is the same as that found in the previous investigations of cadmium,[1] lead^{II},[18] and nickel.[2] No mechanism to explain this effect has been formulated.

The rate expression

The results presented above indicate that the precipitation of zinc by thioacetamide at pH values greater than 4.5 is predominantly controlled by a direct reaction similar to that reported for the precipitation of cadmium, lead^{II}, and nickel. The rate expression has the form

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_d \frac{[\mathrm{Zn(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}} \tag{1}$$

and k_d, the direct reaction rate constant, is calculated to be $(4.2 \pm 0.1) \times 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min^{-1} at 90°.

The direct reaction at higher hydrogen ion concentrations

Rate measurements in solutions having pH values of 2.4 were made while nitrogen was bubbled through the reaction solution to prevent any reaction of zinc with the hydrogen sulphide formed by hydrolysis of thioacetamide at this pH. The rate constant for expression (1) above, obtained from these measurements, was 4.3×10^{-4} litre$^{1/2}$ mole$^{-1/2}$ min^{-1} at 90°. This agreement indicates that the precipitation at this pH is taking place by the direct reaction. Similar qualitative experiments at pH 1 indicated that precipitation by the same reaction occurred; no supersaturation was observed.

Effect of buffer concentration on direct reaction

Rate measurements were made to determine whether the concentration of formate in the buffer solution affected the rate of the direct reaction. The calculated rate constants are shown in Table III. It is evident from the agreement of these values that the formate does not affect the rate significantly over the concentration range studied; the rate of the reaction was the same within the limits of experimental error. This indicates that only a very weak zinc-formate complex, if any, is formed under these conditions, or—as appears unlikely—that complex formation does not affect the rate.

TABLE III.—EFFECT OF BUFFER CONCENTRATION AND TEMPERATURE ON THE RATE OF PRECIPITATION OF ZINC SULPHIDE.

pH 5.70; initial zinc, 0.011 *VF*
initial thioacetamide, 0.10 *VF*

Temp., °C	Formate concentration	$[\mathrm{HCOO^-}]/[\mathrm{Zn^{++}}]$	$k_d \times 10^4$ [a]
90	0.30	30	4 ± 1
90	0.15	15	4.1 ± 0.1
90	0.60	60	4.2
80	0.60	60	2.2 ± 0.1
70	0.60	60	0.92 ± 0.05

[a] Calculated from the expression

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_d \frac{[\mathrm{Zn(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

Temperature effect on the direct reaction

The rates of the direct reaction between zinc and thioacetamide in solutions initially 0.011 *VF* in zinc nitrate and 0.10 *VF* in thioacetamide at pH 5.70 were determined at 70°, 80°, and 90°. Since it had been demonstrated that the rate of the direct reaction is the same in buffer solutions containing either 0.15*F*, 0.3*F*, or 0.6*F* formate, these measurements were made in the most concentrated buffer in order to obtain a higher buffer capacity. The rate constants obtained were $(9.2 \pm 0.5) \times 10^{-5}$, $(2.2 \pm 0.1) \times 10^{-4}$, and 4.2×10^{-4}, respectively (Table III). From a plot of log k_d versus $1/T$ the energy of activation for this reaction over the temperature range from 70 to 90° was determined as 19 ± 2 kilocalories per mole. These data demonstrate the potentialities which exist for controlling the rate of precipitation of zinc sulphide by thioacetamide by varying the solution temperature.

Evidence for the non-existence of a zinc-thioacetamide complex

The rate values presented above indicate the absence of any stable zinc-thioacetamide complex. However, since metal-thioacetamide complexes have been observed by various investigators,[8,11,12] a spectrophotometric investigation of zinc-thioacetamide solutions was made to determine if evidence for a complex could be observed.

TABLE IV.—ULTRAVIOLET ABSORPTION OF ZINC AND THIOACETAMIDE SOLUTIONS.

Beckman DU spectrophotometer
25°C

1-cm quartz cells
H_2O reference
Zinc, 1.2×10^{-4}*VF*
Thioacetamide, 1.0×10^{-5}*VF*

Wavelength, mμ	Absorbancy, *As*		
	$ZnSO_4$	TAA	$ZnSO_4$ + TAA
220	0.002	0.076	0.082
230	0.000	0.048	0.056
240	0.000	0.087	0.089
250	0.000	0.164	0.165
255	0.000	0.201	0.203
260	0.000	0.223	0.223
265	0.000	0.214	0.214
270	0.000	0.170	0.170
280	0.004	0.055	0.055

Thioacetamide has a wavelength of maximum absorption in the 261–263 mμ region.[4,15] Zinc sulphate was used in this study rather than the nitrate since nitrate ion absorbs significantly in the 220–290 mμ region and sulphate has no appreciable absorption in this region. The spectra of 1.2×10^{-4}*VF* zinc sulphate, of 1×10^{-5}*VF* thioacetamide, and of a solution containing both 1.2×10^{-4}*VF* zinc sulphate and 1×10^{-5}*VF* thioacetamide, all in neutral solution, were measured in the 220–400 mμ region by means of a Beckman DU Spectrophotometer and matched 1-cm quartz cells. The pertinent results are presented in Table IV.

Since the spectra of the thioacetamide and zinc-thioacetamide solutions are essentially identical there is no evidence for the presence of a zinc-thioacetamide complex. A 12-fold excess of zinc over thioacetamide was used and no change in the spectrum of thioacetamide was observed. In order for a zinc-thioacetamide complex to exist and give these results, the absorbancy index of the complex at all wavelengths in this region would have to be of a magnitude such as to exactly compensate for the loss of thioacetamide by complexation. Thus it was concluded that there is no significant zinc-thioacetamide complex formation under these conditions.

The hydrolysis-controlled precipitation

Measurements of the rate of precipitation were made in solutions having pH values of 2 and 2.5 where the rate of the direct reaction would be small compared to the rate of the acid hydrolysis of thioacetamide. These measurements were complicated by the fact that there was an initial period during which no zinc sulphide precipitate formed. Consequently measurements were made after six to eight minutes, when visible precipitation commenced.

In order to obtain evidence that zinc sulphide was precipitated by the hydrolysis mechanism at high acidity, semi-quantitative measurements were carried out at pH 2. Essentially the same procedure as was used for the direct reaction rate measurement was followed, except that the volumes of zinc sulphide precipitated were compared with those precipitated from standard solutions under the same conditions. Calculations showed that under the conditions prevailing the rate of precipitation of zinc sulphide by the hydrolysis-controlled reaction should have been 2.7 mg of zinc per 5 minutes. The quantities of zinc precipitated as zinc sulphide, once the precipitation began, were found to be 2–3 mg per 5 minutes. This indicates that the precipitation is predominantly hydrolysis-controlled.

Since the rate constant for the direct reaction had been previously determined at lower hydrogen ion concentrations and checked at pH 2 by bubbling nitrogen through the system, the contribution of this reaction to the total rate of precipitation could be calculated. The total rate of precipitation of zinc sulphide at pH 2.5, after initial precipitation began, conformed to the expression

$$-\frac{d[\mathrm{Zn}^{++}]}{dt} = k_h [\mathrm{H}^+][\mathrm{CH_3CSNH_2}] + 4.2 \times 10^{-4} \frac{[\mathrm{Zn}^{++}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H}^+]^{1/2}} \tag{2}$$

where k_h was calculated to be 0.23 ± 0.08. The previously determined value[18] for k_h is 0.21 ± 0.02.

Direct reaction rate constant correlations

A rough correlation between the rate constants for the direct reactions of lead$^{\mathrm{II}}$, cadmium$^{\mathrm{II}}$, nickel$^{\mathrm{II}}$, and zinc$^{\mathrm{II}}$ with thioacetamide and the solubility products of the metal sulphides has been observed. Numerous conflicting values for the solubility products of these sulphides are to be found in the literature so only one source[19] was used in the comparison.

Waggoner[19] has evaluated the solubility product constants of the metal sulphides by means of the best available thermodynamic data. A comparison of the direct reaction constants observed so far with the solubility product constants of Waggoner (Table V) points out that, in general, the less soluble the precipitated sulphide, the faster is the rate of the direct reaction.

It is to be pointed out that these rate constants were obtained at 90° and the solubility products reported for 25°. In addition, the solubility product values certainly are not quantitatively applicable to solutions containing high concentrations of foreign electrolytes. For these reasons, no quantitative correlation between the rate constants and solubility products has been attempted.

Also, a correlation between the direct reaction rate constants of the above mentioned elements and the ionic radii of those elements has been observed. This correlation would seem to lend substantiation to the claim that the reactions of lead, cadmium, nickel, and zinc ions to form sulphides in the pH 3–6 region is a direct reaction between the metal ion and thioacetamide.

TABLE V.—CORRELATION OF DIRECT REACTION RATE CONSTANTS WITH SOLUBILITY PRODUCTS OF METAL SULPHIDES

Metal	$k_d \times 10^4$ (90° C)	k_{SP} (25° C)
Ni^{II}	2.2	1.8×10^{-21}
Zn^{II}	4.2	8.8×10^{-25}
Cd^{II}	8.1	7.8×10^{-27}
Pb^{II}	11.3	8.4×10^{-28}

If the dielectric constant of the medium and the charge of the ion are kept constant, it can be shown that the logarithm of the rate constant should exhibit a linear relationship with the reciprocal of the square of the radius of the ion, for an ion-dipole interaction. The logarithms of the experimentally determined direct reaction rate constants for lead,[18] cadmium,[1] nickel,[2] and the zinc were plotted versus the reciprocal of the square of the crystal radii of these ions as given by Pauling[13]. A surprisingly linear relation was obtained for the cadmium, nickel, and zinc ions, with the slope of this plot in the theoretically predicted direction. The point for lead fell somewhat off this straight line in the direction which would be predicted from the knowledge that lead forms a formate complex of some stability under the conditions of the reaction carried out by Swift and Butler[18].

Analytical considerations

Plots of the calculated rates of precipitation of zinc sulphide by thioacetamide at various pH values as a result of the hydrolysis and of the direct reactions are shown in Figure 2. The calculated rates are on the basis of solutions 0.01 *VF* in zinc and 0.10 *VF* in thioacetamide and at 90°. This graph is similar to those which have been shown for lead[18] and cadmium.[1] The effects on these rates of varying the thioacetamide, hydrogen ion, and zinc ion concentrations can be predicted from the rate expressions.

If one assumes solutions having the composition stated above, the following calculations can be made: $R_h = R_d$ at pH 3.1, where R_d and R_h are the rates of the direct and hydrolysis controlled reactions; $R_h = 1.6 \times 10^3 R_d$ at pH 1; and $R_d = 630 R_h$ at pH 5. The minimum rate of precipitation of zinc sulphide will occur at pH 3.3.

It is apparent from Figure 2 and the above calculations that in solutions having pH values of 2 or less the hydrolysis-controlled reaction predominates and at pH values of 4 or greater the direct reaction controls the precipitation rate. It should be kept in mind that the foregoing discussion neglects any supersaturation effects such as were observed in the hydrolysis-controlled region, and also neglects any effect which a complex-forming ligand might have on the rate of the direct reaction.

Sulphide separations by the use of thioacetamide. Some of the pitfalls involved in the substitution of thioacetamide for hydrogen sulphide as a means for effecting separations have been discussed in previous papers from these laboratories.[1,2,18] In order to ascertain if similar liabilities exist with sulphide separations involving zinc,

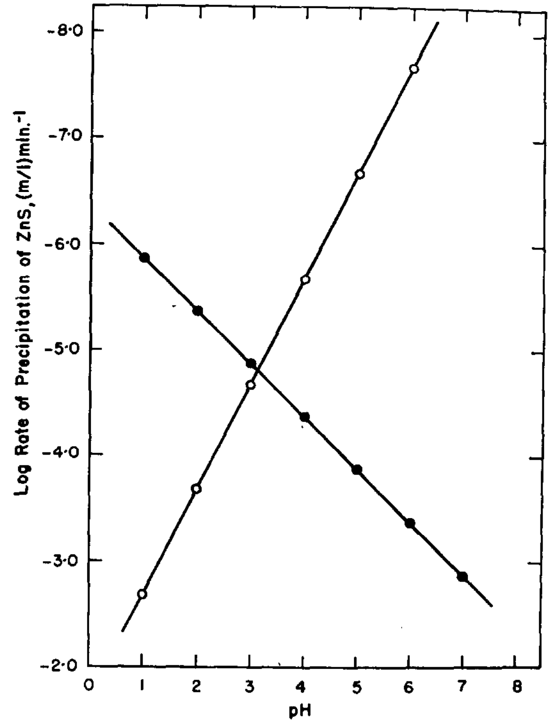

FIG. 2.—Calculated rates of zinc sulphide precipitation at various pH values by the hydrolysis and by the direct reactions.
Temperature: 90°.
0.01 *VF* $Zn(NO_3)_2$
0.10 *VF* CH_3CSNH_2
○ Hydrolysis of thioacetamide
● Direct reaction

the effectiveness of thioacetamide and hydrogen sulphide as precipitants for the separation of lead from zinc and of zinc from nickel were compared. A rigorous quantitative study of all variables was not the intent, but simply the gathering of adequate data to provide a basis for comparing the effectiveness of the two reagents under identical conditions.

Separation of lead from zinc. A hydrogen ion concentration of 0.3 *VF* and a chloride concentration of 0.6 *VF* are frequently recommended for the separation of the conventional Hydrogen Sulphide Group elements (lead, bismuth, copper, cadmium, mercury, arsenic, antimony, and tin) from zinc and the other common elements remaining in the solution. Since similar conditions are used for quantitative separations of these elements from zinc, a study was made of the relative effectiveness of thioacetamide and hydrogen sulphide for the separation of lead from zinc.

Preliminary qualitative experiments, summarized in Table VI, were carried out with solutions containing only zinc in order to obtain information on the effect of the concentrations of various acids and of the time allowed for the precipitation. The findings confirmed the expectation that the direct reaction between zinc and thioacetamide, even at high acidity, can proceed at such a rate as to cause more zinc to precipitate with lead than does hydrogen sulphide, at least without modification of procedure.

TABLE VI.—QUALITATIVE OBSERVATIONS ON THE PRECIPITATION OF ZINC SULPHIDE FROM ACID SOLUTION UNDER VARIOUS CONDITIONS

6 mg Zn^{2+}/ml 50-ml solution 0.40 *VF* CH_3CSNH_2
90° or saturated with H_2S

Conditions	Precipitant	Time, *min*	ZnS precipitated, *mg*
0.3 *VF* $HClO_4$	CH_3CSNH_2	15	> 100
0.3 *VF* $HClO_4$	H_2S	10	> 100
0.3 *VF* HCl	CH_3CSNH_2	20	1–2
		65	> 2
0.3 *VF* HCl	H_2S	65	Slight turbidity
1 *VF* $HClO_4$	CH_3CSNH_2	25	~ 1
1 *VF* $HClO_4$	H_2S	130	Clear solution
1 *VF* HCl	CH_3CSNH_2	60	Slight turbidity

The qualitative results showed that thioacetamide precipitated zinc in solution where hydrogen sulphide did not; presumably the precipitation was a result of the direct reaction. The only experiment shown in Table VI in which a significant amount of zinc sulphide was not produced by thioacetamide after one hour was that in which the solution was 1 *VF* in hydrochloric acid.

In order to evaluate quantitatively the relative effectiveness of hydrogen sulphide and thioacetamide, separations of lead from zinc by each precipitant were carried out in solutions 0.3 *VF* in hydrogen ion and 0.6 *VF* in chloride. Under the experimental conditions prevailing over one half of the thioacetamide should have hydrolyzed after 10 minutes; however, detailed calculations show that with 50, 100, and 200 mg of zinc initially present 0.3, 0.6, and 1.2 mg respectively should be precipitated from 40 ml of solution by the direct reaction in 60 minutes. Because of supersaturation effects, these calculations are subject to some uncertainty and the experimental results shown in Table VII are evidence of this. It is obvious, however, that the direct reaction causes a larger amount of zinc to precipitate with the lead than is the case with hydrogen sulphide. This is in accord with the observations of Lehrman and Schneider[10], who substituted thioacetamide for hydrogen sulphide as a precipitant for the Hydrogen Sulphide Group elements. Schweitzer and Correll[17] found less post-precipitation of zinc sulphide with copper sulphide when thioacetamide was used as the precipitant but these results are not easily comparable because of the different conditions involved.

The amount of zinc precipitated by means of the direct reaction can be minimized by proper control of hydrogen ion concentration and time of precipitation. Thus if the precipitation were begun at a higher hydrogen ion concentration and after an appropriate period this concentration decreased to the required value, precipitation by the direct reaction will be decreased. In addition, if the time of the precipitation is decreased the contribution of the direct reaction is minimized. This time effect is illustrated in Table VII in those experiments in which the time was limited to 15 min.

This study shows that before thioacetamide can be used with confidence as a substitute for hydrogen sulphide for this separation the above factors should be thoroughly studied.

Separation of zinc from nickel. Jeffreys and Swift[9] have outlined the optimum conditions for the separation of zinc from nickel by the precipitation of zinc sulphide with hydrogen sulphide. They recommend the use of a sulphate-hydrogen sulphate buffer of pH 1.8 with a total sulphate concentration of 0.35*VF*. The effectiveness of thioacetamide as compared with hydrogen sulphide as a precipitant under these conditions was studied.

TABLE VII.—COMPARATIVE EFFECTIVENESS OF THIOACETAMIDE AND HYDROGEN SULPHIDE FOR THE SEPARATION OF LEAD FROM ZINC

90° C	Hydrogen ion, 0.3*VM*
40 ml of solution	Chloride, 0.6*VF*
100 mg lead initially	0.40*VF* thioacetamide[1] or saturated with hydrogen sulphide

Zn estimated with Beckman DU spectrophotometer

Zinc initially, *mg*	Precipitant	Time, *min*	Zinc precipitated, *mg*
50	CH_3CSNH_2	15	0.001
50	CH_3CSNH_2	30	0.002
50	CH_3CSNH_2	60	0.067
100	CH_3CSNH_2	15	0.013
100	CH_3CSNH_2	30	0.037
100	CH_3CSNH_2	60	1.5
100	H_2S	15	0.002
200	CH_3CSNH_2	15	0.029
200	CH_3CSNH_2	30	0.18
200	CH_3CSNH_2	60	4.8
200	H_2S	15	0.024
200	H_2S	60	0.089

[1] Hydrogen sulphide equivalent to the lead should have been produced from the thioacetamide after 1 min.

Under the conditions shown in Table VIII one can calculate that at pH 1.7 about 25 minutes is required for the hydrolysis of thioacetamide to give a quantity of hydrogen sulphide equivalent to 100 mg of zinc. However, Bowersox, Smith, and Swift[2] have shown that in this time interval a significant amount of nickel sulphide would be produced by the direct reaction and the data in Table VIII show this effect. Again, these results are not in quantitative agreement with calculated values, but the pattern is as expected. Contamination of the zinc sulphide precipitate exceeded that found when hydrogen sulphide was the precipitant. The observations of Hahn and Shellington[6] that thioacetamide was less effective than hydrogen sulphide for the quantitative separation of zinc from cobalt suggest that cobalt sulphide, like nickel sulphide, may be precipitated by a direct reaction.

TABLE VIII.—COMPARATIVE EFFECTIVENESS OF THIOACETAMIDE AND HYDROGEN SULPHIDE FOR THE SEPARATION OF ZINC FROM NICKEL

90° — pH = 1.7 (25°); $0.3F\ HSO_4^-–SO_4^=$ buffer
40 ml of solution — $0.38\ VF$ thioacetamide[1] or saturated in hydrogen sulphide
100 mg zinc initially[1]

Nickel initially, *mg*	Precipitant	Time,[1] *min*	Nickel precipitated, *mg*
100	CH_3CSNH_2	15	< 0.02
100	CH_3CSNH_2	30	< 0.02
100	CH_3CSNH_2	60	0.06
100	CH_3CSNH_2	120	1
100	H_2S	15	< 0.02
100	H_2S	120	< 0.02
200	CH_3CSNH_2	15	< 0.02
200	CH_3CSNH_2	30	< 0.02
200	CH_3CSNH_2	60	0.08
200	CH_3CSNH_2	120	1.4
200	H_2S	15	0.02
200	H_2S	120	0.06

Hydrogen sulphide equivalent to 100 milligrams of zinc formed from thioacetamide after 25 min under these conditions.

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Zusammenfassung—Die Geschwindigkeit der Fällung von Zinksulfid durch Thioacetamid in Lösungen mit pH kleiner als 2·5 ist durch die Geschwindigkeit der Hydrolyse des Thioacetamid zu·Schwefel wasserstoff kontrolliert. Ubersättigungserscheinungen treten am Beginne der Fällung auf. Die Reaktion ist erster Ordnung in Bezug auf die Konzentration von H^+-Ion und Thioacetamid. In Lösungen mit pH-Werten zwischen 4·5 und 6·3 verläuft die Fällung direkt nach der Geschwindigkeitgleichung

$$-\frac{d[Zn^{+2}]}{dt} = kd\,\frac{[Zn^{+2}][CH_3CSNH_2]}{[H^+]^{1/2}}$$

Die Geschwindigkeitskonstante, K_d, ist $4{\cdot}2 \times 10^{-4}$ $Liter^{1/2} \times Mole^{-1/2} \times Min.^{-1}$ bei 90°C. Die Aktivierungsenergie ist 19 ± 2 kcal pro Mol im Gebiete 70–90°C.

Fällungen nach dieser Geschwindigkeitsgleichung traten auf bei Wasserstoffionenkonzentrationen die höher sind als jene, bei denen Zinksulfid durch Schwefelwasserstoff niedergeschlagen wird. Studien über die relative Wirksamkeit von Thioacetamid und Schwefelwasserstoff bei der Trennung von Blei und Zink durch Sulfidfällung aus ca. 0·3 m salzsaurer Lösung ergaben, dass durch Thioacetamid mehr Zink gefällt wird als durch Schwefelwasserstoff. Dies wird durch die obige, direkte Reaktion erklärt. Durch geeignete Modifikation der Methode, richtige Zeitkontrolle and korrekte Wasserstoffionenkonzentration ist eine völlige Trennung mittels Thioacetamide möglich.

In ähnlicher Weise wurde mehr Nickel mit Zink niedergeschlagen, wenn Thioacetamid als Fällungsmittel bei pH 2 verwendet wurde. Spectrophotometrische Studien gaben keine Evidenz für die Bildung von Zink-Thioacetamidkomplexen in neutraler Lösung.

Résumé—La vitesse de précipitation du sulfure de zinc par la thioacétamide à partir de solutions ayant des pH inférieurs à 2,5 est contrôlée par la vitesse d'hydrolyse de la thioacétamide en hydrogène sulfuré; il peut y avoir initialement une sursaturation importante. La réaction est du premier ordre par rapport aux concentrations en ion hydrogène et en thioacétamide. Dans des solutions ayant des

pH compris entre 4,5 et 6,3 la précipitation a lieu par une réaction directe conforme à l'expression

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = k_d \frac{[\mathrm{Zn(II)}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

La constante de vitesse k_d est égale à 4, $2 \cdot 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min^{-1} à 90°C et l'énergie d'activation à 19 ± 2 kcal par mole dans le domaine 70–90°C.

La précipitation conforme à l'expression de la vitesse avait lieu pour des concentrations en ion hydrogène plus élevées que celles pour lesquelles on pouvait obtenir la précipitation par l'hydrogène sulfuré. Des études sur l'efficacité relative de la thioacétamide et de l'hydrogène sulfuré pour séparer le plomb à l'état de sulfure du zinc par précipitation à partir de solutions approximativement 0,3 *VF* en acide chlorhydrique ont montré que l'on précipitait plus de zinc par la thioacétamide que par l'hydrogène sulfuré; la précipitation est attribuée à la réaction directe ci-dessus. Par une modification du procédé et un contrôle convenable du temps et de la concentration en ions hydrogène on peut faire une séparation efficace avec la thioacétamide.

D'une manière analogue, on précipitait plus de nickel avec le sulfure de zinc à partir de solutions de pH environ 2 quand la thioacétamide était le réactif precéipitant.

Des études spectrales n'ont pas donné la preuve de la formation de complexes zinc-thioacétamide dans les solutions neutres.

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PRELIMINARY COMMUNICATION

The reactions of certain metals with thioacetamide

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DURING the past several years a programme of investigations has been in progress in these laboratories on the reactions involved in the precipitation of metal sulphides from aqueous solutions by thioacetamide. Because of the present interest in this general topic we have decided to publish certain preliminary results which have been obtained, since in some cases it seems unlikely that the investigations can be completed within the near future. Other investigators wishing to concern themselves with these phenomena should feel free to do so.

Preliminary experiments by C. B. Moore have established that in acid solutions the rate of the precipitation of silver sulphide by thioacetamide (TAA) is controlled by the hydrolysis of the TAA at pH values less than 2, and by a direct reaction between the TAA and silver ion when the pH is greater than 3. Under the conditions prevailing, the rate of precipitation by the direct reaction was decreased by an increase in the concentration of TAA and the inhibition effect was observed to be third order. The kinetic evidence indicated the formation of a silver-TAA complex, and preliminary potentiometric studies by J. D. Lamb have established that in solutions of pH 2 to 3, in which the concentration of TAA is 5 to 10 times the silver concentration, a complex of the type $Ag(TAA)_4$ exists. The stability of this or similar complexes is such that precipitates of silver sulphide can be dissolved by concentrated TAA solutions.

Silver is the first metal for which the rate of precipitation of the sulphide by the direct reaction has been observed to be inhibited by TAA. Subsequent experiments by D. M. Smith and D. V. Owens have established a similar inhibition in the precipitation of mercury^{II} sulphide by TAA from acetate buffer solutions having a pH of 4.

Frank Booth has observed that in ammoniacal solutions of copper^{II} and TAA there is a rapid reaction to form a brown-black precipitate, presumably a sulphide, which appears to be complete in less than a minute at room temperature. In solutions having pH values of 1 or less, and with an initial ratio of TAA to copper^{II} of 10 or greater, there is a very rapid, apparently quantitative, reduction of copper^{II} to copper^{I} accompanied by the formation of finely divided sulphur. A single determination of the amount of sulphur precipitated agreed within 5% with the stoichiometric value.

It appears that the resulting copper^{I} is strongly complexed by the TAA, since passage of hydrogen sulphide through the solutions after the reduction produced no noticeable effect. In addition, solutions resulting from the reduction could be left standing in the cold for up to 36 hours without precipitate formation. If these solutions were heated to 50° or higher, brown-black precipitates quickly formed. Visual comparisons of sulphur precipitates indicated that the rate of formation of sulphur is first order with respect to the hydrogen ion, the TAA, and the copper^{II} concentrations.

When the initial ratio of TAA to copper^{II} was increased to 50 and the pH was approximately 3, the rate of the reduction appeared to be slower, but sulphide formation took place within a relatively short time after the reduction appeared to be quantitative. At higher pH values sulphide formation began before the reduction of the cupric copper appeared complete.

Experiments by Glenn Crabbs indicated that it is possible to obtain quantitative precipitation of approximately 1 millimole of tin^{IV} by about 6 millimoles of TAA from 100 millilitres of $0{\cdot}3F$–$0{\cdot}6F$ hydrochloric acid solutions in 10–15 minutes at approximately 90°. No rate measurements were made.

Experiments by M. J. Kallerud indicated that precipitation of a sulphide from molybdenum^{IV} solutions by TAA appears to take place through both the hydrolysis of the TAA and a direct reaction.

The direct reaction predominates at pH values of 4 and greater. The rate of the reduction of molybdenum^{IV} appeared to decrease as the pH was increased.

Experiments by F. C. Anson have shown that the addition of hydrazine to acid solutions of TAA accelerates sulphide formation. This acceleration was most obvious at pH values between 4 and 7, where the acid hydrolysis is inconveniently slow for analytical purposes. Thus, sulphide formation is increased by approximately 16,000-fold when a solution buffered by an acetic acid-acetate buffer to a pH of 5 and with a TAA concentration of 0·03 *VF* is also made 0·08 *VF* in hydrazine. Because of the obvious analytical implications of this effect a study of the reactions involved is in progress.

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SHORT COMMUNICATION

Radiochemical separations by amalgam exchange

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A RAPID and selective radiochemical separation procedure has been developed using the techniques of amalgam exchange. Separation of the radio-isotope takes place by virtue of the rapid exchange occurring between an element present in a dilute amalgam and its ions in solution. If there are many more inactive atoms of the element in the amalgam than there are of its radio-isotope in solution, amalgam exchange will result in almost all of the activity being incorporated in the amalgam. (In this it is somewhat similar to the isotopic exchange separation of silver.[1]) Selectivity is obtained since ions of other elements in solution will not exchange with the desired element in the amalgam. In the case of cadmium, thallium, lead and bismuth, amalgam exchange has been reported to be exceedingly rapid,[2,3] thus the method can be useful for the separation of short-lived isotopes. In this preliminary survey of the method it appears that amalgam exchange can give satisfactory yields in short periods of time for a number of radio-elements.

EXPERIMENTAL

Apparatus and reagents

A 50-ml round-bottom centrifuge tube was used for all extractions. The aqueous and mercury layers were vigorously agitated by a glass stirring rod rotated at 1500 to 2000 r.p.m. by an electric stirrer. All aqueous solutions were made with distilled water from salts of analytical reagent purity. Mercury and other solid metals used to make the amalgams were of analytical reagent purity, and in some cases of spectroscopic standard purity.

Preparation of amalgams

Amalgams of bismuth, cadmium, gallium, indium, lead, tin, thallium, and zinc were prepared by direct combination (with heating) of metal with the mercury. The strontium amalgam was prepared by reducing a solution of strontium nitrate with sodium amalgam. All amalgams were made to contain 2% by weight of the element to be exchanged.

Procedure

To test the method 2 ml of a solution containing a particular electrolyte and tracers of the element to be exchanged were added to the centrifuge tube. One half gram of the amalgam was added to the solution with a calibrated micro pipette and the solution stirred for five minutes. An aliquot of the solution was then measured for activity.

In all of the experiments a volume ratio of 40 : 1 was maintained between the aqueous solution and the amalgam.

RESULTS AND CONCLUSIONS

A short summary of typical yield results for several different electrolytes is shown in Table I. Individual amalgams containing milligram amounts of cadmium, thallium, bismuth, strontium, zinc, indium, or lead have been found to remove trace amounts (μgm or smaller) of their respective radioactive isotopes from dilute acid or salt solution with a yield of at least 50% in five minutes of stirring. Tin and gallium did not exchange.

One problem arises in that these amalgams have a reducing power comparable to the reducing power of the pure metal of which the amalgam is made.[4] These contaminants as well as other oxidizing agents (MnO_4^-, $Cr_2O_7^{2-}$, etc.) can cause a considerable reduction in the yield of the desired

TABLE I. EXCHANGE OF AN ELEMENT WITH ITS AMALGAM
(Five minute stirring time)

Isotope and amount	Solution	Exchange %
^{212}Bi (*)	5M HCl	49
^{115m}Cd (24 μg)	0.5M $NaClO_4$	94
	0.5M $Na_2C_2O_4$	94
	0.5M $NaNO_3$	94
	5M $HClO_4$	94
^{72}Ga (1 mg)	0.5M $NaNO_3$	none
	sat'd NaCl	none
	2M $HClO_4$	none
	2M HNO_3	none
^{114}In (1 mg)	5M HCl	50
^{212}Pb (*)	0.5M $NaNO_3$	90
^{113}Sn (1 mg)	0.5M $NaNO_3$	none
	sat'd NaCl	none
^{90}Sr (*)	0.5M $NaNO_3$	50–60
^{204}Tl (21 μg)	0.5M $NaNO_3$†	85
^{65}Zn (40 μg)	0.5M $NaNO_3$	90

* Carrier free.
† This value is taken at two minutes stirring.

metal. This potential source of contamination in the separation might be avoided, however, by bringing the solution into contact with an amalgam made of an element (scavenger) which is just below the desired element in the electromotive series. This separation would then be followed by contact with a larger amount of amalgam of the desired element.

The potentialities of this method can be shown in the separation of cadmium from zinc. This usually difficult separation was accomplished in three minutes with a decontamination factor for zinc of 10^4 by agitation of the cadmium amalgam with a solution of the cadmium and zinc.

At the end of the separation the desired activity is in the amalgam. Direct gamma-ray counting of the amalgam may be possible without too large an error caused by absorption losses, although β counting might prove more troublesome. In any case it may be possible to strip the element selectively from the mercury, either by a wash with an oxidant or by electrolytic stripping.

A detailed evaluation of this method for elements which demonstrate the exchange is being made by measuring the purity of activity separated from solutions containing many representative tracers. Problems of the accurate assay of the activity separated by this amalgam method are also being studied.

Acknowledgement—This work was supported in part by the U.S. Atomic Energy Commission.

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Talanta, 1960, Vol. 3, pp. 300 to 301. Pergamon Press Ltd. Printed in Northern Ireland

JAROSLAV HEYROVSKÝ

Nobel Prizewinner in Chemistry 1959

THE recent announcement of the award of the Nobel Prize in Chemistry for 1959 to Professor Jaroslav Heyrovský is one that will be received with acclaim, the world over. All chemistry is based essentially on good analysis and it is therefore fitting that the prize should once more be awarded for the evolution of an analytical technique.

The polarographic method of analysis first formulated by Heyrovský in a paper to *Chemické Listy* in 1922 has found application in all fields of chemistry. It has been used for purposes as diverse as measuring *in situ* the oxygen content of blood within the heart and the direct analysis of trace metals in fused salt media. Extensive applications have been found in inorganic, physical and organic chemistry where the method may be applied with equal facility to the determination of traces of metals, the study of reaction kinetics, the analysis of antibiotics, etc.

In the early stages the adoption of polarography as a standard method was curiously slow. During the 1930's some momentum was gained, but the war years brought recognition when dust-covers were removed from many instruments that had lain idle since the first flush of enthusiasm which led to their purchase. The high sensitivity and discrimination of polarography even with simple inexpensive equipment, and its toleration of high concentrations of indifferent electrolyte, ensured its speedy application when the need arose. Now the popularity of the method has burgeoned forth to such an extent that few institutions in industry or academic life can function properly without a polarograph. No longer does one hear references to "the polarographer's art"; the method has come of age and is accepted universally with respect.

And this, apart from the inherent merit of the method itself, is largely due to Heyrovský the man. In his laboratories and latterly his world-famous institute, like another Nobel prizewinner beloved of microanalysts, he has *taught* chemists of all nations with consummate skill and fired them with his own burning enthusiasm. (The enthusiasm of polarographers is well known.) No one who has met this quiet, gentle, unassuming Czech can fail to be impressed or to cherish the memory. It is difficult to decide which is the greatest: Heyrovský the scientist, the teacher or the man.

Heyrovský was born in Prague on December 20th, 1890, the son of Leopold Heyrovský, Professor of Roman Law at the Czech University. His chemical studies began there in 1909 and were continued at University College, London, where he took his B.Sc. in 1913, under the professorship of Sir William Ramsay. Whilst holding the post of University demonstrator there, his interest in electrochemistry was aroused by Professor F. G. Donnan.

After the war, Heyrovský, now at Charles University, Prague, and still interested primarily in electrochemistry, accepted a suggestion by Professor G. Kucera that he should investigate some mysterious inflections which the latter had observed in the electrocapillary curve for mercury when a dropping mercury electrode was used in a solution containing reducible ions. This eventually led to the "discovery" of polarography in 1922. The first polarograph was described by Heyrovský and his Japanese co-worker Shikata in 1925, and the mathematical theory was worked out by the Czech physicist D. Ilkovič in 1934. In 1922 Heyrovský was appointed Associate Professor at Charles University and in 1926 he became its first full Professor of physical chemistry. From that date the development and teaching of polarography proceeded hand in hand.

In 1950 Heyrovský was appointed director of the newly formed Polarographic Institute and in 1951 his country honoured him with the national laureateship. In 1952 the Polarographic Institute was incorporated in the Czechoslovak Academy of Sciences and in 1955 he was awarded the Order of the Czechoslovak Republic. He holds several honorary degrees and is an honorary member of nine foreign chemical societies. He has travelled extensively on lecture tours throughout Europe and the far East, and is a well known figure to many outside his own country.

His influence on the course of chemistry in Czechoslovakia and in the world generally has been most marked and it is indeed fitting that he should have been awarded the highest international scientific honour in this year of his sixty-ninth birthday.

T. S. WEST

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BOOK REVIEWS

Comprehensive Analytical Chemistry, Volume 1A: Classical Analysis. Edited by Cecil L. Wilson and David W. Wilson. Elsevier Publishing Company, Amsterdam: D. Van Nostrand Company, Ltd., London: D. Van Nostrand Company, Inc., New York. 1959. Pp. xix + 577. 105s.

The announcement of the project of a new comprehensive work on analytical chemistry was received by analysts with great interest, and it is fair to say that all who heard of it were filled with curiosity to see how the Editors would tackle their task, and how comprehensive the result would turn out to be. It was clear from the advance advertisements that the work would be of great calibre, and this expectation was if anything enhanced by the eminence of the collaborators engaged on the text.

It is not long since emphasis was laid on the desiderata of textbooks on analytical chemistry in articles that appeared on both sides of the Atlantic; and the view was expressed with firmness in the United States of America that one could no longer expect a single specialist to master the whole subject. On the other hand, it was thought that each chemist might tend to think too much in terms of his own special group of methods, and so be unable to command the whole field of the subject. And it has to be recognised that this field becomes daily wider. What was needed, it was said, was an integration of such groups of methods into the whole scheme of analytical chemistry. "Unfortunately", it is written in *Analytical Chemistry*, "we do not find the climate of our Universities conducive to such growth... We trust that some editor-in-chief... may in his more mature years have gained sufficient wisdom, knowledge and inspiration to write a definitive work on how the various techniques should be integrated in solution of analytical problems so that the answer is obtained quickly. This is a challenging task, but we believe it is not impossible if the writer thinks in terms of analytical chemistry and not as a specialist."

These words have been quoted before, but no apology is needed for their re-appearance; they are surely fundamental to the matter of any new book on the subject under review. For not only are up-to-date descriptions of the newer techniques required in all parts of the work, but it is their assimilation into a comprehensive whole that must be achieved as well if the work is to reach its objective of presenting its subject as a living, vibrant whole.

And what subject could prove more fascinating to any craftsman? It is true that analysts are scientists, but the practising analyst must also be a craftsman, and one of a very high order of skill. The first volume of this work deals with *Classical Analysis*, a subject that has rudely been defined as beaker and filter work, but nevertheless one that offers the finest opportunities for the application of skill that are to be found. If, indeed, it tends sometimes to seem out-of-date and cumbersome to those newly entering the practice of analytical chemistry, one would advise them to see how closely they can match the more famous determinations, perhaps of atomic weights, in accuracy or precision of result.

This test is a severe one, and likely to be undertaken only by those who have already a feeling of pleasure in things well done for their own sake. Let us not, however, think that it is only classical analysis that can command such feelings. Some of the newer techniques lose in accuracy while having been made simpler to operate, and some "push-button" instruments are obviously not so accurate as the longer and more difficult methods they replace; but on the other hand many others of the newer methods of approach to analysis gain in delicacy from their mechanisation; and in skilful hands give information that could never have been derived by the more massive chemical separations. Often it is purely physical methods that give the extra delicacy of separation, but not always. Not a few of today's advances come from a refining of the already highly polished methods of yesterday. Compare, as this volume, does, the analytical balance of yesterday and today with the micro-balance and the ultra-micro balance; and the advance made in a decade or two is at once plain. Apply the study of Statistics to analytical work, and see how it will bring certainty, even if only certainty of how large is the uncertainty of one's work, to chemical analysis. Consider the need for accuracy in sampling, today an advanced subject, and see how much one relied on chance for accurate replication of results in the past, and how much more precise thay may be made now.

But this is to mention a very few of the branches of the subject that are dealt with in this first volume. It is right to mention all the headings: After a general introduction by the Editors, there is a chapter dealing with the *Materials* used for analytical vessels (G. H. Wyatt), *Sampling* (R. C. Tomlinson), *Statistics* (E. C. Wood), *Weighing* (G. F. Hodsman), *Measurement of Volume* (R. Goulden), *Solvent Extraction* (G. H. Morrison and H. Freiser), and *Organic Reagents in Inorganic Analysis* (F. Holmes).

Gas Analysis is described in the third chapter by A. E. Heron and H. N. Wilson. P. W. West, H. Weisz and A. O. Parks deal with *Inorganic Qualitative Analysis*, and A. McGookin with *Organic Qualitative Analysis*. The sixth and final chapter is on *Inorganic Gravimetric Analysis;* it is introduced by Professor C. L. Wilson, and written by F. E. Beamish and W. A. E. McBryde and L. Gordon. This last chapter discusses the preparation of precipitates, their filtration and washing, and subsequent weighing; the purity of reagents, the use of organic reagents, and practical and theoretical considerations; filtering media, crucibles, heating devices, desiccators and miscellaneous apparatus; and finally precipitation from homogeneous solution of hydroxides and various anions. Generally speaking this chapter may be said to review the subject of gravimetric inorganic analysis pretty thoroughly in the course of rather more than 100 pages; but the reader will not find in it the specialised directions for the determinations of each cation and anion that would have appeared in most of the older textbooks on analysis, except in a few instances.

The Editors have rather been at pains to achieve what has been looked for of late, and to review the whole subject covered by their title page. Emphatically they have not produced just another cookery-book.

It is too early to foresee just how the remaining volumes of this great work will turn out. A study of the first section leaves one full of respect for the Editors and authors and of pleasure at what they have already achieved. Let us hope that all concerned will go from strength to strength, and that the completed work will fully justify the promise of its start.

K. A. WILLIAMS

Laboratory Glassblowing. L. M. PARR and C. A. HENDLEY. George Newnes Ltd., London, 1956. Pp. vii + 160. 21s.

VERBAL or written instructions of the technique of glassblowing can become extremely involved and detailed, but remain, at the same time, completely inadequate. The authors have avoided many of the usual faults of this type of book and have presented adequate details of most glassblowing techniques in a simple and lucid manner: in particular, their many diagrams are extremely clear and accurate. Two unusual aspects of this book deserve comment: first, for certain articles the authors give methods of construction which give satisfactory results but which are not necessarily employed by professional glassblower (indeed, he would probably be horrified with some of the details); second, as well as those for standard glassblowing exercises, details are given for the making of stopcocks, metal-to-glass seals and calibrated apparatus which the reader would not expect to find in such a small volume. The book is well-indexed, and contains appendices which list important data such as standard joint and tap specifications and sources of supply of glassblowing equipment.

The book is very readable, so much so that the text could be described as "gripping" in that it is difficult to put down the book until the job in hand is successfully completed. The book is also written with some gentle humour, not all of which is intentional; the legend "no sudden construction" at the end of an arrow pointing to the centre of a diagram of the requirements of a stopcock is wholly accurate for a beginner, if not wholly proof-read!

Because of the nature of glassblowing it is doubtful whether a complete novice would soon become a highly competent glassblower with the aid of this book alone. However, a worker with a little knowledge of the technique will become a much more accomplished glassblower in a much shorter time if he has this book at his side.

D. A. PANTONY

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D. A. PANTONY

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NOTICES

The following meetings have been arranged:

Tuesday 12 *January* 1960: **Society for Analytical Chemistry,** Midlands Section and Microchemistry Group. *Micro Gas Analysis:* G. J. MINKOFF, D.Sc., D.I.C. Mason Theatre, The University, Edmund Street, Birmingham, 3, England. 6.30 p.m.

Wednesday 20 *January* 1960: **Society for Analytical Chemistry,** Biological Methods Group. *Antibiotic Assay in Body Fluids:* Professor L. GARROD, M.A., M.D., F.R.C.P. Burlington House, London, W.1. 7.0 p.m.

Monday–Thursday 25–28 *January* 1960: Thirteenth Annual Symposium on *Modern Methods of Analytical Chemistry.* Louisiana State University, Baton Rouge, Louisiana, U.S.A. The speakers will include Dr. ROGER BATES, Dr. T. S. BURKHALTER, Dr. JAMES FRITZ, Dr. RUSSELL KEIRS, Dr. I. M. KOLTHOFF, Dr. HERBERT LAITINEN, Dr. SEAN MCGLYNN, Dr. G. W. C. MILNER, Dr. ROBERT MITCHELL and Dr. JAMES W. ROBINSON.

Wednesday 27 *January* 1960: **Society for Analytical Chemistry,** Microchemistry Group. London Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

Friday 29 *January* 1960: **Society for Analytical Chemistry,** Scottish Section. Annual General Meeting followed by an address by D. W. KENT-JONES, B.Sc., Ph.D., F.R.I.C. Glasgow, Scotland. 1.30 p.m.

Saturday 30 *January* 1960: **Society for Analytical Chemistry,** North of England Section. Annual General Meeting followed by *Analytical Methods in Clinical Biochemistry:* H. VARLEY, M.Sc., F.R.I.C. Nag's Head Hotel, Lloyd Street, Manchester, England. 2.15 p.m.

Wednesday 3 *February* 1960: **Society for Analytical Chemistry.** Organised by the Physical Methods Group in conjunction with the **Society of Chemical Industry,** Oils and Fats Group. *Spectroscopic Investigation of Fats.* Burlington House, London, W.1. 7 p.m.

Registration forms for the Third Gas Chromatography Symposium, of which a preliminary notice appeared in our issue for August 1959, are now available. They may be obtained from Miss P. E. HUTCHINSON, Assistant Secretary, The Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1., or Mr. L. BREALEY, Standards Department, Boots Pure Drug Co., Ltd., Station Street, Nottingham, England, or Mr. D. H. DESTY, British Petroleum Co., Ltd., Research Station, Chertsey Road, Sunbury-on-Thames, Middlesex, England.

The fifteenth Annual General Meeting of the Physical Methods Group of the Society for Analytical Chemistry was held on Tuesday 24 November 1959 in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Group, Mr. R. A. C. ISBELL, A.Inst.P. The following Officers were elected for the forthcoming year:

Chairman:	Dr. G. W. C. MILNER, F.R.I.C., A.Inst.P.
Vice-Chairman:	Dr. W. CULE DAVIES, F.R.I.C.
Hon. Secretary and Treasurer:	Dr. T. L. PARKINSON. B.Sc., F.R.I.C., Product Research Division, Beecham Foods Ltd., Beecham House, Great West Road, Brentford, Middlesex, England.

The Annual General Meeting was followed by the 69th Ordinary Meeting of the Group. Dr. MILNER was in the Chair, and the retiring Chairman gave a lecture on *The Design of Optical Instruments for Chemical Analysis.*

The *B.S.I. News* announces, among others, the following new British Standard:

B.S. 3145, 1959: *Laboratory potentiometric pH meters.* This specifies input current, details of calibration, stability, sensitivity, temperature compensation, auxiliary pH control, electrode-connexion and screening. (Price 3s.)

The following Standards have been revised:

B.S. 1016: *Methods for the Analysis and testing of coal and coke*, Part 8, 1959: *Chlorine in coal.* This deals with the determination of chlorine in coal by the Eschka and high temperature methods. (Price 4s. 6d.) Part 12: 1959: *Caking and swelling properties of coal.* This deals with the determination of the crucible swelling number and of the Gray-King coke type of coal. (Price 6s.)

B.S. 1309: 1959: *Methods of sampling and analysis of vegetable-tanned and chrome-tanned leathers.* In this, instructions for sampling are given, together with diagrams. Methods for the determination of volatile matter, total ash and *p*-nitrophenol in both vegetable-tanned and chrome-tanned leathers, water-soluble matter, sulphated total ash, sulphated ash of water-soluble matter, insoluble ash, oils and fats, nitrogen and hide substance, degree of tannage, sugars, magnesium salts, pH of aqueous extract and acid figure in vegetable-tanned oils and grease, and uncombined sulphur and chromium in chrome-tanned oils are provided. (Price 8s. 6d.)

The Optical Society of America announces a translation, *Optics and Spectroscopy*, of the Russian Journal *Optika i Spektroscopiya.* This monthly Journal of the USSR Academy of Sciences commenced publication in 1956 and publishes the work of leading Russian scientists in all branches of optics and spectroscopy, including X-ray, ultra-violet, visible, infra-red, and micro-wave; thin layer optics, filters, detectors, diffraction gratings, electroluminescence thermal radiation backgrounds, infra-red polarizers, and their many other applications in science and industry. The English translation, which is being published with a grant-in-aid from the National Science Foundation, starts from Volume 6, January 1959, and it is the aim of the Society that *Optics and Spectroscopy* will appear within four months of the Russian original.

Further information may be obtained from Professor MARY WARGA, Executive Secretary, Optical Society of America, Executive Office, 1155 Sixteenth Street, N.W., Washington, 6, D.C., U.S.A.

Developments in Analytical Chemistry

The Birmingham and Midlands Section of the Royal Institute of Chemistry has arranged a Spring Lecture Course on *Developments in Analytical Chemistry* at the College of Advanced Technology, Birmingham, on the mornings of the Saturdays in March, 1960.

Registration forms and further particulars may be obtained from Dr. M. WILLIAMS, Hon. Asst. Secretary, B.M.S., R.I.C., 24, Conchar Road, Sutton Coldfield, Warwickshire.

Talanta, 1960, Vol. 3, p. 306. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

The analysis of beryllium and beryllium oxide—I: The determination of iron. J. O. Hibbits, W. F. Davis and M. R. Menke. (23 *November* 1959).

The analysis of beryllium and beryllium oxide—II: The determination of copper. J. O. Hibbits, W. F. Davis and M. R. Menke. (23 *November* 1959).

The analysis of beryllium and beryllium oxide—III: The determination of molybdenum. J. O. Hibbits, W. F. Davis, M. R. Menke and S. Kallmann. (23 *November* 1959).

Spectrophotometric determination of zirconium in uranium alloys of the fission elements. R. P. Larsen, L. E. Ross and Gwendolyn Kesser. (23 *November* 1959).

Spectrophotometric determination of fluoride using lanthanum chloride. Kiyoko Hayashi, Taeko Danzuka and Keihei Ueno. (23 *November* 1959).

Radiochemical separations by amalgam exchange. James R. DeVoe, Chong K. Kim and W. Wayne Meinke. (23 *November* 1959).

The minimum ignition temperature of aluminium oxide precipitates. Oscar I. Milner and Louis Gordon. (23 *November* 1959).

A new method for the determination of the actual content of acid chloride in the chlorides of carboxylic acids. K. Burger and E. Schulek. (30 *November* 1959).

The chromatography of sugars. R. W. Bailey and J. B. Pridham. (30 *November* 1959).

The separation of carrier-free ^{234}thorium (UX_1) from uranium by anion-exchange. S. S. Berman, Lorna McKinney and M. E. Bednas. (1 *December* 1959).

Utilization of ternary and ion-association complexes in chemical analysis—II: Polarographic determination of indium. M. Kopanica and R. Přibil. (8 *December* 1959).

The determination of tantalum in rocks by neutron-activation analysis. D. F. C. Morris and A. Olya. (9 *December* 1959).

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TITRIMETRIC ANALYSIS OF 3:5-DINITROBENZOATE DERIVATIVES

W. T. Robinson, Jr., R. H. Cundiff, A. J. Sensabaugh and P. C. Markunas
R. J. Reynolds Tobacco Company, Winston-Salem, N.C., U.S.A.

(*Received* 10 *August* 1959)

Summary—The neutralization equivalents of 3:5-dinitrobenzoate ester derivatives of alcohols and ethers were ascertained by refluxing with pyridine followed by potentiometric titration of the pyridine solution with 0.01*N* tetrabutylammonium hydroxide.

INTRODUCTION

Perhaps the most useful means of isolation and identification of alcohols is through the preparation of their 3:5-dinitrobenzoate derivatives. Although some of the 3:5-dinitrobenzoate esters have low melting points, they crystallize readily and are easily obtained in a pure form. Dinitrobenzoate derivatives are also employed to a lesser extent in the identification of some aliphatic ethers, phenols, mercaptans and amino acids. These derivatives have been identified by melting point data, elemental analysis, infrared and absorption spectroscopy and chemical microscopy.

Fritz, Moye, and Richard[1] demonstrated that anilines substituted in the 2:4 or 2:4:6 positions with at least two nitro groups, or with one nitro group and one or more chloro groups can be titrated as acids in pyridine with a quaternary ammonium hydroxide base, and Sensabaugh, Cundiff and Markunas[2] showed that 2:4-dinitrophenylhydrazones can be titrated as weak acids in pyridine with 0.01*N* tetrabutylammonium hydroxide.

In the present study, 3:5-dinitrobenzoates were found to be sufficiently acidic to be analyzed in a similar manner; however, refluxing of the pyridine solutions, before titration, was necessary to obtain stoichiometric values. If the proposed procedure is combined with the traditional qualitative analysis techniques, it can be a most valuable supplementary adjunct for the identification of unknown alcohols.

EXPERIMENTAL

Reagents and apparatus

Tetrabutylammonium hydroxide, 0.01*N*: Prepare 0.1*N* tetrabutylammonium hydroxide as described previously.[3] Add 30 ml of methanol to 100 ml of this solution and dilute to 1 litre with benzene. Standardize against benzoic acid in pyridine solution. The dilution contains approximately 25 parts of benzene to one part of methanol and is stable for at least 30 days.

Precision-Dow Recordomatic Titrometer (Precision-Scientific Company, Chicago, Illinois).

The remainder of the reagents and apparatus are as described in a previous article.[3]

Procedure

Accurately weigh 2 to 20 mg of the 3:5-dinitrobenzoate into a standard tapered 125-ml Erlenmeyer flask, dissolve in 50 ml pyridine and reflux for 30 minutes. Cool to room temperature, transfer to a 250-ml electrolytic beaker and titrate potentiometrically under nitrogen with 0.01*N* tetrabutylammonium hydroxide. Determine the potentiometric end-point and correct for the solvent blank.

RESULTS

Fig. 1 shows a typical potentiometric curve for titration of an alcohol 3:5-dinitrobenzoate. Table I lists the results obtained in the analysis of representative 3:5-dinitrobenzoates. *d*-Mannitol 3:5-dinitrobenzoate is hexabasic and diethylene glycol 3:5-dinitrobenzoate is dibasic, while the remainder of the compounds listed are monobasic. All results listed are the average of at least two determinations.

TABLE I.—ANALYSIS OF 3:5-NITROBENZOATES BY TITRATION WITH 0.01*N* TETRABUTYLAMMONIUM HYDROXIDE

3:5-Dinitrobenzoate of	Melting Point, °C	Neutralization Equivalent		% Purity
		Theoretical	Experimental	
d-Mannitol	90.5	224.46	224.88	99.82
Methyl alcohol	106–107	226.17	225.90	100.33
Ethyl alcohol	92.5–93	240.19	241.80	99.34
Diethylene glycol	152–154	247.16	248.96	99.37
Allyl alcohol	46.5–47	252.21	252.87	99.74
n-Propyl alcohol	71.5–72	254.19	253.01	100.47
*iso*Propyl alcohol	122.5–123	254.19	255.65	99.43
n-Butyl alcohol	61–61.5	268.23	268.30	99.98
*iso*Butyl alcohol	82–83	268.23	265.18	101.16
sec-Butyl alcohol	74.5–75.5	268.23	268.55	99.88
tert-Butyl alcohol	143.5–144	268.23	272.23	98.53
tert-Amyl alcohol	106–108	282.25	282.19	100.03
*iso*Amyl alcohol	58–59	282.25	285.05	99.20
Ethylene glycol monoethyl ether	73–74	284.22	283.50	100.25
*cyclo*Hexanol	111–111.5	294.26	300.41	97.96
Benzyl alcohol	114–114.5	302.23	302.68	99.86
β-Phenylethyl alcohol	106.5–108	316.26	320.25	98.76
n-Octyl alcohol	60.5–61	324.32	323.68	100.20
Phenylpropyl alcohol	85–86	330.29	330.91	99.82
n-Nonyl alcohol	49–50	338.85	333.55	101.45
l-Menthol	157.5–158	350.36	348.45	100.55
n-Decyl alcohol	55–56	352.38	347.78	101.34
l-Tetradecanol	62.5–63.5	408.48	402.93	101.38
l-Octadecanol	74–75	464.58	466.41	99.61
Solanesol[4]	61.5–63	825.14	800.33	103.10

DISCUSSION

Among the *m*-dinitrobenzenes and derivatives, only 1:3:5-trinitrobenzene and 3-dinitrobenzene have been reported as being sufficiently acidic to be titrated as acids in nonaqueous systems[1,5]. Brockman and Meyer[5] titrated 3-dinitrobenzene in ethylenediamine with sodium aminoethoxide and obtained two inflections in the titration curve. In this laboratory *m*-dinitrobenzene was titrated in pyridine with tetrabutylammonium hydroxide and found to be an exceedingly weak acid. The single inflection in the potentiometric titration curve was slight and the stoichiometry was erratic.

Since acidity is known to increase as other electron-withdrawing groups are introduced into the aromatic ring, it seemed reasonable to expect that a 3:5-dinitrobenzoate would be a much stronger acid than 3-dinitrobenzene. This assumption was correct. In preliminary investigations the 3:5-dinitrobenzoates were titrated directly after solution in pyridine. Although suitable potentiometric curves were realized, these titrations were not stoichiometric in that low neutralization equivalents were obtained. The most anomalous results were obtained on analysis of the dinitrobenzoates of the tertiary alcohols. If the solutions of dinitrobenzoates in pyridine were allowed to stand 48 hours, and then titrated, quantitative results were realized in most instances, although the precision was poor. Consistently accurate and precise results were obtained only when the dinitrobenzoates were refluxed in pyridine before titration.

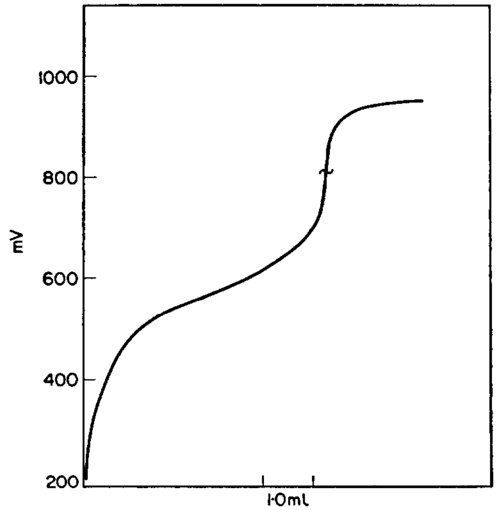

Fig. 1.—Titration of 3:5-dinitrobenzoate of *n*-butyl alcohol in pyridine with 0.01*N* tetrabutylammonium hydroxide.

Other solvents were substituted for pyridine in an effort to eliminate the refluxing time required with pyridine. These solvents included acetone, acetonitrile, dimethyl formamide, ethylenediamine, *iso*propyl alcohol and *n*-propyl alcohol. The lower molecular weight 3:5-dinitrobenzoates analyzed satisfactorily in acetone, but poor results were realized with the higher molecular weight derivatives. None of the other solvents were suitable in this analysis.

The method has been used also for the determination of 3:5-dinitrobenzoates of symmetrical ethers and some phenols. However, the phenol derivatives, especially those of the highly substituted phenols, do not titrate quantitatively and the present method is not recommended for their analysis. Although this procedure has not been tested for the analysis of the dinitrobenzoate derivatives of mercaptans and amino acids, there is no apparent reason why it should not be applicable to these derivatives also.

Indicators cannot be used in the discernment of the end-points, as all solutions were highly coloured.

Zusammenfassung—Die Neutralisationsäquivalente von Estern der 3:5-Dinitrobenzoesäure wurden bestimmt durch Erhitzen am Rückflusskühler mit Pyridin und anschliessende potentiometrische Titration der Pyridinlösung mit 0.01 n Tetrabutylammoniumhydroxyd.

Résumé—Les auteurs ont déterminé les "équivalents de neutralisation" des dérivés ester 3-5 dinitrobenzoate des alcools et des éthers par chauffage au reflux avec la pyridine suivi d'un titrage potentiométrique de la solution de pyridine avec l'hydroxyde de tétrabutylammonium 0,01 N.

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COLORIMETRIC DETERMINATION OF BORON IN NITRATE SOLUTIONS

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Summary—A method has been developed for the determination of microgram amounts of boron in nitrate solutions. Nitrate is destroyed with formic acid and sulphuric acid under reflux conditions. As much as 3 millimoles of nitrate are reduced completely by refluxing 1 ml of the nitrate solution with 1 ml of 88% formic acid for 15 minutes. Boron is determined by the carminic acid method after forming the colored complex *in situ*. This method has been applied to the determination of boron in uranyl nitrate solutions after extraction of uranium with tri-*n*-octylphosphine oxide dissolved in *cyclo*hexane.

THE colorimetric determination of boron in a variety of media has been the object of a considerable number of investigations during the past few years. In this laboratory, the carminic acid, spectrophotometric method[2] has been used frequently for the measurement of boron in aqueous solutions. Nitrate was found to bleach the colour of both carminic acid and the boron-carminic acid complex at room temperature in the presence of hydrochloric acid. Nitrate and strong oxidants interfere similarly with the other widely used chromogenic reagents (quinalizarin,[2] 1 : 1-dianthramide,[5] and curcumin[6]). Methods proposed for the removal of nitrate from boron solutions include: (1) ignition of an alkaline medium,[8] (2) reduction with ferrous sulphate or sodium sulphite.[3] The ignition method has been utilized successfully in the analysis of organic compounds wherein ashing of the sample is a requisite for dissolution; however, such a technique is inconvenient for the determination of boron in acidic solutions. Previous investigations in this laboratory have revealed that iron, in amounts greater than 1 g, interferes with the carminic acid method. Although quantitative reduction of nitrate can be achieved with the mercury cathode, the sample solution is diluted considerably during transfer from the electrolytic cell.

This study was undertaken to develop a method for the determination of boron in concentrations less than 100 ppm in 0.5*M* to 3*M* nitrate solutions. Carminic acid was chosen as the colorimetric reagent. Formic acid was selected as the most feasible reagent for destroying nitrate since only volatile products are formed in this redox reaction. The probable reactions involved are shown below.

$$HCOOH + 2NO_3^- + 2H^+ \rightleftharpoons CO_2 + N_2O_4 + 2H_2O \tag{1}$$

$$3HCOOH + 2NO_3^- + 2H^+ \rightleftharpoons 3CO_2 + 2NO + 4H_2O. \tag{2}$$

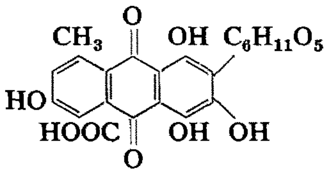
Since these reactions must be carried out at the boiling point of the solution, a reflux condenser is required in order to prevent loss of boron.

The maximum volume of the test solution was set at 2 ml. Larger volumes are impractical since inordinately large amounts of concentrated sulphuric acid would be necessary in order for the reaction between carminic acid and boric acid to proceed to completion.[2]

The method was applied to the determination of boron in nitrate solutions of uranium.

Effect of nitrate on the absorbance of carminic acid

The bleaching effect of nitrate on carminic acid is postulated to be due to the destruction of the quinoidal structure of the carminic acid molecule, I.



I

The relationship between degree of bleaching and concentration of nitrate was established with a series of solutions that contained 0.001 to 1.6 millimoles of nitric acid. These solutions were prepared by adding two drops of hydrochloric acid, 10 ml of sulphuric acid, and 10 ml of carminic acid to 2 ml of the nitrate solution. The absorbance of each of these solutions was measured versus that of a solution that contained no nitrate. The bleaching effect of nitrate is readily observed in Fig. 1. The net absorbance of the carminic acid solution decreases logarithmically with increasing concentration of nitrate. As little as 0.001 millimoles of nitrate reduces the absorbance by 0.025 units. Even trace amounts of nitrate are thus detrimental to the development of the colour of carminic acid in sulphuric acid medium and must be removed before the addition of the chromogenic agent.

When N_2O_4 is produced from the reaction between nitric and hydrochloric acids, the colour of the carminic acid solution is initially green rather than deep red. In solutions that contain one millimole of nitric acid, the deep red colour is restored on waiting the customary 45-minute period; however, in the 1.6-millimole solution, the final colour of the carminic acid solution is yellow, not red.

Decomposition of nitrate with formic acid

The degree to which nitrate is reduced when refluxed for 20 minutes with formic acid was investigated with synthetic solutions wherein the molar ratio of formic acid to nitric acid was varied from 1 to 13. Each solution contained 3 millimoles of nitric acid, 4 millimoles of sulphuric acid, and 3 to 40 millimoles of formic acid in a total volume of either 2 or 5 ml. After being refluxed for 20 minutes the solution was cooled and transferred to a 10-ml volumetric flask. The apparatus was rinsed with water and the rinse solution added to the sample. The amount of nitrate that remained after the solution had been refluxed was determined spectrophotometrically[1,7] by measurement of the absorbance of the solution versus water at 301 mμ. The effects of solution volume and ratio of the reactants on the percentage of nitrate destroyed are presented graphically in Fig. 2.

The reduction of nitrate with formic acid can be achieved with less formic acid if the solution volume is kept to a minimum. In the case of 2-ml test solutions, a molar

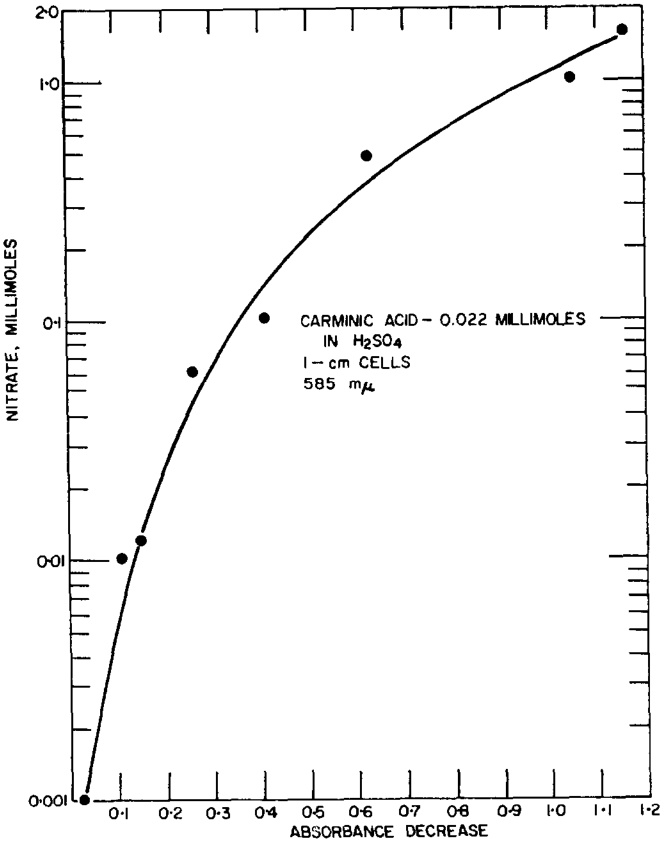


FIG. 1.—Effect of nitrate on the absorbance of carminic acid

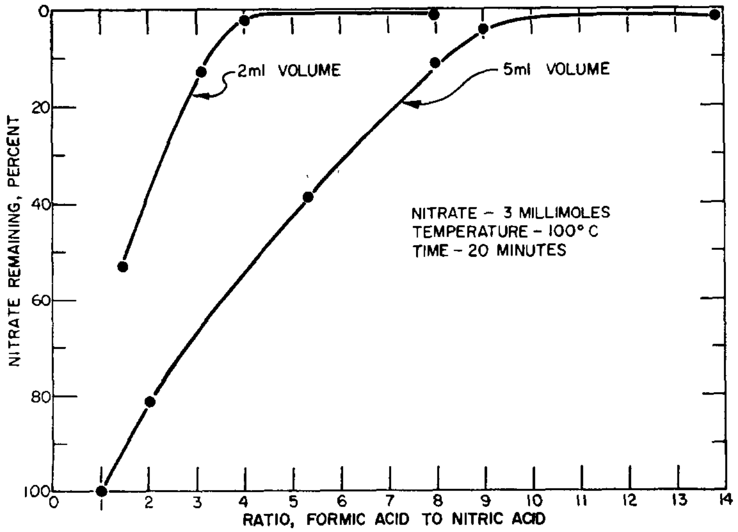


FIG. 2.—Reduction of nitrate with formic acid

ratio ($HCOOH:NO_3^-$) of four is sufficient to reduce, to an extent exceeding 99%, 3 millimoles of nitrate. For a similar ratio in 5-ml test solutions, the corresponding reduction was only 45% complete. In order to attain 99% reduction in 5-ml test volumes, the ratio of formic acid needed was approximately ten.

As shown in Fig. 2, complete reduction is approached asymptotically. Trace amounts of nitrate were found in every test conducted. This nitrate is assumed to be transported physically to the upper portion of the condenser during reflux and thus is not adequately contacted by the formic acid. The amount of nitrate that is so transferred is constant for practical purposes and does not vary appreciably with the shape and size of the apparatus or when the amount of nitrate originally present is reduced to as low as 0.75 millimoles. No enhancement in reduction of nitrate was achieved by doubling the concentration of sulphuric acid; however, slight impairment was observed when this acid was left out of the solution. Essentially no reduction occurred in solutions wherein the reactant ratio was 8 when 6 millimoles of sodium hydroxide were added. This amount of base was sufficient to neutralize the 3 millimoles of nitric acid present but insufficient to achieve neutralization of 23 millimoles of formic acid.

Although the amount of nitrate that remains after refluxing the solutions under optimum conditions is sufficient to cause partial bleaching of carminic acid, this source of error can be eliminated by rinsing the condenser with 10 ml of concentrated sulphuric acid followed by 10 ml of the carminic acid solution. This rinse, which in effect constitutes development of the boron-carminic acid complex, serves to complete the reduction of nitrate as a consequence of the exothermic reaction that takes place when the acids come in contact. For example, when 3 millimoles of nitric acid are refluxed with 24 millimoles of formic acid, in a total volume of 2 ml, for 20 minutes, and the carminic acid colour developed in the reaction, the absorbance of this solution does not vary from that of a reagent blank solution by more than 0.01 units.

Choice of wavelength

A selection of the optimum wavelength for measurement of the absorbance of the boron-carminic acid complex was made after carrying out a spectral study of this complex with a Cary recording spectrophotometer, Model 14M. Two lots of carminic acid were used in the preparation of reagents. The spectra of solutions that contained 1 μg of boron per ml (20 μg of boron per 22 ml) exhibited constant absorbance between 580 mμ and 615 mμ when measured versus a corresponding reagent reference solution. The slit width was smallest, 0.14 mm, in the spectral region of 585 mμ to 600 mμ and increased to 0.17 mm at 580 mμ and 610 mμ and to 0.18 mm at 615 mμ. A wavelength of 585 mμ was selected for this investigation primarily because this wavelength had been used in several previous methods for the determination of boron in this laboratory. The original choice of wavelength was based on the work of Hatcher and Wilcox.[8] Recently, Callicoat and Wolszon[4] have expressed a preference for 610 mμ as the optimum wavelength for measuring the intensity of the boron-carminic acid colour.

Effect of formic acid on the absorbance of carminic acid

Since the quinoidal structure of carminic acid can be reduced to the corresponding hydroquinone form by zinc in acetic acid,[9] the effect of formic acid, a much weaker reducing agent, was investigated to determine if carminic acid is reduced by relatively large amounts of this reagent. The absorbance of carminic acid in solutions that contained 16 and 23 millimoles of formic acid was measured at 585 mμ versus an equivalent concentration of carminic acid in sulphuric acid. No change in absorbance was observed at either concentration of formic acid.

EXPERIMENTAL

Apparatus and reagents

A Beckman spectrophotometer, Model DU, and Cary recording spectrophotometer, Model 14 M, with 1-cm matched silica cells were used for measurement of absorbance.

Either Pyrex or Vycor flasks can be used without significant contamination if they are washed in hydrochloric acid and rinsed with water.

Boron: standard solutions. A stock solution that contained 500 μg of boron per ml was prepared by dissolving 440 mg of $Na_2B_4O_7 \cdot 10H_2O$ in 100 ml of water in a polyethylene bottle. Dilute solutions that contained 100, 50, 25, and 5 μg of boron per ml were prepared by diluting aliquots of the stock solutions with water.

Carminic acid solution: 0.1 % (w/v) in H_2SO_4. (Carminic acid is obtainable from National Aniline Division, Allied Chemical and Dye Corporation.)

Formic acid: 88%. Analytical, reagent-grade.

Sulphuric acid. C. P. grade acid obtained from the General Chemical Division of Allied Chemical and Dye Corporation.

Procedure for the development of the boron-carminic acid colour

Two ml of aqueous solution that contains 40 μg of boron is transferred to a 50-ml Vycor beaker. Two drops of concentrated hydrochloric acid are then added to the beaker. The beaker is cooled in an ice bath, following which 10 ml of concentrated sulphuric acid and 10 ml of carminic acid solution are added by pipette and the solution is stirred thoroughly with a Teflon stirring rod. The beaker is then removed from the ice-bath and allowed to stand at least 45 minutes, after which the absorbance of the boron-carminic acid is measured at 585 mμ versus a reagent blank. The amount of boron in the solution is established by reference to a calibration curve or calculated by means of an empirical factor.

The colour of the complex attains maximum development in 30 to 40 minutes, remains constant for approximately 1·5 hours, and then fades slowly.

Determination of boron in synthetic nitrate solutions

Synthetic boron solutions that contained various amounts of nitrate were prepared by combining 1 ml of standard boron solution, 0·2 ml of sulphuric acid and 0·2 ml of various concentrations of nitric acid. The nitrate was reduced by the addition of 1 ml of formic acid in two, 0·5-ml increments. The boron-carminic acid colour was developed *in situ* by adding the necessary reagents through the condenser and subsequently was measured versus a reagent blank. The results are shown in Table I.

The coefficient of variation for the determination of 25 μg of boron is 1 %. This order of precision was obtained in the presence of varying concentrations of nitric acid. The precision for determining smaller amounts of boron is less, 5 % for 12.5 μg of boron. One of the contributiong factors to this decrease in precision is the presence of minute bubbles of carbon dioxide in the final solutions. These bubbles are formed by the decomposition of excess formic acid with concentrated sulphuric acid. Even on long standing, some gas remains which naturally affects the absorbance readings somewhat. The over-all effect is greatly minimized by frequent agitation of the solution while awaiting complete colour developement.

Determination of boron in synthetic solutions of uranyl nitrate

Because of its high capacity for absorbing neutrons, the concentration of boron in nuclear fuels must be kept to a minimum. The analysis of boron in uranium is thus one of the more common analyses in nuclear technology. Boron must generally be separated from uranium before its determination since at a weight ratio of 1000 (U : B) the error for the carminic acid method is about 15%.

TABLE 1.—DETERMINATION OF BORON IN NITRATE SOLUTIONS

NO_3, *Molarity*	Boron, μg			Coefficient of Variation, *Per Cent*
	Present	Found	Average	
0.4	12.5	11.4		
		12.4		
		12.8		
		12.0		
		11.4	12.0 ± 0.6	5
	25	24.8		
		26.0		
		24.8		
		24.0		
		25.6		
		24.7		
		25.0		
0.8	25	25.5		
		25.6		
1.5	25	27.4		
		26.8		
2.3	25	24.4		
3.0	25	24.4		
		24.9		
		24.8	25.2 ± 0.3	1

Boron is readily separated from uranium by ion-exchange resins;[10] however, this method results in considerable dilution of the sample so that concentration by evaporation is required. In order to avoid this step, liquid-liquid extraction separation was used with a *cyclo*hexane solution of tri-*n*-octylphosphine oxide (TOPO) as the reagent. This compound, dissolved in *cyclo*hexane, is an excellent extractant for uranium from either acidic nitrate or chloride solutions.[12] One millimole of TOPO in *cyclo*hexane can be used to extract 80 mg of uranium from $2M$ HNO_3.[11] Boron is not extracted and is retained in the aqueous phase.[12]

A series of synthetic solutions was prepared to contain 12 mg of uranium and 50 μg of boron in 5 ml of $2M$ HNO_3. These solutions were equilibrated with 5 ml of $0.1M$ TOPO for 10 minutes to extract uranium. One-ml aliquots of the aqueous phase were then transferred to a reflux flask, following which the nitrate in the solution was reduced with 1 ml of HCOOH, and boron was then determined by the carminic acid method. The average result of these determinations was 50.5 μg with a coefficient of variation of 1%. The extraction of uranium with *cyclo*hexane solution of TOPO, therefore, does not cause any error in the determination of boron in the resulting aqueous phase.

Procedure

Transfer 1 ml of the solution that contains 5 to 40 μg of boron to a 10-ml reflux flask and then add 0.2 ml of sulphuric acid and 0.5 ml of formic acid. Connect the flask to a water-cooled reflux condenser and heat the contents of the flask until all coloured oxides of nitrogen are expelled through the condenser. Cool the flask to $<100°$ and then add 0.5 ml of formic acid to the flask through the condenser. Heat the solution to reflux temperature for 15 minutes and then cool in an ice bath. Add 2 drops of hydrochloric acid, 10 ml of sulphuric acid, and 10 ml of carminic acid solution (in this order) to the flask by allowing these reagents to wash down the inner wall of the condenser. When the temperature of the solution is less than $\sim$25°, remove the flask from the condenser, stir the solution and then transfer it to a 50-ml Vycor beaker. Set the solution aside for at least 45 minutes before measuring its absorbance at 585 mμ versus a reference solution that contains 2 ml of water, 2 drops of hydrochloric acid, 10 ml of sulphuric acid and 10 ml of carminic acid solution. Determine the concentration of boron by referring the absorbance to a calibration curve or calculate it by means of a calibration factor.

Work carried out under contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Zusammenfassung—Eine Methode zur Bestimmung von Mikrogrammengen Bor in Nitratlösungen wurde entwickelt. Nitrat wird mittels Ameisen-Schwefelsäure unterm Rückflusskühler zerstört. Bis zu 3 Millimolen Nitrat werden völlig reduziert wenn 1 ml der Nitratlösung mit 1 ml 88 % iger Ameisensäure für 15 Minuten unter Rückfluss gekocht wird. Bor wird nach der Carminsäuremethode photometrisch bestimmt. Die methode wurde auf die Borbestimmung in Uranylnitratlösungen nach Extraktion des Urans mit Tri-*n*-octylphosphinoxyd in Cyclohexanlösung angewendet.

Résumé—Les auteurs ont mis au point une méthode pour le dosage de microgrammes de bore dans des solutions de nitrate. Le nitrate est détruit par l'acide formique et l'acide sulfurique par chauffage au reflux. On réduit des quantités aussi importantes que 3 millimoles de nitrate par chauffage au reflux de 1 ml de solution de nitrate avec 1 ml d'acide formique à 88 % pendant 15 minutes. Le bore est dosé par la méthode de l'acide carminique après formation du complexe coloré "in situ". On a appliqué cette méthode au dosage du bore dans des solutions de nitrate d'uranyle après extraction de l'uranium par l'oxyde de tri-*n*-octylphosphine dissous dans le cyclohexane.

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SPECTROPHOTOMETRIC ESTIMATION OF PHENOL IN SOLUTIONS CONTAINING TYROSINE, TRYPTOPHANE, HISTIDINE OR CHYMOTRYPSIN

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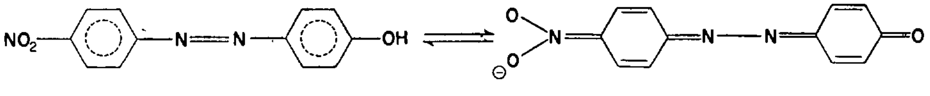
Summary—A sensitive spectrophotometric method for the estimation of phenol ($10^{-5}M$) in solutions containing tyrosine, tryptophane, histidine or chymotrypsin is described. The method employs diazotised *p*-nitroaniline as reagent.

THE direct estimation of low concentrations of phenol in alkaline solution by measurement of the intensity of absorption of phenoxide ion at 234 mμ has been described earlier.[1] This method is unsuitable for the estimation of phenol in the presence of alkali-labile phenyl esters. Furthermore it is difficult to apply accurately in the presence of low concentrations of aromatic amino-acids (particularly tyrosine) or proteins, on account of their high background absorption in the ultra-violet.[2,3]

The present method avoids these difficulties by utilising a sensitive colour reaction of phenol.[4] When dilute aqueous phenol solutions are treated with diazotised *p*-nitroaniline at pH 8, 4-(4′-nitrobenzene-azo) phenol (I) is formed.[5] The latter gives rise to the intensely red anion (II) in alkaline solution.[6]



I II

The intensity of absorption of the species II, which shows a prominent maximum in the visible region[7,8] (λ_{max} 480 mμ, ε_{max} 2,000; Fig. 1), may be conveniently determined spectrophotometrically, thereby affording the concentration of phenol in the original solution.

Coupling of the diazo reagent with phenol is optimal in the neutral pH region. At the same time this pH region favours decomposition of the diazo species into *p*-nitrophenol and nitrogen.[9–11] The *p*-nitrophenol reacts with more diazo reagent forming coloured products which tend to increase the background absorption of the solution. These undesirable side-reactions may be largely eliminated by reducing the reaction time to a minimum. In practice a small excess of diazotised *p*-nitroaniline is allowed to react with the phenol solution in phosphate buffer (pH 8) for one minute, and the product is then made strongly alkaline. The strongly alkaline conditions at once check further coupling,[9] and give rise to the desired red ion II.

It is evident (Fig. 5) that phenol couples almost instantaneously with the diazo solution at pH 8. This behaviour makes it possible to estimate phenol in the presence of tyrosine, tryptophane or histidine, which are found to react with the diazo solution

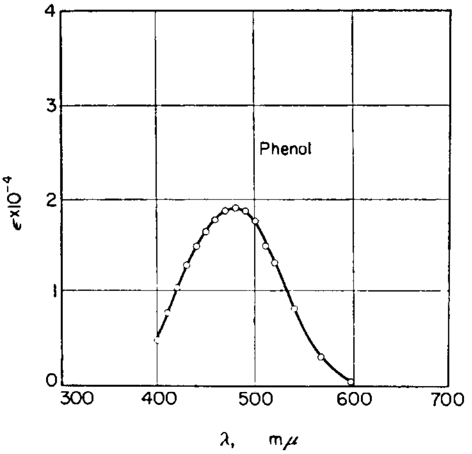


FIG. 1.—Absorption maximum produced by treatment of buffered phenol solution with diazo reagent, and making alkaline after 30 min.

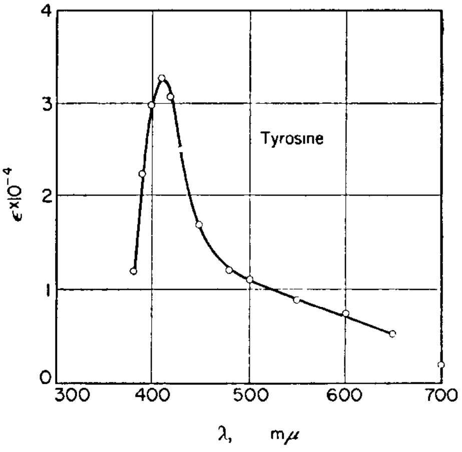


FIG. 2.—Absorption maximum produced by treatment of buffered tyrosine solution with diazo reagent, and making alkaline after 30 min.

much more slowly (Fig. 5). Proteins themselves are known to undergo coupling with diazo solutions,[12,13] but the presence of low concentrations of protein does not seriously interfere with phenol estimation under the experimental conditions of this method. Linear dependence of optical density at 480 mμ on phenol concentration, in the presence of the enzyme-protein chymotrypsin ($2.14 \times 10^{-5}M$) is shown in Fig. 6.

EXPERIMENTAL

Apparatus and reagents

Measurements were carried out using a Unicam S.P. 500 spectrophotometer (Cambridge, Instrument Co.), with 1-cm silica cells. Small volumes of solution were measured using a micrometer syringe.

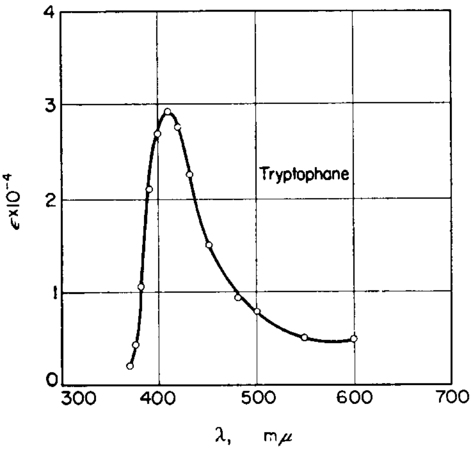


FIG. 3.—Absorption maximum produced by treatment of buffered tryptophane solution with diazo reagent, and making alkaline after 30 min.

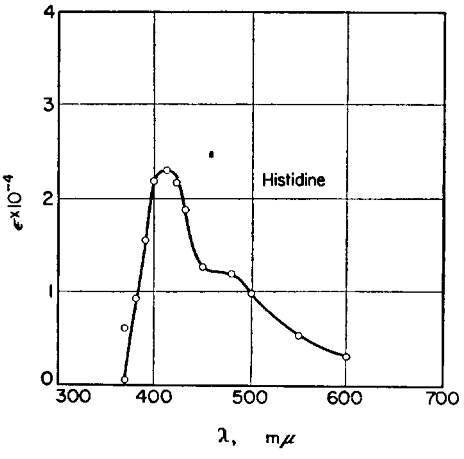


FIG. 4.—Absorption maximum produced by treatment of buffered histidine solution with diazo reagent, and making alkaline after 30 min.

Diazo reagent: p-Nitroaniline (1·5 g) was dissolved in concentrated hydrochloric acid (40 ml) and made up to 500 ml with distilled water. For phenol estimations, 5-ml portions of this stock solution were withdrawn and cooled in ice, and solid sodium nitrite was gradually added until a slight excess of nitrous acid persisted. Solutions of *p*-nitrobenzene diazonium chloride prepared in this manner, were stored for minimum periods in the dark.

Procedure

Determination of optimum concentration of diazo reagent required: Increasing amounts of diazo reagent were added to 3 ml of $3 \times 10^{-5}M$ phenol in 0·1*M* aqueous sodium phosphate buffer (pH 8·0). After maintaining at 20° for one minute, 1 ml of 0·2*N* aqueous sodium hydroxide was added, and the optical density at 480 mμ was measured. (Table I.) Maximum optical density was obtained by the addition of only 0·02 ml of reagent. To ensure an excess of reagent 0·03 ml was added in subsequent estimations.

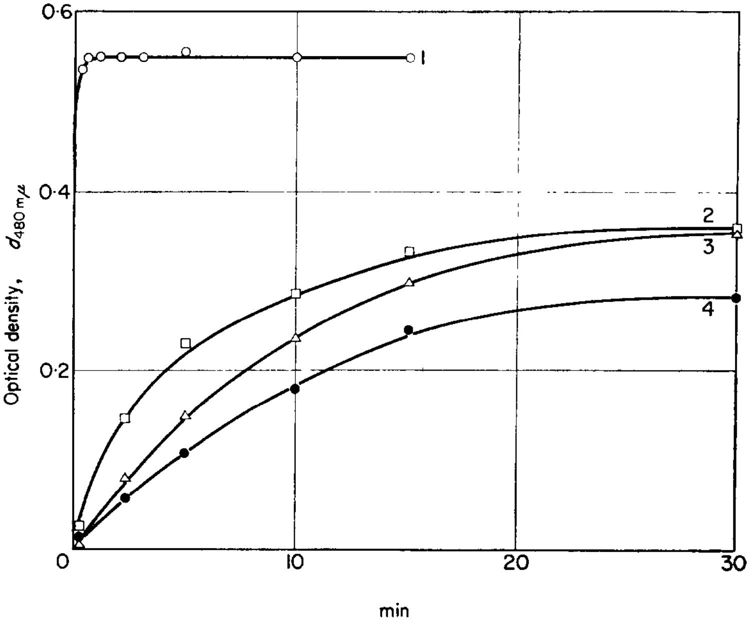


Fig. 5.—Comparison of rates of colour development on treatment of buffered solutions of phenol (1), tyrosine (2), tryptophane (3), and histidine (4) ($3 \times 10^{-5}M$) with diazo reagent, and subsequently making alkaline.

Table I.—Dependence of optical density (d_{480}) on volume of diazo reagent added to 3 ml of buffered phenol solution ($3 \times 10^{-5}M$) under the prescribed conditions

Diazo reagent, *ml*	$d_{480 m\mu}$
0·01	0·265
0·02	0·555
0·03	0·550
0·05	0·540
0·10	0·555
1·00	0·545

Dependence of optical density (480 mμ) *on phenol concentration:* Three ml of solutions of phenol in $0{\cdot}1M$ sodium phosphate buffer were treated with 0·03 ml of diazo reagent, and set aside for one minute at 20°. After making alkaline with 1 ml of $0{\cdot}2N$ aqueous sodium hydroxide, the optical density at 480 mμ was measured. A linear plot of $d_{480 m\mu}$ against phenol concentration over the range $1 \times 10^{-5}M$ to $5 \times 10^{-5}M$ phenol was obtained (Fig. 6).

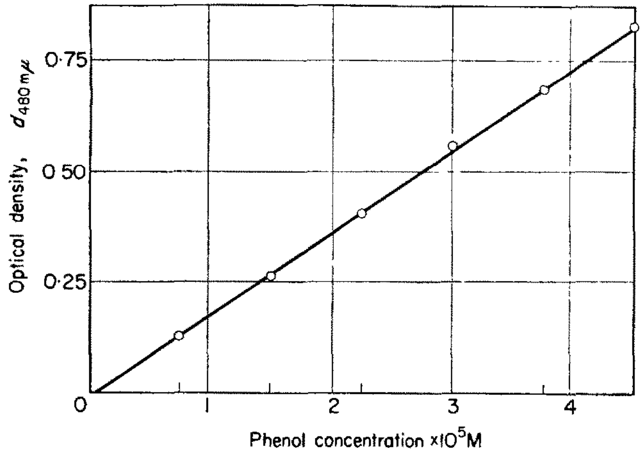


Fig. 6.—Dependence of optical density (d 480 mμ) on phenol concentration in buffered solutions, after treatment with diazo reagent, and making alkaline.

Stability of colour: Solutions of phenol, treated with the diazo reagent in the foregoing manner, showed no change in optical density after standing overnight. Similar preparations in the presence of chymotrypsin ($3 \times 10^{-5}M$) showed a slow decrease of optical density at 480 mμ (Table II) with time.

Table II.—Time dependent effect of chymotypsin ($3 \times 10^{-5}M$) on the optical density (d_{480}) produced on treatment of phenol solutions ($3 \times 10^{-5}M$) with diazo reagent and making alkaline in the prescribed manner

Time, *min*	$d_{480 m\mu}$
5	0·430
16	0·420
31	0·412
60	0·410
overnight	0·320

Reaction of phenol, tyrosine, tryptophane and histidine solutions with the diazo reagent: Solutions of phenol, tyrosine, tryptophane and histidine ($3 \times 10^{-5}M$) were prepared in $0{\cdot}1M$ sodium phosphate buffer and 0·03 ml of the diazonium reagent was added to 3 ml of each. The mixtures were maintained at 20° for 30 minutes, made alkaline by the addition of 1 ml of $0{\cdot}2N$ aqueous sodium hydroxide and their absorption spectra in the visible region measured against a blank cell containing sodium phosphate buffer treated in the same manner as the reactant solutions (Figs. 1–4).

Comparison of rates of colour development of phenol, tyrosine, tryptophane and histidine: Solutions of phenol, tyrosine, tryptophane and histidine ($3 \times 10^{-5}M$), in $0{\cdot}1M$ sodium phosphate buffer, were treated with the diazo reagent as in the previous experiment. The solutions were made alkaline with 1 ml of $0{\cdot}2N$ aqueous sodium hydroxide, after increasing time intervals, and optical densities were measured at 480 mμ against a blank phosphate-diazo solution. The rate curves are shown in Fig. 5.

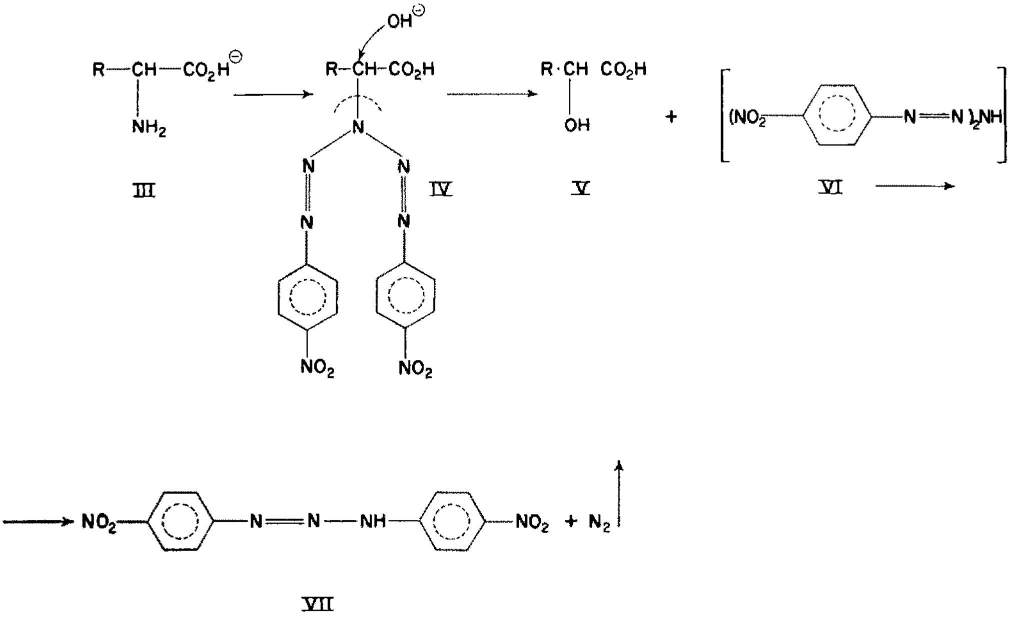
Rate of colour production in phenol solutions at 0°*:* Solutions of phenol (3-ml portions, $3 \times 10^{-5}M$) in 0·1*M* sodium phosphate buffer, were maintained in an ice-bath. To each portion, 0·03 ml of diazonium reagent was added, followed by 1·0 ml of 0·2*N* aqueous sodium hydroxide after increasing time intervals. The optical densities were measured at 480 mμ. (Table 3). This information is useful when phenol estimations are required for kinetic studies at 0°.

TABLE III.—RATE OF COLOUR PRODUCTION AT 0° IN PHENOL SOLUTIONS ($3 \times 10^{-5}M$) TREATED WITH DIAZO REAGENT IN THE PRESCRIBED MANNER

Reaction time (*sec*)	$d_{480 mu}$
15	0·360
30	0·526
60	0·618

DISCUSSION

Comparison of the visible absorption spectra of phenol, tyrosine, tryptophane and histidine solutions, after the standard treatment with diazotised *p*-nitroaniline, reveals interesting features. Phenol solutions, on the one hand, show the absorption maximum of the ion II at 480 mμ (Fig. 1). Tyrosine, tryptophane and histidine solutions, on the other hand show a distinctly different absorption maximum 410 mμ (Figs. 2-4) which is apparently common to all three amino-acids. A closely similar maximum (410 mμ) was obtained from a solution of 4:4′-dinitrodiazoaminobenzene[14] (VII) buffered similarly to pH 8. It would appear that tyrosine, tryptophane and histidine do not undergo appreciable nuclear coupling with the diazo solution under these conditions, for this would yield different chromophoric species.[15,16] Instead, these amino-acids



evidently react with diazotised *p*-nitroaniline affording the dinitrodiazoaminobenzene (VII) and the corresponding α-hydroxy acids (V).[17–19] In line with earlier work we suggest that this reaction proceeds through the α-amino-bis-diazo compound (IV). The latter may then undergo subsequent nucleophilic attack by OH^- yielding the α-hydroxy acid and the unstable pentazine[20–22] (VI) which immediately decomposes into nitrogen and the dinitrodiazoaminobenzene.

Acknowledgement—Thanks are due to Mr. P. M. Newman for helpful discussion.

Zusammenfassung—Eine empfindliche spectrophotometrische Methode zu Bestimmung von Phenol (10^{-5} m) in Lösungen, die Tyrosin, Tryptophan, Histidin oder Chymotrypsin enthalten, wird beschrieben. Diazotiertes *p*-Nitroanilin wird als Reagenz verwendet.

Résumé—Les auteurs décrivent une méthode spectrophotométrique sensible pour le dosage du phénol ($10^{-5}M$) dans des solutions contenant de la tyrosine, du tryptophane, de l'histidine ou de la chymotrypsine. La méthode utilise comme réactif la *p*-nitroaniline diazotée.

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THE ANALYTICAL CHEMISTRY OF THE PYRIDINE THIOCYANATES—II

THE SEPARATION OF RUTHENIUM AND PALLADIUM

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Summary—A procedure is described for the separation and subsequent colorimetric determination of ruthenium and palladium as complex and ammine-type thiocyanates respectively, using solvent extraction. Suggestions are put forward as to the nature of the ruthenium complex occurring in solution.

A NUMBER of organic reagents have been employed in the solvent extraction of the platinum metals, but the use of these has been largely restricted to palladium and platinum. One difficulty in the way of easy formation of chelate compounds is the fact that the commonest form for these metals is in stable complex ions such as $(PtCl_6)^{2-}$, $(RuCl_5OH)^{3-}$. This class of compounds, involving hexachloro-complexes etc., is presumably essentially ionic in character and will exist as entities only in the solid state; reagents forming such compounds would not be expected to assist the solvent extraction of the platinum metals. A second category, however, apparently consists of non-ionic substances related to $Pd(NH_3)_2Cl_2$, and solubility in organic solvents may be expected. Thus Ryan[1] extracted the *p*-nitrosodiphenylamine complex, $Pd(C_{12}H_{10}N_2O)_2Cl_2$, into ethyl acetate, ether and chloroform, while Yoe and Kirkland[2] used *p*-nitrosodimethylaniline for a similar purpose. The covalent complex Pd py_2Cl_2 (py = pyridine) has been known for many years,[3,4] but the analytical possibilities of similar complexes with thiocyanate ion in place of halogen appear either not to have been noted in the literature or to have been completely neglected, although Rubinshtein[5] prepared a series of substituted pyridino-chlorides of palladium, without investigating their extractability into organic solvents.

A survey of the literature reveals that little attention has been paid to the solvent extraction of thiocyanate complexes of the platinum metals. Ogburn[6] first noted the formation by Ru^{III} of a red colour with thiocyanate ion, which is extracted by suitable organic solvents.[7] Recently[8] the red complex $[Pd(SCN)_4]^{2-}$ has been extracted with butyl alcohol or *iso*-amyl alcohol at pH below 5, in the presence of Pt^{IV} and Ir^{IV}. Apart from such investigations, however, it would appear that the analytical value of the complex and ammine-type thiocyanates of ruthenium and palladium has not been examined to any extent.

This paper describes a procedure for the separation and determination of ruthenium and palladium through the formation of compounds of both the above types.

PRELIMINARY INVESTIGATIONS

The replacement of Cl by SCN in Pd py_2Cl_2 was undertaken and the conditions under which a pyridine thiocyanate of palladium is formed were examined. It was found that if excess thiocyanate is added to a palladous chloride solution and the pH adjusted to between 4 and 6, the addition, dropwise, of pyridine causes the red-brown solution to become pale yellow in colour. After a moment the solution becomes completely colourless with the formation of a yellow flocculent precipitate, which is only obtained from solutions containing palladium alone. In the presence of other platinum metals no precipitate is obtained from the pale yellow solution and this effect is also observed in the presence of excess pyridine or in alkaline solution. The yellow precipitate was analysed both by ignition to PdO and by C, H and N determinations; all results accorded with the formula Pd $py_2(SCN)_2$. Both this precipitate and the pale yellow aqueous solution from which it is obtained were found to be very readily and completely extracted, even from solutions of pH up to 12, by organic solvents such as chloroform, ethers, ketones and tributyl phosphate, in all cases yielding a pale yellow solution in the organic phase. The species extracted was thought to be the molecular species Pd $py_2(SCN)_2$, since both chloroform and hexone (methyl *iso*-butyl ketone) yield similarly coloured solutions, very different in colour from that of the palladium thiocyanate complex extracted into hexone from acid solutions. Palladium here closely resembles nickel in the behaviour of its complex and ammine-type thiocyanates.[9]

The behaviour of ruthenium complex thiocyanates was next investigated. Ruthenium was present in the tervalent state as the complex $[Ru(H_2O)Cl_5]^{2-}$, soluble in water or dilute hydrochloric acid. In 0·1*N* acid solution, on the addition of excess thiocyanate, a crimson extractable complex is obtained, which is stable provided that the solution is not heated. On heating the solution, however, the colour changes to deep blue, this process being complete at about 50° in 0·1*N* acid solution and being independent of the particular acid used. In neutral solution it is necessary to maintain the temperature near to the boiling point for a few moments in order to bring the reaction to completion, but in both cases an odour of hydrogen sulphide is observed. The blue colour obtained is considerably intensified if the solution is made 1*N* or more in acid concentration, when it appears very stable and showed no fading after standing for one week.

From neutral or only weakly acid solutions this blue complex is extracted only partially by hexone or a 1 : 5 tributyl phosphate/*cyclo*hexane mixture and not at all by chloroform, ethers or acetates. From a 2*N* hydrochloric acid solution, however, it is rapidly and completely extracted by the first two solvents mentioned above, partially extracted by ethers and acetates, and not at all by chloroform.

On the basis of these preliminary observations it was found possible to effect a separation of ruthenium and palladium. It was decided to employ an absorptiometric method for the determination of the metals and as a first step the absorption spectrum of Pd $py_2(SCN)_2$ in hexone was determined. This is shown in Fig. 1. The maximum at 345 mμ is very suitable for measurement and was used throughout. For known amounts of palladium a calibration curve was prepared, from which the minimum amount which could be determined with certainty was 25 μg.

The absorption spectrum of the dark blue ruthenium thiocyanate complex in hexone is shown in in Fig. 2, the maximum at 570 mμ being employed in subsequent measurements. For known amounts of ruthenium a calibration curve was prepared, from which the minimum amount which could be determined with certainty was 25 μg.

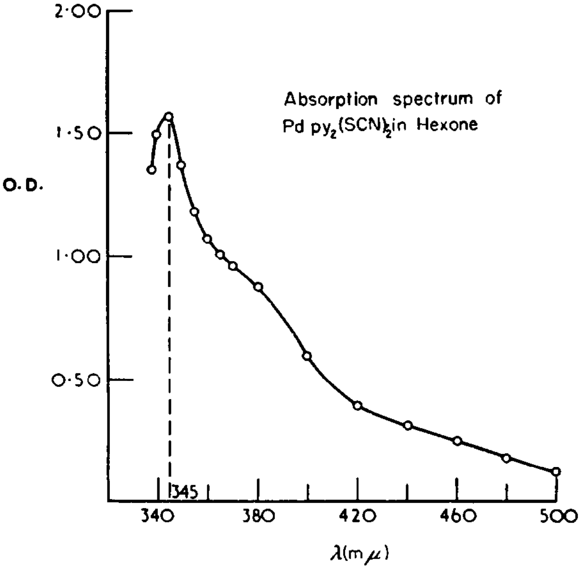
Absorption spectrum of
Pd $py_2(SCN)_2$ in Hexone
2·00
1·50
O.D.
1·00
0·50
345
340
380
420
460
500
λ(mμ)

FIG. 1.

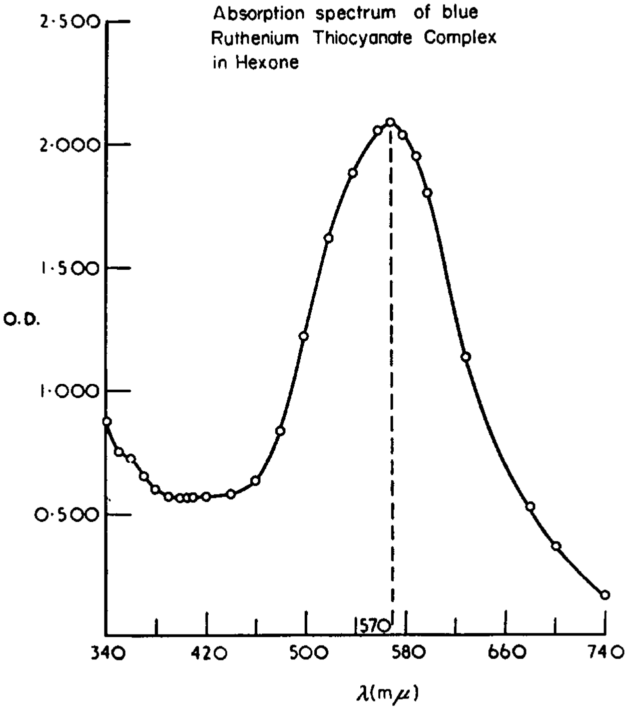
Absorption spectrum of blue
Ruthenium Thiocyanate Complex
in Hexone
2·500
2·000
1·500
O.D.
1·000
0·500
570
340
420
500
580
660
740
λ(mμ)

FIG. 2.

PROCEDURES

To about 20 ml of the solution for analysis, which should contain not less than 25 μg palladium and 25 μg ruthenium and have pH 1·5–2·0, add 10*N* sodium hydroxide solution rapidly until the pH is 11 to 12. It is essential that this adjustment should be made quickly with a strong alkali solution.

Transfer the solution to a separating funnel and use 0·05*N* sodium hydroxide to rinse the beaker, adding these washings to the main solution. To the pale green solution add 0·5 ml (excess) of a 40% solution of potassium thiocyanate, followed by 5 drops of pyridine. The solution becomes pale yellow in colour due to the formation of the pyridine thiocyanate of palladium.

Extract the solution twice with 10-ml portions of hexone and make up to 25 ml. The hexone solution contains all the palladium present in the original aqueous solution. Under these conditions a thiocyanate complex of ruthenium is not formed, or, if formed, is not extracted.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. This operation removes tiny globules of air or water which may be present. Measure the optical density of this solution at 345 mμ, with reference to hexone as standard, and read off the concentration of palladium present from the prepared calibration curve.

Determination of ruthenium

Transfer the pale green aqueous solution remaining after the extraction of palladium to a 50-ml beaker. This solution contains potassium thiocyanate (excess), a trace of pyridine, ruthenium, if present, and has a pH of approximately 11.

Add 1 ml of concentrated (11*N*) hydrochloric acid rapidly with stirring and heat the solution to about 90°, when an odour of hydrogen sulphide is observed. The time taken to reach this temperature should be about 4 minutes. While still hot, add a further 5 ml of concentrated hydrochloric acid down the sides of the beaker. This has the effect of intensifying the colour of the blue complex and, allowing for wash liquor, renders the solution approximately 2*N* in hydrochloric acid. Cool the beaker and contents to about 20°.

When cool, transfer solution to a separating funnel, extract twice with 10-ml portions of hexone and make up to 25 ml. This solution will contain all the ruthenium present in the original aqueous sample.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. Measure the optical density of this solution at 570 mμ, with reference to hexone as standard, and read off the concentration of ruthenium present from the prepared calibration curve.

Notes

It is necessary to carry out the extraction of $Pd\ py_2(SCN)_2$ at pH above 11, since this is not formed below pH 4, while at pH 4–8 a hydrous oxide of ruthenium is precipitated. It cannot be too strongly emphasised that the initial adjustment to pH 11 of the ruthenium–palladium mixture must be made very rapidly using a concentrated alkali solution, under which conditions no precipitation is observed. The same precaution is also necessary on later acidification *i.e.* concentrated hydrochloric acid must be rapidly added.

RESULTS

To test the validity of the proposed method, a number of "unknown" mixtures were analysed by one of us (J. H. W. F.). The results are recorded in Table I. Where the experimental results differ from the actual composition, the latter is recorded in parentheses.

These results were extremely satisfactory, especially for palladium. The method shows great promise in the separation and subsequent concentration and determination of small amounts of ruthenium; results are easily reproducible and precision is very good.

DISCUSSION

In 1952 Yaffe and Voigt,[10] through a spectrophotometric study, claimed to have established the formula $Ru(SCN)^{2+}$ for the deep blue complex formed by the reaction of Ru^{III} and Ru^{IV} perchlorates with thiocyanate ion. In the case of Ru^{IV}, reduction to Ru^{III} occurred at the expense of the thiocyanate, and no evidence was found for higher complexes. However, during the present investigations it was found that both the crimson Ru^{III} thiocyanate complex and the blue complex later obtained were, in fact, anionic in nature, being readily adsorbed on the anionic-exchange resin Amberlite IRA-410. In neither case did any adsorption take place on the cationic-exchange resin Dowex 50. These observations conflict directly with the findings mentioned above.

TABLE 1

No. of Sample	Palladium, μg	Ruthenium, μg
1	450	30 (25)
2	295 (300)	155 (150)
3	97·5 (100)	405 (400)
4	—	250
5	745 (750)	25
6	50	495 (500)
7	247·5 (250)	—

From their experimental data, for the reaction,

$$A + nB \rightleftharpoons AB_n$$

Yaffe and Voigt obtained best agreement with experiment when *n* was chosen as unity. They endeavoured to fit their results to other values for *n*, but found these to be less satisfactory. From their published curve, the deduction must be that at least some of their results were capable of being fitted to the assumption that *n* could equal 2, 3, or even 4. The formation of a negatively charged Ru^{III} thiocyanate complex capable of being adsorbed on an ionic-exchange resin, as observed in the present work, would require it to be formulated as $Ru(SCN)_4^-$ or $Ru(SCN)_5^{2-}$, *i.e.* $n = 4$ or 5; and this may be regarded as at least a possibility, if the behaviour of Fe^{III} thiocyanate[11,12] is taken into account. It is, therefore, suggested that the crimson Ru^{III} thiocyanate may be represented by one or both of the above formulae, at high thiocyanate concentration.

Again it is known,[13,14] that aqueous solutions of Ru^{III} chloride turn deep blue when treated with strong reducing agents, ruthenium being reduced to the Ru^{II} state. It is suggested that the odour of hydrogen sulphide observed on formation of the blue thiocyanate complex is due to the reduction of Ru^{III} to Ru^{II} at the expense of the thiocyanate, catalysed by the metal. $Ruthenium^{II}$ then forms the blue anionic thiocyanate complex, which could be formulated as $Ru(SCN)_4^{2-}$ or $Ru(SCN)_3^-$, and would be capable of adsorption on anionic-exchange resins. At very low thiocyanate concentrations the formation of the complex $Ru(SCN)^+$ would be possible. Investigation with such solutions showed that it was, in fact, possible to form a blue ruthenium thiocyanate complex which was not completely adsorbed on anionic-exchange resins, and this is considered evidence for the existence of one or both of the complexes $Ru(SCN)^+$, $Ru(SCN)_2$. Yaffe and Voigt evidently failed to take into consideration the possibility of such a reduction to Ru^{II}, or the possibility of the existence of a whole series of cationic and anionic complexes at different thiocyanate concentrations, as in the case of $iron^{III}$. Babko[12] has postulated the coexistence at the same thiocyanate concentration of two complexes of $iron^{III}$ and the incomplete adsorption referred to above indicated the probability of a similar phenomenon in the case of $ruthenium^{II}$. Although $ruthenium^{II}$ is certainly unstable in alkaline solution, as instanced by the apparent non-existence of the oxide RuO,[14] yet under the fairly strongly acid conditions in which the most intense colour of the blue thiocyanate complex is observed, stabilisation of this relatively unfamiliar oxidation state appears to be possible.

Acknowledgement—One of us (J. H. W. F.) gratefully acknowledges a research grant from the Imperial Chemical Industries Ltd., (Billingham Division), which enabled him to take part in this work.

Zusammenfassung—Eine Methode zur Trennung und nachfolgenden kolorimetrischen Bestimmung von Ruthenium und Palladium als Komplex bzw. Thiocyanate des Ammintyps unterverwendungvon Solventextraktion wird beschrieben. Die Natur der in der Lösung auftretenden Rutheniumkomplexe wird diskutiert.

Résumé—On décrit un procédé pour la séparation puis la déterminationcolor imétrique du ruthénium et du palladium à l'état de complexes amminés et thiocyanates respectivement, en utilisant l'extraction par solvant. On a proposé quelques hypothèses sur la nature du complexe du ruthénium en solution.

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THE ANALYTICAL CHEMISTRY OF THE PYRIDINE THIOCYANATES—III

THE SEPARATION OF RHODIUM, PALLADIUM AND PLATINUM

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(*Received* 22 *August* 1959)

Summary—A procedure is described for the separation and subsequent colorimetric determination of rhodium, palladium and platinum through the formation of complex and ammine-type thiocyanates, using solvent extraction. Suggestions are put forward as to the nature of the complexes in solution.

PART II[1] of this series of papers outlined a procedure for the separation of ruthenium and palladium through the formation of their complex and ammine-type thiocyanates respectively, using solvent extraction. The success achieved in this manner led to further investigations of such compounds, with a view to including other platinum metals within the scheme. In this connection, the thiocyanate system appears to have been completely neglected, even McBryde's comprehensive review[2] making no reference to it.

For platinum, at least, the possibility arises of forming non-ionic compounds, $R_2M^1X_2$, resembling those formed by palladium, with a high probability of successful extraction into organic solvents. Thus, in the cold, platinum^{IV} does not react with such organic reagents as *p*-nitrosodiphenylamine, but, on warming, a coloured extractable product is obtained.[3] It is believed that the effect of heating is to cause reduction of platinum^{IV} to the II state, in which it does react with this and certain other reagents in the same manner as palladium. Complexes of platinum containing thiocyanate ion do not appear to have been investigated in this context.

Little information is available on the behaviour of rhodium in thiocyanate solution, although it has been stated[4] that the action of potassium thiocyanate on potassium chlororhodite yields the stable complex $K_3Rh(SCN)_6$ and that the addition of dilute sulphuric acid to a solution of this salt liberates the free acid, $H_3Rh(SCN)_6$, which may be extracted by amyl alcohol.

This paper describes a procedure for the separation and determination of rhodium, palladium and platinum through the formation of both complex and ammine-type thiocyanates.

PRELIMINARY INVESTIGATIONS

The conditions for formation of the ammine-type thiocyanate of palladium, Pd $py_2(SCN)_2$, have been discussed in Part II of this series.[1] It was found that this procedure can be applied for the removal of palladium by extraction with hexone (methyl *iso*-butyl ketone) in presence of both rhodium and platinum, with the advantage that it is unnecessary to use strong alkali for rapid pH adjustment. If pyridine is used instead to adjust the pH to 6·0–6·5, the Pd $py_2(SCN)_2$ compound is formed in solution, while, in the cold, the complexes of rhodium^{III} and platinum^{IV}, if formed at all, are not extracted.

In the cold, platinum^{IV}, present as $PtCl_6^{2-}$, is not extracted, even from acid solution, in the presence of excess thiocyanate, by any of the usual organic solvents. However, if such a solution, approximately 0·1*N* in hydrochloric acid concentration, is heated almost to boiling point, an odour of hydrogen sulphide is observed and the solution becomes golden yellow in colour. This colour is quite stable and is readily extracted by hexone at pH below 6·5, giving a golden yellow colour in the organic layer. The process occurring here is presumably reduction of platinum^{IV} to platinum^{II}, with formation of an extractable thiocyanate complex. As in the case of ruthenium, this complex is anionic in nature, as shown by its ready adsorption on the anionic-exchange resin Amberlite IRA-410. This is the case even in the presence of pyridine or acids other than hydrochloric, the rate of formation of the complex being to some extent dependent on acid concentration. It is possible that this species could be formulated as $Pt(SCN)_4^{2-}$, although Ayres[5] has shown the danger of assuming simplified structures for platinum complexes.

Solutions of ammonium chlororhodite or chlororhodate behave very similarly to the $PtCl_6^{2-}$ ion in their reaction with potassium thiocyanate, a golden yellow colour being developed on heating. This, however, is only completely extracted from about 3*N* hydrochloric acid solution by hexone or oxygen-containing solvents and is not extracted from solutions of pH above 1·5. Once again, the rhodium thiocyanate complex is anionic in nature.

On the basis of these observations it was found possible to effect a separation of rhodium, palladium and platinum and to employ an absorptiometric method for their determination. The absorption spectrum of $Pd\,py_2(SCN)_2$ in hexone is shown in Part II of this series.[1] For known amounts of palladium a calibration curve was prepared, from which the minimum amount which could be determined with certainty was 25 μg.

The absorption spectrum of the platinum^{II} thiocyanate complex in hexone is shown in Fig. 1, the maximum at 385 mμ being employed in subsequent measurements. For known amounts of platinum a calibration curve was prepared, from which the minimum amount of platinum which could be determined with certainty was 50 μg.

Fig. 2 shows the absorption spectrum of the rhodium thiocyanate complex in hexone, subsequent optical density measurements being made at 380 mμ. From the calibration curve prepared, the minimum amount of rhodium determinable was 50 μg.

PROCEDURE

Determination of palladium

To about 20 ml of the solution for analysis, which should contain not less than 25 μg palladium, 50 μg platinum, 50 μg rhodium, and should have a pH about 2·5, add pyridine dropwise with stirring until the pH reaches 6·0–6·5.

Transfer the pale yellow solution to a separating funnel, add 0·5 ml (excess) of a 40% potassium thiocyanate solution, swirl the mixture and allow to stand for two minutes. Extract the solution twice with 10-ml portions of hexone and make up to 25 ml. The hexone solution contains all the palladium present in the original aqueous solution. Under these conditions, thiocyanate complexes of platinum and rhodium are not formed, or, if formed, are not extracted.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. This operation removes tiny globules of air or water which may be present. Measure the optical density of

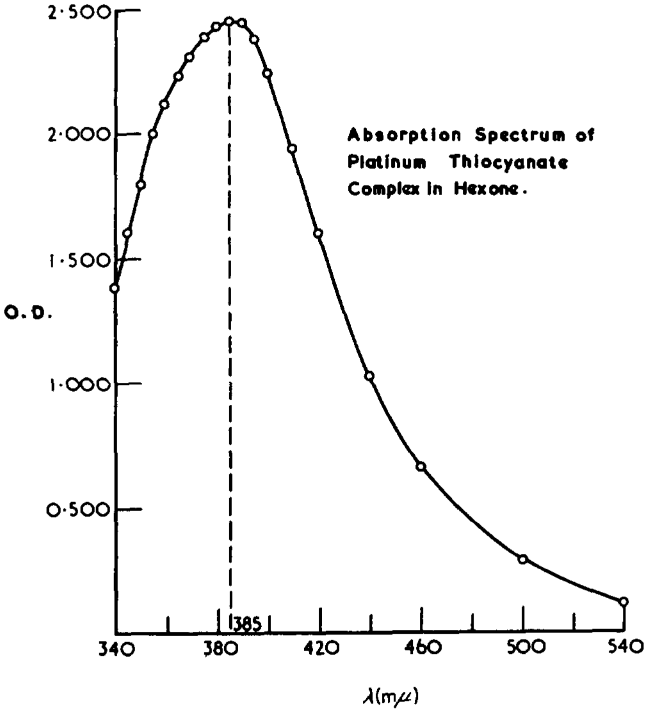
2·500
2·000
1·500
1·000
0·500
O.D.
Absorption Spectrum of Platinum Thiocyanate Complex in Hexone.
385
340
380
420
460
500
540
λ(mμ)

FIG. 1.

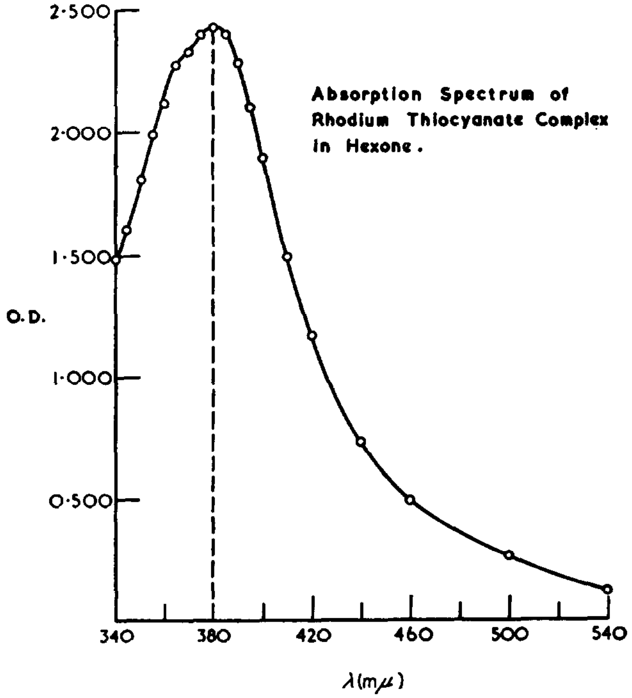
2·500
2·000
1·500
1·000
0·500
O.D.
Absorption Spectrum of Rhodium Thiocyanate Complex in Hexone.
340
380
420
460
500
540
λ(mμ)

FIG. 2.

this solution at 345 mμ with reference to hexone as standard and read off the concentration of palladium present from the prepared calibration curve.

Determination of platinum

The colourless solution remaining after the extraction of palladium contains potassium thiocyanate (excess), a little pyridine, platinum and rhodium, if present, and has a pH approximately 6·0. Adjust the pH to 2·0–2·5 using hydrochloric acid and heat the solution. On first heating a cloudiness appears at about 40°, a golden yellow colour being developed. The reaction is complete at about 90° and the time taken to reach this temperature should be about 4 minutes. Cool the beaker and contents to about 20°.

When cool, transfer the solution to a separating funnel, extract twice with 10-ml portions of hexone and make up to 25 ml. This hexone solution will contain all the platinum present in the original aqueous sample. Under these conditions the rhodium thiocyanate complex, although present in solution, is not extracted.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. Measure the optical density of this solution at 385 mμ, with reference to hexone as standard, and read off the concentration of platinum present from the prepared calibration curve.

Determination of rhodium

To the yellow aqueous solution remaining after the extraction of palladium and platinum add 0·5 ml (excess) of 40% potassium thiocyanate solution, followed by concentrated hydrochloric acid until the acid concentration of the solution is 3–4*N*. Cool the beaker and contents to about 20°.

When cool, extract the solution twice with 10-ml portions of hexone and make up to 25 ml. This hexone solution will contain all the rhodium present in the original aqueous sample.

Filter the hexone extract and pour into the absorption cell of the spectrophotometer. Measure the optical density of this solution at 380 mμ with reference to hexone previously saturated with 2*N* hydrochloric acid as standard and read off the concentration of rhodium present from the prepared calibration curve.

RESULTS

To test the validity of the proposed method a number of "unknown" mixtures were analysed by one of us (J. H. W. F.). The results are recorded in Table I. Where the experimental results differ from the actual composition, the latter is recorded in parentheses.

TABLE I.

No. of sample	Palladium	Platinum	Rhodium
1	100	110(100)	95(100)
2	202·5(200)	260(250)	65(50)
3	50	105(100)	90(100)
4	52·5(50)	245(250)	215(200)
5	255(250)	55(50)	210(200)
6	205(200)	260(250)	50(50)
7	100	100	75
8	100	105(100)	220(225)

The results, especially for palladium, are extremely satisfactory. The procedure described is rapid in application, a complete separation and determination of the three elements taking about 1½ hours.

DISCUSSION

Although ruthenium forms two thiocyanate complexes, one of which is thought to result from reduction from the III to the II state, rhodium forms only a single complex, and this fact operates against the hypothesis of reduction of rhodium to the II state. The fact that platinum also forms only one observed thiocyanate complex is no bar to the hypothesis of the reduction of platinum^{IV} since the bivalent state is also stable. Rhodium presents the important difference that, although the ion Rh^{2+} is probably stable, yet in the presence of chloride it is readily oxidised[6] to $RhCl_6^{3-}$. From these considerations it is probably safest to assume that the extracted species is a thiocyanate complex of rhodium^{III}. On the other hand, although the sulphide Rh_2S_3 is normally precipitated from acid solutions by hydrogen sulphide, yet under the conditions described this is not the case. Very recently Jackson[7] separated rhodium from iridium by precipitation with thioacetanilide after treatment with chromous chloride and suggested that a bivalent complex was formed by rhodium. In either case, some evidence exists for the formation of more than one complex in a varying range of thiocyanate concentration.

Acknowledgement—One of us (J. H. W. F.) gratefully acknowledges a grant from the Imperial Chemical Industries Ltd., (Billingham Division), which enabled him to take part in this work.

Zusammenfassung—Eine Methode zur Trennung und anschliessenden kolorimetrischen Bestimmung von Rhodium, Palladium und Platin durch Bildung von Thiocyanaten des Ammintyps, unter Verwendung von Solventextraktion wird beschrieben. Die Natur der in der Lösung auftretenden Komplexe wird diskutiert.

Resume—On décrit un procédé pour la séparation puis la détermination colorimétrique du rhodium du palladium et du platine par la formation de complexes amminés et thiocyanates en utilisant l'extraction par solvant. On a proposé quelques hypothèses sur la nature des complexes en solution.

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THE EFFECT OF PLATINUM OXIDE FILMS ON REACTION KINETICS AT PLATINUM ELECTRODES

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Summary—It has been known for some time that the pre-treatment of platinum electrodes often effects subsequent electrochemical reactions. Part of the effect of pre-treatment is due to the fact that anodized or chemically oxidized platinum electrodes become coated to some degree with a film of platinum oxide. This work was concerned with quantitative measurement of kinetic parameters as a function of the extent of oxide film formation. Whenever possible, variations in reaction mechanisms are proposed.

Most of the experimental evidence has been taken from current-potential curves but the techniques of chronopotentiometry and microscopy were also used.

The reduction of vanadium^{V}, chromium^{VI}, arsenic^{V}, iodate and oxygen were investigated as well as the oxidation of vanadium^{IV}, arsenic^{III}, oxalic acid, and formic acid. The presence of the platinum oxide film effected the reactions studied in a variety of ways but in every case some variation in the kinetic parameters of the reactions studied was recorded. For a number of cases, a modified oxygen bridge theory was found useful.

INTRODUCTION

MANY workers have found that a platinum electrode which has a coating of platinum oxides exhibits quite different behaviour from an unoxidized electrode.[1–7] Kolthoff and Nightingale[6] have shown that the ferrous-ferric couple acts more reversibly at an oxidized electrode than at an unoxidized one. They have proposed the formation of oxygen bridges between the oxidized electrode and the reacting ions to account for this fact. Similarly Anson[7] has proposed that the enhancement of the reduction of iodate ion by platinum oxide films is due to the fact that "the first step in the reduction of iodate ion at an oxidized electrode can be imagined to consist of the transfer of an electron to iodate from the electrode by means of a platinum oxide bridge which can only serve as an electron-carrying bridge at potentials where the platinum oxide itself begins to be reduced."

Although the oxide-bridge theory explains the more nearly reversible behaviour of many reactions at oxidized electrodes, some reactions, especially those of anions, are rendered less reversible and are sometimes completely suppressed by a coating of oxide film on the working electrode.[2,3] Inhibition of the oxidation of ferrous and arsenious ions by oxide films has been reported by Baker and MacNevin.[4]

This work was undertaken in an effort to measure quantitatively the effect of oxide film formation and to discover some of the causes of the various effects observed. Wherever possible the approach was to measure the kinetic parameters α and $k_{s,h}$ (the electron transfer coefficient and the heterogeneous rate constant respectively)[8] as a function of the extent of oxidation of a platinum electrode. As many chemical systems as possible were investigated but only a limited number yielded useful results

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since the values of $k_{s,h}$ and α must be within certain limits for reasonably accurate results to be obtained with the technique used. In addition, strong reducing or oxidizing agents had to be avoided so that the oxide coating on the electrode would not be too greatly affected by chemical action alone. Although it seems that each reaction must be considered individually, the presence of an oxide film on the electrode seems to effect either the heterogeneous rate constant alone or both the rate constant and the transfer coefficient. In the latter case it is quite probable that the rate determining step is completely altered.

EXPERIMENTAL

The current-potential curves, from which the log *i* versus *E* plots were derived, were obtained with a potentiostat and a current integrator[9] secured from Analytical Instruments, Inc., Bristol, Connecticut, U.S.A. The method of measurement and the treatment of results have been described by Meites.[10] In this work each point on the current-potential curves was obtained by reading the current integrator at the beginning and at the end of a 100-second period of time. A period of 50 seconds was allowed after each change in potential to assure steady readings. The reading of millifaradays per 100 seconds at each potential was then easily converted to microamperes since the value of the faraday is accurately known. Some typical log *i* versus *E* plots are shown in Fig. 1.

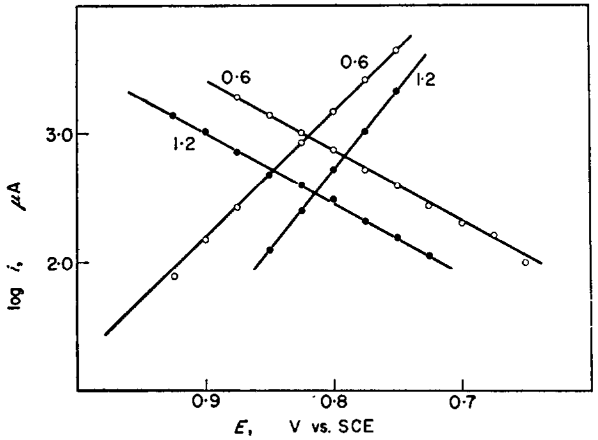

FIG. 1.—Log *i* versus *E* curves for the Vanadium^{V}–Vanadium^{IV} couple.
Open circles—Electrode pre-reduced at +0.60 v. vs. S.C.E. after oxidation.
Closed circles—Electrode pre-reduced at +1.20 v. vs. S.C.E. after oxidation.

A large H-type cell with a working electrode compartment of 100-millilitre capacity was used. A platinum-foil working electrode, whose area was 71.4 cm^2 (both sides), was held in the cell by means of a hole in a rubber stopper. The stopper also contained holes which held an ordinary Beckman asbestos-fibre saturated calomel reference electrode and a glass tube through which purified, oxygen-free nitrogen could be passed. The platinum wire auxiliary electrode was placed in the smaller side of the H-cell and was thus separated from the working electrode compartment by a sintered-glass disk. Stirring was provided by a magnetic stirrer.

The platinum working electrode was pre-treated by oxidation in a solution of argentic oxide in 6*M* nitric acid and then reduction at controlled potential in a 1*M* sulphuric acid solution. The treatment with an argentic solution not only oxidized the electrode but also removed oxidizable impurities. The reduction of the electrode by means of the potentiostat was continued for ten minutes after the current integrator stopped registering when set at its most sensitive range (until the current dropped below about 10 microamps). This method of electrode treatment gave a reproducible amount of oxide on the electrode surface provided that the electrode was well soaked in the argentic solution previous to reduction. Sometimes the electrode became "fouled" by being reduced at potentials below about +0.2 volts versus S.C.E. but the electrode could always be restored to the desired conditions provided it was soaked in the oxidizing solution for a long enough time. Several hours was the maximum found necessary.

Experimental conditions were chosen such that the rate of reaction was independent of diffusion. Relatively concentrated solutions of reactants were used (approximately $0.01M$) together with a low current density which rarely exceeded 30 microamps per cm^2. The fact that the current was indeed independent of diffusion was verified by changing the rate of stirring over about a ten-fold range. The current was found to be independent of the stirring rate. Each run was performed with a fresh solution to avoid depletion of substance undergoing reaction even though less than 1 % was oxidized or reduced during a run. This method may be thought of as measuring a very small section at the foot of a typical polarographic wave.

The experimental arrangement for chronopotentiometric measurements was similar to that described by Anson and Lingane,[11] except that a Sargent Potentiometric Recorder was used.

Pictures of the surface of the platinum electrode were obtained with a Zeiss Standard Metallurgical Microscope. A magnification of about 600 × was achieved by the appropriate selection of objective lens supplied with the instrument. The electrode was treated exactly as it had been for the electrochemical experiments, that is, oxidation was accomplished in an argentic ion solution and the electrode was reduced at controlled-potential in $1M$ sulphuric acid.

The chemicals used in this work were reagent grade or better and were used as obtained without further purification. The arsenic solutions were prepared from National Bureau of Standards arsenious oxide (100.00 %) especially to avoid the difficulties due to antimony observed by Baker and MacNevin.[4] Only when the working electrode was strongly reduced was any effect of impurities apparent. Potentials below +0.2 volts versus S.C.E. were therefore avoided and the electrode was cleaned by oxidation between each run.

One molar sulphuric acid was used as the medium for all experiments except the reduction of iodate, which was carried out in $1M$ acetic acid—$1M$ sodium acetate buffer.

RESULTS AND DISCUSSION

The log current versus potential diagrams were interpreted by means of the following relationships:

$$\log i_c = \log nFAC_0k^\circ_{f,h} - \frac{1}{2{,}3}\frac{\alpha nF}{RT}E \tag{1}$$

$$\log i_a = \log nFAC_Rk^\circ_{b,h} + \frac{1}{2{,}3}\frac{(1-\alpha)nF}{RT}E \tag{2}$$

$$k_{s,h} = k^\circ_{f,h}\exp\left[-\frac{\alpha nF}{RT}E^\circ_c\right] = k^\circ_{b\,h}\exp\left[\frac{(1-\alpha)nF}{RT}\right]E^\circ_e \tag{3}$$

These symbols are those in general use and are defined by Delahay.[8] The values of the current are given by i; the electron change, by n; the faraday, by F; the electrode area by A; the gas constant, by R; the absolute temperature, by T; the potential, by E; the heterogeneous rate constants, by k; and the transfer coefficient, by α. Experimental conditions were chosen so that it was reasonable to assume that E differs considerably from the equilibrium potential and that C_0 or C_R may be set equal to the analytical concentration of the substance under investigation. The values of α and $1 - \alpha$ were easily found from the slope of the log i versus E plots. The question of how to interpret the heterogeneous rate constants is not easily answered. One difficulty is that the values of $k^\circ_{b,h}$ and $k^\circ_{f,h}$ depend on the potential scale used (in this work the saturated calomel electrode) and show wide variation in absolute value depending on the reaction under investigation. Ideally $k_{s,h}$'s are more useful, since they are truly characteristic of the reaction being studied. However, the value of E°_c must be known or must be able to be accurately determined.

Another difficulty is the problem of what value to use for the electrode area in the calculation of the rate constants. At first thought the gross area would seem sufficient but even a polished platinum electrode is not even approximately smooth as can easily be seen from Fig. 3. It is also possible that even with solid electrodes the "effective area" might be variable as will be discussed later. For these reasons the product of the area and $k_{s,h}$'s are reported since it is not absolutely certain which of these is caused to vary by the presence of the oxide film. When the value of E°_{c} (see equation 3) is not known, values of $Ak_{s,h}(E)$ are reported, where E is some arbitrary potential selected for convenience only, but whose value is recorded so that the appropriate calculations could be made if the value of E°_{c} is ever determined.

Variation of the Area—Rate Constant Product

When vanadium$^{\mathrm{V}}$ was reduced and vanadium$^{\mathrm{IV}}$ or arsenic$^{\mathrm{III}}$ was oxidized, variation of the extent of oxidation of the electrode surface seemed to mainly effect the area-rate constant product. The values of α and $1 - \alpha$ showed only slight variations. Tables I and II show the values obtained with the working electrode oxidized, and then reduced at various potentials. Only in the case of the vanadium$^{\mathrm{V}}$–vanadium$^{\mathrm{IV}}$ couple was it possible to study the reaction in both directions. For some unknown reason the log i versus E plots for the reduction of arsenic$^{\mathrm{V}}$ were not straight lines and no conclusions could be drawn from them. Fig. 1 shows two sets of log i versus E plots for vanadium. Since the concentrations and other experimental conditions were identical for both reduction and oxidation, the values of the potential and the current at the intersection of the reduction line and the oxidation line were used to calculate $Ak_{s,h}$ and the formal potential of the couple. The value of the latter is in fair agreement with that reported by Swift[12] for $1M$ sulphuric acid.

TABLE I.—THE EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE VANADIUM$^{\mathrm{IV}}$—VANADIUM$^{\mathrm{V}}$ COUPLE

Treatment (E vs. SCE)	$Ak_{s,h} \times 10^7$ (a)	α	$1 - \alpha$	Sum	E_c° vs. S.C.E.
0.40	2.6	0.74	0.32	1.06	0.818
0.50	2.9	0.52	0.41	0.93	0.786
0.55	11.9	0.59	0.47	1.06	0.792
Red. (Fe^{2+})	13.2	0.67	0.29	0.96	0.810
0.60	7.9	0.59	0.32	0.91	0.815
0.75	5.5	0.70	0.34	1.04	0.812
0.90	4.4	0.67	0.38	1.05	0.820
1.20	3.3	0.73	0.32	1.05	0.812
Ox (Ag^{2+})	2.7	0.74	0.30	1.04	0.825
Average		0.64	0.35	1.005	0.809

(a) Units of $cm^3\ sec^{-1}$.

The values of $A\ k_{s,h}$ for the vanadium$^{\mathrm{V}}$–vanadium$^{\mathrm{IV}}$ couple increase as the oxide film is removed, reach a maximum, and then decrease again. By examination of Tables I and III it is possible to notice that the variation of $A\ k_{s,h}$ follows closely the removal of the oxidized film. The maximum value of $A\ k_{s,h}$ occurs with the electrode from which most, but not all of the film is removed. Several explanations for this behaviour are possible.

It could be that the reduction or oxidation of the electrode serve simply to increase the measured values of the current. This possibility can be rejected at once on the grounds that the current for the oxidation or reduction of the electrode alone is very small (less than 1% of the currents measured for the reduction or oxidation of vanadium). Also curved log i versus E plots should be observed if the two different reactions were making a significant contribution to the total current.[13]

TABLE II.—EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE OXIDATION OF ARSENIC^{III}

Treatment (E vs. SCE)	$Ak_{s,h}$(+0.475 v. vs. SCE) × 10^8 (a)	$(1 - \alpha)n_a$
0.30	2.5	0.76
0.40	4.2	0.77
0.50	5.2	0.81
0.55	17.5	0.80
0.60	53.0	0.71
0.70	66.8	0.70
0.80	66.7	0.71
Oxidized (Ag^{2+})	66.6	0.71

(a) Units of $cm^3\ sec^{-1}$.

A mechanism involving the induction of the vanadium oxidation or reduction by the simultaneous oxidation or reduction of the electrode must also be considered. However, one would expect the maximum value of $Ak_{s,h}$ to be found when the electrode was the most completely oxidized for reductions, and the most completely reduced for oxidations.

The most logical explanation seems to be a slight modification of the oxide bridge theory, which proposes that the greater ease of reduction (or oxidation) at an oxide-coated electrode can be attributed to the formation of a bridge between oxygen of the film and the ion undergoing reaction, thus facilitating the electron transfer between the electrode and the ion.[6,14] Since the theory as originally stated cannot account for the decrease in $Ak_{s,h}$ when the electrode is fairly strongly oxidized (Table I) it should be modified to state that oxygen bridges can form only when a slight or very thin coating of oxide is present.

The proposed change in the oxygen bridge theory can be used to explain several other experimental observations as well as the variations of $Ak_{s,h}$ with the extent of electrode oxidation. Fig. 2 shows a chronopotentiogram of vanadium^{V} in 1M sulphuric acid taken with an oxidized platinum electrode. When the current is first applied, the potential changed rapidly in a reducing direction but then reversed itself forming a small "dip" before the potential hold up for the reduction of vanadium^{V} occurred. The "dip" was not observed if a reduced platinum electrode was used. This "dip" is due to the fact that the oxide on the electrode is first partly reduced but, when the oxide coating is such that oxygen bridges can form and facilitate

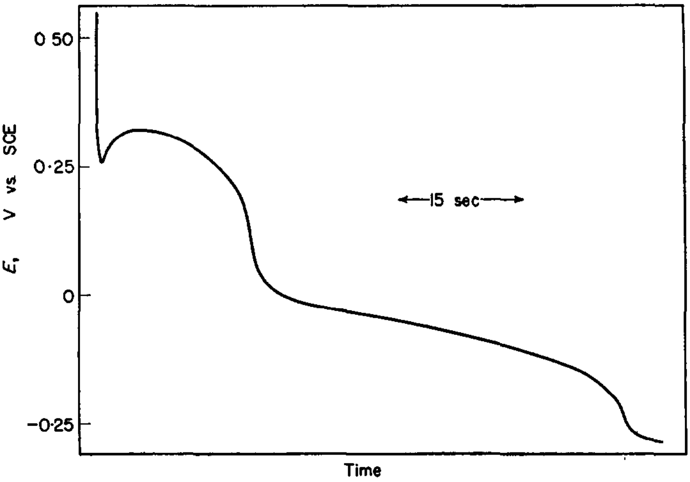

FIG. 2.—Chronopotentiogram for the reduction of $0.1M$ vanadium^{V} in $1M$. Sulphuric acid.
Electrode area, 0.2 square centimeters.
Current, 1.0 milliampere.

electrode exchange, the potential shifts anodically to a value determined by the reduction of vanadium^{V}. Exactly the same behaviour was noticed when iron^{III} was reduced in $1M$ sulphuric acid with an oxidized electrode.

Apparently a heavy oxide film has the ability to suppress rather than enhance the electrode reaction of the iron^{III}–iron^{II} couple as well as the vanadium^{V}–vanadium^{VI} couple. Indeed this has been noticed by Baker and MacNevin[4] in the process of investigating the oxidation of iron^{II} by controlled-potential electrolysis. Their findings were confirmed in this laboratory.

TABLE III.—REDUCTION OF AN OXIDIZED ELECTRODE BY CONTROLLED-POTENTIAL ELECTROLYSIS IN AIR-FREE $1M$ SULPHURIC ACID

E vs SCE	Total milliequivalents × 10^6
1.00	1
0.90	0
0.80	3
0.75	2
0.70	2
0.65	6
0.60	8
0.55	26
0.50	8
0.40	6

Evidently only a slight amount of oxide is necessary—or in fact desirable—for oxygen bridge formation. The amount seems to be something less than a monolayer. (Table III and Reference 15). With these facts in mind a microscopic study of the surface of the working electrode was undertaken. Some typical photographs are shown in Fig. 3. The only noticeable difference between the surface of an oxidized and a reduced electrode is that the grain boundaries are darker in the former case. The results of this study seem to indicate that the PtO and PtO_2 form principally at the grain boundaries. Quite possibly the condition of maximum effectiveness of a platinum electrode occurs when the grain boundaries and possibly other areas, which may be considered active sites, are completely covered with a monolayer of PtO. More than a monolayer can undoubtedly form but the oxide then loses its ability to make electron transfer easier.

Fig. 2 also shows a second wave just following the one attributed to the reduction of vanadium^{V}. This second wave was found to be absent when a reduced electrode was used. Apparently the power of the oxide film to facilitate electron transfer is so great that the notoriously irreversible vanadium^{IV}–vanadium^{III} couple is made quite reversible. The belief that this second wave is truly due to the reduction of vanadium^{IV} to vanadium^{III} is supported by the fact that $\frac{(\tau_1 + \tau_2)^{1/2}}{\tau_1^{1/2}}$ was found to be equal to 1.9. The theoretical value for this fraction would be 2.0 if the vanadium^{V} were reduced in two consecutive one-electron steps.[16]

When vanadium^{IV} is reduced at an oxidized electrode a wave similar to the second wave in Fig. 2 is obtained. If the chronopotentiogram is retaken without re-oxidizing the electrode the wave for the reduction of vanadium^{IV} becomes smaller and smaller and, after about four or five runs, the potential drops immediately to the value at which hydrogen ion is reduced.

It is convenient then to think of an oxidized electrode as possessing a variable "effective area." An electrode which is just sufficiently oxidized so that a monolayer of PtO is covering the grain boundaries and other active sites, may be said to possess maximum "effective area." A heavier oxide film tends to inhibit electron transfer, and likewise when part of the monolayer is reduced the "effective area" is decreased. It is rather difficult to reduce the last bits of PtO from an oxidized electrode as is apparent from the fact that several repeated runs still give waves for the reduction of vanadium.^{IV}

Variation of Reaction Mechanism

Iodate: Several of the reactions studied showed not only variation of the area-rate constant product but also variation in the value of $n_a\alpha$, where n_a is the number of electrons involved in the rate determining step. Apparently the presence of the oxide film changes the whole reaction mechanism, and does not just facilitate the electron transfer process.

The results for the reduction of iodate ion, shown in Table IV, seem to confirm the proposal of Anson.[7] The reduction of iodate is facilitated by the simultaneous reduction of the platinum oxide on the electrode. The current densities measured +0.450 volts versus SCE are greater, the greater the amount of oxide. When the oxide is completely removed from the electrode—reduced below about +0.25 volts—there is an abrupt shift in $n_a\alpha$ from 0.79 to 0.35. If it is assumed that α is about 0.35, then this shift may be interpreted to mean that the rate-determining step has changed from a two-electron to a one-electron one. It is also possible that α is equal to 0.16 or 0.17 making the rate-determining step for the oxidized electrode a five-electron reduction, whereas a two-electron step would occur at a reduced electrode. Generally α is considered to be larger than 0.16, however.

Delahay and Strassner[17] have studied the reduction of iodate at a dropping mercury electrode but they propose an n_a value of 2 and an α of 0.3 in the pH range studied here. DeMars and Shain have found $n_a\alpha$ to be 0.39, also with a mercury electrode,[18] which is in good agreement with the values determined with a reduced platinum electrode.

TABLE IV.—THE EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE REDUCTION OF IODATE (1*M* ACETIC ACID—1*M* SODIUM ACETATE, pH = 4.7)

Treatment (E vs SCE)	Current density at +0.450 v. vs. SCE, microamps per cm^2	$n_a\alpha$
0.15	0.0025	0.35
0.30	0.79	? (curved line)
0.45	7.88	0.79
0.60	11.7	0.79
0.90	65.6	0.77
Oxidized (Ag^{2+})	111.0	0.69

Oxalic acid: The rate-determining step of oxidation of oxalic acid appears to be different depending on whether the electrode is oxidized or not. (See Table V.) If one assumes that $1-\alpha$ is about 0.5, as is generally the case, then $n_a = 1$ with an oxidized electrode, but $n_a = 2$ with a reduced one. In addition, there is a maximum in the $Ak_{s,h}$ at the electrode which has just a small amount of surface oxidation. It is possible that there is some sort of bridge formation between the oxygen of the platinum oxide and oxalic acid or one of its intermediate oxidation products. In any case the partially oxidized electrodes (treatment 0.60 and 0.70 volts) have $n_a(1 - \alpha)$ values intermediate between those of the strongly oxidized and strongly reduced electrodes. The reason for this behaviour is not apparent from this work.

TABLE V.—THE EFFECT OF ELECTRODE OXIDATION ON THE KINETICS OF THE OXIDATION OF OXALIC ACID

Treatment (E vs SCE)	$Ak_{s,h}$(+0.675 v. vs. SCE) × 10^7 (a)	$n_a(1 - \alpha)$
0.40	6.9	1.02
0.50	6.8	1.02
0.60	15.3	0.70
0.80	3.12	0.70
1.00	1.21	0.49
Oxidized (Ag^{2+})	1.56	0.49

(a) Units of cm^3 sec^{-1}.

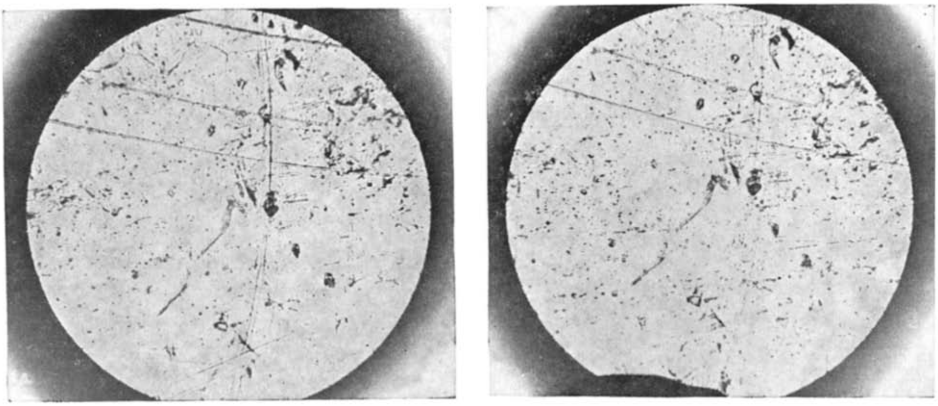

FIG. 3a. FIG. 3b.

FIG. 3.—Photomicrograph of the surface of the platinum working electrode.
Magnification—600×
A—Oxidized
B—Reduced.

Chronopotentiometric studies[2] have shown that the wave due to the oxidation of oxalic acid could be suppressed by oxidation of the electrode, which is in general agreement with this study.

Oxygen: Values for $n_a\alpha$ for the reduction of oxygen are reported in Table VI. No values of $Ak_{s,h}$ are reported since they proved to be rather variable due to the difficulty of controlling the oxygen concentration. However, oxidation of the electrode appears to facilitate the reduction of oxygen. The sudden shift in the values of $n_a\alpha$ indicates that a change in mechanism occurs when the electrode becomes fairly well oxidized. If α is taken as about 0.6 then $n_a = 2$ for oxidized electrodes but only 1 for reduced electrodes. It is proposed that with an oxidized electrode, oxygen is reduced directly to hydrogen peroxide, but at a reduced electrode the rate determining step is:

TABLE VI.—THE EFFECT OF ELECTRODE OXIDATION ON THE REDUCTION OF OXYGEN

Treatment (E vs. SCE)	$n_a\alpha$
0.30	0.54
0.40	0.53, 0.59
0.50	0.61
0.55	0.67
0.60	0.61, 0.65
0.70	1.21, 1.19, 1.29
0.80	1.29, 1.26
0.90	1.25
Oxidized (Ag^{2+})	1.26

$$H^+ + O_2 + e = HO_2$$

The results at a reduced electrode serve to confirm the results of several workers.[19]

Other reactions: Several other reactions were studied but the results were inconclusive. The oxidation of thallous ion seemed little affected by the presence or absence of an oxide film. Although the log i vs. E plots were not very good $n_a(1 - \alpha)$ was apparently very close to unity.

A study of the oxidation of formic acid[20] was found to give no useful information apparently due to its great irreversibility. The reduction of dichromate proved to be so greatly suppressed at a platinum electrode that no measurements are reported. However, the reduction of dichromate was studied with a gold electrode by the same methods used for the platinum electrode and straight log i versus E plots were obtained, which gave a value of $n_a\alpha = 1.00$. This value of $n_a\alpha$ is in good agreement with the values determined by Baumann and Shain.[13]

CONCLUSIONS

The results of the study indicate that the participation of platinum oxide films in electrochemical reaction is undoubtedly rather complex. The theory that a monolayer of platinum oxide residing on the grain boundaries and other active sites can facilitate electron transfer by means of oxygen bridge formation seems to account for the increase in reversibility observed for a number of reactions. In many other cases the mechanism of the reactions is completely altered by the presence of the oxide film.

Analytical chemists should exercise extreme care when using platinum electrodes in conjunction with controlled-potential electrolysis, chronopotentiometry and other electroanalytical techniques. Corrections for the current used to oxidize or reduce the electrode must be made in many cases.[11,15,21] In addition, the effect on the electrode kinetics must be considered. In many cases advantage may be taken of the increase in reversibility or of the rate constant for a particular reaction. For instance it is advantageous to titrate an oxidant with a reductant, rather than the reverse, when the end-point is located by means of "two electrode" amperometry.[6] Likewise, if iodate ion is to be determined by controlled-potential electrolysis, an oxidized electrode would allow a more rapid and possibly more complete reduction. Oxalic acid should be oxidized with a reduced electrode, in so far as is possible, as should iron^{II}.[4]

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Zusammenfassung—Es ist seit geraumer Zeit bekannt, dass die Vorbehandlung von Platinelektroden häufig von Einfluss auf die elektrochemischen Reaktionen ist. Zum Teil lässt sich der Effekt auf die Tatsache zurückführen, dass anodisch oder chemisch oxydierte Platinelektroden zu einem gewissen Grade mit einem Film von Platinoxyd überzogen sind. Die vorliegende Arbeit beschäftigt sich mit der quantitativen Beziehung zwischen kinetischen Parametern und Ausmass der Oxydfilmbildung. Wo immer möglich werden Änderungen des Reaktionsmechanismuss es vorgeschlagen. Die meisten experimentellen Daten wurden aus Strom-Potential-Kurven gewonnen, doch wurde auch de Technik der Chronopotentiometrie und Mikroskopie angewandt.

Die Reduktion von Vanadin (V), Chrom(VI), Arsen(V) Iodate und Sauerstoff wurden untersucht. Desgleichen die Oxydation von Vanadin(IV), Arsen(III), Oxalsäure und Amseisensäure. Die Anwesenheit von Oxydfilmen beeinflusste die Reaktionen in verschiedenster Weise. Jedoch wurde in jedem Falle eine Änderung der kinetischen Parameter der studierten Reaktionen festgestellt. Für einige Fälle war die Anwendung einer modifizierten Sauerstoffbrückentheorie nützlich.

Résumé—On sait depuis quelques temps que le pté-traitement des électrodes de platine affecte souvent les réactions électrochimiques ultérieures. Une partie de l'effet du pré-traitement est due au fait que des électrodes de platine oxydées anodiquement ou chimiquement se recouvre plus ou moins d'un film d'oxyde de platine. Ce travail est relatif à la détermination quantitative de paramètres cinétiques en fonction de l'importance du film d'oxyde. Lorsque cela a été possible, on a proposé des changements dans les mécanismes des réactions.

La plupart des phénomènes expérimentaux ont été empruntés aux courbes intensité-potentiel, mais les techniques de la chronopotentiométrie et de la microscopie ont été aussi employées. On a étudié la réduction du vanadium (V), du chrome (VI), de l'arsenic (V), de l'iodate et de l'oxygène ainsi que l'oxydation du vanadium (IV), de l'arsenic (III), de l'acide oxalique et de l'acide formique. La présence d'un film d'oxyde de platine affecte différemment les réactions étudiées, mais dans chaque cas, on a enregistré la variation de paramètres cinétiques de la réaction étudiée. Dans un grand nombre de cas, une théorie modifiée du pont d'oxygène a donné satisfaction.

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THE DETERMINATION OF COBALT BY OXIDATION WITH POTASSIUM MOLYBDICYANIDE

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Summary—Cobalt has been determined titrimetrically and coulometrically by oxidation of the bivalent ion with potassium molybdicyanide, $K_3Mo(CN)_8$, in ammoniacal medium. The break in potential at the equivalence-point is approximately 0.6 volt. Manganese is not oxidized stoichiometrically in citrate media, but the total of cobalt and manganese may be obtained in the presence of fluoride. Iron interferes when fluoride, but not when citrate is used as the complexing agent. The method, therefore, is not directly applicable to steels where both iron and manganese are present.

OF the various methods which have been devised for the titrimetric determination of cobalt, the one most widely used is that proposed almost simultaneously by Dickens and Maasen[1] and by Tomicek and Freiberger[2]. In this procedure bivalent cobalt is oxidized to the tervalent state in the presence of ammonia and an ammonium salt by potassium ferricyanide, the end-point being determined potentiometrically. The method suffers the disadvantage that the break in potential at the equivalence-point is only about 0.2 volt, making it necessary that the end-point of inflection be obtained from a plot of the titration curve.

Substitution of ethylenediamine for ammonia lowers the reduction potential of the cobalt^{III}–cobalt^{II} system some 0.5 volt to about −0.55 volt versus the saturated calomel electrode, giving a greatly improved potential break of 0.7 volt at the end-point.[3] However, because the cobalt^{II} ethylenediamine ion is readily oxidized by atmospheric oxygen, careful precautions must be taken to exclude air from the titration vessel and the titrant.

Potassium molybdicycanide, $K_3Mo(CN)_8$, with a reduction potential of 0.73 volt versus the saturated calomel electrode,[4] is a more powerful oxidizing agent by some 0.4 volt than is potassium ferricyanide. The solid compound decomposes rapidly upon exposure to light, but is more stable in solution. Solutions may be readily prepared by oxidation of a solution of the corresponding potassium molybdocyanide, $K_4Mo(CN)_8$, which as the solid is stable in light. This oxidation is most conveniently performed by stirring with lead dioxide in dilute sulphuric acid solution. Solutions of the molybdicyanide prepared in this manner may be kept and used for two to three days if stored away from light and standardized at the time of use.

Using this reagent in place of potassium ferricyanide, cobalt has been successfully determined under conditions similar to those employed in the ferricyanide titration. The break in potential at the equivalence-point is approximately 0.6 volt.

Also, a procedure for the application of the system to constant-current coulometry has been developed which eliminates the necessity for preparation and frequent standardization of potassium molybdicyanide solutions. By adding solid potassium molybdocyanide to a solution containing cobalt^{II} in the presence of ammonia and an ammonium salt and oxidizing the cobalt and/or the molybdocyanide at a platinum electrode under conditions of one hundred percent current efficiency, the amount of cobalt present may be determined from the total current required to effect the oxidation. The end-point may be found by following the potential with a pH meter, using a platinum-calomel electrode system as was done in the titrimetric procedure.

EXPERIMENTAL WORK

Titrimetric Method

Reagents

Potassium Molybdicyanide Solution: A solution of approximately 0.05*M* potassium molybdicyanide was prepared by dissolving 36 g of potassium molybdocyanide, prepared by the method of Willard and Thielke[5], in 500 ml of distilled water. About 10 g of lead dioxide and 4 ml of concentrated sulphuric acid were added and the solution stirred vigorously for 5 minutes. After the addition of the lead dioxide the solution was protected from exposure to light as much as possible. The lead sulphate and unreacted lead dioxide were filtered off on a medium-porosity fritted-glass funnel, the solution diluted to approximately one litre and stored in a dark bottle away from the light. It was standardized potentiometrically against cobalt^{II} sulphate.

Cobalt^{II} sulphate: A standard solution of 0.05*M* cobalt^{II} sulphate was prepared by weighing out accurately 16.617 g of potassium cobalticyanide into a 500-ml conical flask, adding 50 ml of concentrated sulphuric acid and heating gently at first and then strongly until all the cyanide was driven off and about 10 ml of solution remained[6]. After cooling, the solution was transferred quantitatively to a litre volumetric flask and diluted to volume. It was stored in a polyethylene bottle.

Apparatus

A Beckman Model H–2 pH meter with a bright platinum-saturated calomel electrode system was used for the titrations. The titration vessel was a 250-ml beaker with the exterior covered with aluminium foil. Magnetic stirring was used.

Standardization of potassium molybdicyanide solutions

It has been shown by Kolthoff and Tomsicek[4] that decomposition of potassium molybdicyanide in solution is less rapid if the solution is made acid. In the procedure given above for the preparation of molybdicyanide solutions a sufficient excess of sulphuric acid is present to provide the required acidity. A solution prepared by the method given above was stored away from direct light and portions were withdrawn and titrated over a period of eight days. A plot of concentration versus time is shown in Fig. 1. The rate of decomposition may be seen to increase with time. For this work fresh solutions were prepared every two or three days.

Determination of cobalt

For the determination of cobalt a known excess of standard potassium molybdicyanide solution was pipetted into a solution containing up to 50 mg of cobalt to which had been added 15 ml of ammonium citrate and 25 ml of concentrated ammonia. The excess molybdicyanide was then back-titrated immediately with standard cobalt^{II} sulphate. Back-titration is recommended, as equilibrium is reached rapidly after the addition of each increment of titrant. With direct titration it is necessary to wait 30 seconds or so after the addition of each quantity of titrant when in the neighborhood of the end-point to allow the system to come to equilibrium. A titration plot is shown in Fig. 2.

Effect of iron and manganese

Iron^{III} does not interfere, as it is held in solution by the high concentration of citrate present. Iron^{II} if present must be oxidized to the tervalent state. This may be done with hydrogen peroxide, the excess oxidizing agent being removed by boiling.

In the presence of citrate, manganese^{II} was oxidized by molybdicyanide to a mixture of the three and four oxidation states, so that stoichiometric results could not be obtained. Other complexing agents were investigated in an effort to find one in whose presence manganese would be oxidized to some definite oxidation state. Those studied included tartrate, sulphosalicyclate, pyrophosphate, ethylenediaminetetraacetate, N-hydroxyethylene-diaminetriacetate and fluoride. Of this number

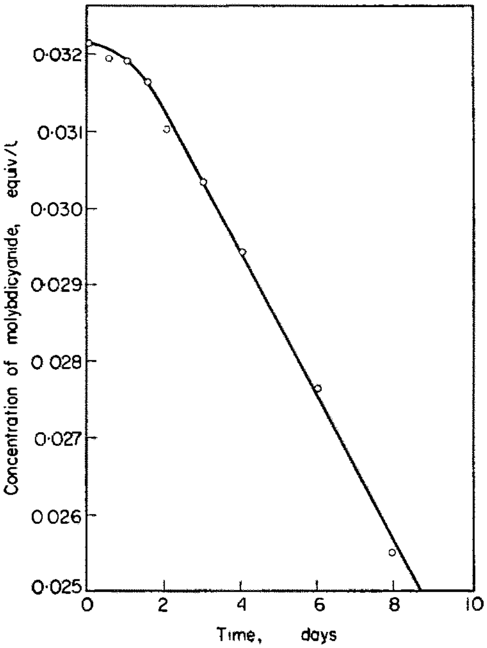

FIG. 1.—Change in concentration of a solution of potassium molybdicyanide in subdued light over a period of eight days

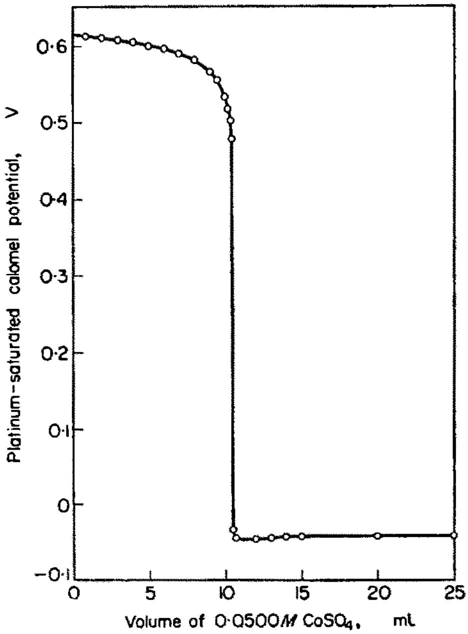

FIG. 2.—Titration of potassium molybdicyanide with cobalt^{II} sulphate in the presence of ammonia and ammomium citrate

only fluoride was found acceptable, for in the presence of fluoride manganese was oxidized quantitatively to the quadrivalent oxidation state and precipitated as manganese dioxide. Unfortunately, the fluoride complex of iron^{III} is not stable enough under the alkaline conditions of the titration to prevent the precipitation of ferric hydroxide, so that the simultaneous presence of iron and manganese could not be tolerated. Attempts to use mixtures of citrate or tartrate and fluoride were unsuccessful because potential readings were not stable. Results of some typical titrations are given in Table I.

Substitution of ethylenediamine for ammonia was also investigated. Upon addition of ethylenediamine to a solution of potassium molybdicyanide the potential drifted steadily downward from 0.72 volt to about 0 volt versus the saturated calomel. Attempts were made to titrate cobalt in the presence of ethylenediamine with molybdicyanide, but in the region of the equivalence-point the potentials drifted seriously, indicating probable attack of the amine by the oxidizing agent.

TABLE I. TITRATION OF COBALT^{II} AND MANGANESE^{II} WITH POTASSIUM MOLYBDICYANIDE

Metal ion titrated	Other metal ion present, *mg*	Complexing agent	Metal taken, *mg*	Metal found, *mg*
Co^{II}	None	Citrate	5.44	5.41, 5.41, 5.44; ave. 5.42
Co^{II}	None	Citrate	48.32	48.41, 48.24, 48.21, 48.28; ave. 48.29
Co^{II}	Fe^{III}, 54.1	Citrate	14.73	14.70
Co^{II}	Fe^{III}, 270.5	Citrate	14.73	14.65
Mn^{II}	None	Citrate[a]	4.91	4.68[b]
Mn^{II}	None	Fluoride	4.91	4.89[b]
Co^{II}	Fe^{III}, 54.1	Fluoride	16.11	14.37[c]

[a] Potential break not sharp

[b] Calculated on basis of oxidation of Mn^{II} to Mn^{IV}

[c] Precipitate of ferric oxide formed

Coulometric Method

Apparatus

A Hewlett-Packard Model 712A power supply was used as a potential source. A 1000-ohm, 100-watt dropping resistor and a calibrated precision resistor of either 2 or 20 ohms were connected in series with the cell. The exact amount of current being passed during each run was determined by measuring the potential drop across the precision resistor with a Leeds and Northrup student potentiometer, the potentiometer being checked frequently against a standard cell. The potential of the power supply was adjusted as required during each run to keep the current constant. Time measurements were made with a stop watch.

A 250-ml beaker was used as a titration vessel, with a circular platinum gauze electrode suspended in the beaker to act as an anode. The cathode, a platinum foil fused to a platinum wire, was placed in a glass tube approximately 1 cm in diameter and 10 cm long into one end of which was fused a fine fritted glass disc. This tube, filled with a catholyte of dilute sulphuric acid (1:1), was placed in the center of the titration vessel. A Beckman Model H-2 pH meter with a bright platinum-saturated calomel electrode system was employed to detect the end-point. Magnetic stirring was used.

Procedure

Into the titration vessel was placed 10 ml of a 25% solution of ammonium citrate and 15 ml of concentrated ammonia. Approximately 0.5 g of potassium molybdocyanide for each 30 mg of cobalt was added. Portions of a solution of cobalt^{II} sulphate, prepared by weight from primary-standard cobalt sulphate, were then pipetted into the cell and the stop watch and current started simultaneously. When the potential of the solution just began to rise rapidly from that of the cobalt^{III}–cobalt^{II} system, the time was noted.

The amount of cobalt present, B, in millimoles, was calculated from the equation

$$B = \frac{It}{nF}$$

where

I = current in milliamperes
t = time in seconds
n = number of electrons per molecule involved in the oxidation
F = Faraday, 96,500 coulombs per equivalent

Results for a series of titrations are given in Table II.

TABLE II. DETERMINATION OF COBALT BY CONSTANT CURRENT COULOMETRY WITH POTASSIUM MOLYBDICYANIDE

Current, *mA*	Cobalt taken *mg*	Cobalt found *mg*
9.98	2.72	2.72, 2.69, 2.70, 2.73, 2.72, 2.72; ave. 2.71
19.96	5.44	5.48, 5.39, 5.46, 5.42, 5.45, 5.42; ave. 5.44
48.83	13.60	13.55, 13.66, 13.67, 13.62, 13.57, 13.54; ave. 13.60
97.66	27.19	27.26, 27.07, 26.91, 27.15, 27.36, 27.27; ave. 27.17

Manganese and iron both interfere in the determination of cobalt by the coulometric method Excessive amounts of current are required to oxidize manganese alone in either citrate or fluoride media, as a film of manganese dioxide coats the platinum anode. When iron^{III} is present the results for cobalt are invariably low by a small amount. It is necessary, therefore, that cobalt be separated from these elements before titration.

Zusammenfassung—Cobalt wurde in alkalischem Medium titrimetrisch und coulometrisch bestimmt durch Oxydation des zweiwertigen Ions mit Kaliummolybdicyanid, $K_3Mo(CN)_8$

Résumé—Les auteurs ont dosé le cobalt volumétriquement et coulométriquement par oxydation de l'ion divalent par le molybdicyanure de potassium, $K_3Mo(CN)_8$, en milieu ammoniacal. La variation du potentiel au point équivalent est d'environ 0,6 volt. Le manganèse n'est pas oxydé stoechiométriquement dans les milieux citrique, mais on peut obtenir la totalité du cobalt et du manganèse en présence de fluorure. Le fer est complexé par le fluorure, mais pas quand on utilise le citrate comme agent complexant. La méthode n'est donc pas directement applicable aux aciers quand le fer et le manganèse sont presénts à la fois.

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THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH AMMONIUM PYROPHOSPHATE

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Summary—A spectrophotometric procedure for determining copper is described, utilising the absorption at 650 mμ of the copper^{II}-ammonium pyrophosphate complex. Optimum conditions have been established and interferences studied. It is suggested that the procedure could be used for the determination of major amounts of copper in various alloys.

INTRODUCTION

It is a well known fact that the pyrophosphate ion is capable of forming complexes with several metallic radicals[1-3] and the range of complexes formed by various ratios of copper^{II}, ammonium and pyrophosphate ions has been studied by Watters and his co-workers[4]. In the course of investigating a similar system[5] it was noticed that the deep blue colour formed between copper^{II} and ammonium pyrophosphate solutions possessed properties that suggested its use as a quantitative procedure for the colorimetric determination of copper.

This paper describes the work that was carried out in developing this idea into a workable procedure and it will be shown that ammonium pyrophosphate is not suitable for determining minute traces of copper. This, it is felt, is an advantage in some respects in that it would enable major amounts of copper to be determined in various alloys without resorting to the undesirable technique of excessive dilution of a small aliquot.

EXPERIMENTAL

Apparatus

All absorption measurements were carried out on a Unicam SP500 spectrophotometer using glass cells.

Reagents

Ammonium pyrophosphate: Dissolve 20 g of pyrophosphoric acid (B.D.H. Laboratory Reagent) in 100 ml of distilled water, filtering the solution if necessary. Whilst cooling this solution in running water, add slowly and with stirring, ammonia solution (s.g. 0·880) until a white precipitate forms. Allow to settle, filter through a Büchner funnel and wash two or three times with ammonia solution (s.g. 0·880). Finally, wash once with acetone, transfer the precipitate to a large clock glass and allow to dry at room temperature, occasionally turning over the precipitate with a spatula. When the precipitate no longer smells of acetone (there is always a faint smell of ammonia) transfer to a stoppered bottle.

Standard metal solutions: All the solutions were prepared from high purity metals (Johnson, Matthey and Sons Ltd., London). They had a final acid concentration of 1% with respect to hydrochloric acid and in every instance 1 ml of standard solution ≡ 1 mg metal.

Other reagents: All other reagents were of AnalaR quality and were used as received.

The absorption curve of the copper^{II}–ammonium pyrophosphate complex

In order to exclude the possible interference of any anions, the following technique was used[5]: A small ion-exchange column, 10 cm long and 1 cm internal diameter, was charged with one or two g of Zeokarb 225 in the hydrogen form and a 0·1*M* solution of copper sulphate was passed through the column until there was complete conversion of the resin to the copper form. The column was washed with water until washings were copper-free, and the resin was then transferred to a small Büchner funnel and dried as much as possible by suction. It was finally transferred to an oven and dried overnight at 60°.

A 0·2 g portion of the resin thus prepared was weighed into a small conical flask, 25 ml of approximately 0·2*M* (50 g per litre) ammonium pyrophosphate were added, the flask was stoppered and set aside for three days with occasional swirling. The resulting dark blue supernatant liquid was carefully decanted into a 50-ml graduated flask and the solution was diluted to standard volume with 0·2*M* ammonium pyrophosphate. The absorption curve was plotted and the result is shown in Fig. 1. It shows a maximum absorption at 650 mμ and this wavelength was used for all readings. Chloride, nitrate, sulphate and perchlorate ions subsequently added as their sodium salts, caused no shift in the absorption maximum.

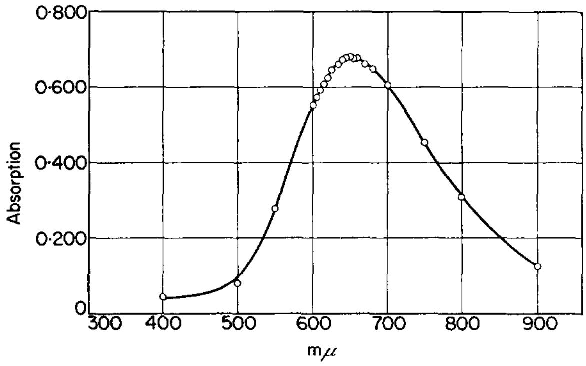

FIG. 1.—The absorption curve of the copper^{II}–ammonium pyrophosphate complex.

DISCUSSION

Effect of reagent concentration

In order to study the effect of excess reagent on the coloured complex, 1-ml aliquots of standard copper solution were added to five 25-ml graduated flasks. Ammonia solution (1 + 4) was added dropwise to each flask until the initial pale blue precipitate just redissolved and then the contents of the flasks were diluted to standard volume with 0·2, 0·3, 0·4, 0·5 and 0·6*M* ammonium pyrophosphate solutions respectively. The absorption readings of all these solutions at 650 mμ were identical within the range of experimental error.

Effect of pH

For successful colour development, the pH of the solution before adding the ammonium pyrophosphate reagent must not be less than 10. Adjustment of solutions to this pH value is made with dilute ammonia solution and checked with wide-range indicator papers.

Stability of the colour to time and temperature

Repeat absorption readings taken after standing for two days at room temperature agreed with the original figures to within the accuracy of the instrument. In addition, identical readings were obtained on the solutions at 35°.

Beer's law

To ascertain the adherence of the system to Beer's law a calibration graph was prepared in the following manner: To a series of 25-ml graduated flasks were added different volumes of standard copper solution, the pH was adjusted to between 10 and 11 by the dropwise addition of ammonia and the solutions were diluted to standard volume with approximately 0·2M ammonium pyrophosphate. The absorption of each solution was measured at 650 mμ against a reagent blank of ammonium pyrophosphate solution. On plotting absorption against concentration (Fig. 2) it is seen that the system obeys Beer's law up to the maximum concentration tested, namely 1·2 mg copper per ml.

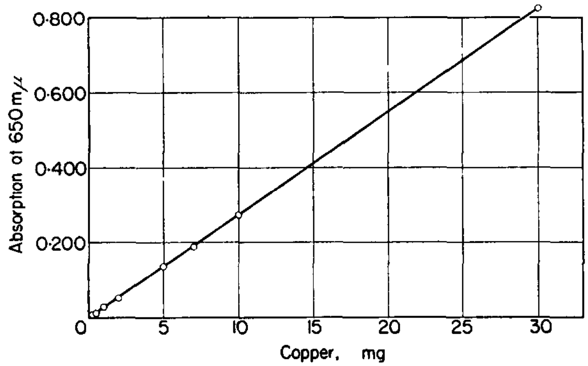

Fig. 2.—Adherence of the copper$^{\mathrm{II}}$–ammonium pyrophosphate system to Beer's law.

Precision and sensitivity of the method

The standard deviation was determined by transferring 10-ml portions of standard copper solution into each of five 25-ml graduated flasks, adjusting the pH to between 10 and 11 with ammonia solution and then diluting to standard volume with 0·2M ammonium pyrophosphate. The results are given in Table I.

Table I.—Standard deviation experiments

Test	Absorption at 650 mμ	Deviation
1	0·277	0·001
2	0·280	0·002
3	0·275	0·003
4	0·277	0·001
5	0·282	0·004

Average 0·278

From these results it follows that the Standard Deviation is 0·002(5) units.

As can be seen from Fig. 2, the proposed reagent is not capable of determining minute amounts of copper. This fact would be useful in applying the method to determining copper as a major constituent in various alloys.

Optimum range and accuracy

The optimum range was determined by Ringbom's procedure[6] a curve being plotted with % absorption as the y axis and log concentration as the x axis. The graph, reproduced in Fig. 3, shows that the optimum range lies between 7 and 30 mg copper *i.e.* the section of the curve with steepest slope.

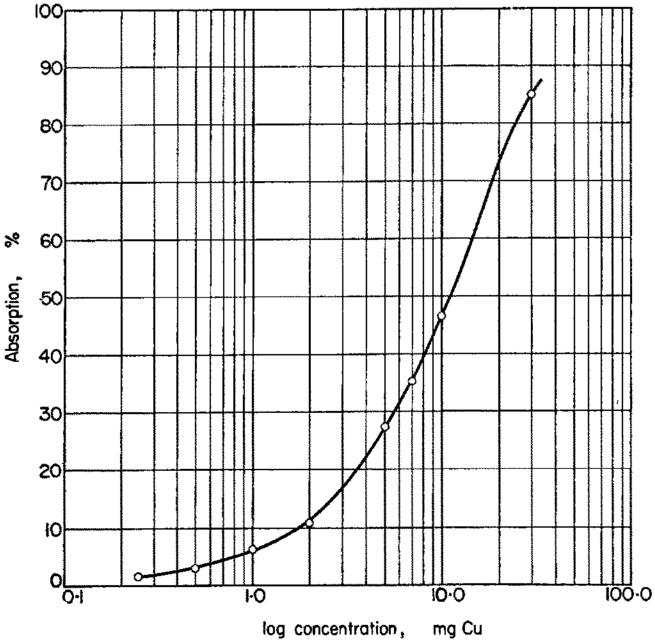

FIG. 3.—Ringbom's curve showing optimum range.

Applying the formula according to Ayres[7]:—

$$\frac{\%\ \text{relative analysis error}}{1\ \%\ \text{absolute photometric error}} = \frac{230}{\text{dI/d log c}}$$

for the range 7 to 30 mg copper, a relative analysis error of 2·9 % is obtained per 1 % absolute photometric error. This is in good agreement with the value of 2·7 % which is the minimum error attainable as imposed by Beer's law.

Interferences

As mentioned previously, common anions such as chloride, nitrate, sulphate and perchlorate do not interfere and in addition, tin^{II}, zinc, cadmium and manganese have no harmful effect. On making the test solution ammoniacal before adding the ammonium pyrophosphate reagent, lead and bismuth form precipitates which can be removed either by filtering or centrifuging the suspension. Cobalt and nickel cause more serious interference and corrections must be made if these elements are present. At 650 mμ 5·0 mg of cobalt give an absorption equivalent to 0·6 mg of copper and 10·0 mg of cobalt are equivalent to 2·0 mg copper. Similarly, 5·0 mg of nickel correspond to 0·55 mg of copper whereas 10·0 mg are equivalent to 1·0 mg of copper.

Acknowledgements—The author records his grateful thanks to Dr. J. E. Salmon and Mr. J. A. R. Genge for helpful discussions and assistance in the preparation of this paper.

Zusammenfassung—Es wird eine spectrophotometrische Methode zur Bestimmung von Kupfer beschrieben, die von der Absorption des Kupfer (II)ammonium-pyrophosphates bei 650 mμ Gebrauch macht. Die optimalen Bedingungen wurden festgestellt und Störungen untersucht. Die Methode wird zur Bestimmung von grösseren Kupfermengen in Legierungen als geeignet erachtet.

Résumé—On décrit un procédé spectrophotométrique pour le dosage du cuivre en utilisant l'absorption du complexe Cu II-pyrophosphate d'ammonium à 650 mμ. On a établi les conditions optimum et étudié les interférences. On a suggéré l'emploi du procédé pour la détermination de grandes quantités de cuivre dans divers alliages.

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DETERMINATION OF DEUTERIUM IN ORGANIC COMPOUNDS BY INFRARED SPECTROPHOTOMETRY*

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Summary—The Trenner–Arison–Walker method for the micro-analysis of deuterium in organic compounds involves oxidation of the compound with copper oxide in a sealed tube, collection of the water by vacuum distillation, and analysis of the water by infrared spectrophotometry. Experience in applying this technique to a variety of organic compounds in our laboratory has suggested a number of procedural modifications. These principally affect the methods of sample handling and water collection. Difficulties associated with temperature changes on the spectrophotometry of the deuterium-enriched water are overcome by differential analysis against natural-abundance water using a double-beam spectrophotometer.

AN infrared method for the determination of the deuterium content of water was first described by Thornton and Condon.[1] This method depends on the fact that HDO has an absorption band at 2520 cm^{-1} which can be observed through the overlapping spectrum of H_2O. At high isotopic dilution, where the concentration of D_2O is negligible, the intensity of the HDO band provides a direct measure of the total deuterium content of the water sample. This technique was developed by Trenner, Arison and Walker[2–5] for the determination of deuterium in organic compounds by assay of the water formed on combustion. In their earlier work[2] these investigators used the conventional Pregl micro-analytical type of combustion train for the oxidation of the organic compound, but subsequently[3] they replaced this by a static oxidation method in which the organic compound is heated with a large excess of copper oxide in a sealed quartz tube at 750–800°.

The object of this paper is to review our experience with this technique, which we have applied to deuterium-enriched organic compounds of various types; during this time a number of changes have been made in the apparatus and procedure. The principal modifications are concerned with the collection of the water sample and its transfer to the micro absorption cell. It has also been found that the determination of HDO is facilitated by differential analysis against natural-abundance water on a double-beam spectrometer in place of the single-beam cell-in/cell-out method used originally. The volatility and other physical characteristics of the compound critically determine the methods which must be used to obtain accurate dilution ratios, and they also influence the procedures to be followed for filling the combustion tube and subsequently evacuating and sealing it. This phase of the technique has not been discussed by previous investigators.

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APPARATUS

The apparatus used for the collection and transfer of the water is shown in Figs. 1-3. The main difference from the distillation train used by Trenner and collaborators is the elimination of the vacuum-controlled capillary system for sample transfer from the collecting vessel to the absorption cell. This simplifies the apparatus and eliminates three of the stop-cocks. In our experience the water sample which finally collects at the bottom of the collecting vessel can be transferred to the micro-cell by withdrawal into a separate glass capillary tube after releasing the vacuum and detaching the collecting vessel at the ground-glass joint. This simplifies the manipulation and allows greater flexibility in collecting the water from the walls of the vessel above the cooling tip.

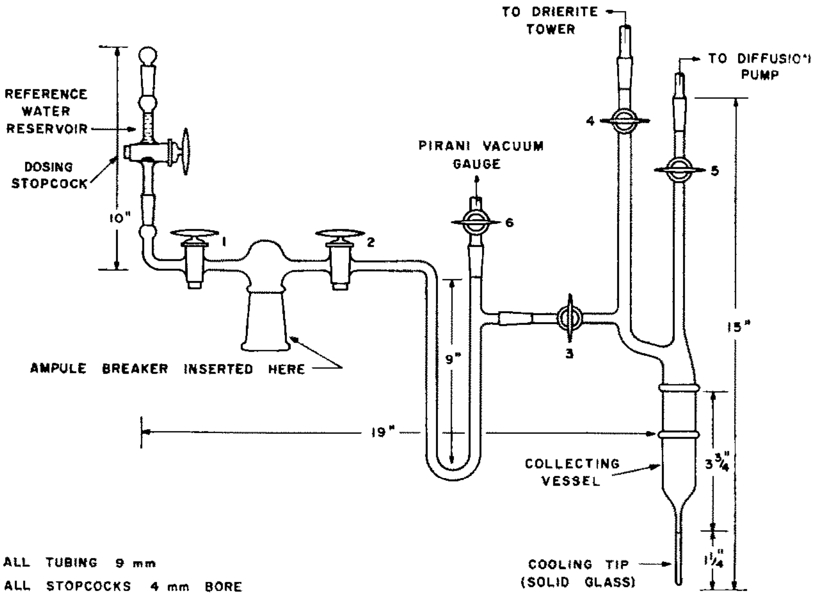


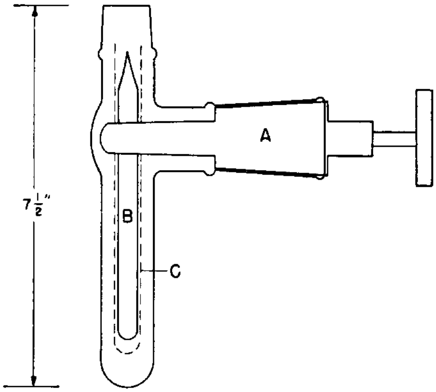
FIG. 1.

The ampule breaker, shown in Figs. 2 and 3, is based on designs kindly supplied to us by Dr. Trenner. The main part, including the standard tapered barrel, is constructed of aluminum, while the piston and plunger are made of brass. It should be noted that the piston, which is advanced by rotation of the screw-threaded plunger, is formed from a separate piece of brass rod, so that it does not rotate as the plunger is advanced. In normal operation the piston is only advanced far enough to break the ampule, and, after the water transfer is completed, it can be reset by means of a brass rod inserted down the breaker tube from the ground joint. A small hole in the anvil, in line with the axis of the screw thread, permits the insertion or removal of the piston without completely unscrewing the plunger. The vacuum seal in this unit is obtained by lubricating the screw thread with a grease formed by mixing hot Apiezon Wax (W-100) and Apiezon grease (T) in equal proportions.

SPECTROPHOTOMETRIC TECHNIQUE

The spectra are measured on a Perkin-Elmer Model 21 spectrophotometer using a sodium chloride prism. A standard Perkin-Elmer micro-cell of 0·2 mm thickness with calcium fluoride windows is used in the reference beam and a macro-cell of matched thickness in the sample beam. To reduce the parasitic volume of the micro-cell the filling tube is removed, as described by Trenner, Arison and Walker;[3] capillary attraction suffices to keep the water in the functional part of the cell over extended periods of time without evaporation or change in the deuterium content; no stoppers are required, and an analysis can be performed with 10 mg of water.

Since the transmission of a 0·2-mm layer of natural-abundance water at 2500 cm^{-1} is only about 5 %, it is necessary to operate the spectrometer with wide slits (100–120 μ) to obtain sufficient energy.



AMPULE BREAKER ASSEMBLY

A - AMPULE BREAKER
B - AMPULE IN POSITION TO BE OPENED
C - WIRE GAUZE

FIG. 2.

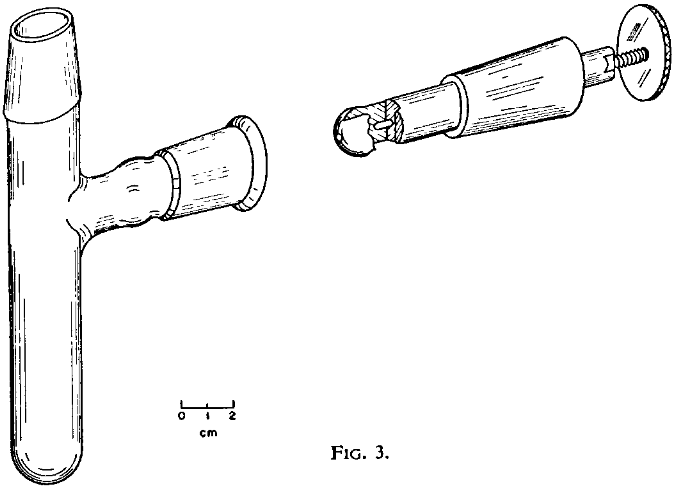


FIG. 3.

Reproducible operating conditions are obtained by first closing the sample beam, and, with no cell in the reference beam, recording the pen displacement produced by a test signal of 0·03 μ volt. This should correspond to an apparent absorption of 40–60% depending on the sensitivity of the spectrometer. The reference cell is next filled with repeatedly distilled natural-abundance water. With the reference cell in place, and no cell in the sample beam, the slit is now adjusted to produce a pen displacement equal to that of the 0·03 μ volt test signal. With natural-abundance water in both cells, the spectrometer is now set to 2500 cm^{-1} and the pen adjusted to read between 0·05 and 0·10 absorbance units, whereupon the background spectrum is recorded from 2800 to 2400 cm^{-1} (Curve A of Fig. 4). Both cells are then removed from the spectrometer, and the micro-cell is emptied, dried and refilled with the deuterium-enriched water. Both cells are next replaced simultaneously in the spectrometer and the spectrum is rescanned to record the HDO absorption peak (Curve B of Fig. 4). By following this procedure, adequate temperature equivalence is maintained in the two cells, and the need to thermostat the cells during measurement is avoided. If additional time is allowed for the cells to reach thermal equilibrium with the spectrometer, a repeat measurement of the spectrum does not change the peak absorbance by more than 0·002 units.

The calibration curve, shown in Fig. 5, is plotted as total mole per cent deuterium oxide against peak absorbance, taking the natural abundance ratio H/D as 6400/1. The plot is linear at least up to 0·7% deuterium oxide and all measurements were made below this concentration. The curve has been checked periodically and has shown no deviation in three years. All standard deuterium-enriched water samples were obtained by dilution of a master standard prepared in turn by dilution of 99·8% deuterium oxide. Dilutions were made gravimetrically with repeatedly distilled natural-abundance water.

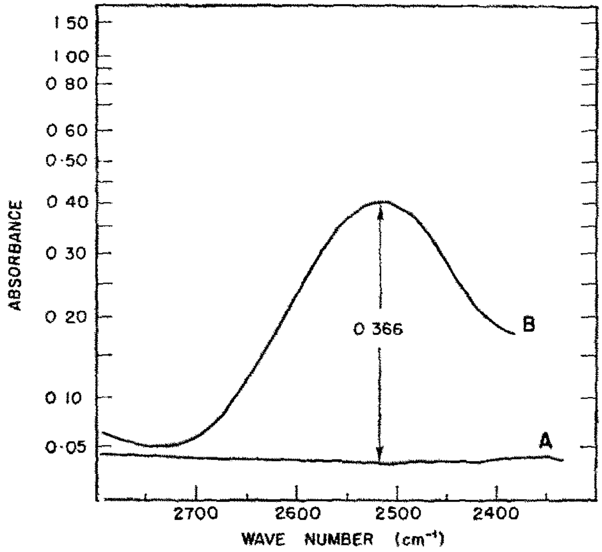


FIG. 4.

ANALYTICAL PROCEDURE

Dilution of the deuterium-enriched compound

Most of the compounds analysed contained between one and eight deuterium atoms per molecule, with molecular weights in the range 50–500. In all cases the deuterium-enriched compounds were diluted with the natural-abundance compound; the approximate deuterium contents of the compounds were known, and the dilution factors were adjusted to yield water samples containing 0·25–0·35% deuterium oxide. This required dilutions in the range 20 to 250.

The method of dilution depends on the physical characteristics of the substance. Crystalline solids are weighed on a micro-balance and then dissolved in a suitable volatile solvent, and the solvent is pumped off in vacuum. Non-viscous liquids are mixed directly, while viscous liquids are dissolved in a suitable solvent, the solvent is removed by distillation and the diluted compound is vacuum distilled.

Combustion

Oxidation is carried out in an ampule formed from a 15-cm length of Vycor quartz tubing. One end of the tube is sealed in an oxy-hydrogen flame, and the other end is attached through a graded seal to a male 14/35 Pyrex standard tapered joint for attachment to a vacuum line. Between 250 and 500 mg of copper oxide (Merck Reagent Grade) is introduced into the combustion tube, which is then evacuated at 105–110° for one hour. After cooling, the vacuum is released and the calculated amount of the diluted compound to yield 10–12 mg of water is added. This normally requires between 5 and 10 mg of compound. Solid compounds are introduced down the tube by means of a cylindrical glass scoop attached to the end of a glass rod, and liquids are added through a glass capillary. Quantitative transfer, of course, is not necessary, but it is important to avoid contamination of the upper section of the Vycor tube. A capillary constriction of 1–2 mm internal diameter is next formed in the Vycor tube near the graded seal. The tube is then evacuated for approximately one hour and while still under vacuum, is sealed at the constriction, with an oxy-hydrogen flame. If the compound under analysis is volatile or heat sensitive, the lower end of the tube is kept cool with ice or solid carbon dioxide during the evacuation and sealing process.

The sealed ampule is next encased in a close-fitting but open-ended refractory jacket and heated in the furnace at 750–800° for 45–60 minutes. For this purpose a semi-micro Pregl-type electrical combustion furnace is used. The whole furnace is confined in a protective box made of $\frac{1}{16}$ inch sheet steel; openings are left in the rear of this box, which faces a blank wall, to allow for blast release in case of an explosion. The temperature during the combustion is monitored by a thermocouple in contact with the outer surface of the Vycor tube. Provided that the tube has been properly evacuated and sealed, explosions do not occur unless the temperature rises above 800°.

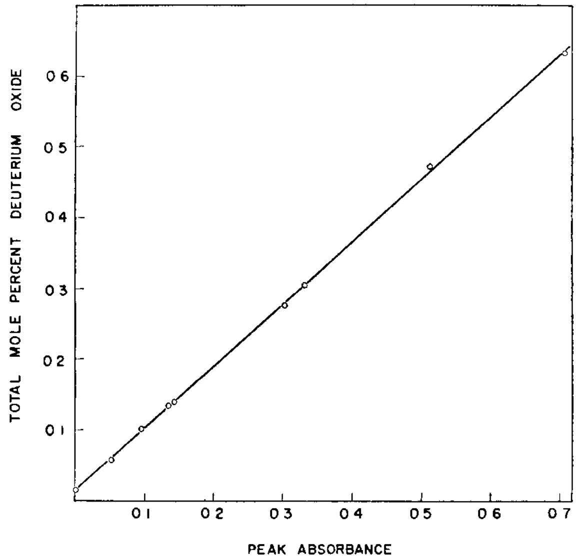


FIG. 5.

Distillation

After the combustion is completed the furnace is allowed to cool and the ampule is surrounded by a protective cylinder of wire mesh and inserted into the ampule breaker (Figs. 2, 3). This is next attached by the standard tapered joint to the thoroughly cleaned distillation apparatus. Particular care is necessary that the collecting vessel is free of any trace of grease and it must be washed each time before use with chromic anhydride cleaning solution and distilled water, followed by acetone and carbon tetrachloride. This is essential if the water sample is to form as a single, easily collectable drop.

With stop-cock 1 open, the distillation apparatus is next tested for vacuum tightness and pumped to 10^{-3} mm. The Pirani vacuum gauge is then disconnected from the system by closing stop-cock 6. Stop-cock 5 is also closed and a 10-mg dose of water containing about 0·3% deuterium oxide is introduced into the system from the water reservoir by means of the dosing stop-cock. Five minutes are allowed for isotopic equilibrium to be established in the system, after which stop-cock 5 is re-opened and the system is pumped for a further 45–60 minutes. Stop-cocks 1 and 5 are now closed, stop-cock 6 to the Pirani gauge is opened, and the system is checked again for vacuum tightness. For proper function of the Pirani gauge it is essential to isolate it when the vacuum system contains water vapor.

If the vacuum holds satisfactorily, stop-cocks 2, 3 and 6 are next closed and the ampule is broken by turning the breaker screw. The U-trap is immersed in liquid air, stop-cocks 2, 3 and 5 are opened in that sequence, and the system is pumped for about one minute. During this time the liberated water collects at the bottom of the U-tube. Stop-cocks 2 and 5 are then closed again and the liquid air reservoir is transferred from the U-tube to the solid glass cooling tip on the bottom of the collecting vessel. Distillation then occurs from the U-tube to the collecting vessel and this can be accelerated by gently warming the U-tube with the palm of the hand. Provided that the apparatus has been properly cleaned, the water now collects as a single mass of ice crystals at the bottom of the collecting vessel. The system is next brought to atmospheric pressure by admitting air through stop-cock 4. As the collecting vessel warms to room temperature, the ice should melt into a single water drop. The collecting vessel is now detached at the ground-joint and the water is withdrawn into a vertically clamped capillary syringe, controlled by a micrometer screw head, and is subsequently discharged into the micro-absorption cell. Initial attempts to provide mechanical support for the micro-cell during this process were discontinued, as it was found that the manipulation could be made more delicately with the cell held in the hand. The water sample is then analysed as described in the section on spectrophotometric technique.

CALCULATIONS AND RESULTS

Although the spectrophotometric analysis requires that the deuterium be all present as HDO, it is more convenient, for purposes of computation, to consider the oxidation in terms of the general formula:—

$$\begin{aligned} C_aH_{(b-x)}D_xO_c + (2a + 0{\cdot}5b - c)\ CuO = (a){\cdot}CO_2 &+ 0{\cdot}5(b - x){\cdot}H_2O \\ &+ 0{\cdot}5(x){\cdot}D_2O + (2a + 0{\cdot}5b - c){\cdot}Cu \end{aligned}$$

where $C_aH_{b-x}D_xO_c$ represents the deuterium-enriched compound or undiluted isotopic mixture.

The combustion of w_1 mg of this material will yield $\dfrac{0{\cdot}5(b - x)}{(m + x)} \cdot w_1$ millimoles of H_2O and $\dfrac{0{\cdot}5x}{(m + x)} \cdot w_1$ millimoles of D_2O, where m is the molecular weight of $C_aH_bO_c$.

The addition of w_2 mg of diluent containing H/D in a ratio of 6400/1 will provide a further $\dfrac{0{\cdot}5b}{m} \cdot w_2$ millimoles of H_2O and $\dfrac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \dfrac{1}{6400}$ millimoles of D_2O.

If D is the total mole per cent of deuterium oxide in the water collected,

$$D = \frac{\left[\dfrac{0{\cdot}5x}{(m + x)} \cdot w_1 + \dfrac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \dfrac{1}{6400}\right] \times 100}{\left(\dfrac{0{\cdot}5x}{(m + x)} \cdot w_1\right) + \left(\dfrac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \dfrac{1}{6400}\right) + \left(\dfrac{0{\cdot}5(b - x)}{(m + x)} \cdot w_1\right) + \left(\dfrac{0{\cdot}5b}{m} \cdot w_2\right)}$$

If the small term $\dfrac{0{\cdot}5b}{(m + b)} \cdot w_2 \cdot \dfrac{1}{6400}$ is neglected in the denominator, it follows algebraically that

$$x = \frac{Db(w_1 + w_2) - m\left(0{\cdot}0156\,\dfrac{bw_2}{(m + b)}\right)}{100w_1 - \dfrac{Db}{m} \cdot w_2 + \left(0{\cdot}0156\,\dfrac{bw_2}{(m + b)}\right)}$$

The results of some typical analyses are listed in Table I. The first four measurements are for deuterium-enriched steroids for which independent assays of the

TABLE I.—REPRESENTATIVE DEUTERIUM ANALYSES OF ORGANIC COMPOUNDS

Compound	*Deuterium Content (Atoms of D per molecule)*	
	Theoretical	*Found*
Cholesterol	0·414*	0·375, 0·372
Δ^4-Androstene-3:17-dione	0·475*	0·486, 0·464
Androstan-3-one	0·101*	0·100
Cholestan-3α-ol acetate	2·55*	2·58, 2·58
n-Dodecane-1-d_3	3	2·89, 2·92
n-Dodecane-1:12-d_6	6	5·81
Methyl laurate-12-d_3	3	2·86, 2·93
Methyl-d_3 laurate-2,2-d_2	5	5·12, 5·09
Methyl laurate-2:12-d_5	5	4·80, 4·45
Methyl-d_3 laurate-2:12-d_5	8	8·09, 8·06
n-Dodecyl-1-ol-1:12-d_5	5	5·10. 4·90
1-Bromo-*n*-dodecane-1:12-d_5	5	4·91, 4·78
Androstan-17-one-16-d_2	2	2·12, 2·09
Androstan-3-one-2:4-d_4	4	3·93, 4·29
Androstan-3:17-dione-2:4:16-d_6	6	5·79
3β-Acetoxy-d_3-androstan-17-one	3	3·25
3β-Acetoxy-androstan-17-one-16-d_2	2	2·18
3β-Acetoxy-d_3-androstan-17-one-16-d_2	5	5·16
17β-Acetoxy-d_3-androstan-3-one	3	3·16
17β-Acetoxy-androstan-3-one-2,4-d_4	4	3·71
17β-Acetoxy-d_3-androstan-3-one-2,4-d_4	7	6.72
3β-Hydroxy-androstan-17-one-16-d_2	2	1·94
17β-Hydroxy-androstan-3-one-2,4-d_4	4	3·65
Benzoic-2:4-d_2 acid	2	2·04, 2·08
Benzoic-2:6-d_2 acid	2	1·95, 1·93
Acetophenone-ω-d_3	3	2·53, 2·57
Acetophenone-2-*d*	1	0·90
Anthracene-9:10-d_2	2	1·70, 1·62
s-trans-(2-Phenyl)-2-*d*-*cyclo*hexylamine	1	0·93, 0·97

* Deuterium values determined by mass spectrometry.

deuterium content had been obtained by mass spectrometry. The satisfactory agreement between the two methods is evident.

Acknowledgements—We wish to acknowledge the helpful advice received from Dr. W. A. Patterson of Baird Associates Inc., and Dr. W. H. Stevens of Atomic Energy of Canada Ltd., in connection with the spectrophotometry. We are also grateful to Dr. N. R. Trenner of Merck and Co. Inc., who provided details of his ampule breaker, and to Dr. M. L. Eidinoff of the Sloan-Kettering Institute for Cancer Research who supplied the deuterium-enriched compounds which had been assayed by mass spectrometry.

Our thanks are also due to Mr. G. Ensell and Mr. A. Nadeau for assistance in the design and construction of the apparatus.

Zusämmenfassung—Die Trenner–Arison–Walker Methode zur Mikrobestimmung von Deuterium in organischen Verbindungen beruht auf Oxydation der Probe mit Kuperfoxyd in abgeschmolzener Röhre, Gewinnung des gebildeten Wassers durch Vakuumdestillation und Analyse desselben durch IR-Spektroskopie. Erfahrungen bei Verwendung dieser Methode zur Analyse verschiedener organischer Verbindungen legten einige Änderungen der Arbeitsvorschrift nahe. Diese betreffen in der Hauptsache die Behandlung des Probenmaterials und das Sammeln des Wassers. Schwierigkeiten, die durch Temperaturänderungen während der spektrophotometrischen Bestimmung des an Deuterium angereicherten Wassers auftreten, werden durch Verwendung einer differentialanalytischen Methode überwunden, indem es gegen natürliches Wasser in einem Doppelstrahlphotometer gemessen wird.

Résumé—La mèthode Trenner–Arison–Walker pour la microanalyse du deutérium dans les composés organiques nécessite l'oxydation du composé par l'oxyde de cuivre en tube scellé, la collection de l'eau par distillation sous vide et l'analyse de l'eau par spectrophotométrie infra-rouge. Pour l'application de cette technique à une variété de composés organiques l'expérience a suggéré un certain nombre de modifications du mode opératoire. Celles-ci affectent principalement les méthodes de manipulation de l'échantillon et de collection de l'eau. On surmonte les difficultés entraînées par les variations de température dans la spectrophotométrie de l'eau enrichie en deutérium en effectuant une analyse différentielle par rapport à une eau naturelle non enrichie en utilisant un spectrophotométre à double faisceau.

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A CRITICAL STUDY OF THE DETERMINATION OF PLATINUM WITH DIMETHYLPHENYLBENZYLAMMONIUM CHLORIDE

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(*Received* 28 *September* 1959)

Summary—A study of the recorded method for the determination of platinum with dimethylphenylbenzylammonium chloride revealed defects which become serious for larger amounts. A revised procedure which yields accurate results for micro and semi-micro amounts is described. Samples which have been fumed in sulphuric acid solution may be handled with a slight modification of the recommended procedure.

THE more familiar methods for the gravimetric determination of platinum have been studied in recent years by Beamish and co-workers.[1,2] These investigations show that of the several precipitants which may be relied upon to provide satisfactory results with macro quantities, only zinc yields adequate precision and accuracy on the micro scale. A procedure which deserves to be regarded as the classical micro method was developed in the same laboratory. This utilizes thiophenol to precipitate platinum as a mercaptide.[3] These methods possess disadvantages, however. The former must be used with careful adherence to conditions and the latter involves a reagent which is unstable in air and possesses a disagreeable odour.

A variety of other organic precipitants for platinum have appeared recently in the literature. A review by Beamish[4] indicates their probable usefulness, but general acceptance of these methods should be preceded by careful re-investigations. We have found 4-phenylthiosemicarbazide[5] to be a convenient reagent but have been unable to avoid serious losses to the filtrate. There seems to be little hope of circumventing the trouble, as the reagent can be dissolved only in media in which its complex with platinum is slightly soluble.

Of the remaining reagents, dimethylphenylbenzylammonium chloride seemed the most attractive and worthy of further study.[6] This reagent precipitates bromoplatinate from hydrobromic acid solution and is thus analogous to ammonium chloride in the ammonium chloroplatinate method. Our initial attempts to make use of it met with little success, however. The sources of error discovered were: (*a*) failure to attain constant weight, (*b*) variable composition of the precipitate under certain conditions, and (*c*) prior fuming with sulphuric acid led frequently to low results. This last phenomenon was not unexpected, for many analytical procedures for platinum fail in the presence of sulphate. The handling of such solutions was considered of sufficient importance to warrant further attention.* These difficulties have been overcome and a modified procedure is described below.

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* Fumed sulphuric acid solutions are frequently encountered in precious metals analysis: for example, see the classical isolation of platinum from the other members of the platinum group by hydrolytic precipitation.[7]

Apparatus and reagents

Weighings were performed on a Sartorius SM 10 balance with intercalibrated weights. The filtering crucibles used were manufactured by the Staatliche Porzellanwerke, Berlin, and were of A2 porosity, sizes M1 and M2.

Standard platinum solution: A stock solution was prepared from 1·9659 g of platinum supplied by Johnson, Matthey and Mallory, Ltd. This was dissolved in a small quantity of *aqua regia* and the solution evaporated to dryness. The residue was treated three times with conc. hydrochloric acid and evaporated each time to dryness. It was then taken up in water and filtered through a 7·0-cm Whatman No. 42 filter paper. The paper was ashed in a porcelain crucible and the residue treated with *aqua regia* and hydrochloric acid in the same fashion as before. The final residue was taken up in water and filtered. The two filtrates were combined and adjusted to 0·05*N* with hydrochloric acid in a 2·000 litre volume. The solution was standardized by means of the thiophenol method.[3] Found: 0·982 and 0·983 mg per ml; Taken: $0{\cdot}982_8$ mg per ml.

Dimethylphenylbenzylammoniumchloride: The compound was prepared as described by Ryan from Fisher Scientific Co. chemicals, Nos. A-746 and B-277. The 5% aqueous solution was filtered through a sintered-glass funnel. Although it was kept in a brown bottle, the solution became visibly oxidized (blue coloration) after two or three weeks. Weakly coloured solutions were used but more strongly coloured ones were discarded.

Hydrobromic acid: The concentrated acid supplied by Allied Chemical and Dye Corporation was distilled once and a colourless product obtained.

Dioxane and cyclohexane: Distillation Products Industries No. 2144 and Fisher Scientific Co. No. C-556, respectively, were filtered through a sintered-glass funnel.

Thermogravimetric study of the weighing form

It was found that precipitates prepared according to the procedure given by Ryan failed to attain constant weight. The losses on heating precipitates obtained from 10 mg of platinum in 100 ml of solution were generally small—of the order of 0·02 mg per hour. Precipitates obtained from 20-mg quantities experienced losses which were invariably serious. Typical weight-time curves for 20- and 40-mg samples are shown in Fig. 1.

Prolonged heating reduced the weight to very much less than the theoretical value and caused the complex to darken or even turn to tar. Drying at slightly lower temperatures in a well-controlled oven failed to improve the situation.

The reason for this apparent decrease in stability with increasing concentration of the original solution was evident when the precipitates were viewed under the microscope. Precipitates prepared from solutions containing 0·1 mg Pt per ml appeared under magnification to have the texture of blotting paper, whereas those formed from solutions containing 0·2 mg per ml or more appeared chalk-like indicating a much smaller particle size. It may be concluded that the decomposition upon heating, which takes place by evaporation of the organic portion of the complex, proceeds more readily when the surface to volume ratio is higher. Extremely slow addition of the reagent failed to produce coarser precipitates.

The solution to this problem consists in washing the precipitate with a highly volatile solvent and drying at a lower temperature. No single solvent was found to be suitable so the aqueous "holdup" was removed with dioxane and this in turn washed out with *cyclo*hexane. To estimate the magnitude of possible losses to the washings, 25-ml volumes of the organic wash liquids were passed through a large portion of the platinum complex and evaporated to dryness. The platinum content of these washings was determined colorimetrically. (See below under *Filtrate Tests.*) The dioxane wash contained 5 μg of platinum and the *cyclo*hexane less than the detectable limit.

Composition of the precipitate

The nature of the precipitation reaction would suggest that the dimethylphenylbenzylammonium ion would be a suitable precipitant for platinum in the semi-micro range as well as the micro. It was found, however, that increasingly low values were obtained for increasing quantities of platinum precipitated from 100 ml of 2% hydrobromic acid solution. This was attributed to the formation of mixed precipitates. The average molecular weights of precipitates prepared from solutions of various concentrations are presented in Table I.

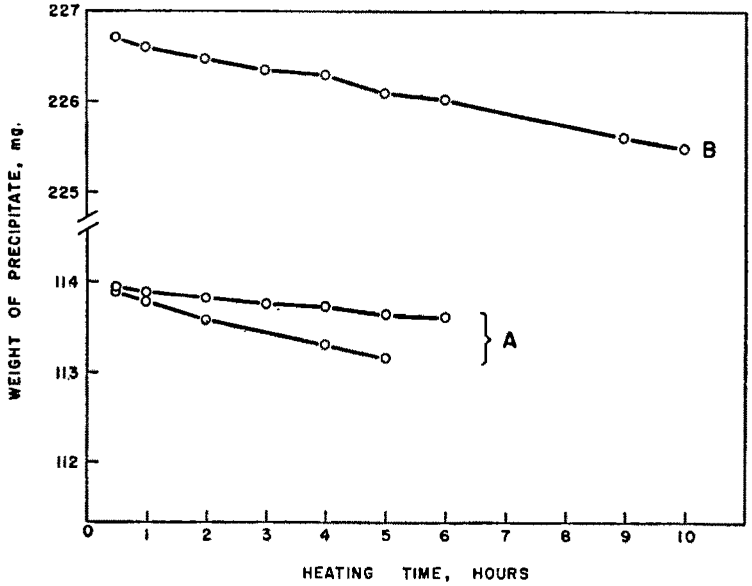

FIG. 1.—Loss of weight upon heating at 110°
A—10 mg of platinum taken
B—20 mg of platinum taken

The most plausible explanation for the decrease in apparent molecular weight assumes that the equilibria:

$$PtBr_6^{2-} + H_2O \rightleftharpoons PtBr_5OH^{2-} + HBr$$

$$PtBr_5OH^{2-} + H_2O \rightleftharpoons PtBr_4(OH)_2^{2-} + HBr \qquad (1)$$

cause an appreciable concentration of the partially hydrolyzed species of lower molecular weight to appear at higher platinum concentrations. An alternative explanation might be based on the reaction:

$$PtBr_6^{2-} + Cl^- \rightleftharpoons PtBr_5Cl^{2-} + Br^- \qquad (2)$$

when large quantities of reagent are added. However, this latter possibility was seen to be at least not the major cause of the effect as essentially the same results were obtained with dimethylphenylbenzylammonium bromide as with the chloride reagent.

It follows that for higher platinum concentrations, the hydrobromic acid concentration must be increased accordingly.

During the course of experiments to determine optimum conditions, it was found that it is unnecessary to add as much reagent as was recommended by Ryan. We found that a final reagent concentration in the supernatant liquid of 0·25 % is adequate. The required amount of washing depends upon the quantity of sodium bromide added. Very little washing is required for solutions containing little or no metal cation. When 5 g of sodium bromide had been added, it was necessary to wash large samples with about 50 ml of 0·1 % dimethylphenylbenzylammonium chloride solution.

TABLE I.—AVERAGE MOLECULAR WEIGHTS OF PRECIPITATES FORMED FROM 2 % HBr SOLUTION

No.	Wt. of Pt in precipitate, *mg*	Average molecular weight
1	31·55	1097·1
2	35·83	1094·8
3	42·69	1096·4
4	49·14	1088·9
5	53·63	1080·8
6	73·57	1077·5

The molecular weight of $(C_{15}H_{18}N)_2PtBr_6$ = 1099·4.

In the light of our new knowledge of the precipitation of platinum with dimethylphenylbenzylammonium ion, the following procedure was arrived at.

Recommended procedure: A solution of bromoplatinate is prepared for precipitation by adjusting the acidity with hydrobromic acid. Four ml or more of the 48 % acid are added for quantities of platinum of 10 mg or less. Approximately 4 ml of acid are added for each additional 10 mg of platinum. If the platinum concentration is entirely unknown, the acidity may be adjusted to as high as 30 %. The sample is made up to approximately a 100-ml volume and a 5 % solution of the precipitant is added slowly with stirring. A volume of 5 ml plus 1 ml for each 10 mg of platinum present is sufficient, but a large excess appears to be not detrimental. After allowing the precipitated sample to stand for 3 hours, it is filtered through a tared fritted crucible. The precipitate is washed with a 0·1 % aqueous solution of the reagent, followed by 3 ml of dioxane and this in turn followed by 4 ml of *cyclo*hexane. The crucible is heated at 80° to constant weight which is attained in 0·5–1 hour.

Treatment of chloroplatinate solutions

Solutions to be precipitated probably should contain but little, if any, hydrochloric acid, otherwise interference from reaction (2) may be encountered. This condition was ensured by evaporating solutions of chloroplatinate to dryness in the presence of sodium bromide. A single evaporation in the presence of very little chloride was sufficient to effect 100 % conversion to bromoplatinate. If much hydrochloric acid was present, it was deemed advisable to repeat the evaporation one or more times after moistening the dry residue with hydrobromic acid. It was frequently found that upon taking up the residue in dilute hydrobromic acid and filtering, a brown or black insoluble residue containing platinum and silica had been formed. This increased with the number of evaporations to which the sample was subjected. The formation of this residue was kept to a minimum by using unetched beakers for the evaporation and a copious excess of sodium bromide.

Procedure: A sample containing relatively little hydrochloric acid is evaporated to dryness in the presence of 0·5 g of sodium bromide. The residue is dissolved in a little diluted hydrobromic acid and passed through a porous-bottom crucible. If any dark residue is found, this is leached with *aqua regia*. The leaching removes all but a yellow stain on the porous bottom. The leach solution is evaporated to dryness, the residue moistened three times with a few drops of hydrobromic acid and evaporated each time to dryness on the water bath. The final residue is taken up in water and filtered. No dark-coloured, insoluble residue should be observed at this stage.

Aliquots of the stock solution were treated as described in the above procedures. The results of these determinations appear in Table II.

TABLE II.—RECOVERY OF PLATINUM FROM CHLOROPLATINATE SOLUTION

No.	Weight of Pt taken, *mg*	Weight of Pt recovered, *mg*	Filtrate loss, *μg*	Gravimetric error, *mg*
1	0·97	0·97	—	0·00
2	0·97	0·97	—	0·00
3	4·87	4·87	2	0·00
4	9·83	9·83	—	0·00
5	9·83	9·86	<2	+0·03
6	9·83	9·83	<2	0·00
7	9·83	9·82	2	−0·01
8	19·66	19·62	2	−0·04
9	19·66	19·67	<2	+0·01
10	34·42	34·43	<2	+0·01
11	49·15	49·17	8	+0·02
12	73·71	73·78	4	+0·07

Blanks were carried through the entire procedure. The weights obtained (not multiplied by the gravimetric factor, 0·1776) were 0·17, 0·14, 0·14, and 0·13 mg.

Treatment of solutions which have been fumed with sulphuric acid

The conversion to bromoplatinate when platinum has been complexed with sulphate is more difficult than the corresponding conversion to chloroplatinate. Whereas the latter may be effected by simple boiling with hydrochloric acid, the weights of precipitates obtained from sulphate solutions of platinum which had been boiled with hydrobromic acid were usually low. The conversion proceeds rapidly, however, at temperatures rather higher than the boiling point of hydrobromic acid. These can be attained if the chief constituent of the solution is sulphuric acid.

Procedure: A sample in sulphuric acid is fumed to about a 2-ml volume and allowed to cool. Approximately 1 ml of water and 10 drops of concentrated hydrobromic acid are added. The sample is heated until fumes of hydrobromic acid are evolved. It is cooled and the fuming repeated after adding a few more drops of hydrobromic acid. Heating must not proceed to a point when hydrobromic acid fumes cease to be evolved. The sample is filtered through a porous-bottom crucible. No insoluble platinum residue should be formed in the process.

Aliquot samples of the stock platinum solution were fumed strongly with 5 ml of concentrated sulphuric acid and treated as described in the preceding paragraph. Results of the gravimetric determinations appear in Table III.

TABLE III.—RECOVERY OF PLATINUM FROM FUMED SULPHURIC ACID SOLUTION

No.	Weight of Pt taken, *mg*	Weight of Pt recovered, *mg*	Filtrate loss, *µg*	Gravimetric error, *mg*
1	9·83	9·78	<2	−0·05
2	9·83	9.83	<2	0·00
3	9·83	9·82	<2	−0·01
4	19·66	19·62	5	−0·04
5	19·66	19·66	5	0·00

Filtrate tests

Filtrates and washings were evaporated to dryness and "wet-ashed" with sulphuric acid and 30% hydrogen peroxide. After treatment with boiling hydrochloric acid, platinum was determined in a 10-ml final volume with stannous chloride.[8]

Zusammenfassung—Die von Ryan veröffentlichte Methode zur gewichtsanalytischen Bestimmung von Platin mit Dimethylphenylbenzylammoniumchlorid wurde eingehender untersucht und die für grössere Platinmengen Fehlerquellen festgestellt. Eine modifizierte Methode, welche für den Mikro-sowie Halbmikro-bereich genaue Resultate erziehlt, wird beschrieben. Platinlösungen welche mit Schwefelsäure abgeraucht wurden, können mit kleinen Änderungen untersucht werden.

Résumé—La méthode de Ryan utilisant le chlorure de diméthyl phénylbenzylammonium pour le micro dosage du platine s'est révélée défectueuse et d'autant plus si les quantités sont grandes. Une modification de cette méthode fourni des résultats aussi précis à l'échelle micro que semi-micro. Même, si l'échantillon est digéré dans une solution sulfurique on peut le traiter en modifiant legérèment le processus opératoire.

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LETTERS TO THE EDITOR

"Metalfluorechromic" indicators

Sir:

A new term, "metalfluorechromic indicators", has been recently proposed by Wilkins[1,2] for compounds called by Körbl and Vydra[3] "metallofluorescent indicators". In our opinion the term "metallofluorescent" expresses better both similarities and differences between these indicators and the metallochromic type. In the case of Fluorescein Complexone (Fluorexon, Calcein) it has been demonstrated[3] that metallofluorescent indicators change only the intensity of fluorescence; they do not in fact change colour, or the colour change is insignificant.

Two different types of reactions of Fluorescein Complexone have been observed[4] and an explanation of these has been offered[5], *viz.* those which result in quenching of the fluorescence (which take place at a lower pH), and those which, on the contrary, cause fluorescence (at a higher pH, *cf.*[6]). This explanation is consonant with the conception of similar colour phenomena with metallochromic indicators[7] but not with the explanation based on the presumed differences in the structure of the "normal" and "indicator reversal" complexes as proposed by Wilkins[6].

Our explanation is based on the known fact that the individual ligand atoms of a polydentate ligand generally are involved in the chelate successively, *i.e.* in the course of increasing pH, according to decreasing constants corresponding to the dissociation of protons from these atoms. Starting in the acidic range the cation bonding is effected first by carboxyl groups and nitrogen atoms; subsequently, but still in acidic medium, phenolic oxygen participates with the majority of cations. The phenolic oxygen bond is at the lower pH quite loose and of an ionic nature, and therefore the electronic structure of the chromophoric or fluorechromic system of the indicator molecule does not differ appreciably from the fully de-protonized anion. Bathochromic colour change of metallochromic indicators, or quenching of the fluorescence of the metallofluorescent indicator takes place. With increasing pH the phenolic oxygen bond is stabilized, whereas the stability of the bonds with the carboxyl groups is decreased. Consequently, the structure of the indicator chelate undergoes a change and the phenolic oxygen bond to the metal changes from ionic to covalent, in the limiting case with the same consequence for the colour or fluorescence properties as in the covalent association of the proton with the phenolic oxygen atom. With the metallochromic indicator a hypsochromic shift takes place; in metallofluorescent indicators fluorescence appears. These facts can be illustrated by the following model experiments:

1. The addition of a solution of Cu^{2+} to a solution of Phenol Complexone[8] in acidic solution produces the same blue colour as is formed with plain iminodiacetic acid. The phenolic hydroxyl does not take part. Only on increasing the pH to approximately 5 does the yellow colour appear which is characteristic for the extension of the chromophoric effect of Cu^{2+} over the ionically bonded phenolic oxygen to the benzene ring.

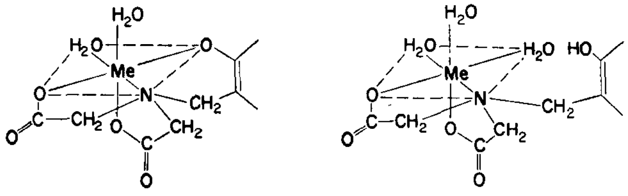
2. A similar reaction of Fe^{3+} with Phenol Complexone in strongly acidic medium again gives the same yellow colour as with the simple iminodiacetic acid. Approximately at pH 3 this colour changes to violet—the phenolate anion in its conducting form is involved. Finally in alkaline medium the solution again turns red and yellow—a non-conducting barrier of a covalent bond is formed between the chromophoric iron atom and the phenolic residue of the molecule.

In contrast to Wilkins' statement[6], both "normal" and "indicator reversal" reactions were noticed even with the same cation and the same indicator. Thus Ca^{2+} and Phenolphthalein Complexone at a lower pH (about 10) produce a red colour (normal reaction—ionic bond between the metal and phenolic oxygen); at a higher pH (13–14) the red colour of the indicator disappears (reversal reaction—covalent bond between the cation and the phenolic oxygen.)[9] This example demonstrates clearly that Wilkins' concept according to which structure *a* (fig. I, *cf.*[6]) should be assumed for the lower pH and structure *b* for the higher pH, both with the same central atom (Ca), is not tenable. In that case a sign of

$$\overset{H^+}{\leftrightarrows}$$

between the two structures could be justified though this would be in sharp contrast to the pH dependence of the existence of the two structures. Similar examples could be instanced for Cu^{2+} and Glycinethymol Blue[10] etc.

In this connection the consideration that the values K^{M}_{MHL} and K^{M}_{ML} can be close together[6] is so far incorrect that these constants cannot as such express to a mutually comparable degree the stability of the corresponding complexes for the given pH. In this case the pH-dependent constants should be compared, and these, of course, differ substantially for the pH ranges involved, because the actual concentrations of L and HL differ.



(a) (b)

FIG. 1.

We conclude, therefore, that the only correct explanation of the fluorescent reaction of calcium with Fluorescein Complexone—and similarly also in other instances—is the assumption of the formation of a covalent bond (similar to the bond with hydrogen) between the phenolic oxygen and the calcium and not the assumption of the actual bonding of hydrogen to the Fluorescein Complexone anion.

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24 *December* 1959

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AN APPEAL

Sir:

For more than twenty years it has been my practice to read, and frequently to test, methods published in journals devoted to analytical chemistry. I have to report not only that the presentation of the papers has not always pleased me but also that in few instances have the methods I tested been as good as the authors claimed. In some instances the methods have not worked at all, and letters addressed to the authors, although always acknowledged, have not given me answers to all my questions; and often those answers I did receive were vague in the extreme. I am forced, therefore, to conclude that many papers describing inferior and suspect methods are being printed. Owing to the apparently ready acceptance of papers by the editors of journals of analytical chemistry, many analysts are submitting for publication methods that are unsound, apparently under the impression that it is better for their prestige to get several inferior papers into print than one good one. Human nature being what it is, this practice will certainly continue unless referees make a more detailed examination of each paper they read and refuse to accept anything slipshod. Directions such as "transfer 0.1000 gm of sample and 0.5000 gm of *sodium peroxide* to the crucible . . . . "[1] indicate only cursory examination by the referee. Careful reading of the author's practical instructions usually throws a lot of light on the soundness of the method and if *any doubt* exists in the referee's mind the paper as it stands should be rejected. Even if such rigorous action reduces the size of the journal, the readers will realise they are getting quality if not quantity. I would like to see published in these journals only sound methods, or methods the shortcomings of which are described in detail. I am a regular reader of five journals of analytical chemistry and what strikes me most forcibly is the fact that no criticisms of previous papers are published except where they appear in papers claiming to carry out the estimation in a better manner. In order to discourage the submission of poor methods and slipshod papers I would suggest that provision be made in every journal for the publication of criticisms of methods already published; and in this connection I would like to point out that it is as important to praise a satisfactory method as it is to condemn one that is unsatisfactory. If this is done and editors take the view that no journal at all is better than one full of indifferent papers we should be able to look forward to the time when every method published is as good as the authors say it is.

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BOOK REVIEWS

Treatise on Analytical Chemistry: A Comprehensive Account in Three Parts. Part I, Theory and Practice, Volume 1. Edited by I. M. KOLTHOFF and PHILIP J. ELVING, with the assistance of ERNEST B. SANDELL. pp. xxvi + 809. Interscience Publishers, New York, 1959. $17.50 (single), $15.00 (subscription).

THE stated object of Kolthoff and Elving's *Treatise*, of which this is the first volume to be published, is to present a "concise, critical, comprehensive, and systematic treatment of all aspects of classical and modern analytical chemistry." The rapid growth of analytical chemistry in recent years has created a need for some such unified treatment of the entire field; the magnitude of this need may be estimated from the bulk of this work, the first two of the projected three parts of which are expected to fill about nineteen volumes.

Part I of the *Treatise*, Theory and Practice, is composed of eight sections, two of which are contained in Volume 1. Each of the nineteen chapters of Volume 1 has been prepared by an expert in the field. The first four chapters, (Section A), deal with material more or less peculiar to analytical chemistry: the general analytical process (E. B. Sandell and P. J. Elving), errors (Sandell), statistics (W. J. Youden), and sampling (W. W. Walton and J. I. Hoffman). Section B, which comprises the bulk of Volume I, consists of fifteen chapters on basic principles of chemistry which are of significance in analysis. The first chapter of this section is a basic discussion of the elements and their compounds in quantum mechanical terms (J. I. Watters). This is followed by treatments of atomic weights (E. Wichers), chemical equilibrium and thermodynamics (T. S. Lee), equilibrium diagrams (L. G. Sillen), electrode potentials (R. G. Bates), pH (Bates), concepts of acids and bases (I. M. Kolthoff), aqueous acid-base equilibria (S. Bruckenstein and I. M. Kolthoff), nonaqueous acid-base equilibria (Kolthoff and Bruckenstein), complexation reactions (A. Ringbom), oxidation-reduction mechanisms (F. R. Duke), oxidation-reduction equilibria (Duke), solubility (D. L. Luessing), precipitates (M. L. Salutsky), and precipitation equilibria (J. F. Coetzee).

Volume 1 confines itself to the theory of analytical chemistry. Each topic is first discussed from a pure chemical point of view, and the ideas presented are then applied more or less specifically to analytical chemistry. Sufficient space has been alloted to permit ample discussion of each topic. Although really exhaustive treatments are not attempted, the presentations go far beyond statements and discussions of elementary principles. Topics have been treated in sufficient depth to make reference to specialized monographs unnecessary in most cases; however, each chapter contains a list of carefully selected specific references, and the important general references are also listed.

In view of the fact that seventeen authors have contributed to this volume, it is particularly notable that the approach to each topic and the quality of authorship are quite consistent, and consistently high. This gives to the work a degree of unity which is rather unusual in a book prepared by so many geographically separated contributors.

The high quality of the entire volume makes it difficult to point out any one chapter or group of chapters as especially praiseworthy; however, the finest feature of the book is probably the central core of chapters which deal rigorously and extensively with equilibria of all sorts. The use of figures is particularly admirable. They are employed only when necessary, they deal with real chemical entities, and they clearly demonstrate what they are intended to demonstrate. One cannot ask for more. Few criticisms can be made: the powerful Lewis concept of acids and bases could have been exploited more fully, and the topic of crystal growth could have been approached from a more modern point of view. These are, however, minor points, and are possibly a matter of taste.

The production of the book is excellent, and the text is nearly free of misprints.

Kolthoff and Elving's monumental *Treatise* is a major contribution to the science of analytical chemistry, and should prove to be an invaluable standard reference for chemists in all fields.

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Column Chromatography in Pharmaceutical Analysis. J. A. P. Stroes. Thesis for the degree of Doctor of Philosophy. University of Groningen. 1959. (In Dutch.)

In this thesis an enquiry has been made into the possibilities of applying chromatography—both ion exchange and partition—to the analysis of some unmixed organic drugs and their combinations as used in pharmacotherapy.

The eluates obtained in the chromatographic separation of mixtures were investigated spectrophotometrically, and this combination of column chromatography and UV-absorption spectrophotometry gave results which were better, more reproducible and more quickly obtained than with the classical methods.

Typical of the combinations investigated are

Acetylbromalum, Isopropylantipyrinum, Caffeinum, phenacetinum and papaverini hydrochloridum.

Acidum acetylsalicylicum, phenacetinum, caffeinum and aluminii hydroxydum colloidale.

Barbitalum and apobarbitalum.

R. J. Magee

Electrophoresis. Theory, Methods and Applications. Edited by Milan Bier. Pp. xx + 563, Academic Press Inc., New York, 1959.

This book is a collection of eleven articles by a number of authors, dealing with the principles and various aspects of electrophoresis. An Introduction by Tiseleus gives an excellent historical background to the subject. The intention is to provide an authoritative survey dealing with theory, methods and applications of electrophoresis and the emphasis has been placed upon the fundamental principles involved, the problems encountered and the means that must be adopted to solve them. All the chapters are of high standard but, as is unavoidable in such collaborative works, there is some unevenness in style and overlapping of material. Some re-arrangement in the order of the chapters might have been an improvement and, in certain cases, the title of the chapter is not an exact guide to the contents.

The book gives a very comprehensive picture of the various branches of the technique and the theory is well-presented with much detail. The descriptions of apparatus are complete and easily followed, the diagrams are excellent and the lists of references are large and valuable. The applications described, however, are very specialised, being mainly confined to proteins and related materials. There is an interesting chapter on the application of electrophoresis to viruses, bacteria and cells, which will be of great interest to those concerned with this field of study. A notable omission is that, although the subject of paper electrophoresis is treated at length, it is mainly confined to low voltage methods. A brief description of attempts to use high voltages is given, but no reference is made, in the relevant chapter, to the high voltage techniques now in fairly common use and only brief reference to them is made elsewhere.

This book must be welcomed as an important addition to the literature of the subject, which it greatly extends. It will be of great value to all workers in the subject, especially those concerned with proteins. In view of the highly mathematical treatment of some of the theory and the mass of specialised material it is not easy to read and beginners may find it confusing unless a selective study of its contents, under guidance, is made. Those with some knowledge of the subject will, however, find it a valuable work of reference and, as such, it is strongly recommended.

G. F. Reynolds
C. D'Oyly-Watkins

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NOTICES

The following meetings have been arranged:

Thursday 18 *February* 1960: **Society for Analytical Chemistry.** Symposium on *Food Analysis. Some Analytical Problems in the Dairy Industry:* K. A. HYDE, B.Sc., F.R.I.C. *Routine Control in the Brewery:* W. A. WHITLEY, M.I.Biol. *Control Tests in the Flour Milling Industry:* J. WILLIAMS, B.Sc., Ph.D., F.R.I.C. *Quality Control Analysis of Pre-packed Foods:* G. WALLEY, B.Sc., F.R.I.C. Council Chambers, Colmore Row, Birmingham, England. Afternoon session 2.30 p.m. Tea 5.00 p.m. Evening session 6.30 p.m.

Friday 19 *February* 1960: **Society for Analytical Chemistry,** Microchemistry Group. Annual General Meeting. Postgraduate Medical School, Ducane Road, London, W.12. 6.0 p.m.

Friday 19 *February* 1960: **Society for Analytical Chemistry,** Microchemistry Group and Biological Methods Group. *Microanalysis in Clinical Biochemistry:* Professor E. J. KING. *Completely Automatic Methods in Microanalysis:* Dr. I. D. P. WOOTTON. *Automatic Titration Apparatus:* Dr. RUTH HASLAM and Dr. I. D. P. WOOTTON. *Flame Photometric Analysis of Divalent Cations in Biological Materials:* Dr. IAN MACINTYRE. *Optical Rotatory Dispersion:* Dr. W. KLYNE. Postgraduate Medical School, Ducane Road, London, W.12. 7.0 p.m.

Wednesday 24 *February* 1960: **Society for Analytical Chemistry,** Midlands Section: **Royal Institute of Chemistry,** Birmingham and Midlands Section. *Some Analytical Aspects of Non-aqueous Reactions:* Professor V. GUTMANN. The University, Birmingham 15, England. 7.0 p.m.

Friday 26 *February* 1960: **Society for Analytical Chemistry,** Scottish Section. *Analytical Methods on the Hygienic Control of Industrial Atmospheres:* J. G. GAGE, B.Sc., F.R.I.C. *Analytical Problems in the Isolation and Measurement of Traces of Radioactivity in Foods:* Professor J. HAWTHORN, B.Sc., Ph.D., A.R.C.S.T., F.R.I.C. Central Hotel, Glasgow, C.1, Scotland, 7.15 p.m.

Wednesday 2 *March* 1960: **Society for Analytical Chemistry,** Annual General Meeting. Queen's Hotel, Birmingham, 2, England. 4.30 p.m.

Wednesday 2 *March* 1960: **Society for Analytical Chemistry.** *Bernard Dyer Memorial Lecture. The Contribution of Analytical Chemistry to Medical Progress:* Professor A. C. FRAZER. Queen's Hotel, Birmingham, 2, England. 5.0 p.m.

Wednesday 9 *March* 1960: **Society for Analytical Chemistry,** Midlands Section. *Plant Growth-promoting Substances—Some Analytical Aspects:* Professor R. L. WAIN. The University, Birmingham 3, England. 6.30 p.m.

Friday 11 *March* 1960: **Society for Analytical Chemistry,** Western Section: **Royal Institute of Chemistry,** South Wales Section: *Advantages and Disadvantages of Visual Colorimetry:* G. J. CHAMBERLAIN. Swansea, South Wales.

Saturday 12 *March* 1960: **Society for Analytical Chemistry,** North of England Section. *The Analysis of Non-soapy Detergent Products:* G. F. LONGMAN, B.Sc., F.R.I.C. Manchester, England. 2.15 p.m.

Wednesday 16 *March* 1960: **Society for Analytical Chemistry,** Microchemistry Group: London Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

Friday 18 *March* 1960: **Society for Analytical Chemistry: Society for Chemical Industry,** Fine Chemicals Group. *Techniques of Automatic Analysis.* London. 6.30 p.m.

Wednesday 23 *March* 1960: **Society for Analytical Chemistry,** Midlands Section. Annual General Meeting. Nottingham and District Technical College, Burton Street, Nottingham, England. 7.0 p.m.

Friday 25 *March* 1960: **Society for Analytical Chemistry,** Scottish Section. *Volumetric Determination of Nitrogen as Nitrate:* A. F. WILLIAMS, B.Sc., F.R.I.C. *Control of Quality in Synthetic Foodstuff Colours:* H. E. STAGG, B.Sc. Royal Society of Edinburgh, 22, George Street, Edinburgh, 2, Scotland. 7.15 p.m.

Monday–Thursday 11–14 *April* 1960: **American Chemical Society,** Division of Analytical Chemistry. *Fisher Award Symposium* Honouring PHILIP J. ELVING. Programme Chairman, I. ROSENTHAL, Rohm and Haas Co., Philadelphia, Penna. *Gas Chromatography:* Programme Chairman, ROBERT A.

DINERSTEIN, Standard Oil Company, Whiting, Ind. *The Analysis of Fluoro-Containing Compounds:* Programme Chairman, A. STEYERMARK, Hoffman-LaRoche Company, Nutley 10, N.J. *Thermal Methods of Analysis,* (a) *Thermogravimetry,* (b) *Differential Thermal Analysis,* (c) *Zone Refining:* Programme Chairman, E. L. SIMONS, General Electric Company, Schenectady, N.Y. Cleveland, Ohio, U.S.A.

Thursday–Friday 14–15 *July* 1960: **Society for Analytical Chemistry,** Midlands Section. Symposium on *Analytical Methods in the Service of Agriculture. Determination of pesticide residues:* Dr. J. T. MARTIN. *Determination of Metals in Soils and Plants:* Dr. R. L. MITCHELL. *Analytical Aspects of Dairy-farming:* Dr. J. A. F. ROOK. *Determination of Systemic Insecticides:* K. GARDNER: *Analysis of Herbicides.* L. A. HADDOCK. *The Protection of the Consumer against Harmful Effects of Pesticide Residues:* Dr. E. J. MILLER. *Determination of Additives in Feeding Stuffs (with special reference to Prophylactics):* Dr. R. F. PHIPERS. The programme will also include a visit to a horticultural or agricultural research station, Nottingham University, Nottingham, England.

The fee for the Symposium will be £3–3s. An informal dinner at a cost of about £1–1s will be held on Thursday 14 July, and hostel accommodation will be available at Nottingham University.

Registration forms may be obtained, together with further information, from C. A. JOHNSON, B.Sc., B.Pharm., F.P.S., A.R.I.C., Standards Department, Boots Pure Drug Co., Ltd., Station Street, Nottingham, England.

The fifteenth Annual General Meeting of the Biological Methods Group of the Society for Analytical Chemistry was held on Wednesday 9 December 1959 in the Meeting Room of the Chemical Society Burlington House, Piccadilly, London, W.1. The Chairman of the Group, Dr. J. I. M JONES, F.R.I.C. presided.

The following were elected Officers of the Group for the forthcoming year.

Chairman:	Dr. J. I. M. JONES
Vice-Chairman:	Mr. J. S. SIMPSON
Hon. Secretary and Treasurer:	Mr. K. L. SMITH, Standards Department, Boots Pure Drug Co., Ltd., Nottingham, England.

American Chemical Society, Division of Analytical Chemistry. The following Officers have been elected for 1960:

Chairman:	H. A. LIEBHAFSKY
Chairman-elect:	CHARLES N. REILLEY
Secretary–Treasurer:	L. B. ROGERS, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, 39, Mass., U.S.A.

The *B.S.I. News* announces, among others, the following new British Standard:

B.S. 3156, 1959. *Methods for the sampling and analysis of fuel gases.* This describes methods of sampling and analysis applicable to coal gas, water gas, carburetted water gas, producer gas, methane, sewage gases, blast-furnace gases, Mond gas, Tully gas and oil gas. The constant-volume method and the soap-film method are given as alternatives for the determination of carbon dioxide, oxygen, saturated hydrocarbons, hydrogen, carbon monoxide, saturated hydrocarbons and nitrogen: the Metro method for nitrogen is also described. Methods for determining sulphur compounds, condensable vapours, nitrogenous gum, tar fog, ammonia, naphthalene, water vapour, hydrogen cyanide, iron carbonyl, specific gravity, calorific value and various arbitrary characteristics are given. (Price 25s.)

The following Standard has been revised:

B.S. 1428. *Microchemical apparatus,* Group A, *Combustion trains for the determination of elements.* Part A 2: 1959. *Nitrogen combustion train (micro-Dumas).* This specifies the components with dimensional drawings and an assembly drawing of the whole train. It describes a carbon dioxide generator using solid carbon dioxide as an alternative to the Tucker type. It refers to B.S. 1428, Part D 3 for the micro-nitrometer, and to B.S. 1428, Part A 1 for components common to both types of train. (Price 4s. 6d.)

DINERSTEIN, Standard Oil Company, Whiting, Ind. *The Analysis of Fluoro-Containing Compounds:* Programme Chairman, A. STEYERMARK, Hoffman-LaRoche Company, Nutley 10, N.J. *Thermal Methods of Analysis,* (a) *Thermogravimetry,* (b) *Differential Thermal Analysis,* (c) *Zone Refining:* Programme Chairman, E. L. SIMONS, General Electric Company, Schenectady, N.Y. Cleveland, Ohio, U.S.A.

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Talanta, 1960, Vol. 3, p. 377. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Dalzin (diallyl dithiocarbamido-hydrazide) as a micro reagent—I: Estimation and separation of copper and nickel. N. K. Dutt and A. Dutta Ahmed. (11 *December* 1959).

Acid chlorides of substituted succinic and glutaric acids as hydrolytic agents for the determination of water. R. Belcher, L. Ottendorfer and T. S. West. (14 *December* 1959).

Determination of ultramicro amounts of sulphate as methylene blue—I: The colour reaction. Lilly Gustafsson. (14 *December* 1959).

Determination of ultramicro amounts of sulphate as methylene blue—II: The reduction. Lilly Gustafsson. (14 *December* 1959).

Comments on fluorechromic indicators. J. Körbl and V. Svoboda. (24 *December* 1959).

The reactions of certain metals with thioacetamide. Ernest H. Swift and Fred C. Anson. (24 *December* 1959).

Analytical chemistry of α-benzoinoxime complexes of molybdenum, tungsten, vanadium and chromium. Henry J. Hoenes and K. G. Stone. (31 *December* 1959).

New methods of analysis for glyoxal. Eugene Sawicki and Walter Elbert. (11 *January* 1960).

A derivatographic study of potassium hydrogen phthalate. R. Belcher, L. Erdey, F. Paulik and G. Liptay. (11 *January* 1960).

Separations involving sulphides—XIII: Separation of quinquevalent antimony from alkaline earths G. B. S. Salaria. (19 *January* 1960).

Thiourea complexes of some noble metals: A polarographic determination of rhodium. Francesco Pantani and Pier Giorgio Desideri. (20 *January* 1960).

Calcein Blue: A new metalfluorechromic indicator for chelometric titration. Donald H. Wilkins. (28 *January* 1960).

Talanta, 1960, Vol. 3, p. 378. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Actas do XV Congresse Internacional de Química Pura e Aplícada (Quimíca Analítica), Volume II. Lisboa, 1958, Communications presented in Sections IV, V and VI. Pp. 1046.

Trace Techniques Using the K1000 Cathode Ray Polarograph, Vol. I. J. Hetman. Southern Instruments Limited, Camberley, Surrey, 1959. Pp. 49. 25s.

Optics and Spectroscopy, January 1959, Vol. VI, No. 1. Translated from the Russian on the initiative of the Optical Society of America, Inc. Distributed with the Journal of the Optical Society of America. Pp. 84.

The following publications have been received and are available from the Office of Technical Services, Department of Commerce, Washington, 25,/D.C., U.S.A.

Neutron and Gamma Effects in Dilute Aqueous Solutions: James R. Barcus. SCTM 22-59 (16) *March* 1959. Pp. 22. $0.75.

Solution of Multistage Separation Problems by Using Digital Computers: John H. Duffin. UCRL 8787. *August* 1959. Pp. 267. $4.00.

Dissolution of Thorium in Mixtures of HNO_3 and HF: D. G. Karraker. DP-399. *September* 1959. Pp. 15. $0.50.

Reactor Technology, Report No. 10—Chemistry. KAPL-200-7. *September* 1959. Pp. ix + 62. $2.00.

Effect of Dissolved Stainless Steel Components on Vapour-Liquid Equilibria in Aqua-regia: B. E. Paige. IDO-14483. *October* 1959. Pp. 23. $0.75.

Spectrophotometric Determination of Cobalt in Sodium Metal: Louis Silverman and Rachel L. Seitz. NAA-SR-4005. *October* 1959. Pp. 10. $0.50.

Sulfex Process: Depassivisation of Stainless Steel: T. A. Gens. ORNL-2785. *November* 1959. Pp. 14. $0.50.

Solubility Relations among Rare-Earth Fluorides in Selected Molten Fluoride Solvents: W. T. Ward, R. A. Strehlow, W. R. Grimes and G. M. Watson. ORNL-2749. *November* 1959. Pp. 14, $0.75.

ERRATUM

Volume 3, page 50, Table I, last three column headings, replace *mV* by *V*.

TALANTA

An International Journal of Analytical Chemistry

VOLUME 2 1959

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