as are decomposed by the phosphoric acid and potassium iodide reaction can be analyzed with rapidity and the results are accurate. Manganates, permanganates and precipitated oxides fall into this class. The method finds application also to the more easily decomposed pyrolusite ores. With some pyrolusite samples, especially those containing a large amount of iron oxide, considerable care must be taken to insure a complete reaction. For such samples the method is not recommended.

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TITRATION OF MAGNESIUM.

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This paper deals with the titration of magnesium as applied to water analysis. Two methods are available, one consisting in the precipitation of magnesium as magnesium-ammonium phosphate and titration with 0.10 *N* HCl after filtration; the other in the precipitation as magnesium-ammonium arsenate and titration of the iodine liberated after treating with acid and KI.

Stolba[1] suggested that magnesium be determined by titrating the precipitate of magnesium-ammonium phosphate with HCl, using methyl orange as indicator, assuming that one mol of $MgNH_4PO_4$ requires 2 mols of acid. Mead[2] speaks of the accuracy of the method, but points out that nothing is gained by using it owing to the tediousness of washing with alcohol. Cohen,[3] however, besides mentioning the difficulty of washing, also reports that it is impossible to obtain concordant results.

After working on this method for some time, we overcame the difficulty of washing the precipitate by filtering with aid of suction, using a "Black Ribbon" filter with a protected cone. Concordant results, however, were not always obtained when the precipitate produced by the usual procedure was titrated, *i. e.*, when the precipitation was made directly in the solution from which the calcium had been removed. Since extreme care was taken to remove all the free ammonia, we concluded that the errors came from impurities in the precipitate. The success of the method depends entirely upon the complete precipitation of the magnesium as pure $MgNH_4PO_4$. The conditions for such a precipitation have been pointed out by Gooch and Austin,[4] and by Neubauer.[5] These are, that the solution be neutral and as free as possible from ammonium salts, and that the

[1] *Chem. Centr.*, **1866**, 728.

[2] THIS JOURNAL, **21**, 746 (1899).

[3] *Ibid.*, **29**, 1464 (1907).

[4] *Am. J. Sci.*, [4] **7**, 187 (1899).

[5] *Z. angew. Chem.*, **9**, 839 (1896).

ammonia be added after the phosphate solution has been added. The first and last precautions were carefully observed, but no special effort was made to see that the second one was fulfilled.

Now the standard acid added reacts with the PO_4^{---} present in the precipitate forming $H_2PO_4^-$. If some of the magnesium is present as $Mg_3(PO_4)_2$ or as $Mg(NH_4)_4(PO_4)_2$ the results in the former case will be too low and in the other too high. The tendency for the formation of the two compounds should be eliminated. The former can be avoided by keeping the solution just alkaline while adding the precipitant, and the latter by avoiding an excess of ammonium salts.

In water analysis all but the latter condition is easily avoided. Ammonium salts do accumulate in the solution and to such an extent as to contaminate the precipitate. These salts must be removed by evaporation and ignition before the titration of magnesium can be made successful. This operation required time and in ordinary routine work is not always resorted to. If the precipitate is to be titrated, however, this step is necessary. A number of waters were analyzed for magnesium by the titration method and by the pyrophosphate method both with and without previous evaporation and ignition with the following results:

PARTS PER MILLION OF MAGNESIUM.

Ammonium salts absent.		Ammonium salts present.	
Pyrophosphate.	Titration.	Pyrophosphate.	Titration.
25.00	24.00	26.00	24.90
33.29	30.20	35.60	34.80
40.19	40.26	42.14	43.00
36.76	36.80	40.20	38.40
51.92	51.85	53.64	52.15
60.87	60.80	62.48	63.24
75.86	75.81	77.98	76.74
74.92	74.79	76.83	75.80

In every case where the ammonium salts were not removed too high results were obtained by the titration method. Strict attention must be given to details in obtaining a pure magnesium precipitate if it is to be titrated. Evaporation and expelling of ammonium salts requires time, and so much so that this one operation defeats the end for which the method was devised, namely a hastening of the magnesium determination. Accurate results can, however, be secured by using it, for, in comparing the two methods by using pure salts concordant results were obtained each time. For reference we give the procedure which we found to give the best results.

The solution containing magnesium is evaporated to dryness and the ammonium salts are carefully removed by heating. The residue is taken up in a small volume of water, acidified with HCl and, after filtering, made slightly alkaline with ammonium hydroxide. Microcosmic salt solution is slowly added to the cold solution with stirring, and after the precipitate has formed, a volume of ammonium hydroxide equal to one-third of the total volume added, and the solution allowed to stand 18 hours. The precipitate is filtered off on a "Black Ribbon" filter with the aid of suction and washed with 25 cc. of alcohol. The precipitate is washed with hot water from the filter into the beaker in which the precipitation took place. A known excess of 0.10 *N* HCl is added and the excess titrated back with 0.10 *N* NaOH, using methyl orange as indicator.

The second method applicable to water analysis was suggested by Meade[1] and later revised by Cohen.[2] The latter reports favorably on the method provided starch solution is not used in the titration. This method consists in making the concentrated and acid solution decidedly alkaline with ammonia, and precipitating the magnesium with sodium arsenate, agitating the solution while the reagent is being added. After settling, the precipitate is filtered and washed with dilute ammonia solution and then dissolved in hot water. Sulfuric acid is added and after cooling, KI. The liberated iodine is titrated with thiosulfate without starch.

In using the method in our laboratory, several sources of error not mentioned by the above investigators were found. For the complete precipitation of the magnesium a decided excess of sodium arsenate is required. The excess of arsenate must, however, be at a minimum so as to reduce the wash water to a minimum and thereby avoid solution of the precipitate. An excess of 25% arsenate was the least that could be used if comparable results were to be obtained. This quantity was found to be completely removed by 20–25 cc. of wash water.

The solution in which precipitation takes place should be made decidedly alkaline with ammonia by the addition of 10 cc. of ammonia in excess of that necessary to neutralize the acid and should be free from ammonium salts. Since in water analysis the solution after precipitation of calcium is rich in ammonium salts, it is necessary to evaporate to dryness and remove by ignition, in order to obtain a pure precipitate of $Mg(NH_4)AsO_4$. This requires time and, hence, this method is open to the same objection as the one previously discussed.

The second great error occurs in the titration of the liberated iodine. Mead suggested the use of thiosulfate after the arsenate had been reduced with KI in acid solution, the following reaction taking place:

$$2H_3AsO_4 + 4H^+ + 6I^- = 2H_2AsO_3 + 2H_2O + 3I_2$$

This reaction is reversible, the value for the mass law constant being:

$$\frac{(H_3AsO_4)^2(H^+)^4(I^-)}{(H_3AsO_3)_2(I_2)^3} = K$$

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[1] THIS JOURNAL, **29**, 746 (1907).

[2] *Ibid.*, **29**, 1464 (1907).

In order for the reaction to go to the right the solution must be decidedly acid; that is, the (H^+) must have such a value as to materially increase the oxidizing power of the arsenic acid,[1] otherwise the reaction will not go in the desired direction. The volume of the solution during the titration should, therefore, be not greatly increased or else the concentration of H^+ will be so decreased that the reaction will reverse itself. At no time should the volume of the acid (specific gravity 1.16) be less than one-tenth of the volume of the solution.

Again, acidulated solutions of potassium iodide are also very easily oxidized by the air, whereby the concentration of the I_2 is considerably increased. Excessive HCl also liberates iodine and also decomposes thiosulfate. These errors are small and to a large extent neutralize each other. The errors from the other sources mentioned, however, are all positive and lead to higher values than the theoretical. At least such was our experience even with careful manipulation and strict attention to details so as to avoid such conditions as produce errors. After careful experimentation on various procedures which differed only as to concentrations of reagents used, the following procedure was found to give more nearly theoretical results:

The solution is entirely freed from ammonium salts by evaporation and ignition. The residue is taken up by a small quantity of HCl and filtered. The solution is cooled and an excess of 10 cc. of ammonia added. A 10–20% excess of sodium arsenate is added slowly and with vigorous stirring, the stirring being continued for about 10 minutes after no further precipitation takes place. The solution is allowed to stand in a cool place to allow the precipitate to settle, and is then filtered and washed with ammonia water (3%). The precipitate is dissolved in hot water and washed into the beaker in which precipitation took place and 10 cc. HCl (conc.) and 0.3 g. KI added for every 100 cc. of liquid. The liberated iodine is titrated with 0.10 *N* thiosulfate. Some typical results follow:

MAGNESIUM IN PARTS PER MILLION.

By titration.	By pyrophosphate.	By titration.	By pyrophosphate.
25.61	26.41	50.73	52.00
25.82	26.38	80.98	81.65
35.40	36.00	80.87	81.92
35.55	36.49	100.50	101.25
50.62	51.23	100.45	101.56

Better results were obtained by using a method suggested by Gooch and Browning[2] in which the arsenious acid was titrated with iodine after expelling the liberated iodine in the original solution by boiling with sulfuric acid. One modification, however, was made. Instead of using the

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[1] Stieglitz, "Qualitative Analysis," Pt. 1, 283.

[2] *Am. J. Sci.*, [3] **3**, 40, 66 (1890).

sodium bicarbonate as neutralizing agent, we made use of sodium phosphate[1] along with sodium hydroxide, which procedure more easily permits keeping the H^+ ion concentration of the solution at the proper value than the use of sodium bicarbonate. For every 100 cc. of 0.10 *N* iodine used, 11 g. of $Na_2HPO_4.12H_2O$ are necessary in a volume of 250 cc. to keep the ratio $Na_2HPO_4/NaH_2PO_4 = 2$ at the end point, which insures a concentration for H^+ of 10^{-7}. This quantity of iodine would be equivalent to 480 mg. of magnesium per liter, a quantity rarely found in water. To aid in keeping the ratio at the proper value, we found it convenient to start with a volume of about 100 cc. and at the end of the titration, if added reagents did not make the volume 250 cc., distilled water was added. The phosphate solution was made up so that 50 cc. contained 11 g. of salt. The volume necessary to add is then half the volume of 0.10 *N* iodine used. The following are a few typical results:

MAGNESIUM IN PARTS PER MILLION.

By titration.	By pyrophosphate.	By titration.	By pyrophosphate.
25.47	25.51	50.70	50.72
25.90	25.94	75.80	75.90
35.62	35.60	75.87	75.90
35.75	35.72	100.23	100.26
50.61	50.59	100.37	100.35

The procedure used follows: The solution from the calcium precipitation is evaporated to dryness and the ammonium salts are removed by ignition. The residue is taken up in hot water, acidified with HCl, filtered and an excess of 10 cc. of ammonium hydroxide added. Sodium arsenate is added in excess, 10–20%, and the whole solution cooled and shaken or stirred for ten minutes. The precipitate is allowed to settle in the cold, after which it is filtered and washed in dilute ammonia water (3%). The precipitate is dissolved in hot water, and the solution caught in an Erlenmeyer flask. An excess KI is added and 10 cc. H_2SO_4 (1 : 1). The whole is boiled rapidly with a trap in the Erlenmeyer flask until iodine vapors are no longer visible. While still hot, the small trace of iodine remaining is destroyed with sulfurous acid and the whole cooled quickly. The acid solution is neutralized with 0.10 *N* NaOH, using phenolphthalein as the indicator, adding from time to time some of the phosphate solution. When titration is complete, the volume of phosphate solution added should be equal to one-half the volume of the iodine solution. The volume should be about 250 cc. and if greater than this, more phosphate must be added in proportion to keep the concentration of H^+ at the right value. The arsenious acid is titrated as usual, using 0.10 *N* iodine.

Judging from our experience, the magnesium can be determined volu-

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[1] Washburn, THIS JOURNAL, 30, 37 (1908).

metrically provided great care is taken in the formation of the phosphate precipitate on the one hand, and on the other that special precautions are taken in the titration of iodine liberated by the arsenate precipitate from potassium iodide or the arsenious acid remaining after all the iodine has been expelled. Detailed procedures have been given which have been found to give results comparable with those by the usual gravimetric procedure.

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THE APPLICABILITY OF THE FERRO-FERRICYANIDE ELECTRODE TO THE MEASUREMENT OF THE ACTIVITIES OF ELECTROLYTES IN CONCENTRATED SOLUTIONS.

BY G. A. LINHART.

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The two fundamental concepts Fugacity and Activity which were developed by G. N. Lewis[1] have been applied in numerous cases to the study of dilute electrolytic solutions. Concentrated solutions, however, have been studied very little from this point of view. Potassium chloride was chosen for the present investigation because there are sufficient and reliable data in the literature from which to calculate the activity products of the potassium and chloride ions for a considerable range of concentration.

In a paper by Lewis and Sargent[2] on the Potential of the Ferro-Ferricyanide Electrode, it is shown that in the presence of potassium chloride of definite concentrations, the activities of the potassium ferro-ferricyanides are proportional to their total concentrations. This fact suggested the possible use of the ferro-ferricyanide electrode as one of the reference electrodes in the present experiments, the other being the calomel or the silver chloride electrode. The study of the relation between the potentials of the latter two electrodes in different concentrations of potassium chloride has been one of the secondary purposes of the present investigation; and, it was found that the e. m. f. between the silver chloride and the calomel electrodes, over the range of concentrations given in Table I, remained constant[3] at 0.0456 ± 0.0001 volt. The object of measuring simultaneously the ferro-ferricyanide electrode against the silver chloride or calomel electrode, was to test if there is any irregularity in either electrode as the concentration of the potassium chloride

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[1] Lewis, *Proc. Am. Acad. Art. Sci.*, 43, 259 (1907).

[2] Lewis and Sargent, THIS JOURNAL, 31, 355 (1909).

[3] *i. e.*, constant for any one silver chloride electrode. Differently prepared silver chloride electrodes, however, may differ from one another by as much as 0.001 volt.