Para cresol absorbs bromine much more slowly than either of the other cresols. Under similar experimental conditions, $4\frac{1}{2}$ hours' standing in contact with free bromine results in absorption of only 95.73 per cent. of the theoretical quantity (Exps. 1, 2, and 3). If concentration of free bromine is increased and the usual quantity of HCl decreased one-half, the bromine in combination exceeds the amount necessary for the formation of a dibrom-*p*-cresol brom or tribromcresol compound and 18 hours' standing does not result in sufficient decomposition even though the quantity of KI is doubled (Exps. 4, 5, 6, 7, 8 and 9).

However, an increase in both HCl and KI results in a most pronounced reversal¹ which is due to the decomposition of dibrom-*p*-cresol brom into dibrom-*p*-cresol (Exps. 10 and 11).

Here again the result is directly dependent upon conditions and previous knowledge is necessary on part of the operator.

Now when iodine reacts with *p*-cresol in presence of the condensing agent, sodium acetate, diiodo-*p*-cresol is formed in theoretical quantity if sufficient time is allowed for reaction to complete itself.

This reaction is made the basis of a method for the determination of *p*-cresol (Exps. 12, 13, 14, 15 and 16). The procedure is exactly the same as that given under *o*-cresol.

SUMMARY.

1. Usual bromine methods for determination of cresol depend upon fixed conditions presupposing a previous knowledge on the part of the operator, and while they may be of service they do not satisfy the demand for a desirable method.

2. Tribrom-*o*- and *p*-cresol brom compounds can not be formed in a manner analogous to the production of 2,4,6-tribrom phenol brom. Dibromcresol brom compounds are formed and finally tribromphenol brom; however, *o*- and *p*-cresols can not be determined volumetrically by a conversion into these compounds.

3. Meta cresol is determined by a conversion into tribrom-*m*-cresol.

4. Ortho and para cresols form diiodo compounds, and this reaction is made the basis of a method for their determination.

5. Meta cresol does not yield diiodo compounds under the same conditions; hence, cresol U. S. P. or any mixture containing *m*-cresol can not be determined by a volumetric iodine method.

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THE ACCURATE VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID IN PHOSPHATE ROCK.

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The method of determining the phosphoric acid content of phosphate rock here described is a modification of Pemberton's caustic alkali titration, which

has the great advantage of being quicker than other volumetric or gravimetric methods. The difficulty experienced in the use of the Pemberton method has been invariably a low result compared with that obtained by the standard method of weighing the phosphoric acid as magnesium pyrophosphate. After close observation of the successive operations whereby the yellow precipitate is dissolved in an excess of standard alkali and this excess titrated after addition of a few drops of phenolphthalein, it was noticed that the final end point was considerably delayed, and this was the more marked the greater the amount of phosphoric acid present or the larger the aliquot parts taken.

In the belief that if this behavior of the indicator toward phosphoric acid could be overcome the method would be very accurate, the suggestion of Sutton² was adopted, namely, to precipitate out the phosphoric acid with barium chloride in excess before titrating the excess of alkali. The results stated below show how the method is improved by this modification.

In the first place low results being obtained in dealing with phosphate rocks by standardizing the alkali solution against microcosmic salt in the old way, it was thought possible that the other salts in the rock solution interfered with the titration. A rock solution whose phosphoric acid content was accurately determined gravimetrically was taken as the standard. The average of four results (32.69, 32.82, 32.88 and 32.93) obtained by using different aliquot² parts of a 2 gram solution was found to be 32.83 per cent. P_2O_5 . Double precipitations were made after weighing the first precipitate, any calcium sulfate or silica being removed by its solution in sulfuric acid with alcohol. The second weights were only 0.1 to 0.3 mg. less, so that this correction could be disregarded.

The next step was to take an aliquot part, preferably 0.1 gram, add 20 cc. of strong ammonia (sp. gr. 0.90), make acid with 1:1 nitric acid, and add slowly 25 cc. of warm molybdate solution (about 40° C.). The temperature of formation of the yellow precipitate here is most important, the limits being 45° to 55° C. After shaking for five minutes the precipitate is let stand till cool, then filtered through a 9 cm. No. 590 S. & S. paper and washed, once with a 2 per cent. nitric acid solution and then with a 2 per cent. potassium nitrate solution till the washings cease to redden blue litmus. Paper and precipitate are then transferred to the original flask and dissolved in an excess of standard alkali; diluted slightly with cold water; three drops of phenolphthalein solution are added and one drop of methyl orange (to give a sharper end point). Excess of alkali is then titrated with standard acid, either nitric or hydrochloric. Next, about 8 cc. excess of alkali are again added and 10 cc. of a 10 per cent. solution of neutral $BaCl_2$, which is usually sufficient to precipitate all the phosphate, the molybdate, and also any carbonate. The important feature is the elimination of the phosphate. After again titrating the excess of alkali the two readings show 32.6 cc. and 33.1 cc. The results of several

¹ "Zur Quantitativen Bestimmung des Phenols und Parakresols in Gemischen derselben und ihre Anwendung auf den Harn," *Pharm. Zentralhalle*, 1911, 1288.

² *Volumetric Analysis*, 9th Ed., p. 113.

² Pipettes used were standardized to the flask.

determinations gave this difference of 0.5 cc. Dividing the amount of P_2O_5 present, 0.03283 gram, by 32.6 and by 33.1 gives two values per cubic centimeter, namely, 0.001007 and 0.000992 gram P_2O_5 , a difference of 1.5 per cent.

Again, taking the value per cubic centimeter as 0.001007 gram P_2O_5 and multiplying this by 33.1, the correct number of cubic centimeters required for 0.1 gram of the standard rock solution, the percentage of P_2O_5 found is 33.33, which is 0.51 per cent. too high in P_2O_5 , or a 1.5 per cent. actual error corrected by the use of $BaCl_2$.

A solution of microcosmic salt was then prepared by dissolving 2.088 grams in some water containing 40 cc. 1 : 1 nitric acid and diluting to 500 cc. Several portions of 25 cc., equivalent theoretically to 0.03546 gram P_2O_5 , were taken and their content, determined gravimetrically, was found to be 0.03575 gram P_2O_5 . Exactly the same value was found by using 50 cc. of solution. A volumetric determination was now made on 25 cc., which required 35.5 cc. of alkali, barium chloride not being used. Excess of alkali was again added with 10 cc. of $BaCl_2$ and the excess titrated. The result of the second titration was 36.0 cc. Multiplying the value of the alkali solution previously obtained against the standard phosphate rock we have $36.0 \times 0.000992 = 0.03571$ gram P_2O_5 , which is the exact amount taken for analysis. If the first burette reading is used we have $35.5 \times 0.000992 = 0.03522$ gram P_2O_5 , a difference of 0.5 per cent. of P_2O_5 , or 1.5 per cent. actual error, as before.

Although this calculation proves that microcosmic salt can be safely used in standardizing the alkali solution, still, in order to show more strongly that such salts as calcium nitrate have no effect on the titration figure, sufficient pure dry calcium carbonate was added to the nitric acid solution of the microcosmic salt to form tricalcium phosphate with all the phosphoric acid. The same aliquot portions were taken, precipitated, and titrated with these results: without $BaCl_2$, 35.5 cc.; after addition of $BaCl_2$, 36.0 cc. These check the results first obtained.

The value of the alkali solution having in this way been fixed very accurately, analyses of a series of eight phosphate rocks (from different localities in order that all probable variations might occur in the composition of the rock solution) were made in the regular way by both volumetric and gravimetric methods. Two grams of the rock powder were put with a little water in a small covered casserole and digested on the steam bath with 40 cc. of 1 : 1 nitric acid for 20 minutes or more. The filtered solution

Volumetric, per cent.	Gravimetric, per cent.	Differences.
31.68	31.70	-0.02
25.42	25.74	-0.32
31.79	31.99	-0.20
14.40	14.34	+0.06
24.83	24.67	+0.16
20.66	20.42	+0.24
24.43	24.49	-0.06
37.82	37.93	-0.11

Sum, -0.25

Average difference = 0.03 per cent.

was made up to 200 cc., a portion amounting exactly to 0.1 gram being taken for the volumetric and 0.5 gram for the gravimetric determination. In the preceding table will be found the results of single determinations.

Examination was next made of the insoluble residues. Four of these were combined and the papers were ashed in a large platinum crucible and fused with sodium carbonate. Silica was removed by evaporation of the acidified solution in a porcelain dish, the residue taken up with hot 1 : 1 nitric acid, and test made for P_2O_5 . Only a trace was found. The papers of the second four were ashed, the silica volatilized with HF and H_2SO_4 , the HF being practically all expelled by repeated evaporation on the steam bath. After oxidation with HNO_3 , filtration, addition of ammonia and about 10 grams of NH_4NO_3 , the P_2O_5 found after dividing by 8 was 0.05 per cent. Several other tests have been made of residues insoluble in hot dilute nitric acid and only once was as much as 0.10 per cent. found, the usual result being no more than a trace.

The curve below shows the effect of $BaCl_2$ on the titration when increasing amounts of phosphate solution are used.

These are the actual percentages:

Portions (gram).....	0.04	0.100	0.150	0.200	0.250
With $BaCl_2$	33.02 ¹	32.84	32.84	32.84	32.84
Without $BaCl_2$	32.50	32.34	32.14	32.14	32.01

The following results compare the two methods just described, the old method of weighing the yellow precipitate direct, and Blair's method² of reducing the molybdic acid followed by titration with $KMnO_4$.

¹ Single determination. About 0.2 per cent. high. See curve.

² *Analysis of Iron*, 6th Ed., p. 92.

The factor used for P_2O_5 in the ammonium phosphomolybdate was 0.03782. The yellow precipitate was washed well with 2 per cent. nitric acid and dried in a porcelain Gooch crucible at $125^\circ C.$ to constant weight.

Weighed as ammonium phosphomolybdate.

	Gram.	Per cent. P_2O_5 .
Portion taken.....	0.250	32.66
Fresh sample.....	0.500	32.70

REDUCTION METHOD.

Portion taken.	Gram.	Per cent. P_2O_5 .
	0.025	32.94
	0.050	32.94
	0.050	32.51
	0.050	32.51

Blair's reduction method¹ gives accurate results when extreme care is taken to wash the yellow precipitate entirely free from the molybdate precipitant. Inasmuch as the portion taken here is very small, any slight difference in cubic centimeters of $KMnO_4$ used is multiplied by a large factor four times the factor for the caustic alkali titration. A difference of 0.35 cc. on a 0.05 gram portion gives a difference of 0.40 per cent. in P_2O_5 content.

It is important to bear in mind that the barium phosphate precipitate hydrolyzes rather rapidly, so that the titration should be finished in 15 minutes. If let stand an hour or more the pink color returns to the indicator. The reaction is probably like this:

$$\ddot{B}a_2(\ddot{H}P\ddot{O}_4)_2 + 2\ddot{H}O\ddot{H} \rightleftharpoons \ddot{B}a(O\ddot{H})_2 + \ddot{B}a(\ddot{H}_2P\ddot{O}_4)_2$$

The phenolphthalein is then affected by the barium hydrate. With precipitates containing more than 0.035 gram P_2O_5 it requires more care in order to strike the true end point. The plan followed above was to close the flask and shake it violently a few minutes, keeping it cold. With smaller precipitates there is no difficulty.

The least amount of molybdate solution necessary to completely precipitate 0.030 gram of P_2O_5 was found to be 20 cc. One cc. of this solution contains 0.048 gram MoO_3 and will precipitate, theoretically, 0.002 gram of P_2O_5 . When only 15 cc. were used on a 0.1 gram portion of the standard rock solution 25.5 cc. of alkali were required for solution of the phosphomolybdate. On adding 5 cc. more of molybdate solution to the filtrate and titrating the precipitate, 7.2 cc. more of alkali were used, a total of 32.7 cc., whereas the correct figure was 33.1 cc. To insure a noticeable excess 25 cc. of the molybdate solution are added.

By allowing 20 minutes for solution of the rock the time for a single determination will average not more than one hour.

As a final test, the amount of error due to expansion of the standard solutions was fixed. A standard alkali solution was transferred to a 100 cc. flask up to the mark and its temperature taken. The solution was then heated exactly 10° and the rise in volume noted on the neck of the flask. This increment was then withdrawn by a pipette and its value found by running in from a burette enough to reach the top mark again. This difference due to $10^\circ C.$ was found to be 0.2 cc., an error altogether negligible.

¹ Factor $MoO_3 : Fe$, 0.85714.

In conclusion, it is seen that the greatest accuracy possible by the gravimetric method is 0.50 per cent., or 0.15 per cent. of the P_2O_5 content, and it varies to 0.75 per cent., or 0.25 per cent. P_2O_5 . The accuracy of the caustic alkali method is a trifle over 1 per cent. actual error, or a difference of 0.30 per cent. P_2O_5 in the rock.

STANDARD SOLUTIONS.

Caustic Alkali.—31 grams of the C. P. soda sticks dissolved in water and diluted to 2 liters: 1 cc. equals about 0.001 gram P_2O_5 . The small amount of CO_2 present, about 0.12 per cent., is negligible.

Nitric Acid.—Practically a 2 per cent. solution which is diluted till 1 cc. equals 1 cc. alkali solution.

Phenolphthalein.—A 1 per cent. alcoholic solution.

Methyl Orange.—A 0.1 per cent. solution.

Molybdate Solution.—100 grams MoO_3 , 144 cc. NH_4OH (sp. gr. 0.90), and 271 cc. H_2O ; 489 cc. HNO_3 (sp. gr. 1.42) and 1.148 cc. H_2O .

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THE DETERMINATION OF TOTAL MANGANESE IN SOILS.

By ROSS A. GORTNER AND CLAYTON O. ROST.

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INTRODUCTION.

It is a well-known fact that the gravimetric estimation of small quantities of manganese, such as occur in rocks or soils, is highly inaccurate even when great care is used. The inaccuracy may be caused by a number of factors, including incomplete separation from the iron and aluminium, incomplete precipitation, and contamination of the precipitate by other substances. These errors, because of the small amounts of manganese present, can not be depended on to balance each other.¹ The usual method which is now employed is to determine the manganese colorimetrically after oxidation to permanganic acid. Various means of effecting this oxidation have been employed. The oldest method is the oxidation of the manganese in nitric acid solution by the addition of lead peroxide.² This material proved unsatisfactory owing to the necessity for the removal of the excess of the lead peroxide, which settled very slowly.

Acting on the suggestion of Marshall,³ Walters⁴ substituted ammonium persulfate for the lead peroxide. All of Walters' determinations were made either on steel, pig irons or blast furnace cinders. This method was later adopted by Hillebrand⁵ and Washington⁶ for the determination of total manganese in rocks.

Essentially the method consists in decomposing the rock powder in a platinum basin by means of hydrofluoric and sulfuric acids, expelling the excess of hydrofluoric acid by repeated evaporation with small amounts of sulfuric acid, evaporating almost to dryness, diluting with 1 : 1 nitric acid, filtering, and

¹ See Hillebrand, *Bull.* **422**, 116, U. S. Geol. Survey.

² Pichard, *C. R. acad. sci.*, Dec. 30, 1872.

³ Marshall, *Chem. News*, **83**, 76 (1901).

⁴ Walters, *Ibid.*, **84**, 239 (1901).

⁵ *Loc. cit.*

⁶ Washington, "The Chemical Analysis of Rocks," Wiley and Sons, N. Y., 1910.