The effect of organic matter was next studied. Determinations were made in the presence of soil extract which contained considerable organic matter. Fifty cc. of a standard nitrite solution were added to 50 cc. of a soil extract and the nitrite was determined. Nitrites were determined separately on 50-cc. portions of the soil extract and the proper correction, 0.448 mg., was made.

TABLE III.—EFFECT OF ORGANIC MATTER ON NITRITE DETERMINATION. AMOUNT TAKEN, 10 MG. OF NITROGEN.

Cc. 0.1 N $Na_2S_2O_3$.	Nitrogen found. Mg.	Nitrogen recovered. Mg.	Cc. 0.1 N $Na_2S_2O_3$.	Nitrogen found. Mg.	Nitrogen recovered. Mg.
7.46	10.45	10.00	7.46	10.45	10.00
7.47	10.46	10.02	7.50	10.50	10.05
7.48	10.47	10.03	7.50	10.50	10.05
7.48	10.47	10.03	7.47	10.46	10.00

The organic matter of the extract does not affect the results very materially. In extreme conditions, however, the nitrites may be removed from a second sample by boiling with acetic acid, and the magnitude of the action due to organic matter determined by means of a blank titration.

Small quantities of nitrites may be determined in the open flask while a current of CO_2 is passing through the solution. Table III contains the results of such determinations. For very small quantities of nitrites 0.005 N thiosulfate is used.

TABLE IV.—AMOUNT TAKEN, 0.012 MG. NITROGEN.

Cc. 0.005 N $Na_2S_2O_3$.	Mg. nitrogen.	Cc. 0.005 N $Na_2S_2O_3$.	Mg. nitrogen.
0.19	0.013	0.18	0.012
0.16	0.011	0.17	0.012
0.14	0.009	0.18	0.012
0.19	0.013	0.16	0.011
0.19	0.013		

The results reported in this paper show clearly that nitrous nitrogen can be determined titrametrically when care is taken to expel the air from the titration flask with some gas which will not affect the determination.

The author takes this opportunity to thank Mr. J. J. Kennedy and Dr. E. R. Allen for their assistance in carrying on this work.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY.]

SODIUM PYROGALLATE AS A REAGENT FOR THE DETERMINATION OF OXYGEN.

BY J. W. SHIPLEY.

Received June 21, 1916.

TOPICAL OUTLINE.—Introduction and Historical. Reagents. Apparatus. Range of Concentrations. Specific Absorption of Reagents. Comparison with Potassium Pyrogallate. Volume of Oxygen Absorbed before Rate of Absorption Dropped to Four-minute Limit. Rate of Absorption. Temperature Coefficient. Relation of

Oxygen Absorbed to Amount of Pyrogallol. The Formation of Carbon Monoxide. Rate of Absorption in Various Pipets. Choice of Reagents for Gas Analysis. The Use of Ammonium and Barium Pyrogallate. Summary.

Introduction and Historical.

The purpose of this research was to determine whether sodium pyrogallate might not be substituted for potassium pyrogallate in the absorption of oxygen from gaseous mixtures.

The evidence from the chemical literature available indicated that no one as yet had made a systematic study of the use of sodium pyrogallate in this connection and that chemists had on very doubtful evidence indeed discarded this reagent in favor of the more expensive potassium salt. Particularly at this time when circumstances have made it almost impossible to obtain the latter foreign product in any quantity did it seem desirable to determine whether the home product might not be as serviceable.

Potassium hydroxide is at present universally used in the preparation of alkaline pyrogallate for the absorption of oxygen. All text-books on gas analysis recommend its use and many researches have been carried out to determine the best proportion of alkali, pyrogallate and water to use in the preparation of the reagent. The best conditions for obtaining the most efficient absorption of oxygen by means of this reagent was the subject of a recent exhaustive research by **R.** P. Anderson.[1] Anderson made one determination with sodium pyrogallate in place of potassium pyrogallate, obtaining complete absorption only after twelve minutes' shaking. From this he concludes that such a reagent would scarcely be satisfactory for general use as an absorbent for oxygen.

Weyl and Goth[2] carried out a series of experiments, the results of which tended to indicate that sodium hydroxide might be better than potassium hydroxide in the preparation of this reagent.

Berthelot[3] found that the relative absorbing capacity of sodium and potassium pyrogallate was practically equivalent when the solution contained alkali in the proportion of three parts of alkali to one of pyrogallol. Dilution affected the rate of absorption and the evolution of carbon monoxide but the total absorbing power was not affected until the ratio between pyrogallol and alkali used dropped below 1 : 1. At 1–2 KOH to 1 of pyrogallol the amount of oxygen absorbed was reduced to one-half of that absorbed when the ratio was 3 : 1, respectively.

Lewes[4] prepared a reagent by dissolving 10 g. of pyrogallol in 150 cc. of 20% sodium hydroxide. Such a solution required twenty minutes for the complete absorption of oxygen and could not be used more than three

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[1] Anderson, *J. Ind. Eng. Chem.*, 7, 587 (1915).

[2] Weyl and Goth, *Ber.*, 14, 2659 (1881).

[3] Berthelot, *Ann. Chem. et Phys.*, 77, 294 (1898).

[4] Lewes, *J. Soc. Chem. Ind.*, 10, 407 (1891).

or four times, since carbon monoxide was generated after a certain proportion of oxygen had been absorbed. Had Lewes gone further and used more concentrated solutions with respect to both alkali and pyrogallol he would have found the rate of absorption of oxygen much greater and would not have found any appreciable quantity of carbon monoxide.

The experimental work of Weyl and Goth at relatively low concentrations and of Berthelot at high concentrations indicated that sodium hydroxide might well have been considered in the preparation of alkaline pyrogallate. Chemists[1] have, however, in this as in many parallel cases, accepted the preference for a potassium compound without investigating fully the possible substitution of the cheaper sodium salt.

The results of a few preliminary determinations covering several different concentrations indicated clearly that the absorption of oxygen by sodium pyrogallate was sufficiently rapid to warrant a more extensive investigation. Moreover, no carbon monoxide appeared to be evolved from any of the concentrations used. Accordingly, apparatus and reagents were prepared for determining the best conditions and concentrations of sodium pyrogallate for the absorption of oxygen from gaseous mixtures.

Reagents.—Pyrogallic acid was secured from the 1-pound can product prepared by a reputable firm.

Sodium hydroxide solution was prepared by dissolving electrolytic, pure stick sodium hydroxide in an equal weight of water. The alkali content of this solution was determined by diluting 10.0 cc. to a liter and titrating an aliquot portion against standard acid. Thus 10.0 cc. were found to contain 7.36 grams of sodium hydroxide or about 49.1%. This solution will be referred to as the stock solution.

Oxygen was prepared from the reaction between sodium peroxide and water. The preparation contained 95% of the gas.

Apparatus.—Fig. 1 illustrates in detail a special pipet outwardly resembling the Richard's form and inwardly that of the Orsat model.

Such a double pipet was found to be very efficient. It is com-

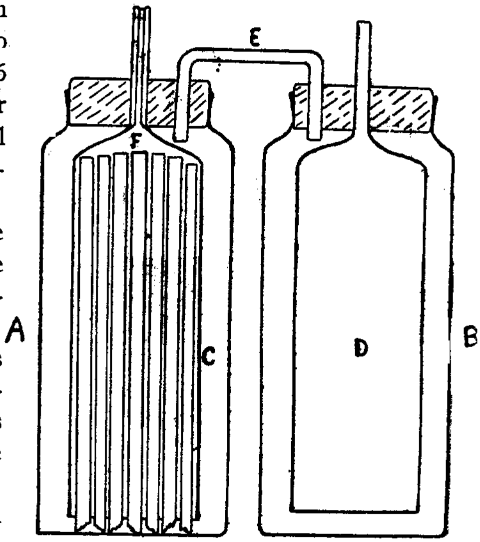

Fig. 1.

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[1] Withrow, *J. Ind. Eng. Chem.*, 8, 486 (1916).

pact, stable, easy to construct or repair, not at all fragile and very convenient for filling or cleaning. The small glass tubes provide a very large absorbing surface and since no shaking is necessary the disadvantage arising from foaming when viscous solutions are used is entirely obviated.

This pipet was used in making the absorptions tabulated in Table I.

A Simple Pipet.—In determining the specific absorption of various alkaline pyrogallate solutions it was necessary to have a simple pipet and that depicted in Fig. 2 was found to give very satisfactory results. This pipet resembled in principle that described in Fig. 1.

A glass tube 6 mm. in diameter was sealed to the lower extremity and to this was attached a levelling bulb filled with mercury. A three-way capillary stopcock, C, Fig. 2, was sealed to the upper end of the pipet;

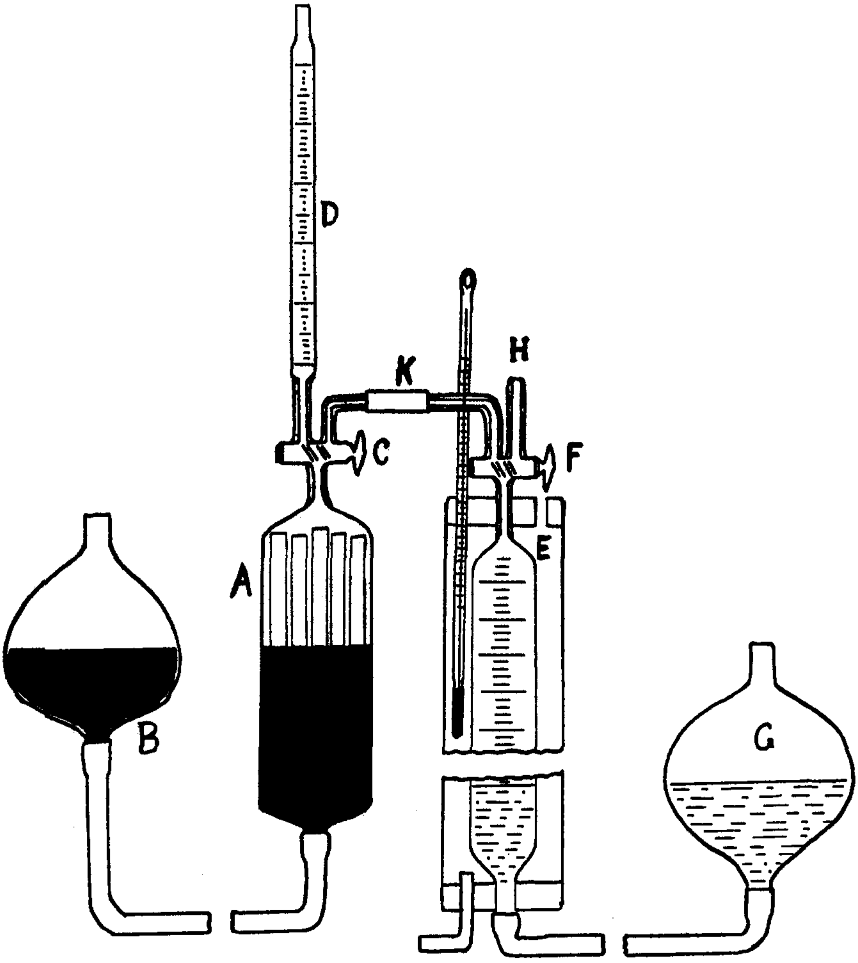

Fig. 2.

one arm led to the gas buret while to the other was sealed a 5 cc. pipet graduated in tenths. The gas buret was likewise provided with a three-way capillary stopcock, F, one arm being connected at K by pressure tubing with the corresponding arm of the absorption pipet, while the other, H, permitted the filling of the buret with air or with oxygen from the oxygen tank.

The carbon monoxide absorptions were made in the ordinary pipet of the Orsat apparatus.

Range of Concentrations.—A series of determinations was made for the purpose of finding out the range of concentration over which the rate of absorption was sufficiently rapid for the purpose in question. A weighed portion of pyrogallic acid was placed directly into the pipet, Fig. 1, followed by a few cubic centimeters of water to prevent caking when the alkali solution was added. Depreciation of the reagent through contact with the air was obviated by filling the pipet with illuminating gas before adding the alkali.

The results collected in Table I represent the average of a number of determinations for each solution carried out by passing 50.0 cc. portions of air back and forth over the reagent three times in four minutes.

TABLE I.

Time of Absorption of Oxygen by Sodium Pyrogallate.

	Composition of reagents in grams.			Time for complete absorption of oxygen from 50.0 cc. air.
	Pyrogallol.	NaOH.	H_2O.	
1	10.0	110.4	114.3	Incomplete in 15 min.
2	15.0	117.8	131.9	4 minutes
3	20.0	73.6	96.2	2 minutes
4	20.0	73.6	106.2	2 minutes
5	20.0	73.6	156.2	4 minutes
6	20.0	73.6	206.2	Incomplete in 1 hr.
7	10.0	92.0	105.2	4 minutes
8	10.0	92.0	155.4	4 minutes
9	10.0	92.0	205.2	4 minutes
10	10.0	92.0	255.2	7 minutes

Specific Absorption of Reagents.—Since complete and rapid absorption of the oxygen over a considerable range in concentration was secured, the determinations of the specific absorption of the reagent for various concentrations was next carried out. This was done in the pipet already described in Fig. 2. The reagent with predetermined proportions of alkali, acid, and water was always prepared in a small dropping funnel. The required weight of pyrogallic acid together with from one to four cubic centimeters of water—to prevent caking—was placed in the funnel and the air swept out with illuminating gas, by connecting the funnel in series with a Bunsen burner. The lighted burner disposed of the excess gas. Ten cubic centimeters of alkali from the stock solution were next run in from a pipet and the funnel stoppered. The stem of the funnel was also provided with a stopper to prevent the gas from being displaced by air. The mixing of the alkali and pyrogallol was always accompanied by a considerable rise in temperature, but this apparently had no deleterious effect upon the reagent.

After cooling, five cubic centimeters of the reagent were transferred to the graduated pipet of the absorption apparatus, care being exercised to prevent any contact whatsoever with the air. The absorptions were carried out with 1.5 cc. portions of the reagent measured into the pipet by means of the graduate. Oxygen in measured volumes was introduced through the gas buret and passed to and fro between the pipet and buret until the rate of absorption had dropped to one cubic centimeter per ten minutes. To have waited for complete exhaustion of the reagent would have made the determinations interminable, so this arbitrary ending of the reaction was chosen. For comparative purposes and for the purposes of this investigation the data so secured were quite sufficient. The time required for an absorption was about one and one-half hours. Between each determination the gas buret was detached from the pipet, the residual liquor run out through K, and the pipet cleaned and dried.

TABLE II.

Volume of Oxygen Absorbed by Sodium Pyrogallate.

	Pyrogallic acid (g.).	Water (g.).	Stock soln. NaOH (cc.).	Proportions by weight of absorbing constituents.			Oxygen absorbed by 1.5 cc. reagent (cc.).
				NaOH.	Pyrogallic acid.	Water.	
1.	1	+1	10.0	7.36	1.00	8.62	46.6
2.	1.5	+1	10.0	7.36	1.50	8.62	69.0
3.	2.0	+1	10.0	7.36	2.00	8.62	81.5
4.	2.5	+1	10.0	7.36	2.50	8.62	104.0
5.	3.0	+1	10.0	7.36	3.00	8.62	113.0
6.	5.0	+3	10.0	7.36	5.00	10.62	132.0
7.	7.0	+3	10.0	7.36	7.00	10.62	170.7
8.	10.0	+3	10.0	7.36	10.00	10.62	232.2
9.	10.0	+4	10.0	7.36	10.00	11.62	222.6
10.	12.0	+4	10.0	7.36	12.00	11.62	265.2

The densities of reagents No. 1 and No. 9 were determined at 20°/4 in an Ostwald-Sprengel pycnometer. Knowing the composition by weight of these reagents the density formed a ready and accurate means of determining the concentration of the constituents in the 1.5 cc. volume used.

Comparison with Potassium Pyrogallate.—Comparative determinations were made in the same apparatus using potassium pyrogallate instead of the sodium salt. 10 cc. of a solution of potassium hydroxide, made by dissolving 73.4 g. of stick alkali in 73.4 cc. of water were added to 10 g. of pyrogallic acid. 1.5 cc. of this solution absorbed 223 cc. of oxygen before the rate of absorption dropped to 1 cc. in 10 minutes. This is practically the same volume as that for sodium pyrogallate of the same concentration. But absorption of the oxygen from 50 cc. of air under conditions identical with those for sodium pyrogallate required from 6 to 10 minutes instead of from 2 to 4 minutes as with the sodium salt.

3.5 cc. of the reagent, as prepared above, were diluted with 1 cc. of water. 1.5 cc. of this solution absorbed 197 cc. of oxygen before the rate of absorption had dropped to 1 cc. in 10 minutes. Complete absorption in four minutes was also obtained, but this continued only until 60 cc. of oxygen had been absorbed.

The dropping off in the rate of absorption for solutions containing a high concentration of pyrogallol limits the use of potassium pyrogallate to solutions of relatively low specific absorption. Anderson found that the specific absorption with 15 g. of pyrogallol in 100 cc. of solution was almost equal to that with 20 g. per 100 cc. But with sodium pyrogallate there is no such dropping off in specific absorption, and reagents containing 50 g. of pyrogallol per 100 cc. of solution are perfectly practicable.

It was also considered desirable to determine in our apparatus the absorption of oxygen by the potassium pyrogallate reagent recommended by Anderson as being the best solution for use in the Hempel double pipet. 1.5 cc. of this reagent absorbed about 30 cc. of oxygen from the air before the absorption was incomplete in 4 minutes and about 70 cc. of 95% oxygen before the rate of absorption dropped to 1 cc. in ten minutes. In comparison, the sodium pyrogallate of reagent No. 9 absorbed 154 cc. of oxygen from the air before absorption was incomplete in four minutes, and 222.4 cc. before the rate fell below 1 cc. in ten minutes. The reagent proposed by us has, therefore, five times the specific absorption of that recommended by Anderson as being the best for potassium pyrogallate.

Volume of Oxygen Absorbed before Rate of Absorption Dropped to Four-minute Limit.—For practical purposes the value of a reagent for the absorption of a gas ceases when the rate of absorption has decreased below a certain value. In this work complete absorption of the oxygen from 50.0 cc. of air when absorbed in the simple pipet, Fig. 2, was chosen as the limit.

1.5 cubic centimeter portions of solution No. 9 were treated with successive 50.0 cc. volumes of air at 20°, the residual gas being run off after each absorption. This was continued until absorption failed to be complete in four minutes with two transfers of the gas back to the buret. The average of three closely agreeing results gave 180 cc. of oxygen absorbed. Three similar absorptions carried out by first absorbing 125 to 130 cc. of oxygen from the 95% sample and then completing the determinations with 50.0 cc. volumes of air gave 154, 155 and 154 cc. of oxygen absorbed before the rate dropped below the four-minute limit.

Similar determinations on 1.5 cc. portions of solution No. 1 gave an absorption of about 20 cc. before the four-minute limit was reached. The difference in the specific absorptions as found above for the same solution depending on the percentage of oxygen used, is, according to Hempel and Anderson,[1] the result of the deleterious effect of high temperature. With 95% oxygen the rise of temperature in the reagent was very marked indeed.

Rate of Absorption.—Two series of measurements of the rate of absorption of oxygen by the proposed reagent were made. The first consisted in observing the volume of oxygen absorbed by 1.5 cc. of the reagent in four minutes from successive 50.0 cc. portions of air together with the time required for complete absorption. The results for solution No. 9 are included here but they are typical of all. Only the last six observations are given, since all before these were identical with the 1st and 2nd.

50.0 cc. portion of air.	Vol. absorbed in 4 minutes. Cc.	Time for complete absorption of oxygen. Minutes.	50.0 cc. portion of air.	Vol. absorbed in 4 minutes. Cc.	Time for complete absorption of oxygen. Minutes.
1st	10.4	4	4th	9.2	11
2nd	10.4	4	5th	7.6	18
3rd	10.0	6	6th	4.0	50

The time necessary for complete absorption increased very rapidly. This is of special significance to the gas analyst. As soon as the rate of absorption of alkaline pyrogallate begins to drop off the reagent should be replaced by fresh solution, thus obviating the danger from incomplete absorption in a reasonable interval of time.

The second series of observations was made on the falling off in the rate of absorption when complete exhaustion of the reagent was being approached. The results for three solutions are plotted in Fig. 3. The ordinates represent the volume of oxygen absorbed by 1.5 cc. of the reagent when a considerable excess of 95% gas was present, while the abscissae indicate the time intervals in minutes corresponding to the volume reading. These observations were taken with the special apparatus already described and were accompanied by frequent passing back and forth of the gas between the pipet and the buret. Curve A is for solution No. 8 and requires to have 90.0 cc. added to it, since observations were not taken until the curve began to leave the vertical. Similarly Curve B, representing solution No. 6, must have 20 cc. added to it, while Curve C is that for solution No. 2 and represents the total volume of oxygen absorbed. The curves end when the rate of absorption had dropped to that of 1 cc. in ten minutes. The vertical portion of the curves, representing 210 cc. for solution No. 7, 120 cc. for No. 6 and 50 cc. for No. 2, indicates the volume of oxygen that might be absorbed by 1.5 cc. of

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[1] Anderson, *Loc. cit.*

the respective reagents before exhaustion made further use of the reagent in gas analysis doubtful. The three curves are practically parallel and have the general direction of curves representing a reaction following the law of mass action.

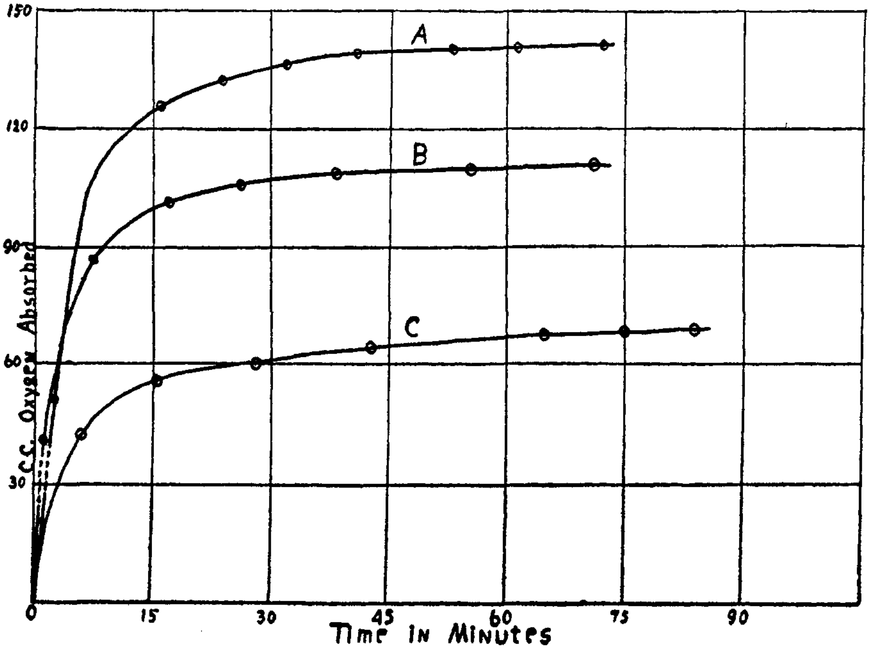

Fig. 3.

Temperature Coefficient.—A series of determinations was carried out to establish the relationship of temperature to the rate of absorption. The time required by solution No. 9 to completely absorb the oxygen from equal volumes of air at different temperatures was taken as the basis for comparison. The absorption pipet was surrounded by a bath kept at the desired temperature and 50.0 cc. portions of air were run in from the gas buret, the time for complete absorption being noted. The gas was run back and forth twice in each case, excepting at the higher temperatures where absorption was complete without doing so. At temperatures above 40.0° absorption was so rapid that the time measurements could not be made with any degree of accuracy. The series, however, follows in general the law of Ostwald that the speed of a reaction doubles for each 10° rise in temperature. It also disposes of the contention[1] that alkaline pyrogallate is very much less active at a temperature of 7° than at 15°.

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[1] Hempel, "Gas Analysis," 1916, p. 149.

Table III.—Temperature Coefficient.

Temperature centigrade	0.0°	10.0°	15.0°	20.0°	25.0°	30.0°	40.0°	45.0°
Time for complete absorption, minutes	8–10	8	6	4–5	3	2	1	1

Relation of Oxygen Absorbed to Amount of Pyrogallol.—Table II contains the results of determinations made with ten different proportions of acid, alkali and water, ranging in concentration from a reagent containing but 10 g. of pyrogallol in 110 cc. of solution to a reagent from which sodium pyrogallate separated on cooling. It will be observed that the absolute alkali content was not varied throughout the series, that the water content was changed twice while the pyrogallic acid content was increased for each determination. At high concentration it was found necessary to increase the water content in order to prevent the crystallization of sodium pyrogallate and the consequent clogging of the apparatus. The composition of solutions No. 1 and No. 9 in respect to pyrogallol alkali and water may easily be calculated from the weight of these constituents used and the determined densities. The density of any of the intermediate solutions of Table II lies between that of 1.490 for No. 1 and 1.405 for No. 9. A slight increase in volume occurs as the pyrogallic acid content of a water solution increases so that direct comparison between the 1.5 cc. portions of the reagents used and the volumes of oxygen absorbed does not give the exact relation existing between pyrogallic acid and oxygen absorbed. But the results given in Table II indicate clearly that the absorption capacity is roughly directly proportional to the pyrogallic acid content.

Another cause of irregularity in this proportion was occasioned by the variable conditions under which the absorption of oxygen took place. A rapid rise in temperature always occurred and this rise was more marked for the solutions containing the higher proportions of pyrogallol. Moreover, since the gas used contained only 95% oxygen the residual gas contained varying proportions of oxygen for each determination. The residual gas containing the least proportion of oxygen would reach the chosen limit of absorption first. Replacing the residual gas with 60 cc. of 95% oxygen gave an increased absorption of 10 cc. to reagent No. 9 before the limit was reached.

Solution No. 10 was very viscous and on standing sodium pyrogallate crystallized out. For this reason further experimentation was carried out with the less concentrated solution No. 9.

The volume of oxygen absorbed by each gram molecule of $C_6H_6O_3$ present in reagents No. 1 and No. 9 was calculated from the known weight of alkali, acid and water taken and the determined densities. Calculations based on the results given in Table II gave an absorption of 63.1 g. of oxygen for each gram molecule of $C_6H_6O_3$ present in reagent No. 9

and 59.1 g. for reagent No. 1. The result for the former was based on the complete exhaustion of the reagent while for the latter only to when the rate of absorption had become 1 cc. in ten minutes. Berthelot[1] found that for complete absorption with the sodium pyrogallate and potassium pyrogallate reagents he used, 48.5 g. of oxygen were absorbed per gram molecule of $C_6H_6O_3$, or three atoms of oxygen per molecule of $C_6H_6O_3$. Our results are from 30% to 40% higher than this and apparently do not follow so simple a proportion. Calculating the intermediate reagents of Table II on the basis of a density of 1.49 or 1.41 (between which limits the densities of the solutions must lie) gave results in every case much higher than those of Berthelot. With ammonium pyrogallate Berthelot obtained 66.4 g. of oxygen absorbed per gram molecule of $C_6H_6O_3$. Considering the variety of the oxidation products formed it seems unlikely that a simple relationship would exist between the oxygen absorbed and the $C_6H_6O_3$ present, but that this relation would be a function of several variables such as temperature, viscosity, nature of absorbing vessel, relative concentration of oxygen, acid and alkali, etc. This view is consonant with the experimental evidence,[2] for by changing the conditions of oxidation for the same reagent carbon monoxide may or may not be formed, indicating clearly a marked change in the nature of the oxidation products. Moreover, it has been frequently observed that the temperature at which absorption takes place and the percentage of oxygen in the gas reacting affects the amount of oxygen absorbed.

De Forcrand[3] was not able to prepare pure mono and disodium pyrogallate from the reaction between sodium hydroxide and pyrogallic acid in aqueous solution. He always obtained a product containing a considerable proportion of resinous matter, and this when the reaction was carried out in an atmosphere of hydrogen. Trisodium pyrogallate on the other hand separated pure. One might expect, therefore, that with an excess of alkali present the absorption of oxygen would be more uniform, but Berthelot found that so long as he did not reduce the molecular proportions of alkali and pyrogallol below that of 1 : 1 the amount of oxygen absorbed remained the same as when the proportion was 3 : 1.

The Formation of Carbon Monoxide.—Throughout the course of this research numerous determinations were made for the detection of carbon monoxide in the residual gas after complete exhaustion of the reagents. The excess oxygen from the residual gas was absorbed in an Orsat pipet containing sodium pyrogallate reagent No. 5, Table II. After the complete absorption of the oxygen as indicated by no further change in volume on remaining in contact with the reagent for some time the gas was passed

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[1] Berthelot, *Loc. cit.*

[2] Clowes, *Loc. cit.* This paper, p. 1699.

[3] De Forcrand, *Compt. rend.*, 115, 46, 48 (1892).

into another Orsat pipet containing freshly prepared ammoniacal cuprous chloride. Two such pipets were prepared, but as carbon monoxide was only found in one instance the second pipet was quite superfluous. To remove ammonia the gas was finally passed into a pipet containing a dilute solution of sulfuric acid. In order to be sure that the cuprous chloride pipet was functioning properly, air containing carbon monoxide was passed through the system of pipets in the same order as was the residual gas. A decrease in volume corresponding to the known amount of carbon monoxide in the gaseous mixture occurred in the cuprous chloride pipets. This check was run twice during the course of the analyses and once at the close.

No measurable quantity of carbon monoxide was detected in any of the reagents included in Table II. Special attention was given the proposed reagent No. 9, exhaustion being brought about under the varying conditions likely to occur in the application of this reagent for use in gas analysis. Speedy exhaustion with 95% oxygen and consequent high temperature of reaction, slow successive additions of oxygen without rise of temperature and exhaustion by successive volumes of air, all alike gave no appreciable absorption in freshly prepared cuprous chloride solution. One sample of gas was kept in contact with the reagent for a week after exhaustion was about complete, but no carbon monoxide was evolved. The potassium pyrogallate reagent, as recommended by Anderson, also failed to evolve any appreciable quantity of this gas. Experiments were next carried out with the sodium hydroxide reagent of Lewes. No generation of carbon monoxide was obtained when successive volumes of air were employed, but when 95% oxygen was used over 3.0 cc. of carbon monoxide was formed. This is in agreement with Clowes, who found that no carbon monoxide was formed when the gas contained less than 28% oxygen, but above that percentage the quantity became appreciable and increased as the alkali content was diminished. Evidently the alkali content used in the series of Table II was sufficient to prevent the formation of this objectionable gas in appreciable amounts. The non-formation of carbon monoxide was indirectly corroborated for the above reagents by the complete absorption of the oxygen from the air. Many determinations on 50.0 cc. volumes of air were made when the rate of absorption was under investigation. If carbon monoxide had been evolved in appreciable amounts it would have been indicated as incomplete absorption. Such did not occur in any one of the reagents listed in Table II. The volume of oxygen absorbed always agreed with that corresponding to the percentage composition in the atmosphere.

Concerning the conditions favoring the formation of carbon monoxide it may be pointed out that solution No. 9 contains only 2.3 molecules of sodium hydroxide per molecule of pyrogallol while 3 molecules would be necessary for complete neutralization. The absence of carbon monoxide does not, therefore, appear to be dependent upon having an excess of alkali present as Clowes[1] contends.

Rate of Absorption in Various Pipets.—It was deemed desirable to try the proposed reagent in several different pipets. The table below gives briefly the results of these determinations.

TABLE IV.

Time of complete absorption of oxygen from 100.0 cc. air.

Reagent.	Hempel pipet.	Richards pipet.	Orsat pipet.	New pipet.
No. 9..........	10–15 min.	10–15 min.	4–6 min.	4–6 min.
No. 5..........	.....	.....	4–6 min.	4–6 min.

Complete absorption was obtained with from three to four transfers for the Orsat and the New pipet while with the Richards and the Hempel pipets double as many transfers combined with continual shaking failed to obtain complete absorption in less than ten minutes. Rhodes[2] found that nine minutes accompanied by nine transfers back and forth were necessary to obtain complete absorption of the oxygen from 100.0 cc. sample of air using the Orsat pipet and potassium pyrogallate.

It is hard to understand why the Hempel pipet should be longer used for any but very special work. It is difficult to fill with any reagent and especially so if the reagent is somewhat viscous. The long bent capillary is a source of weakness in structure and of irregularity in use. The enormous friction of the liquid in the capillary requires, even with comparatively fluid reagents, a considerable excess of pressure to overcome and prohibits entirely the use of many concentrated reagents because of their viscosity. Moreover the pipet requires a special and expensive stand while shaking has to be resorted to in order to obtain efficient absorption. Should the pipet be broken anywhere only an experienced glass blower can repair it.

The Richards pipet is much simpler but is objectionable because of the necessity for shaking. Moreover having the bulbs above the stoppers with a comparatively long stem extending down to the bottom of the bottles gives an objectionable hydrostatic pressure when the apparatus is in use. The new pipet combines the good points of the Richards model with those of the Orsat type.

Choice of Reagents for Gas Analysis.—Table V gives the relative absorption capacity of 150 cc. of solutions No. 1 and No. 9 and the best KOH reagent as proposed by Anderson.

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[1] Clowes, *J. Soc. Chem. Ind.*, 15, 170 (1896).

[2] Dennis, "Gas Analysis," p. 82.

TABLE V.

Volume of oxygen absorbed by 150 cc. of reagent before reaching four-minute limit.

Reagent	No. 1	No. 9	Best KOH reagent
Volume of oxygen absorbed, liters	2.2	15.3	3.0

Such a reagent as No. 9 is, therefore, five times as efficient an absorbing agent for oxygen as the best potassium pyrogallate solution.

Reagent No. 9 is somewhat viscous and in pipets provided with capillaries less than 1.5 mm. in internal bore, difficulty may be found in driving over the last portions of gas. With larger capillaries this reagent causes no difficulty whatsoever. Should a particular pipet have a small-bore capillary it would be advisable to use a more fluid reagent, such as No. 3 or No. 5.

Should difficulty in observing the position of the meniscus in the capillary be encountered because of the highly colored and viscous nature of the oxidation products, the running over of a very little water from the gas buret readily clears the tube for the final reading.

Such a reagent as No. 9 should replace in technical gas analysis the use of the more expensive and less efficient potassium solution. The saving of time and trouble in using a reagent lasting five times as long should alone decide in its favor. For use in a laboratory course in gas analysis, where only a comparatively small volume of oxygen is to be absorbed, reagent No. 3 would be found eminently satisfactory. Reagents No. 3 and No. 9 have been used in the laboratory classes of Ohio State and have proved quite satisfactory in every respect. No deterioration in the reagents was observed over a period of three months.

The Use of Ammonium and Barium Pyrogallate.—A reagent prepared by dissolving 10.0 g. of pyrogallic acid in 10.0 cc. of 29% ammonium hydroxide precipitated on cooling a white crystalline substance soluble on heating but again separating on cooling. On adding 10.0 cc. more of the ammonium hydroxide the precipitate failed to dissolve. Evidently the trihydroxy benzene compound with ammonia is much less soluble than those of sodium hydroxide and potassium hydroxide. A second solution prepared by dissolving 10.0 g. of pyrogallol in 10.0 cc. of water and adding 160 cc. of 29% ammonium hydroxide gave complete absorption of the oxygen from 50.0 cc. of air in five minutes. Apparently, if occasion required, ammonium pyrogallate might be used for absorbing oxygen.

The insoluble barium compound of trihydroxy benzene made it impracticable for use in any but a very dilute solution. Moreover, the oxygen compound formed appeared to be insoluble and tended to clog the capillary connecting tube of the absorption apparatus while at the same time the rate of absorption was very low.

Summary.

(1) A new double pipet for liquid reagents in gas analysis is described.

(2) The use of sodium pyrogallate as a reagent for the determination of oxygen in gases is proposed. Complete absorption in four minutes was secured from a number of solutions containing pyrogallol, sodium hydroxide and water in varying proportions. No carbon monoxide was detected in using the proposed reagent under varying conditions and the specific absorption of the best practicable solution was found to be five times that of the corresponding best solution for potassium pyrogallate.

(3) The total volume of oxygen absorbed was found to be in excess of the proportion of 3 atoms of oxygen for each molecule of pyrogallol.

(4) Ammonium and barium pyrogallate were found to be impracticable for general use in gas analysis.

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[CONTRIBUTION FROM THE KENTUCKY AGRICULTURAL EXPERIMENT STATION.]

THE ESTIMATION OF THIOSULFATE SULFUR IN LIME-SULFUR SOLUTIONS BY IODINE TITRATION.

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The question of the accuracy of the so-called "Iodine Methods" for the estimation of thiosulfates and polysulfids in commercial lime-sulfur solutions has vexed agricultural chemists for some years past. Recently one of us[1] published a paper in which he proved that the substance titrated with iodine after removing polysulfids, actually was thiosulfate, by means of a process in which tetrathionate was reconverted to thiosulfate and estimated.

Roark[2] stated that in the iodine titration there is reason to believe that iodine may cause an increased formation of sulfate, thus introducing an error.

We have undertaken to test the accuracy of the iodine method for thiosulfate in another fashion, namely, by converting the tetrathionate formed to sulfate and comparing this value with the titration figure.

Experimental.

The following experiments were conducted with two objects in mind: to ascertain whether the oxidation of thiosulfate or tetrathionate to sulfate occurs sufficiently rapidly and in such quantity, particularly under poor working conditions, as to cause serious analytical errors; and to learn as much as possible about the chemistry of the lime-sulfur titration after the removal of polysulfid sulfur.

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[1] S. D. Averitt, *J. Ind. Eng. Chem.*, 8, 623 (1916).

[2] *J. Assoc. Off. Agr. Chem.*, 1, 65.