

AN ABSTRACT OF THE THESIS OF

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Title-----A CERIMETRIC METHOD FOR THE DETERMINATION OF-----
-----MAGNESIUM-----

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Abstract Approved
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Determination of Magnesium. The determination is based on a precipitation of magnesium ammonium arsenate hexahydrate from an ammoniacal solution, reduction of the arsenate by distillation with hydrazine sulfate in a solution of hydrochloric acid, and titration of the volatilized arsenous chloride with standard ceric sulfate solution.

A 0.2 gram sample is weighed and dissolved in 55 ml. of water and enough hydrochloric acid to remove any turbidity. One-half gram of sodium arsenate, Na_3AsO_4 , and 3 grams of ammonium chloride, are added and then 20 ml. of concentrated, 28%, ammonia solution is added all at once. The flask is swirled frequently while standing at room temperature for 90 minutes. The precipitate is filtered off on a Gooch-asbestos filter and is washed till free from chlorides with a 2.5% ammonia solution. It is then dissolved and transferred to a 125-ml. distilling flask with 75 ml. of concentrated hydrochloric acid and 25 ml. of a solution containing 20 grams of hydrazine sulfate and 20 grams of sodium bromide in 1000 ml. of 1:4 hydrochloric acid solution. Distillation is carried out as in the A. O. A. C. method for determination of arsenic in Paris green with the exception that only one replacement of hydrochloric acid is made. Time required for the distillation should be about 90 minutes. The distilled arsenous chloride and hydrochloric acid are gathered into one flask, 25 ml. of concentrated hydrochloric acid and 7 ml. of iodine monochloride solution are added, and titration is carried out at 50° C. with standard ceric sulfate solution. The indicator used is a 0.025 molar solution of ortho-phenanthroline ferrous complex.

The results of the method compare within 0.2 % of results obtained by the gravimetric phosphate hexahydrate method and may be duplicated with a precision of 0.3 %

An alternate method of reduction with sulfurous acid is described but is not recommended.

A CERIMETRIC METHOD FOR THE
DETERMINATION OF MAGNESIUM

by

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TABLE OF CONTENTS

	Page
Introduction	1
Theoretical Considerations	4
Preparation and Standardization of Solutions	8
Sodium Arsenite, 0.1000 N.	8
Ceric Ammonium Sulfate, 0.1 N.	8
Sodium Arsenate	9
Hydrazine Sulfate	9
Ammonia Wash Water	10
Iodine Monochloride	10
Ortho-Phenanthroline Ferrous Complex	10
Experimental Procedures	11
Table I--Dick's Conditions for Precipitation of Magnesium ammonium arsenate hexahydrate	11
Table II--Effects on Gravimetric Analysis of Varying Conditions of Precipitation	12
Experimental Results	19
Table III--Results Comparing Methods of Determining Magnesium	19
Recommended Procedure for Determination of Magnesium	21
Solution of Sample	21
Precipitation	21
Filtration	21
Reduction of arsenic	21
Titration	22

Discussion	23
Summary	25
Bibliography	26

A CERIMETRIC METHOD FOR THE DETERMINATION OF MAGNESIUM

INTRODUCTION

Almost all of the methods previously available for the determination of magnesium have depended on an ultimate weighing of some compound containing the element. It has long been desirable, therefore, to develop some sort of procedure which will eliminate the manipulations required in the drying, igniting, and weighing of a precipitate. In recent years considerable work has been done on this problem. One of the most recent methods which have been developed consists of precipitating magnesium with 8-hydroxyquinoline and oxidizing the precipitate with a standard solution of ammonium hexanitrate cerate (10) or with a standard solution of potassium bromate-bromide (2,5).

In 1935 Daubner (3) proposed another titrimetric method for the determination of magnesium which consists, briefly, of a precipitation of magnesium ammonium arsenate hexahydrate, reduction of the arsenate to arsenite with sulfurous acid, and titration of the arsenite with a standard solution of iodine after expulsion of the excess of sulfur dioxide from the solution. It was thought that an improvement in this method could be accomplished by using a solution of ceric sulfate for the standard oxidant instead of iodine. This would be a definite step forward because

none of the instability encountered in iodine solutions is met with in the case of a standard solution of ceric sulfate. There are the added advantages that the indicator is stable whereas starch solution, for iodine titrations, is not; and the end point of the final titration is more easily detected than it is in the iodine-arsenite titration. Even with this improvement, however, there still remained the tedious necessity of a slow reduction of arsenic with sulfurous acid and also the equally tedious, and uncertain, elimination of the excess of sulfur dioxide. A possible escape from these difficulties was suggested by Mehlig and Johnson (9) who determined arsenic in Paris green by the use of hydrazine sulfate as a reducing agent and the A. O. A. C. procedure for distillation (1) for arsenous chloride prior to titration with a standard solution of ceric sulfate.

The object of the present work was, then, to determine the feasibility of a determination of magnesium by a combination of the above procedures. In the following discussion a method will be described consisting of a precipitation of magnesium ammonium arsenate hexahydrate, reduction of the arsenic to the trivalent state, and oxidation of the trivalent arsenic back to the pentavalent condition with a standard solution of ceric sulfate. The two methods available for reduction of arsenic will be compared and described. It will be noted that the method is an indirect, titrimetric

one which employs no drying, igniting, or weighing of a precipitate as would a gravimetric determination.

THEORETICAL CONSIDERATIONS

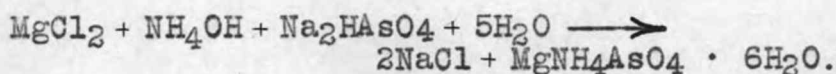
The determination of magnesium as proposed in this work consists of three main steps; the precipitation of magnesium, the reduction of arsenic to the trivalent condition, and the titration with ceric sulfate solution. These three will be considered in order with regard to theory involved.

The precipitation is made in a manner similar to the precipitation of magnesium ammonium phosphate in the familiar gravimetric determination and is subject to the same errors as are encountered in that procedure. It is made from a strongly ammoniacal, basic solution in the presence of ammonium chloride, the precipitating reagent being disodium hydrogen arsenate. The conditions of this precipitation must be carefully controlled if good results are to be obtained. First, no other metals than those of the alkali group may be present; since the arsenates of almost all the other metals are precipitated in a solution basic with ammonium hydroxide. Second, the composition of the precipitate formed depends upon the concentrations of hydroxide ion and ammonium ion and the conditions of precipitation as regards time and temperature. Since it is essential for titrimetric calculations that the ratio of arsenic atoms to magnesium atoms in the precipitate be known, it is in order at this point to review the effect of too high or too low a concentration of each of the above mentioned ingredients,

as well as the effect of changing the time allowed for the formation of the precipitate.

It will be remembered from the gravimetric determination, after precipitation of magnesium as magnesium ammonium phosphate hexahydrate (6,8), that the concentrations of ammonium chloride and of ammonium hydroxide are of the utmost importance (6). Similar effects prevail in the arsenate precipitation. Though the solubility of magnesium ammonium arsenate decreases with increasing concentrations of ammonia, there is a limit to the concentration of ammonium hydroxide which is permissible. If this concentration is too high, high basicity results in the formation of some trimagnesium arsenate $Mg_3(AsO_4)_2$, which has an arsenic to magnesium ratio of two to three. Furthermore, the concentration of ammonium ion is important, because if an excess of it is present, formation of monomagnesium ammonium arsenate, $Mg(NH_4)_4(AsO_4)_2$, results in an arsenic to magnesium ratio of two to one. Though, as shown, an excess of ammonium ion is to be avoided, presence of a certain amount is required to prevent formation of magnesium hydroxide, $Mg(OH)_2$, through a repression of hydroxide ion concentration. It is easily seen, then, that since an arsenic to magnesium ratio of one to one is assumed in the final calculation from titrimetric data, conditions of precipitation must be standardized within certain limits.

The equation for a correct precipitation is as follows, assuming the sample to be magnesium chloride:



The reduction of arsenic to trivalency presented a problem that was not solved to the extent desired. The requirements for a reducing agent are that it reduce all arsenic to the arsenous state and that there be some method of separating the reduced arsenic from the excess of reducing agent. It is desirable, of course, that the reduction consume as little time as possible and that the elimination of the excess of reducing agent be easily and quickly accomplished. As has previously been mentioned, two reducing agents were tried, the two being sulfurous acid and hydrazine sulfate. Both, however, left much to be desired. Sulfurous acid was time consuming and entailed an unsatisfactory elimination of its excess while hydrazine sulfate requires a distillation. The equation for the sulfurous acid reduction is as follows:

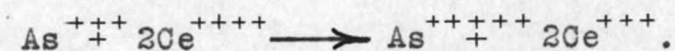


The equation for the reduction with hydrazine sulfate is not definite, a mixture of compounds being formed.

The equation for the final titration of arsenite with ceric sulfate is:



and the one for the final titration of arsenous chloride is:



Iodine monochloride was used to catalyze the reaction, but its effect is not well understood at present (12,15). The temperature of the solution during titration at the endpoint must be approximately 50° C. to insure rapid oxidation by the ceric ions. The indicator used was ortho-phenanthroline ferrous complex. The acidity of the solution should be close to 2 molar with sulfuric acid, lower acidity resulting in slow oxidation and a correspondingly sluggish endpoint (15).

PREPARATION AND STANDARDIZATION OF SOLUTIONS

Sodium Arsenite, 0.1000 N. was prepared by dissolving 1.2366 grams of pure arsenous oxide with 1.25 grams of sodium hydroxide in 50 ml. of distilled water, adding 3.25 ml. of concentrated hydrochloric acid and then, with stirring and in small portions, 2.25 grams of sodium bicarbonate, transferring to a 250-ml. volumetric flask, cooling and making up to the mark accurately with distilled water. This solution was used only in standardizing the solution of ceric sulfate.

Ceric Ammonium Sulfate 0.1 N. This salt was used in preference to ceric sulfate itself because it is more easily dissolved. For each liter of solution desired, 28 ml. of concentrated sulfuric acid were mixed with enough distilled water to give a volume of 500 ml. Then 64 grams of ceric ammonium sulfate were dissolved in this acid solution. The solution was permitted to stand overnight to permit all insoluble matter to settle to the bottom. The liquid was then filtered through glass wool and asbestos to remove the insoluble material. This solution is 0.5 M. with sulfuric acid (11).

This solution was standardized against arsenic by two different methods. In the first method, the standard solution of sodium arsenite was used. From a burette,

25 ml. of arsenite solution were run into a 250-ml. Erlenmeyer flask. Seventeen ml. of concentrated hydrochloric acid, 6 ml. of 0.005 M. iodine monochloride solution, one or two drops of a 0.025 M. solution of ortho-phenanthroline ferrous complex, and 55 ml. of water were added; and the solution was titrated with the ceric sulfate solution. The titration was made at room temperature till the brown or reddish color of the indicator returned only slowly after addition of each drop of oxidant. Then the solution was warmed to 50° C., using a thermometer as a stirring rod; and the titration was completed to a pale blue endpoint.

The second method of standardization employed involved the same distillation as will be described for the reduction of arsenic by hydrazine sulfate. A 0.1000 gram portion of arsenous oxide was weighed out and washed into a 125-ml. distilling flask with 75 ml. of concentrated hydrochloric acid and 25 ml. of hydrazine sulfate solution. Distillation and subsequent titration were carried out as in the procedure followed in the determination of magnesium.

Sodium arsenate for use as the precipitant was prepared by dissolving 50 grams of disodium hydrogen arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$, in distilled water and diluting to 250 ml. This solution contained the equivalent of approximately one gram of trisodium arsenate, Na_3AsO_4 , per 10 ml. of solution.

Hydrazine sulfate solution for use as the reducing agent was prepared by dissolving 20 grams of the salt and either

20 grams of sodium bromide or the equivalent amount of potassium bromide in 1000 ml. of 1:4 hydrochloric acid (1).

Ammonia wash water was prepared as a 2.5% NH_3 solution by diluting 39.6 ml. of ammonia (28%) to 400 ml. with distilled water.

Iodine monochloride, for catalyzing the reaction between arsenous arsenic and ceric ions, was prepared as a 0.005 M. solution. Ten grams of potassium iodide and 6.74 grams of potassium iodate were dissolved in a solution of 90 ml. of water and 90 ml. of concentrated hydrochloric acid. Five ml. of chloroform were then added and any red color in the chloroform was removed by adding 0.005 M. potassium iodate dropwise till the color in the chloroform became very faint. Ten ml. of this solution were diluted to one liter (13).

Ortho-phenanthroline ferrous complex, the indicator used in the titration, was obtained already prepared as a 0.025 M. solution from the G. F. Smith Chemical Company. One drop, or at most two, is sufficient for a titration(14).

EXPERIMENTAL PROCEDURES

For the successful completion of a magnesium determination by the method being discussed, the various steps in the analysis must be carried out in a careful manner and with due regard to details in treatment. Much time was spent in working out the best set of conditions and procedures, and much experimentation was done to determine the effects produced by varying one factor at a time.

Probably the most delicate point during an analysis is encountered in the precipitation and subsequent treatment of magnesium ammonium arsenate hexahydrate prior to the dissolving and reducing processes. Table I lists the recommendations made by Dick (4) in a study of the optimum conditions for precipitation in the gravimetric magnesium determination.

TABLE I

DICK'S CONDITIONS FOR PRECIPITATION
OF $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$

Weight of Mg sample	0.1 gm. Mg
Total volume of solution	70 ml.
Weight of NH_4Cl	3-5 gm.
Weight of precipitant	1 gm. of Na_3AsO_4 or 1 gm. of $(\text{NH}_4)_3\text{AsO}_4$
Volume of conc. $\text{NH}_4\text{OH}(28\%\text{NH}_3)$	about 23 ml.
Temperature of precipitation	cold water
Time of precipitation	90 min.
Composition of wash water	2.5% NH_3

Since the first results obtained in the development of the present method were not entirely satisfactory, studies were carried out to check on certain of Dick's findings. In order to do this the analyses were made gravimetrically before continuing with the titrimetric process. Factors studied included the weight of ammonium chloride, the weight of precipitant, the concentration of ammonium hydroxide, and the length of time of the precipitation. The results, for the most part, served only to verify the earlier conclusions; but in certain instances minor differences were noted. The results of this investigation are shown in Table II.

TABLE II

EFFECTS ON
GRAVIMETRIC ANALYSIS OF VARYING
CONDITIONS OF PRECIPITATION

Percentage Mg found by gravimetric phosphate determination — 25.30

NH_3 (28%) ml	NH_4Cl gm.	Na_3AsO_4 gm.	Time min.	Mg %
18	3	1	90	26.77
25	3	1	90	26.86
20	3	1	90	26.81
20	5	1	90	27.20
20	6	1	90	27.42
20	3	0.7	90	26.53
20	3	0.5	90	26.59
20	3	0.6	180	26.48
20	3	0.6	180	26.50

It was concluded from this data that; the concentration of ammonium hydroxide may vary considerably without any appreciable effect, that the weight of ammonium chloride should not be more than 3 grams, that the weight of disodium hydrogen arsenate should be approximately 0.5 gram rather than one gram as suggested by Dick, and that ninety minutes is sufficient time for precipitation. It will be noticed that even the best results obtained are very high. It seems likely that occluding of some substance present or more hydration than theoretical might be responsible for these high results. The fact that a lowering of concentration of precipitant lowers the weight of the precipitate obtained seems to support the theory that arsenate occlusion is responsible. Titrimetric data which will be presented later, however, point toward either excess hydration or occlusion of chlorides as the offending factor. Probably both took place.

The details of precipitation and subsequent treatment for titrimetric analysis will be presented later; but it might be well to describe, at this point, the procedure employed in drying and weighing the precipitate. After the precipitate was filtered on a Gooch and washed with a dilute solution of ammonium hydroxide till free from chlorides, it was washed with three separate 15-ml. portions of 95% ethanol followed by two portions of ether of the same volume.

Air was sucked through for 10 minutes and then the crucible was transferred to a calcium chloride dessicator where it was kept for 20 minutes. The Gooch crucible and contents were then weighed and the weight of precipitate obtained by subtracting the previously determined weight of the prepared crucible and asbestos.

While ethanol was used for almost all the runs, methanol also was tried but was found to be altogether unsatisfactory. It was found that three washings with methanol as described for ethanol dissolved as much as one tenth of the precipitate. This, of course, eliminated the possibility of using methanol as a substitute for ethanol.

The precipitation itself was carried out as follows. A sample of about 0.2 gram was weighed out and transferred to a 250-ml. Erlenmeyer flask the sides of which were subsequently washed with 30 ml. of distilled water. If insoluble in water, enough dilute hydrochloric acid was then added dropwise from a pipette to effect solution. In case the sample was soluble in water no treatment with acid was necessary. The solution was boiled briefly to expel any carbon dioxide, was cooled, and 30 ml. more of distilled water were added followed by 3 grams of ammonium chloride. The flask was shaken gently till all ammonium chloride was dissolved, and then 5 ml. of the arsenate solution were added. After mixing thoroughly again, 20 ml. of concentrated,

28%, ammonia solution were added all at once. The flask was swirled well, corked, and immersed in cold water. Dense, white precipitate formed on addition of the ammonia. The flask was left in the water for 90 minutes, with frequent shaking, and was then removed and filtered on a Gooch-asbestos, suction filter.

When determining magnesium by the titrimetric procedure, the precipitate was not dried or weighed, of course, but was washed till free from chlorides with a 2.5% solution of NH_3 . (It was found that arsenates would be absent when all the chlorides had been removed.) The precipitate was then dissolved in acid, the acid used depending on the reducing agent to be employed. If sulfurous acid was to be the reducing agent, sulfuric acid was used, hydrochloric not being at all suitable because of the volatility of arsenous chloride in a boiling solution. The precipitate and asbestos were transferred from the Gooch crucible into a 250-ml Erlenmeyer flask with as little as possible of 1:2 sulfuric acid. Then one gram of sodium sulfite was added after washing the crucible with enough water to make the total volume of liquid in the flask up to approximately 100 ml. The flask was corked, shaken, and set aside for at least one hour, preferably longer. Subsequently it was equipped with a two hole stopper with a tube leading into the liquid from a tank of carbon dioxide and another leading from the flask to a larger flask containing some solution of sodium hydrox-

ide for conversion of sulfur dioxide to sodium sulfite. A fume chamber could probably be used equally well. The contents of the flask were then heated to boiling while carbon dioxide was led in from the tank at a moderate rate. The carbon dioxide was to prevent oxidation of arsenic by air. This boiling was continued till the vapors issuing from the flask were free from sulfur dioxide as shown by the fact that they no longer decolorized a dilute solution of potassium permanganate. This operation usually required about an hour. In case the volume of solution in the flask became too low during the elimination of sulfur dioxide, it was restored to about 100 ml. with 1:2 sulfuric acid.

If the reduction was to be made with hydrazine sulfate, the acid used for dissolving the precipitate had to be hydrochloric; because the volatile arsenous chloride was now not only desirable but required. In this case, after washing the precipitate with dilute ammonium hydroxide, the precipitate was dissolved by sucking 75 ml. of concentrated hydrochloric acid followed by 25 ml. of hydrazine sulfate solution through the crucible into a 125-ml. distilling flask. The distilling flask was then connected as part of the distillation apparatus used in the A. O. A. C. method for determining arsenic by distillation (1).

Mahin (7) gives an excellent diagram of the apparatus which consists of a 125-ml. distilling flask provided with

a dropping funnel and connected through a water condenser to three receiving flasks with capacities of 500 ml., 1000 ml., and 100 ml., respectively. The three flasks are connected in series in the order named and the first two are surrounded by ice water. Forty ml. of water were placed in the first receiver, 100 ml. in the second, and 50 ml. in the third.

Distillation was started and maintained at such a rate that the liquid in the distilling flask barely boiled. A micro burner was used and is recommended. When the volume of liquid in the flask was reduced to 40 ml., 50 ml. of concentrated hydrochloric acid were added through the dropping funnel and distillation was continued. It was found that the lengthy distillation required by the A. O. A. C. method for arsenic in Paris green, in which much larger amounts of arsenic are used, was not necessary. Complete distillation of arsenic was found to have taken place after the first extra 50 ml. portion of acid had been added and the volume of liquid in the flask had been reduced to 40 ml. for the second time. Time required for the entire distillation was about ninety minutes.

After the distillation was complete, the condenser and connecting tubes were washed with water and the washings, together with the contents of the other two receivers, were added to the first receiving flask. The solution was then ready for titration.

Whether reduction was made with sulfurous acid or with hydrazine sulfate the titration was carried out in practically the same manner. If sulfurous acid was used, the volume of the solution was first made up to about 125 ml. In either case 20 ml. of concentrated hydrochloric acid were added, the solution was heated to 50° C., a drop of the ~~ortho~~-phenanthroline ferrous complex solution and 7 ml. of iodine monochloride solution were added, and titration was made with the standard solution of ceric sulfate. The color change was from reddish brown, through an orange-yellow, to a final pale blue. The change to pale blue was sharp and easily observed. Since the action of the oxidant was sometimes sluggish at the endpoint, return of reddish color was encountered occasionally. Therefore, readings were taken only after the blue color had remained for one minute.

EXPERIMENTAL RESULTS

The results of the determination of magnesium in three samples by the methods described are shown in Table III, together with the values obtained by the familiar gravimetric determination as magnesium ammonium phosphate hexahydrate (8).

TABLE III

RESULTS COMPARING METHODS
OF DETERMINING MAGNESIUM

Phosphate	Arsenate		H ₂ SO ₃ as Reductant		N ₂ H ₄ ·H ₂ SO ₄ as Reductant	
<u>% Mg</u>	<u>% Mg</u>	<u>Dev.</u>	<u>% Mg</u>	<u>Dev.</u>	<u>% Mg</u>	<u>Dev.</u>
10.00	10.17	+0.17	10.49	+0.49	10.08	+0.08
10.00	10.25	+0.25	10.28	+0.28	10.11	+0.11
10.00	10.21	+0.21	10.14	+0.14	9.95	-0.05
25.30	26.59	+1.29	25.89	+0.59	25.23	-0.07
25.30	26.50	+1.20	25.90	+0.60	25.62	+0.32
25.30	25.89	+0.59	26.19	+0.89	25.40	+0.10
9.87	10.52	+0.65			10.10	+0.23
9.87	10.39	+0.52			10.01	+0.14
9.87	10.61	+0.74			9.97	+0.10

The first column gives the percentage magnesium as determined by the gravimetric phosphate hexahydrate method. This value is used as the basis for comparison. The second column gives results obtained with the gravimetric arsenate hexahydrate method, the third gives results obtained titri-

metrically using sulfurous acid as the reducing agent, and the fourth gives the results obtained titrimetrically using hydrazine sulfate as the reductant.

RECOMMENDED PROCEDURE FOR
DETERMINATION OF MAGNESIUM

Solution of sample. Weigh out a 0.2 gram sample and if it is freely soluble in water dissolve it in 55 ml. of distilled water in a 250-ml. Erlenmeyer flask. If the sample is a carbonate, add 30 ml. of water and then dilute hydrochloric acid, dropwise and with swirling, till the solution clears. Boil to expel carbon dioxide, cool, and add 30 ml. more of water.

Precipitation. Add 3 grams of ammonium chloride, five ml. of the disodium arsenate solution, and, if a precipitate forms, add concentrated hydrochloric acid dropwise till turbidity disappears. Then add, all at once, 20 ml. of concentrated, 28%, ammonia solution, shake well, cork, and leave at room temperature for ninety minutes, shaking frequently. (See "Discussion", p. 24.)

Filtration. Filter the contents of the flask with the aid of suction in a Gooch crucible. Use the 2.5% ammonia solution for transferring any adhering precipitate from the flask to the filter. When all precipitate is transferred, continue washing with the dilute ammonia solution till the washings no longer give a test for chlorides when treated with silver nitrate-nitric acid solution.

Reduction of arsenic. The hydrazine sulfate-distillation method is preferable here and will be given. Dissolve

the precipitate and transfer it to a 125-ml. distilling flask by sucking 75 ml. of concentrated hydrochloric acid followed by 25 ml. of the hydrazine sulfate solution through the crucible and into the distilling flask. Connect the flask in the distillation apparatus (1) and distill using a micro burner and maintaining a distillation rate of approximately 20 drops per minute. When the volume of liquid remaining is about 40 ml., add 50 ml. more of concentrated hydrochloric acid through the dropping funnel and continue distillation till the volume of residual liquid is again about 40 ml. Stop the distillation, empty the contents of the second and third receiving flasks into the first receiving flask, and wash the emptied flasks, condenser, and connecting tubing with warm water, collecting the washings also in the first flask.

Titration. Add about 7 ml. of iodine monochloride solution, 20 ml. of concentrated hydrochloric acid, and one drop of ortho-phenanthroline ferrous complex to the solution. Heat the liquid to 50° C., using a thermometer as a stirring rod, and titrate with standard ceric sulfate solution. Take a one minute endpoint. The temperature should not be allowed to drop below 45° C.

DISCUSSION

The method developed, using hydrazine sulfate as the reducing agent, is capable of giving results which compare favorably with any of the better methods for determination of magnesium. The hydrazine sulfate reduction of the arsenate is more easily carried out, requires less time, and gives better results than the sulfite reduction. With the hydrazine sulfate reduction the method takes no more time, if anything a little less, than does the gravimetric phosphate hexahydrate method and certainly less time than the procedure involving ignition to pyrophosphate. No alcohol-ether washing and drying or igniting of a precipitate is necessary as in the gravimetric methods. The accuracy is superior to that in the iodometric method and in addition, the standard solution and indicator are stable over a much longer period.

There are, of course, some chances for errors; but few of these cannot be avoided by careful work. The conditions of precipitation and of the distillation must be carefully controlled and much care must be exercised in washing the precipitate and transferring it to the distillation flask. The results are rather consistently high, showing that there is some sort of error involved which is inherent in the method.

From tabulated data it is seen that titrimetric results

were lower, and better, than the arsenate gravimetric results obtained on the same sample. This could not be explained by assuming that arsenates were occluded by the precipitate, so it seems likely that either chlorides are occluded or that there are more than six water molecules in each molecule of precipitate. It is possible, of course, that ammonia might adhere somehow to the precipitate; but this does not seem probable. The cause for disagreement between gravimetric and titrimetric results provides an interesting problem for future study. It is a curious observation that on one sample of magnesium sulfate which had lost some of its water of hydration, the agreement between arsenate gravimetric results and titrimetric results is good. There seems to be no good explanation for this.

During the experimental work on the titrimetric phase of the investigation, it was discovered that better results were obtained if the precipitation of magnesium ammonium arsenate hexahydrate was made at room temperature instead of at the temperature of a cold water bath. This is not in accord with Dick's findings, and may not be true for a gravimetric determination; but the improvement in the titrimetric results was definite.

The precision of the determination is, from Table III, about 0.3 %; and the accuracy is 0.2 %.

SUMMARY

A ceriometric method has been developed for the titrimetric determination of magnesium. It depends upon the formation of insoluble magnesium ammonium arsenate hexahydrate in an ammoniacal solution, reduction of the arsenate by distillation with hydrazine sulfate in the presence of hydrochloric acid, and titration of the volatilized arsenous chloride with standard ceric sulfate solution. Results given by the method compare favorably with those obtained by the usual gravimetric methods.

An alternate method of reducing the arsenate with sulfurous acid has been described but is not recommended.

The advantages over both the gravimetric and iodometric methods have been indicated.

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