

140. *Qualitative Semimicro-analysis with Reference to Noyes and Bray's System : The Copper and the Tellurium Group.*

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A scheme of analysis differing from that of Noyes and Bray is presented for the detection and approximate estimation of 0.25—50 mg. of bismuth, cadmium, or copper, 0.25—10 mg. of molybdenum, rhenium, iridium, rhodium, or tellurium, and 0.25—2 mg. of lead, in mixtures containing a maximum of 50 mg. referred to the metals. Tellurium is precipitated as the element, and confirmed by means of calcium hypophosphite. In separate portions of the residual solution molybdenum and rhenium are converted into their complex thiocyanates, rhodium is reduced by means of stannous chloride, iridium oxidised to a blue compound, copper precipitated as copper zinc mercury thiocyanate, and bismuth detected with thiourea. Lead and cadmium are separated from the other metals, and confirmatory tests with sodium rhodizonate and *p*-nitrobenzenediazoaminoazobenzene ("casion") applied. Throughout, full attention is paid to the possible interfering effects of group contaminants.

SCHEMES of semimicro-analysis for four groups of Noyes and Bray's system ("A System of Qualitative Analysis for the Rare Elements," 1927) have recently been submitted by Miller and Lowe (J., 1940, 1258, 1263) and Miller (this vol., p. 72). The extension of the methods to the copper and the tellurium group, which have been analysed on the micro-scale by Alstodt and Benedetti-Pichler (*Ind. Eng. Chem., Anal.*, 1939, 11, 294), is now described.

In Noyes and Bray's scheme, the perchloric acid-containing filtrate from the precipitate composing the thallium group is, after suitable preparation, treated under carefully controlled conditions of acidity with hydrogen sulphide, so as to precipitate essentially the sulphides of bismuth, cadmium, copper, iridium, rhodium, tellurium, molybdenum (carried through to this group by phosphate), and lead in small quantity escaping precipitation in the thallium group. Kao and Chang (*J. Chinese Chem. Soc.*, 1934, 2, 6) have since reported that rhenium should be included in these groups, and have prescribed conditions for its detection. Accordingly, provision has been made for the detection and approximate estimation, in mixtures, of all these metals within the limits set forth in the summary.

The scheme presented, which is for the combined groups, differs in several respects from that of Noyes and Bray. For instance, after the removal of tellurium, six metals are separately tested for in portions of the solution. For the detection and estimation of lead and cadmium it has, however, been found necessary to separate them from the other metals, and from each other, by a method differing only slightly from Noyes and Bray's. Attention is directed to the important use made of organic solvents, in testing for rhodium, iridium, rhenium, and molybdenum, and to the simplicity and directness of application of most of the tests, even in the presence of metals, not normally components of the groups, that may be carried down on the semimicro-scale to the extent of a few tenths of a mg., e.g., arsenic and indium especially, selenium, germanium, antimony, tin, zinc, and titanium, or in traces (<100 γ), e.g., cobalt, nickel, gallium, iron, mercury, platinum, and tungsten (cf. Noyes and Bray, *op. cit.*, pp. 134—136, 292, 306—309, 375—377).

EXPERIMENTAL.

Preparation of the Group for Analysis.—Mixtures containing sodium tellurite, sodium molybdate, potassium perchlenate, the chlorides or nitrates of the other metals, a little nitric acid, and 0.35 ml. of 9N-perchloric acid were evaporated as far as possible on the steam-bath in

Copper and Tellurium Groups.

Precipitate. Sulphides of Te, Cu, Bi, Rh, Ir, Re, Mo, Pb, and Cd. Dissolve this as far as possible in hot, concentrated HCl, and then add a little hyperol. If a dark precipitate is left, separate it, and heat it gently with *aqua regia* until only S remains (1). Add to the combined solutions 20 mg. of NaCl, and evaporate to dryness in a 3-in. tube, using an air current (2). Take up in 0.6–1 ml. of concentrated HCl, saturate in the cold with SO₂, and, if necessary, remove **Se**. Dilute with water to make 2.7N in HCl, and resaturate with SO₂. Heat to coagulate Te (15 mins.), and separate and wash it twice with N-HCl. (3)

Precipitate. Black Te. Estimate if desired. To confirm a small amount, dissolve in 0.25 ml. of concentrated HCl and a minimum quantity of hyperol. Expel Cl₂, dilute with 0.25 ml. of water, and heat with an excess of calcium hypophosphite at 50°. Compare a black precipitate of **Te** with standards. (4)

Solution. Contains Pb, Bi, Cu, Cd, Ir^{III}, and Rh^{III} chlorides, perchlenate, and molybdate. Evaporate just to dryness as above, add a drop of concentrated HNO₃, and re-evaporate to oxidise. Expel HNO₃ by evaporating twice with 0.1 ml. of HCl, take up in 1–2 ml. of 6N-HCl, and examine portions as follows.

(a) Test 1–2% for Cu. Add water to make 0.05 ml., 0.05 ml. of 10% aq. NH₄F, 0.05 ml. of 0.5M-ZnSO₄, and stir. Finally add 0.05 ml. of ammonium mercury thiocyanate reagent (30 g. of HgCl₂ and 33 g. of NH₄SCN in 100 ml. of water). A violet or almost black precipitate shows **Cu**. Compare with standards. (5)

(b) Test 1–2% for Bi in <0.5 ml. of cold, 1–2N-HNO₃, adding 0.05 ml. of 10% aq. NH₄F, and solid thiourea in excess. A yellow solution shows **Bi**. Estimate. If a maximum excess of Rh interferes by giving a pinkish-brown colour, test for Bi after the removal of Rh. (6)

(c) Test 10% for Rh. Make up to 0.5 ml. in 6N-HCl, add 0.1 ml. of α-SnCl₄ in 6N-HCl, and heat for 1 min. If the solution is coloured, cool, extract with 0.5–2 ml. of n-butyl acetate, and, if a yellow ester layer results, wash it with 0.1 ml. of 6N-HCl. Next add 0.2 ml. of 6N-HCl to the ester layer, and, while heating, just sufficient hyperol to discharge the yellow colour. Heat until effervescence ceases, re-reduce with SnCl₄ as above, and compare a yellow ester layer, which shows **Rh**, with standards. If Pt may contaminate, separate the ester layer, add 6N-HCl and 0.005 ml. of thioglycolic acid, and shake the mixture for 10 secs. (7)

(d) Test 10% for Ir. If Rh is present add 0.5 ml. of concentrated HCl, heat, and add a little hyperol to oxidise Ir fully. Cool, add hyperol again, and water to make 1 ml. Extract once with 1 ml. of isoamyl alcohol. Evaporate the alcoholic layer to dryness (hot plate), and heat the residue with hyperol and <0.5 ml. of concentrated H₂SO₄, until strong fuming occurs. Add ~20 mg. portions of NH₄NO₃ at intervals, with continued strong fuming, until a maximum blue-purple colour showing **Ir** has developed. Cool, and compare with standards. Double the estimate (8). If Rh is absent omit the initial oxidation and partial (50%) extraction of IrCl₄, and oxidise directly with NH₄NO₃ in H₂SO₄.

(e) Test 10% for Re. Add water to make N in HCl, and extract twice with the same volume of isoamyl alcohol. Wash the combined extracts with 0.2 ml. of N-HCl. Add 1 ml. of ca. 12N-HCl, 0.02 ml. of α-SnCl₄ in 6N-HCl, and 10–20 mg. of KSCN. Shake, leave for a few mins., and, if the alcohol layer is coloured, separate it, and add to it again 1 ml. of 12N-HCl. Heat for 1 min. A completely miscible, yellow solution shows **Re**. Compare with similar standards. (9)

(f) Test 10% for Mo. Make up to 1 ml. in N-HCl, add 0.005–0.01 ml. of thioglycolic acid, and, after 2 mins., 20–40 mg. of KSCN. If Cu is present ensure its complete precipitation as white CuSCN, and then the full development of a yellow or red colour that may be due to Mo. Remove the precipitate, wash it with 0.1 ml. of N-HCl, and extract the solutions with n-butyl acetate. Compare an orange-red or red ester layer, which shows **Mo**, with similar standards. Should the interference of iron be suspected confirm Mo by means of toluene-3:4-dithiol, see (10).

(g) Test >0.5% for Cd. Add 4 times the volume of water, and saturate with Rochelle salt. Spot thin, ashless filter paper, impregnated with p-nitrobenzenediazaminoozobenzene, with this solution, and then with an excess of 2N-NaOH. A pink colour shows **Cd**. Contaminating Hg may interfere. (17)

(h) If Mo is present, or as an alternative to (f), extract 50% 2 or 3 times with the same volume of n-butyl acetate. Wash the combined extracts with a few drops of 6N-HCl, and add the washings to the aqueous layer (11). If Mo has been tested for and found to be absent proceed immediately as follows.

Ester layer. Contains Mo, which is tested for if necessary. (10)

Aqueous layer. Contains Pb, Bi, Cu, Cd, Ir, and Rh chlorides, and perchlenate. Evaporate just to dryness, add 0.02 ml. of glacial HOAc, 0.5 ml. of water, and 0.5 ml. of 2M-NaNO₂. Heat at 60–70° for 5 mins., cool, and add dropwise, with constant stirring, N-NaOH until red litmus paper is turned deep blue. Separate and wash a precipitate with hot water. To the centrifugate add 0.25 ml. of m-NaHCO₃, and, if necessary, separate a small precipitate of PbCO₃, and combine it with the other. (12)

Precipitate. Mainly Pb, Bi, Cu, and Cd hydroxides. Dissolve in 0.2 ml. of concentrated HCl, and add 0.3 ml. of water. Reprecipitate with concentrated NH₄OH, added dropwise, until 3–4 drops in excess are present. Separate and wash a precipitate with 0.1N-NH₄OH. (13)

Solution. Contains perchlenate, and the complex nitrites of Rh and Ir. Reject.

Precipitate. Pb(OH)₂ and Bi(OH)₃. If Bi is >1 mg., dissolve the precipitate in a minimum amount of HNO₃, and add water to make 1 ml. Precipitate BIONO₂ in the cold with NH₄OH (finally 0.1N), until thymol-blue present as an indicator just turns yellow. Wash the precipitate with water. Omit the precipitation if Bi is <1 mg. (14)

Solution. Contains Cu(NH₃)₂Cl₂ and Cd(NH₃)₂Cl₂. Decolorise with solid KCN, and pass H₂S for 30 secs. to deposit yellow CdS, of which a large precipitate may be estimated. If the precipitate is very discoloured, or practically white, making the presence of Cd doubtful, or assessment difficult, digest it at the b. p. with N-HCl, and reject a small dark precipitate. Evaporate the solution to dryness, and follow (a) or (b), using the latter if the presence of Cd is uncertain. (16)

Precipitate. BIONO₂. Reject.

Solution. Contains Pb(NO₃)₂ and a little Bi(NO₃)₃. Evaporate to dryness and expel NH₃ salts (hot plate). Dissolve the residue in >0.5 ml. of 2N-HNO₃, and add to the cold solution < the same volume of thiourea (15% in N-HNO₃). Stir

(a) Take up in a small volume of 0.25N-HCl, and pass H₂S in the cold. Estimate yellow CdS.

briskly, centrifuge, and wash the separated precipitate twice with a little cold ethyl alcohol. Dissolve it in water, add fresh, saturated aq. sodium rhodizonate in excess, and centrifuge. Compare a reddish-purple precipitate, which shows **Pb**, with standards. Finally, add to the separated precipitate, without stirring, a drop of 2N-HCl. A blue-purple colour confirms the presence of Pb. (15)

(b) Take up in 1 ml. of water or less, and place 0.01 ml. of the solution on thick, drop reaction paper, impregnated with p-nitrobenzenediazaminoozobenzene. Allow 0.2N-NaOH to diffuse centrally over the spot, at a slow rate, until the periphery is violet. A pink spot shows **Cd**. Estimate. (17)

tubes, 3" × $\frac{3}{4}$ ", over which a current of air played. Finally, the tubes were placed to a depth of $\frac{3}{4}$ " in a metal block, and heated until the temperature of the liquid just exceeded 200°. 2.5 ml. of water were then added to the cold solutions, the acidity was adjusted, and the metal sulphides were precipitated and washed, essentially as prescribed by Noyes and Bray, but on one-tenth of their scale. The final heating under pressure for an hour at 100°, in a solution 4.5N in acid, was conducted in a 15 ml. centrifuge tube, closed with a rubber stopper, and fixed in the frame of a 150 ml. pressure bottle. Rhenium(VII) sulphide was satisfactorily precipitated under these conditions (cf. Geilmann and Weibke, *Z. anorg. Chem.*, 1931, **195**, 289). The subsequent analysis of the group was in accordance with the tabulated scheme. The figures in parentheses are referred to in "Notes on Methods and Tests."

Notes on Methods and Tests.

The experimental technique was referred to by Miller and Lowe (*loc. cit.*). Vigorous shaking and brief centrifuging always preceded the separation of two liquid layers. One layer was then simply and effectively withdrawn, mouth suction being used, by means of a pipette prepared with a 12 cm. capillary part of 1½ mm. diameter bent at an angle of 120° to the main body of 6 mm. diameter and 20 cm. length. All evaporations were done on a steam-bath, and heatings by inserting tubes in boiling water, except where otherwise stated. Organic solvents were fractionated.

Note 1. Hyperol (Booer, *J. Soc. Chem. Ind.*, 1925, **44**, 1137) in association with hydrochloric acid readily dissolved most of the sulphides, including rhenium sulphide. Iridium sulphide required *aqua regia*.

Note 2. Sodium chloride was added to ensure the retention of rhenium (cf. Kao and Chang, *loc. cit.*). Tellurium chloride was partly volatilised if the solution was evaporated in a basin. The method adopted was adequate.

Note 3. The separation of tellurium was necessary, because it adversely affected the tests for a few of the other group components, and its own confirmatory test required the absence of large excesses of certain metals.

Note 4. The reduction with hypophosphite proceeds in 6N-hydrochloric acid, and by heating at $\gt 50^\circ$ no interference from arsenic can occur (Challis, *Analyst*, 1941, **66**, 58). At least 10γ of tellurium were detectable in the presence of large excesses of all the group components, except rhodium, iridium, and molybdenum, of which only 10-fold excesses were permissible, and of all the group contaminants (see p. 786) except selenium. Many other metals might also be present.

Note 5. There is an abundance of tests for copper. That prescribed (Montequi, *Anal. Soc. Fis. Quím.*, **25**, 52, through *Chem. Zentr.*, 1927, **I**, 2453) was very reliable and selective, and its application in distinctly acid solutions was a great advantage. Straumanis and Ence (*Z. anorg. Chem.*, 1936, **228**, 334) showed that all the copper is involved in the formation of mixed crystals (violet), when about twice as much zinc as copper is present. In order to render the test suitable for estimations, it was necessary to use a constant amount of zinc, at least twice as great as the maximum amount of copper anticipated, and sufficient ammonium mercury thiocyanate to ensure its complete precipitation. Under the conditions given, which precluded serious interference with the bulk, and therefore the colour of the precipitate by other (*e.g.*, cadmium) mercury thiocyanates, 1—500γ of copper was capable of assessment, the colour ranging from pale heliotrope, through violet, to black. It was immaterial whether the copper solution contained dilute acetic or mineral acid, and the acid concentration was not critical. 5 Mg. of ammonium fluoride, added *before* the thiocyanate reagent, effectively prevented the similar reaction of 500γ of iron(III) without appreciably influencing the test for copper. The group components, and many other metals, did not interfere, unless by giving coloured solutions (*e.g.*, rhodium) which could be removed. There was practically no interference from the small amounts of other metals that might contaminate the group. For instance, cobalt and nickel, which were most liable to interfere, did not prevent the detection of the same, and 10 times the amount of copper, respectively. Cobalt rendered the estimations more difficult.

Note 6. This selective test was used in analysing the thallium group (Miller, *loc. cit.*). Towards tellurium and antimony, which also give yellow colours, the reagent was respectively 25 and 100 times less sensitive. Fluoride, in moderate amount, without affecting the detection of bismuth, quenched the reaction of antimony, but not that of tellurium, hindered a slow formation of molybdenum blue, and prevented a violet colour due to iron. 200γ of iridium gave in the cold the equivalent of $< 1\gamma$ of bismuth. Rhodium, which gave a brown colour in hot solutions, did not seriously influence the test *in the cold*, except when its maximum amount rendered uncertain the detection of a minimum amount of bismuth. The latter had then to be

detected in conjunction with lead, following the removal of rhodium as its complex nitrite. The remaining group components and the likely contaminants did not interfere, provided that an excess of thiourea was used. At higher concentrations of bismuth Beer's law was not followed, and a comparison with several standards was advisable.

Note 7. The tests for rhodium and iridium (*Note 8*) represent the final results of an investigation undertaken to improve the methods of detection used in the gold group (Miller and Lowe, *loc. cit.*). Alstodt and Benedetti-Pichler (*loc. cit.*) applied the stannous chloride reduction test of Iwanow (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 460, through *Chem. Zentr.*, 1923, IV, 135) to rhodium, after a somewhat lengthy scheme of separations that has been found unnecessary. The following are the salient features of the present method. The rate of reduction of rhodium(III) chloride with stannous chloride in hydrochloric acid solution, to form an orange-brown solution, increased with increasing acid concentration, and the reaction was virtually complete in 1 min. in 6*N*-hydrochloric acid at 100°. Rhenium and molybdenum gave brown solutions, and iridium a yellow-brown solution, 50 times less intense than that for rhodium. From 6*N*-hydrochloric acid *n*-butyl acetate extracted neither the rhenium nor the molybdenum reduction product, and very little iridium, whereas the reduction product of rhodium was readily removed from 4—6*N*-acid solutions. <5γ of rhodium were detectable.

In the systematic analysis of mixtures, generally containing both iridium and molybdenum, there was sometimes produced in the ester a brown colour due to iridium. The only effective means of eliminating it was to reoxidise and repeat the reduction as outlined. A large number of metals were without influence on the test. When other reducible substances were present it was essential to use sufficient stannous chloride (0.1 ml. of fresh *m*-SnCl₂) to ensure their full reduction, as well as that of rhodium. The only contaminant of the group (see p. 786) that behaved like rhodium was platinum. The final treatment with thioglycollic acid eliminated the colour due to <25γ of platinum.

Note 8. The test for iridium with sulphuric and nitric acid, as formerly applied, was inadequate in the presence of the larger excess of rhodium encountered here. The method now prescribed separated 50% of the available iridium(IV) chloride from rhodium(III) chloride. The reliability of the test was enhanced by the substitution of solid ammonium nitrate for nitric acid (cf. Rüdüsüle, "Nachweis, Bestimmung, und Trennung der chemischen Elemente," 1916, vol. IV, p. 40). As 10 mg. of lead, bismuth, copper, or cadmium, <2 mg. of molybdenum, rhenium, or tellurium, and <50γ of any other metal that might contaminate the group did not prevent the detection of 10γ of iridium in 0.5 ml. of sulphuric acid, the *isoamyl* alcohol extraction was resorted to only when rhodium was present. Colour comparisons of large amounts of iridium were best made in test tubes, with a concentration of iridium >250γ per ml.

Note 9. The formation of the yellow complex thiocyanate of rhenium, probably ReO(SCN)₄, in hydrochloric acid solutions, by reducing Re^{VII} to Re^{VI} with stannous chloride in the presence of potassium thiocyanate (Geilmann, Wrigge, and Weibke, *Z. anorg. Chem.*, 1932, 208, 217; Hurd and Babler, *Ind. Eng. Chem., Anal.*, 1936, 8, 112) afforded a convenient and sensitive test if the interference of molybdenum and rhodium could be prevented. It was found that the proportion of rhenium(VII) extracted by *isoamyl* alcohol, from hydrochloric acid solutions, diminished only slightly as the acid concentration decreased. For example, in *N*-acid the procedure given effected the removal of ~90%. Molybdenum was correspondingly extracted to the extent of 5%, and rhodium very slightly. The rate of formation of the rhenium-thiocyanate complex greatly increased as the concentration of hydrochloric acid increased, the best results being obtained when *ca.* 12*N*-acid was added with the reagents to the alcohol layer. This acid simultaneously enfeebled the reaction of molybdenum (cf. Hiskey and Meloche, *Ind. Eng. Chem., Anal.*, 1940, 12, 503). The effect of a large amount of molybdenum might not be fully eradicated, but a second treatment with 12*N*-hydrochloric acid and brief heating were remedial. The test outlined permitted the detection of 5γ of rhenium in association with all the group components, except tellurium, in their maximum amounts, and at least 100-fold excesses (tungsten, 10-fold) of the recognised group contaminants (see p. 786), except selenium, which had to be absent. 1 Mg. of rhodium gave the equivalent of ~3γ of rhenium.

Note 10. For the detection of molybdenum as its complex thiocyanate Miller and Lowe (*loc. cit.*) used thioglycollic acid and potassium thiocyanate. Although these gradually reacted with rhenium, giving a dark brown colour, the interference of rhenium could be avoided by using a solution of low acidity at room temperature, and extracting molybdenum thiocyanate soon by means of *n*-butyl acetate. For a satisfactory extraction it was impracticable to have the acidity < *N*. At least 5γ of molybdenum were detectable in association with <1000-fold excesses of lead, bismuth, copper, and cadmium, and 200-fold excesses of the remaining group components,

including tellurium, and all the likely group contaminants (see p. 786), except titanium, of which a 10-fold excess was permissible, and iron. Finely-divided cuprous thiocyanate was removed before the extraction, with which it interfered.

The interference of iron was more troublesome. It behaved as follows. 50 γ in 1 ml. of *n*-hydrochloric acid gave, on the simultaneous addition of thioglycollic acid and potassium thiocyanate, a red-brown colour, which changed to a deep purple-red that was extracted by *n*-butyl acetate. If the iron solution were left in contact with thioglycollic acid for <2 mins., before the addition of potassium thiocyanate, no red colour appeared in the aqueous solution, but, on the addition of the ester, a light violet-pink colour developed in it, and did not change appreciably in 10 mins. In order to obtain this paler colour it was essential to add the ester last. Iron in such an experiment did not prevent the detection of at least a similar amount of molybdenum, but caused it to be over-estimated. Normally, contaminating iron will be masked by the procedure given. The interference of iron could be eliminated entirely by heating the contaminated ester solution containing molybdenum thiocyanate with 1 ml. of *n*-hydrochloric acid and 2—3 mg. of toluene-3 : 4-dithiol. The intense green "dithiol" complex of molybdenum was produced (see Miller, this vol., p. 792), and even 500 γ of iron were decolorised.

Note 11. *n*-Butyl acetate was preferred to ether (see Noyes and Bray, *op. cit.*). The removal of molybdenum was effective, *e.g.*, 95% for 10 mg., if 3 extractions were made, the extraction of other metals, except rhenium (*ca.* 25% removed), was negligible, and the ester solution could be immediately utilised, if desired, to detect molybdenum (see Note 10).

Note 12. This process of Noyes and Bray did not give an entirely satisfactory separation of iridium and rhodium, although a more dilute solution of sodium hydroxide was used. However, only lead and cadmium remained to be tested for, by methods that were not adversely affected by small quantities of the other metals.

Note 13. For the subsequent detection of lead by means of thiourea and sodium rhodizonate it was necessary to separate it in the form of lead nitrate from appreciable amounts of copper and bismuth. The dissolution of the hydroxides in hydrochloric acid, and reprecipitation with an excess of ammonia readily removed copper and cadmium, leaving the bismuth associated with the lead.

Note 14. A quantitative separation of bismuth from lead was not required. The gradual reduction of the acidity until the p_H was 2—3 removed nearly all the bismuth and left in solution the small amount of lead normally present.

Note 15. This process has been described for the thallium group (Miller, *loc. cit.*). As a small volume of solution was essential for the precipitation of the thiourea complex of a minimum amount of lead, and high concentrations of the other group components might lead to their partial precipitation (*e.g.*, copper, bismuth, and rhodium), or hinder the precipitation of the lead complex (*e.g.*, iridium and rhodium), a more direct application of the thiourea test was not feasible. The formation of a small precipitate with thiourea was not confirmatory for lead, but no other group component or contaminant reacted with sodium rhodizonate and hydrochloric acid in the same manner as lead.

Note 16. Noyes and Bray precipitated cadmium sulphide thus, dissolved it in 1·2*N*-sulphuric acid, and reprecipitated it in the diluted (0·3*N*) solution. *N*-Hydrochloric acid was preferred, as its easy removal facilitated the reprecipitation of cadmium sulphide in a small volume of solution, and provided a neutral solution for the application of the "cation" test (see Note 17).

Note 17. For the detection of cadmium there is probably no reagent as sensitive and selective as *p*-nitrobenzenediazoaminoazobenzene, "cation" (see Hopkin and Williams, "Organic Reagents for Metals," 1938, p. 85). When a slightly acid solution, saturated with Rochelle salt to prevent the subsequent precipitation of certain metallic hydroxides (*e.g.*, of copper, iron, etc.), was spotted on thin, dry, ashless filter paper, previously impregnated with a 0·05% solution of cation in alcohol and acetone (9 : 1), and then with 2*N*-sodium hydroxide in excess, a pink spot resulted if cadmium was present. Cadmium was detected thus in a 0·005% solution with <1000-fold excesses of lead, bismuth, and copper; 100-fold excesses of all the other group-components and contaminants, except mercury which itself gives a salmon-pink spot; and many other metals. Consequently, in the absence of contaminating mercury, cadmium could be detected in a minute portion of the solution of the group. If no pink spot was observed it was unnecessary to examine further for cadmium. This test cannot be used for determining cadmium save in neutral solutions free from other metals.

When the rate of reaction with sodium hydroxide of 0·01 ml. of a neutral cadmium chloride solution spotted on drop reaction paper (Whatman, No. 120, "double thickness"), impregnated with cation, was controlled by allowing the dilute hydroxide to diffuse *very slowly* out of a burette

like that of Clarke and Hermance (*Ind. Eng. Chem., Anal.*, 1937, 9, 292), pink spots, related in size to the concentration of the cadmium, were obtained. Thus one sheet of paper gave 7½, 14½, 19, and 24½ mm. diameter spots for 0.01, 0.05, 0.1, and 0.25% solutions of cadmium (as chloride), respectively. For estimations the most desirable concentration range was 0.01—0.1%. Although the concentration of sodium hydroxide was not critical, the best results were obtained when it was between 0.1N and 0.2N. The size of the spots diminished if cadmium acetate replaced the chloride, and increased if, *e.g.*, zinc chloride was also present: 0.05% of zinc caused the same amount of cadmium to be overestimated 5-fold. If more than a trace of zinc entered the copper and the tellurium group it would be necessary to use procedure (a) for the estimation of cadmium.

Analysis of Mixtures.—Fifteen mixtures, mainly of unknown composition, were analysed to test the scheme. Nos. 1—5 contained only salts of the normal metallic components of the group. The solutions were evaporated to dryness with hydrochloric acid to remove nitrate, and analysed without the prior precipitation of the sulphides. Nos. 6—10, which were similarly analysed, contained, in addition, arsenic and indium (1 mg. of each), antimony, germanium, selenium, tin, titanium, and zinc (0.25 mg. of each), and cobalt, gallium, iron, mercury, nickel, platinum, and tungsten (0.05 mg. of each) (see p. 786). In nos. 11—15 precipitations with hydrogen sulphide were conducted in solutions containing the normal group components and 10 mg. quantities of other metals that might be present in systematic analyses, and exert an influence, if inadvertently brought into the group by a faulty precipitation. Thus nos. 11, 12, and 15 contained nickel, cobalt, and zinc, respectively; no. 13, chromium, iron, and titanium; and no. 14, gallium and indium. In addition, nos. 11, 14, and 15 contained, respectively, 5, 10, and 0.5 mg. of phosphoric acid. The results shown in the table are the estimated weights in mg. of the group components found. Where these differed from the actual amounts taken the latter are shown in parentheses.

Element.	Te.	Bi.	Cu.	Rh.	Ir.	Re.	Mo.	Pb.	Cd.
No. 1	1	28 (32)	0	0	0	7 (9)	0	0	0.05, 0 (0.25)
2	0	20 (21)	0.25	7 (10)	0.25	0	0	0.1 (0.25)	0
3	0.25	0	40 (36)	0	0	0	7 (8)	0.75 (0.6)	1, 0.5 (1)
4	5 (7)	0.25	3	0.1 (0.25)	6 (8)	0.25	0.25	1 (2)	50, 16 (27)
5	0	2 (3)	0	1.5 (3)	1	0.5 (1)	4 (2)	0	5, 6 (5)
6	6 (10)	0	0.25	1.5 (1)	1	2 (3)	0	1 (0.5)	8, 8 (10)
7	0	16 (15)	1	0	0.25	0	0	0 (0.25)	0.1, 0.1 (0.5)
8	0	0	0	0.25	0	0.75 (0.5)	10	1.5 (2)	0.5, 0.25 (1)
9	0.1 (0.25)	1 (0.5)	0.5	5 (6)	5 (6)	0	0	0	0
10	2.5 (2)	0	5	0	0.5	10 (7)	0.5 (0.25)	1	2
11	0	0	0.5	0	6 (7)	0	5 (6)	1	4, 3 (3)
12	0	0.5 (0.25)	0.25	5 (6)	0.1 (0.25)	0	0	1 (2)	6, 3 (5)
13	0	0.5	10 (12)	0.25	0	0	0	0.5	0.25, 0 (0.25)
14	0.5	2	0	0	0.25 (0.5)	7 (10)	0.5	0	0.5, 0.25 (1)
15	3	0	13 (17)	0	0.5 (1)	0.25	0.25	0	0.25, 0.1 (0.5)

In general, the results are satisfactory. Particularly good are the estimations of bismuth and copper, which, with the exception of that for bismuth in no. 12 (rhodium interfering), were made on 1—2% of the solution. Cadmium was estimated in every experiment by means of cadion (first estimate shown) as well as on the bulk of the first (Cd > 5 mg.) or second (Cd < 5 mg.) sulphide precipitate (second estimate shown). The first estimations are surprisingly good, considering that in, *e.g.*, no. 4 the final test was made with 0.05% referred to the original solution. It is possible that compensating errors (see Note 17) caused the estimations made with cadion to be generally higher than those attributable to cadmium sulphide. Had cadion not been employed cadmium would have been missed in nos. 1 and 13.

The detection of the smallest amounts of lead, and the estimation of corresponding amounts of cadmium, were less certain than for the other metals, mainly because losses were incurred in the various separation processes. Thus in no. 7 lead apparently escaped into the filtrate containing iridium, etc., because when the hydroxide-nitrite treatment was omitted, and a direct precipitation with an excess of ammonia made, 0.25 mg. was found. In nos. 1 and 7 cadmium seemed to be partly retained by the large precipitate of bismuth hydroxide. At present more direct tests suitable for estimations cannot be given.

Nos. 6—10 show that small amounts of the common group contaminants did not influence the results. In nos. 11—15 the precipitation of the sulphides was successfully conducted. The adjustment of the acidity before the precipitation was, however, difficult if the solutions were deeply coloured, and care was required. A means of improving on Noyes and Bray's technique, using methyl-violet, has not been found, nor has any other indicator been found superior to methyl-violet. Neither molybdenum nor rhenium was detected in the group filtrates, but in nos. 11, 12, 14, and 15 the amounts of iridium in the filtrates corresponded closely to the amounts

by which the estimations were low. Noyes and Bray (*op. cit.*, p. 377) refer to the incomplete precipitation of iridium. It is satisfactory that even the minimum amount under consideration was detected.

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