

1938

# The coprecipitation of magnesium on hydrous ferric oxide.

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BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

THE COPRECIPITATION OF MAGNESIUM ON HYDROUS FERRIC OXIDE

by

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(B.S., Bowdoin College, 1935)

Submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

1938

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## INTRODUCTION

A. The importance of coprecipitation in the precipitation of hydrous ferric oxide.

The phenomenon of coprecipitation, defined as "the contamination of a precipitate by substances normally soluble under the conditions of the precipitation", is of importance to several fields of chemistry, both pure and applied. For a comprehensive discussion of the subject, the reader is referred to some standard text, such as Kolthoff and Sandell, Ch. VIII\*.

The particular problem of coprecipitation on hydrous ferric oxide (which in the following may be referred to as the hydroxide for convenience, or written  $\text{Fe}(\text{OH})_3$  instead of the more accurate  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) is of great importance to the analytical chemist, inasmuch as: a) in both qualitative and quantitative analysis iron is usually separated by precipitation as the hydrous oxide; b)  $\text{Fe}(\text{OH})_3$  always precipitates as a flocculated colloid of amorphous, or at best, of submicroscopic crystalline structure. This is the type of precipitate most likely to involve adsorption due to its enormous specific surface, and is also the type most likely to involve mechanical inclusion of impurities in its porous gelatinous structure. c) Many of the other ions usually present during the analysis are those which would be predicted by the Paneth-Fajans-Hahn rule\*\* to be

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\*Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis", Macmillan, 1930.

\*\*Ibid., p. 107.

the very ones most strongly adsorbed on a hydrous oxide, e.g., Mg and the alkaline earths.

The usual procedure is to redissolve the precipitate, after filtering and washing, and to precipitate it again. Since the concentration of the impurities will be much less in the second precipitation, much less will probably be carried down. The filtrate (and washings) from this second precipitation may be combined with that from the first if the ions therein are to be determined subsequently. This procedure may be repeated until the coprecipitated impurities are reduced to a negligible amount, provided, of course, that the amount of each impurity adsorbed does decrease with decreasing concentration of that impurity. This last assumption will be valid for impurities held mechanically, and is probably valid for all cases of true coprecipitation, for, since the coprecipitated ions are held by surface adsorption, they will in all probability obey more or less closely one of the well-known equations of adsorption. (Exchange adsorption of cations need not be considered, as  $\text{Fe}(\text{OH})_3$  is far more insoluble than any of the other hydroxides concerned.)

It should suffice here to give as examples two of the best known of the various adsorption equations: (1) Freundlich developed empirically the formula  $y = kC^n$ , where  $y$  is the grams adsorbed/gram adsorbant,  $C$  is the conc of adsorbed substance, and  $n$  is an empirical constant usually near  $\frac{1}{2}$ . (2) Langmuir developed on theoretical grounds the equation  $y = \frac{aC}{1 + bC}$ , where  $a$  and  $b$  are constants,  $y$  and  $C$  are the same as above. The latter equa-

tion has been shown to hold well for adsorption in monomolecular layers where the amount adsorbed covers only a fraction of the total surface; the former holds well for a large number of cases, notably where rough or porous surfaces are involved.

For a further discussion of adsorption equations, the reader is referred to any text on physical chemistry, e. g., Getman and Daniels\*, pp. 221-224.

Returning to the question of the precipitation of hydrous ferric oxide, it would seem important in any analysis to have data from which to estimate the number of precipitations necessary to obtain a sufficiently pure precipitate, given a rough idea of the constitution of the sample, as is generally the case in a practical analysis.

The principal interfering cations in the analysis of, for instance, limestone, are Al, Cr, Mn, the alkaline earths (mainly Ca), and Mg; of these, the first three are precipitated by ammonia even in the absence of iron, hence cannot be eliminated by any number of reprecipitations. Of the alkaline earths, Ba and Sr are rare, and their hydroxides are quite soluble; Ca, however, is an important impurity, and its hydroxide is not very soluble (0.77 g/liter @ 100°). Mg is usually present in appreciable amounts; in addition, its hydroxide is so insoluble (0.04 g/liter @ 100°) that it will precipitate almost complete-

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\*Getman and Daniels, "Outlines of Theoretical Chemistry", 6th Ed., John Wiley, 1937.

ly in ammoniacal solution, unless large amounts of ammonium salts (e.g.,  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ ) are present as buffers; even in such buffered solutions, the Paneth-Fajans-Hahn rule (Kolthoff and Sandell, p. 107) predicts that Mg ion will be strongly adsorbed on  $\text{Fe}(\text{OH})_3$ . Under ordinary conditions Mg is the only coprecipitated cation not removed satisfactorily from the  $\text{Fe}(\text{OH})_3$  by one, or, at the most, two reprecipitations, and it seems reasonable to conclude that when the precipitate is free from Mg, it will be free from other coprecipitated cations.

Because it is a widely occurring element, and is very strongly adsorbed on  $\text{Fe}(\text{OH})_3$ , it is logical to select Mg for the present study.

It is perhaps necessary to explain why only cations have been considered in the above discussion, especially since the cation (ferric ion) is in excess during the precipitation of  $\text{Fe}(\text{OH})_3$ , which would be expected to result in greater contamination by foreign anions than by cations (Kolthoff and Sandell, p. 113. Also, *ibid.*, p. 296.)

In the case of sulfate, chloride, or nitrate, which would generally be present during the analysis, no great adsorption would be expected to take place, as the ferric salts of these anions are all fairly soluble. Furthermore, on the ignition which usually follows the iron precipitation, most common ferric salts (except the chlorides) are converted to the oxide, hence would cause no difficulty even if they should persist through the usual reprecipitation.

With phosphate ion in particular, however, the case is just the opposite: this anion forms a rather insoluble ferric salt, which would result in a strong adsorption, especially where the precipitation takes place in the presence of excess cation. Phosphate is almost universally present with iron, even in the metallic states. Any adsorbed phosphate would remain unchanged on ignition, leading to high results; and to make matters worse the phosphates of the alkaline earths and magnesium are quite insoluble in alkaline solution. This last fact leads to the following situation: if phosphate is present with magnesium or an alkaline earth, we have both an anion and a cation strongly adsorbed on the  $\text{Fe}(\text{OH})_3$ , and in addition, the two foreign ions together form an only slightly soluble compound. Also, if the cation is magnesium, the precipitation of  $\text{MgNH}_4\text{PO}_4$  will be promoted at the surface of the precipitate, since ammonium ion is always present.

We are thus drawn to the conclusion that if phosphate ion is present with either magnesium or an alkaline earth, it will be completely precipitated (or coprecipitated) on the surface of the  $\text{Fe}(\text{OH})_3$  (either as the normal, acid, basic, or ammonium phosphate) and will not be removed to any great extent by reprecipitation. Since the various phosphates are only slightly altered by ignition, we can hardly hope to avoid high results in a gravimetric determination of iron if phosphate is present with magnesium or an alkaline earth, unless some other means of precipitation than the hydroxide is employed (See Kolthoff and Sandell,

pp. 79-80, 298-299).

Because of the insolubility of  $\text{FePO}_4$  itself, Kolthoff and Sandell (p. 298) state that phosphate must be absent if iron is to be precipitated as  $\text{Fe}(\text{OH})_3$ .

To sum up: the precipitation of iron as the hydroxide is not advisable in the presence of phosphate (and certain other less common anions, see Kolthoff and Sandell, p. 298). The more common anions, such as sulfate, nitrate, and chloride, do no harm even if they are carried down, as most of them are converted to the oxide on ignition. This makes the question of anion coprecipitation of slight importance, although at least for chloride and sulfate, it would not be difficult to investigate this problem, using the method of separation outlined in the experimental part of this thesis, and a turbidimetric or nephelometric determination of the ion in question.

B. Possible methods of attack on the problem.

In spite of its importance, the problem has been investigated only by Victor and Alter\*, and Chamberlin and Alter\*\*, whose results will be discussed later (p. 74). In both of these investigations a gravimetric method was employed.

The procedure for determining the amount of coprecipitation will vary greatly depending on whether practical or theoretical use is to be made of the results. Let us first consider the former case: we have generally a rough idea of the composition of the sample, and wish to know the minimum number of precipitations which will leave a satisfactorily pure precipitate. We do not care whether the impurity is due to adsorption, mechanical inclusion, or just poor washing; in fact, if a reprecipitation is to be carried out, we purposely give the precipitate only a perfunctory washing before redissolving, as reprecipitation is so much more efficient than washing in removing impurities. Since we are interested in reducing the impurities to a value too small to affect the final ignited weight of the ferric oxide, it is preferable to use this same method for the investigation, i.e., find the gain in weight of the ignited oxide due to coprecipitated impurities.

For practical use of the results in analysis, therefore,

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\*Victor, Master's Thesis, Boston University, 1936.

\*\*Chamberlin, Unpublished Results, Boston Univ., 1937.

we might proceed as follows:

1) Analyze gravimetrically a pure sample of iron or a ferric salt, or standardize a solution of the same, using the largest practical sample.

2) Proceed exactly as in 1), but precipitate the  $\text{Fe}(\text{OH})_3$  in the presence of a known amount of the impurity in question.

3) If this gives a high result, repeat, using one or more reprecipitations, until the result is again normal.

4) Determine the least number of reprecipitations necessary to avoid high results for amounts of impurity covering the whole probable range of occurrence in the materials to be analyzed.

5) Make up a table or chart of the data found in 4). To use this chart, estimate the largest percentage of the impurity likely to be present (a knowledge of the nature of sample usually permits this), then look up in the table the number of reprecipitations required for that amount of impurity.

If, however, we wish to undertake a theoretical study of the phenomena involved in coprecipitation, the case is quite different: for the results to be of any value, we must be able to distinguish clearly between Mg (1) carried down by true coprecipitation, (2) mechanically included, and (3) left with the precipitate because of insufficient washing.

It might appear at first sight that the third of these could easily be eliminated by sufficient washing; however, the

possible effect of such treatment on the truly adsorbed Mg must not be forgotten. The adsorbed Mg ions are in equilibrium with those in solution; the replacement of the original solution with Mg-free wash liquid would result in a new equilibrium with most of the adsorbed Mg going into solution. The fact that contamination of  $\text{Fe}(\text{OH})_3$  by Mg does occur, and is not remediable by mere continued washing, may be due to one of three things:

a) Mg ion is inside the crystals of  $\text{Fe}(\text{OH})_3$  instead of at the liquid-solid interface, b) the coprecipitated Mg which persists through the washing is entirely that mechanically held in, and adsorbed on the surface of, the inaccessible capillarities, or c) the new equilibrium is not approached in the length of time necessary to wash the precipitate.

Taking up these three possibilities in order: a) This is highly improbable; the ferric hydroxide is very nearly amorphous, i.e., has very little crystalline structure (Kolthoff and Sandell, p. 294). Even if there were well developed crystals it seems permissible to assume ohne weiteres that  $\text{Mg}(\text{OH})_2$  or other Mg salts would not form either mixed crystals or a solid solution with it. Therefore, this first possibility will not be considered further.

b) This may well be the true situation; if so, the question of adsorption of Mg on  $\text{Fe}(\text{OH})_3$  would be of little significance in analytical chemistry, and the only thing measured by such experiments as Victor's and Chamberlin's (to be described later) would be the porosity of the precipitate. This, indeed, might

be of importance in choosing analytical conditions giving a precipitate of the least porosity, were it not for the possibility of seriously affecting the physical state of ferric hydroxide by varying such conditions as the speed of addition of  $\text{NH}_4\text{OH}$  (Kolthoff and Sandell, p. 295).

c) This third possibility also might conceivably be true. The speed of attainment of equilibrium by adsorption is often much greater than by desorption, which is a notoriously slow process in many instances (cf., the rates of adsorption and desorption of water vapor on silica gel, for instance).

Whether case b) or c) or a combination of both is the true state of affairs could be decided by the following experiment:

Add the magnesium immediately after, rather than before, the precipitation of the iron, decant after settling, and add a large volume of wash liquid (e.g., 1%  $\text{NH}_4\text{Cl}$ ). Let stand, with occasional stirring for various lengths of time, and analyze the precipitates for Mg. (A method for this analysis will be discussed later.) This procedure should result in little if any mechanical inclusion; any magnesium found in the precipitate would be adsorbed on surfaces exposed to the liquid, and the rate of desorption, if any, could be studied. This experimental method appears to offer one of the most favorable approaches for a theoretical study of true surface adsorption.

It should be remembered that if traces of phosphate, for example, are present, the complete precipitation of this anion

as  $MgNH_4PO_4$  will be promoted at the surface of the  $Fe(OH)_3$ , as pointed out on p. 5. This will not redissolve appreciably in the wash liquid; however, the presence of such a promoted precipitate could be avoided by the use of sufficiently pure reagents.

The question of the proper wash liquid deserves consideration here. In practice, a hot 1%  $NH_4Cl$  (or  $NH_4NO_3$ ) solution is used, the presence of the electrolyte preventing the peptization of the  $Fe(OH)_3$ . This wash liquid will be somewhat acidic due to hydrolysis, which has no effect on the extremely insoluble  $Fe(OH)_3$ , but would undoubtedly cause much more rapid desorption of cations adsorbed on surfaces exposed to the solution. This would be an advantage in practical analysis, but just the opposite in a study of the present kind. It might be preferable to make the wash liquid distinctly ammoniacal; whether or not this is really necessary could be determined by a study of rates of desorption in the presence of the two wash liquids, using the procedure outlined on p. 10.

The objective of our experimental study is to find the mathematical relation between the Mg adsorbed per gram of  $Fe(OH)_3$  and the concentration of Mg in the solution, and to find how this relation varies with different methods of precipitation, different temperatures, and so on. In other words, we wish to find the adsorption equation, and see if it corresponds to some well-known law (see p. 2) or not.

We must be certain that we have eliminated the disturbing effects of mechanical inclusion or insufficient washing, either

of which would vitiate the results. If we are considering the use of a method which requires filtration of the precipitate, we must first make preliminary tests of the sort outlined on pages 10-11, and show that a thorough washing will not result in a serious amount of desorption. It might be necessary to change the wash liquid to prevent loss of adsorbed ion. If we find, however, that desorption during washing is unavoidable, another method must be chosen.

Let us now review the various methods which might be employed in this investigation.

1. The first method, one of the least desirable, is that followed by both Victor and Chamberlin (p. 7, footnotes). They added a known concentration of magnesium to a solution containing a weighed amount of standardized Fe solution and 3-4%  $\text{NH}_4\text{NO}_3$ , heated to boiling, and ran in freshly distilled  $\text{NH}_4\text{OH}$  until just ammoniacal; then filtered and washed the precipitate, and ignited. The increase in weight over that calculated was assumed to be  $\text{MgO}$ .

Their results will be taken up later on, but their significance is open to question, for the following reasons:

- a) The fact that much of the magnesium found by this method may be due to mechanical inclusion was not considered.
- b) The possibility of desorption during washing was not considered.
- c) The increase in weight of the ignited precipitate was considered entirely due to  $\text{MgO}$ ; although this assumption may well

be justified, a determination of Mg itself is certainly a much sounder procedure. Unless the precipitate is ignited in Pt and treated with HF, we can never be sure of avoiding errors due to varying silica content.

d) The behavior of the curve near the origin, which is of particular theoretical interest could not be studied, as the uncertainty in any ignition is not less than 1/10 mg; it was thus impossible to determine with any accuracy less than a milligram of MgO. As a matter of fact, the precision of their results did not exceed 10%, even for their largest values (2 mg of MgO); and at the lower points the variations equaled the values themselves. It is doubtful if these results could be improved, where a very small difference between two large quantities is sought.

II. To overcome the objections inherent in method I, the following changes are proposed:

a) Make a preliminary study of the possibility of desorption during washing, as outlined on p. 10; as pointed out above, if this is not found small enough to be harmless, we must drop any procedure involving filtration and washing.

b) Eliminate mechanical inclusion by adding the magnesium immediately after, rather than before the precipitation. This will perhaps reduce the surface available for adsorption, but the isotherms would be changed only by a constant factor. (Kolthoff and Sandell, p. 111, state that virtually the same contamination is found adding magnesium either before or after precipitation.)

c) Analyze for Mg itself, instead of as a minute increase in the weight of the ignited precipitate. The magnesium may be easily and completely separated from the  $\text{Fe}(\text{OH})_3$  by reprecipitation, leaving it in the filtrate. In the analysis for magnesium, a micro-method is necessary; the choice of method will be discussed in the experimental part of this thesis.

d) By letting the precipitate digest various lengths of time before adding magnesium, the effect of aging may be determined.

III. Proceed as in II, but add the magnesium before precipitation. Determine the extent of mechanical inclusion, which will be the same for any ion, by repeating the experiment with some other ion not appreciably adsorbed, and for which there is some accurate method of micro-analysis. This ion might well be an anion. Subtract the mechanical inclusion from the total contamination to find the true adsorption.

The difference between the results in II and III would give the "internal surface", if any.

IV. The ideal method from a theoretical point of view is as follows: Precipitate the iron in a solution containing an accurately known concentration of magnesium; separate the precipitate from the supernatant liquid either by simply letting settle, centrifuging, or decanting the liquid through a filter. Using an aliquot of this liquid, determine the decrease in concentration of magnesium due to adsorption on the precipitate.

It is easily seen that this procedure very probably measures only the true adsorption, and is the most straightforward of all.

The only drawback, although a serious one, is that we are again determining a difference between two large quantities. This difference, i.e., the amount of magnesium adsorbed, may be increased many-fold in this method by increasing the amount of iron. The largest quantity which may be conveniently filtered and washed is about 0.1 g. (as  $\text{Fe}_2\text{O}_3$ ), whereas in this method, involving no treatment of the precipitate, up to several grams might be used.

A 30-fold increase in adsorbed Mg is an attractive prospect. Conditions could probably be arranged so that some 15% of the Mg present would be carried down; in addition, the quantity of Mg present is large enough so that a micro-method would be unnecessary.

V. It is probably true that, other things equal, the amount of adsorption is directly proportional to the surface area of the precipitate. This brings up the possibility of determining the adsorption curve for a precipitate formed under one set of conditions, and calculating that for a precipitate formed under other conditions from the ratio of the specific areas.

One method of determining the specific area (and more simply the ratio of the specific areas of two precipitates) is that of Kolthoff\*. He showed that Wool Violet above a certain concentra-

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\*Kolthoff and MacNevin, J. Am. Chem. Soc., 59, 1639 (1937).  
Kolthoff and Neponen, *ibid.*, 60, 499 (1938).

tion completely covers the surface of  $\text{BaSO}_4$  in a monomolecular layer; this is shown fairly conclusively for any given dye-precipitate pair if the adsorption reaches a constant value above some minimum concentration of dye. The amount adsorbed is determined colorimetrically by the decrease in coloration.

A suitable dye could probably be found for  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

The data for specific area in terms of exposed ions per gram would be of great value in interpreting the adsorption curves.

The dye method gives very rapid and reproducible results, and is especially suited to aging studies, where a portion of the supernatant liquid may be analyzed colorimetrically and returned, thus allowing one run to be continued for as long as desired.

### C. Analysis for Magnesium.

In methods II and III, part B above, a micro-analysis for magnesium is required, the amounts ranging from a few milligrams down; in method IV, an ordinary macro-method is suitable, the amounts not being below a few mg/liter.

In the former case (see part B, II and III) the thoroughly washed precipitate containing the adsorbed Mg is dissolved and reprecipitated twice or more, leaving the Mg in the filtrate, which may be evaporated down to a smaller volume. If sufficiently pure reagents have been used, the filtrate should be free of anything else except considerable amounts of  $\text{NH}_4\text{Cl}$  (or  $\text{NH}_4\text{NO}_3$ ) used as the buffer (and of course some silica). The ammonium salts may be removed if necessary (see experimental part).

#### Micromethods

1) Briggs' method\* utilizes precipitation as  $\text{MgNH}_4\text{PO}_4$  and determination of the phosphate by the Bell-Doisy reaction, i.e., by adding ammonium molybdate to form phosphomolybdate which is in turn selectively reduced to Molybdenum Blue by hydroquinone. Although this method has been used for years with success by a number of workers, the author has spent a considerable amount of time attempting to apply it to the present problem, with poor results. The analysis for phosphate by the Bell-Doisy reaction is

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\*Yoe, "Photometric Chemical Analysis", Vol. I, p. 264.  
Snell, "Colorimetric Methods of Analysis", Vol. I, pp. 468, 500. (Additional references to the literature may be found in both of these volumes for many of the methods listed here.)

very satisfactory; the difficulty appears to lie in the precipitation of very small amounts of magnesium as  $MgNH_4PO_4$ . This is one of the most soluble precipitates used in quantitative analysis, which fact alone makes it unsafe as the basis for a micro-determination of magnesium. Kolthoff and Sandell (p. 339 et seq.) show that more than a small concentration of ammonium salts increases the solubility of the precipitate, which necessitates the removal of most of these salts, a great disadvantage. This precipitation is more subject than many others to contamination by foreign ions and the reagents themselves. Other criticisms, such as the time consumed by this procedure, will not be taken up; more direct procedures are available and are strongly recommended.

Wheeler\* studied this method and found it inaccurate.

2) Precipitation of magnesium as the oxinate (salt of 8-quinolinol, or 8-hydroxyquinoline, called for brevity "oxine"),  $Mg(C_9H_6ON)_2 \cdot 2H_2O$ . The oxine is used either in alcoholic or acetic acid solution. Most cations are precipitated in hot acetic acid-acetate solution, while magnesium is precipitated from ammoniacal solution (Kolthoff and Sandell, p. 80); thus most foreign cations may be removed by precipitation in the former medium before separating the magnesium.\*\* This procedure is probably unnecessary, since most of the interfering ions would be carried down with the  $Fe(OH)_3$ , if present. The treatment also causes some error, presumably by slight decomposition of the oxine.\*\*\*

\*Wheeler, Am. J. Physiol., 76 233 (1926).

\*\*Snell, p. 475. Alten, Wieland, and Kurmies, Z. Angew. Chem., 46 697 (1933).

\*\*\*Alten, et al. See footnote preceding.

Another objection to Alten's precipitation is the necessity of removing all the  $\text{NH}_4$  ion; furthermore, the only interfering ion likely to be present is Ca, which may just as easily be precipitated as the oxalate and centrifuged out.

The best procedure for the oxine precipitation is probably that of Berg<sup>\*</sup>; this calls for the presence of much  $\text{NH}_4\text{Cl}$ , a distinct advantage, as only part of that already present need be removed.

To determine the amount of oxinate after the precipitation and washing, several methods are available:

a) A micro-gravimetric method should be applicable, especially since the weight factor is nearly 15 for the dihydrate, which is the stable form at  $105^\circ$ . The Pregl filter-tube or Emich's filter-stick technique<sup>\*\*</sup> should be applicable. A micro-balance would be desirable, but with so high a weight factor, an error of only 1 gamma of magnesium is caused by an error of .015 mg. in weighing the precipitate, a precision almost attained by the research balance in this laboratory.

By heating to  $130-140^\circ$  instead of  $105^\circ$ , the precipitate may be weighed as the anhydrous salt; at this temperature any oxine carried down is volatilized, which is important, as a sufficient excess of reagent leads to contamination of the precipitate.

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<sup>\*</sup>Berg, Wolkner, and Skopp, Mikrochemie, Emich Festschr., 1930, 18. Snell, p. 472.

<sup>\*\*</sup>Pregl, "Quantitative Organic Microanalysis", p. 97. Emich, "Microchemical Laboratory Manual", p. 68 et seq. See also: Bailey, Ind. Eng. Chem, Anal. Ed., 9 490 (1937), for an inexpensive micro filter crucible.

(For very minute quantities of magnesium, a large excess of reagent is necessary to start precipitation, and ensure its completeness; for large quantities, a smaller excess is sufficient.) The weight factor for the anhydrous salt is nearly 13.

By igniting under a cover of oxalic acid to prevent volatilization of magnesium, it is possible to weigh as  $MgO$ .\* As we lose the high weight factor, this is disadvantageous for micro work.

Micro-gravimetric technique is so tedious, however, that other methods are universally employed for magnesium. For larger quantities, however, the above procedures are all in use, and will be mentioned again later on.

b) The complex may be dissolved in dilute  $HCl$  and determined as phenol.\*\* The reaction involved is an excellent one for colorimetry, being much used to determine either phenols or phosphate. It depends on the reduction by the phenol of a heteropoly complex acid, such as the phosphomolybdotungstic acid recommended by Folin and Wu, the reduction of one of the oxide molecules in the complex forming a deep blue-colored lower oxide. This color is compared colorimetrically with that formed with a known amount of standard. The latter is made by dissolving a certain weight of magnesium oxinate in dilute  $HCl$  and making to volume.

Berg, et al., give data showing an accuracy of 2% for 15 gamma, down to 10% for 5 gamma.

c) The magnesium oxinate complex gives a green color with

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\*See Hough and Ficklen, footnote, p. 24.

\*\*Snell, p. 471; Berg et al., loc. cit.

iron (Snell, p. 473). This method is rather indirect, as the oxine in the HCl solution of magnesium oxinate is precipitated as ferric oxinate, which is dissolved and compared with a similarly prepared standard.

d) The complex is converted into a dye by coupling with diazobenzenesulfonic acid.\* Alten gives data showing an accuracy of 6% from 10 to 100 gamma and 1-2% above 100 gamma. The color produced by this method is a red with an orange hue, and is not as deep a color as that produced in b) above.

3) Magnesium oleate may be precipitated and determined nephelometrically.\*\* Gregoire and Sola, the originators of the method, claim an accuracy of 1-3%, and a range down to 3 gamma of magnesium. The article was very optimistic, but since no further references to the method have appeared for 14 years, it must have proved disappointing.

(These are about all the methods which seem satisfactory for the range from 10 gamma and up. The following, which may find no use in the present study, are some methods used for estimation of extremely small quantities of magnesium, below 15 gamma.)

4) Titan Yellow is adsorbed from solution by  $Mg(OH)_2$ , changing the color of the solution from yellow-brown to orange with 1 mg. Mg/liter, to red with 5 mg. Mg/liter, and giving a red flocculent precipitate with higher concentrations. The unknown

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\*Snell, p. 474; Alten et al., loc. cit.

\*\*Snell, p. 478; Yoe, p. 266; Gregoire and Sola, Z. anal. Chem., 64, 342 (1924).

is treated with NaOH and dye, and compared with a standard series.\*  
Accurate to 0.1 gamma for quantities below 15 gamma.

Clayton Yellow, which is sometimes used instead of Titan Yellow to measure traces of magnesium, is very closely related chemically to the latter, and doubtless behaves quite the same.

5) Quartaroli\*\* describes a novel method for determining traces of magnesium (below 12 gamma) by the specific negative catalysis which magnesium exerts on the darkening of freshly precipitated  $\text{Cu}(\text{OH})_2$ , probably due to a surface adsorption of  $\text{Mg}(\text{OH})_2$ . The presence of 12 gamma delays for one-half hour the otherwise instantaneous darkening.

6) Hahn\*\*\* gives a method using the change in color of tetrahydroxyanthraquinone with magnesium and comparison with a standard series. It determines from 5 to 12 gamma to the nearest microgram, and estimates down to 1 microgram. Euler discusses the method and states the accuracy at 10 gamma to be 6%.

Other methods have been reported, but do not seem useful for the present purpose.

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\*Snell, p. 476; Kolthoff, Chem. Weekblad, 24, 254 (1927); Hirschfelder, Serles, and Haury, J. Biol. Chem., 104, 635 (1934).

\*\*Quartaroli, Ann. Chim. Applicate, 24, 383 (1934); Chem. Abs., 29, 74 (1935).

\*\*\*Hahn, Mikrochemie, Pregel Festschr., 1929, 127; Emich, loc. cit., 146; Euler, Hellstrom, and Runehjelm, Z. physiol. Chem., 187, 127 (1930).

### Macromethods

In procedure IV, p. 14, the magnesium will range from several mg./liter to 5 or 10 gm/liter; therefore, an ordinary macro-analysis may be employed. If conditions are such that 15% of the magnesium present is carried down (p. 15), an accuracy of 0.1% in the analyses before and after precipitation will give an accuracy for the adsorbed magnesium of 2%, which is satisfactory. Any systematic error in the method of analysis would be eliminated by analysis of the solution before and after precipitation by the same method.

When small concentrations of magnesium are being used, the accuracy may be improved by increasing the volume, taking a very large aliquot for analysis, and using a large amount of iron to increase the fraction of magnesium carried down. A suggested procedure for small quantities of magnesium is as follows: Make up the solution except for the iron (but with Mg and  $\text{NH}_4$  ions in the desired amounts) and dilute to exactly a liter; measure out 500 ml. in a volumetric flask, and analyze for magnesium, evaporating down and removing  $\text{NH}_4$  salts if necessary. To the remaining solution add a measured volume (e.g., a 25 ml. pipet) of analyzed Fe solution, containing as much iron as can be handled when precipitated, but not enough to carry down more than 20-25% of the magnesium present at the most.

Precipitate the Fe by some standardized procedure, measuring the ammonia from a buret, and being careful to duplicate the ex-

cess each time; let settle for the desired time, then decant through a large filter (4-6 inch). Collect 500 ml. of filtrate, and analyze as before. The total volume after precipitation may be added up, the aliquot computed, and the magnesium carried down found by difference. It may be pointed out that the concentration of magnesium in the filtrate after precipitation is the concentration in equilibrium with the coprecipitated magnesium, not the original concentration.

1) With amounts of magnesium above 50 mg., the usual  $MgNH_4PO_4$  precipitation should give good results; most of the ammonium salt present would have to be removed to give the desired accuracy. Any text on quantitative analysis will give the procedure; an excellent discussion of the analysis will be found in Kolthoff and Sandell, Ch. XXII.

2) The oxine precipitation (cf. p. 18) is much used in ordinary work.\* Details will be found in the various references below. After the oxinate is precipitated, it may be determined in several ways:

a) Gravimetrically. The precipitate may be weighed as the dihydrate by heating at  $105^\circ$  (see Kolthoff and Sandell, p. 351); as the anhydrous salt by heating at  $130-140^\circ$ , which volatilizes any reagent carried down; and as MgO by ignition under a cover of

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\*Berg, Z. anal. Chem., 71, 23 (1927); Hough and Ficklen, J. Am. Chem. Soc., 52, 4752 (1930); Snell, p. 474; Redmond and Bright, Bur. Stand. J. Res., 6, 113 (1931); Redmond, *ibid.*, 10, 823 (1933); Kolthoff and Sandell, p. 351.

oxalic acid to prevent loss by vaporization (Hough and Ficklen). The accuracy of the last method (which requires previous separation of Ca by precipitation as oxalate and filtering) is 15% from 1 to 2.5 mg., and 1% above 5 mg. No data could be found on the accuracy of the first two weighing forms, but they are probably at least accurate to 0.1. mg. of Magnesium.

b) Colorimetrically by loss in color of the oxine reagent. This is a very rapid method well adapted to routine analysis, but not capable of great accuracy. Hough and Ficklen (q.v.) report the accuracy as 40% for 0.5 mg., and 10% from 1 to 5 mg.

c) Although not reported in the literature, the precipitate after filtering (and perhaps heating to 130° to remove excess reagent) could be dissolved in 1 N. HCl and determined colorimetrically by its own color against a similarly prepared standard; or an aliquot could be taken and subjected to one of the colorimetric reactions used in microanalysis (p. 20 et seq.). The accuracy probably would not exceed 3%.

d) Volumetrically by  $\text{KMnO}_4$ . This rather crude method consists of dissolving the precipitate in hot dilute  $\text{H}_2\text{SO}_4$ , adding  $\text{KMnO}_4$   $\frac{1}{2}$  ml. at a time, and timing the fading of the purple color. An arbitrary time of exactly 2 minutes was selected as the end-point. Hough and Ficklen report an accuracy of 40% at 0.1 mg., 10% at 0.3 mg., and 2% from 1.5 to 2.5 mg.; brown oxidation products obscure the end-point above 2.5 mg.

e) Volumetrically by  $\text{KBrO}_3$ . This is one of the best methods\*: the precipitate (preferably heated to 140° to remove

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\*Redmond and Bright, and Redmond, loc. cit.

excess reagent) is dissolved in dilute HCl. A measured volume of standard bromate-bromide solution is added, reacting quantitatively with the HCl to give  $\text{Br}_2$ ; exactly two moles of  $\text{Br}_2$  are substituted in each mole of oxine, leaving  $4\text{HBr}$  (thus using 4 moles of bromine for each mole of oxine). KI is now added, which reduces the remaining bromine, yielding  $\text{I}_2$ , which is titrated with standard thiosulfate and starch indicator. The loss of bromine from the solution measures the amount of oxinate.

Although this procedure appears to be rather indirect, all the reactions are clean-cut; furthermore, the volume of bromate-bromide used is standardized against the thiosulfate by the same procedure, which cancels systematic error of the method.

There seems to be no upper limit to the range of this method, it being only necessary to add the bromate-bromide until an excess is present. The accuracy of a routine determination is 1/10 mg. down to 10 mg. present (as magnesium). The time required, starting from a sample of cement in the instance reported, is only  $1\frac{1}{2}$  hours, the fastest of any method.

The exact value of the thiosulfate need not be known as accurately as its ratio to the bromate-bromide, which may be determined quickly before a set of analyses.

Ca, if present, is precipitated as oxalate before precipitation of the magnesium, and is not filtered out.

The oxine precipitation has further advantages in the present problem. The accuracies in many of the above methods were obtained by precipitation in a volume of several hundred cc., and in the

presence of much ammonium salt. Great accuracy was obtained, for example, by Schuman and Berry\* by precipitation in a volume of 400 cc. containing 50 grams of NaCl. It is seen that the large volumes and high salt concentrations of the solutions to be analyzed in the present problem present no difficulties; it is probable that the magnesium oxinate complex is salted out more completely by high electrolyte concentration. The bulkiness of the precipitate is advantageous where small quantities are involved, as well as the lack of any tendency to adhere to glass.

3) Magnesium is sometimes precipitated in routine analysis as the hydroxide by adding NaOH and heating to drive off  $\text{NH}_3$ . This is only suited to cases where speed is desired rather than accuracy; the large concentration of ammonium salts in the case at hand would require so long for removal that even this advantage would vanish.

That sums up all the suitable analyses for magnesium.

N.B. It should be remembered before undertaking any method of colorimetric micro-analysis, that it is necessary for the analyst to spend much time perfecting his technique, constructing a correction curve, etc. An inexperienced man may easily take weeks to become familiar with the colorimeter, prepare and standardize solutions, determine correction curves, and run enough knowns to check the reproducibility and accuracy of the method. Hence, if there is a possibility of choosing between a macro- and a micro-

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\*Schuman and Berry, Ind. Eng. Chem., Anal. Ed., 9, 77 (1937).

analysis, the former is often the wiser choice.

In the author's opinion, the most promising, and by far the most rapid, approach to the problem of adsorption of Mg on  $\text{Fe}(\text{OH})_3$  is to proceed as outlined on p. 23, and analyze for Mg. either gravimetrically, or volumetrically by the bromate-bromide method (pp. 25-26).

## EXPERIMENTAL

## F o r e w o r d.

The author has expended a great deal of time and effort in an attempt to overcome the various obstacles arising in the separation and determination of the small quantity of magnesium down by  $\text{Fe}(\text{OH})_3$  in a procedure similar to II c), p. 14. This procedure proved to be much more difficult than was anticipated, with the result that all of the time spent to date has been consumed in trying to perfect the method, and no final results have been attained.

In the light of his experience, the author is convinced that further work on the problem would be much more profitably applied in the direction indicated on the previous page. The accuracy should be at least as great, and the time consumed far less. The number of operations required would be reduced to a very small number: filtration of  $\text{Fe}(\text{OH})_3$ , precipitation of magnesium oxinate, filtration of the latter, and its determination. By contrast, the time-consuming multiplicity of operations involved in the determination of the coprecipitated magnesium itself is apparent; and added disadvantage is the necessity for meticulous care inevitable in a micro-analysis, which makes even a simple operation a slow one.

### Outline of Work Done.

As mentioned previously, both Victor and Chamberlin in their gravimetric work on the problem used method I (p. 12), which was not sufficiently sensitive to investigate the region of the adsorption curve near the origin. The author undertook to extend the curve toward the origin by using the same procedure for the precipitation of  $\text{Fe}(\text{OH})_3$ , then separating out the adsorbed magnesium, and determining it by a micro-analysis.

The separation of the magnesium from the  $\text{Fe}(\text{OH})_3$  is not difficult, being accomplished by reprecipitation of the latter, leaving magnesium in the filtrates. (The questions of desorption, etc., which might seriously affect the results [see p. 8, et seq.] were not considered.) The micro-determination of magnesium was first attempted by the Briggs method (1, p. 17), which now appears to have been very unfortunate. In spite of its success in the hands of the biochemists, the author could not get satisfactory results, even after the expenditure of a considerable amount of time.

The Briggs method involves precipitation of magnesium as  $\text{Mg-NH}_4\text{PO}_4$ , which requires the removal of most of the ammonium salts present, a problem which took some time to solve satisfactorily. Incidentally, the microanalysis for magnesium by precipitation with oxine also requires removal of much of the large quantity of  $\text{NH}_4$  salts (or all of them, depending on the particular procedure), in contrast to the macro-analysis, in which this is unnecessary.

After the question of removal of ammonium salts was solved,

many runs were made in which a known amount of magnesium was carried through the whole process of separation and determination. The determinations were made by the Briggs method, and although in many cases the check-runs would agree among themselves, the values found were much greater than the values present. It was thought probable that some other ion must be present which gave a phosphate precipitate in ammoniacal solution, so the Briggs method was given up.

Work was begun on the determination of magnesium by Berg's method (p. 20). This seemed to be satisfactory, although certain difficulties arose due to the limitations of the centrifuge available; these will be mentioned later.

In the following pages, the procedures which might be applicable in further study of the problem will be taken up in some detail.

## Procedures

### A. Reagents.

In this paper it may be assumed, unless otherwise stated, that all reagents are of C.P. or Reagent quality, not further treated. Most chemicals are J. T. Baker's Analyzed.

1)  $\text{FeCl}_3$  solution. Victor and Chamberlin prepared this solution from iron wire (Baker's "Iron Wire for Standardization", Fe = 99.8%, no analysis of impurities given); since a wire of this sort may contain up to 0.07% P (= 0.2% as  $\text{PO}_4$ ), it does not seem advisable to use it (pp. 4-6), as errors from this source might easily be large in comparison to the quantity which we are measuring. To avoid this source of error, Merck's "Spec. Phosphorus Free"  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was used, the maximum limit of P being stated as 0.000%. A solution was made up to contain about 0.1 g.  $\text{Fe}_2\text{O}_3$  in a 25 ml. pipet, the samples delivered by this pipet were analyzed gravimetrically (a volumetric analysis would be fully as good). Volumetric measurement of many of the of the reagents was employed, using standardized pipets, as it is very rapid and sufficiently accurate, besides ensuring uniformity.

One-tenth gram of Fe (as  $\text{Fe}_2\text{O}_3$ ) is the quantity used by Victor and Chamberlin, and is about the largest quantity conveniently filtered and washed; for method IV (p. 14) a much more concentrated solution should be made up, to provide samples up to several grams. The Fe solution should contain enough HCl to prevent hydrolysis of the precipitation solution when heated to boiling, but not enough

to increase greatly the ammonium salt concentration when neutralized by ammonia; 10-20 ml. per liter should suffice. This HCl should be added to the ferric chloride before dissolving in water, otherwise a brown solution will result, which will turn light yellow only slowly, even with much acid present. A few ml. of bromine water should be added and boiled off to oxidize all Fe to ferric.

2)  $MgCl_2$  solution. Prepared from magnesium turnings (Eastman). Since qualitative tests showed the absence of Al and the alkaline earths, the magnesium was assumed pure enough to make up the solution accurately by weight. The quantitative solution of the metal in HCl is very troublesome, due to the vigorous reaction; the following procedure, however, works very well.

In a 2 liter conical flask, place 265 ml. conc. HCl (i.e., the calculated amount plus a few ml. excess) and 500 ml. of distilled water; stand in a large ice bath, and provide with a spray-catcher (e.g., a 100 ml. dist. flask with the neck cut off to 2 in., and a 1 cm. hole blown in the side of the bulb). Weigh out exactly 40.00 g. of magnesium, and add in small portions to the flask, replacing the spray-catcher after each addition; if the liquid becomes warm, allow to cool before adding more magnesium. Due to the  $H_2$  involved, keep flames away.

When magnesium is all dissolved, wash down the spray-catcher and flask, and transfer carefully to a liter volumetric flask, diluting to the mark (at 20°). This gives a solution containing 1.000 g. of magnesium in 25 ml.; amounts of 0.4 g. and 0.2 g. may

be measured out by 10 and 5 ml. pipets.

A portion of this solution was diluted to 1/10 strength, using calibrated volumetric flasks; a portion of this latter solution was again diluted, and so, giving: "A" (original solution) with 1.000 g. Mg/25 ml., "B" with 0.1000 g./25 ml., "C" with 10.00 mg./25 ml., "D" with 1.000 mg./25 ml., and "E" with 0.1000 mg./25 ml. The last two solutions furnished known amounts of magnesium for micro work. It is advisable to add a ml. of HCl to the diluted solutions before making to volume, to prevent mold growth and retard the solution of silica.

The accuracy of this procedure was tested by analysis, using the  $MgNH_4PO_4$  method. As no foreign ions were present, only one precipitation was carried out, since the known concentration of magnesium permitted the immediate addition of the optimum  $PO_4$  concentration. The first solution, prepared in March, 1937, and the second, prepared in September, were analyzed in October.

Solution A, old batch ----- 1.002 g. Mg/25 ml.

Solution A, new batch ----- 1.001 g. Mg/25 ml.

Solution C, old batch ----- 9.91 mg. Mg/25 ml.

As the total samples in the last solution were only 10 mg., it was felt that the error here was probably in the analysis itself, and casts no doubt on the reliability of the above method of preparing magnesium solutions. The high value found for the older A solution could easily be due to evaporation during the summer.

3)  $NH_4Cl$  and  $NH_4NO_3$  solutions. (The author used  $NH_4Cl$ .)

A fairly concentrated solution, 5 grams in 25 ml. of solution, was made up so that a pipet could be used to measure out the buffer salt for the precipitation. A 1% solution was made up several liters at a time for washing the  $\text{Fe}(\text{OH})_3$ .

4)  $\text{NH}_4\text{OH}$ . As the ferric hydroxide is not weighed, it was not deemed necessary to distill the ammonia, filtration being sufficient. A volumetric analysis for the  $\text{FeCl}_3$  solution (1) is recommended if a standard solution is available; if it is done gravimetrically, distilled ammonia is required. For the procedure for distilling ammonia, see Victor's thesis (note, p. 7).

## B. Apparatus.

Besides the usual apparatus, the following were required.

1) For filtration. Four Jena sintered glass crucibles ~~#3~~ with gooch adaptors to fit; the latter with stoppers to fit four 500 cc. suction flasks. All these were labeled and numbered to correspond. For convenience, a filter arm was set up to hold the adaptors and crucibles when not in the suction flasks; occasionally, the holes in the arm had to be enlarged to fit. To avoid dust, the crucibles were always kept covered with porcelain crucible covers.

The Jena crucibles will not filter  $\text{Fe}(\text{OH})_3$  alone, but work very well when provided with a mat of filter cellulose. To prepare the mat, a tablet of the cellulose was broken up in a beaker of water, and stirred with a fast motor stirrer until all disintegrated. Enough suspension was poured into the filter to form a mat 1-2 mm. thick, then the water was slowly sucked through. If an even mat was not formed, it was stirred up with a stream from a wash bottle until a uniform suspension was again formed, and again sucked down slowly. The mat was protected with a 2 cm. Witt (perforated porcelain) plate when filtering through the crucible.

During use, fine particles of cellulose, caused partly by action of hot dilute HCl (used to redissolve the hydroxide), gradually clogged up the sintered funnels. To clear them out, they were filled half full of conc.  $\text{HNO}_3$ , then filled to top with conc.  $\text{H}_2\text{SO}_4$ . This mixture was stirred, then sucked through over a period

of several minutes, and the crucible washed well with water. To clear the plate of dirt, etc., the crucible was next held upside down on the adaptor, and several hundred cc. of water sucked through as rapidly as possible. This flushed out the disk well.

2) To provide suction for the filtration, a small wide-mouthed bottle was fitted with a 5-hole stopper, and five glass bends, that to the aspirator extending to the bottom to draw out any liquid sucked in, and the other four provided with heavy pinch clamps and tubing. Lead shot was put in the bottom of the bottle to keep it from tipping over.

To break the vacuum conveniently when desired, it was found advisable to have a similar bottle between the aspirator and the distribution bottle. This latter had a 3-hole stopper, with one bend leading to the apparatus, one (extending to the bottom) to the aspirator, and a glass stopcock in the third hole. The stopcock was not put in the distribution bottle, because the latter was put away when not filtering, and the second bottle was more convenient for general use.

As the ball check valves in the aspirators are not at all dependable, and corrode badly in the ammonia fumes, it is well to remove them and use a bunsen valve instead. Fit a 15 mm. i.d. glass tube 10 cm. in length with one-hole stoppers and glass bends at each end, one of the bends extending  $\frac{1}{2}$  in. in through the stopper; a bunsen valve is slipped on the long bend (inside the large tube). The valve consists of about 6 cm. of regular heavy-wall 1 cm. o.d. rubber tubing, with a glass plug at one end, and a clean slit about 10-15 mm.

long in the middle; this slit is best made by thrusting a small sharp knife blade into the bore of the tubing, and out through the wall. (It is practically impossible to make a good slit by cutting inward.) The whole assembly is connected to the aspirator by a short tube. Such a valve is absolutely necessary to prevent water from flooding back through the aspirator when the faucet is turned partly off to obtain a low suction.

3) Pipets. Pipets of all sizes were calibrated for measuring out the solutions. Transfer pipets from 5 ml. up were kept clean by keeping in a liter graduate full of water, with a half inch of glass beads in the bottom to protect the tips. Smaller pipets were kept in a 250 ml. graduate.

As markings were desired on the pipets, they were etched in with Diamond (HF) ink, as labels were not protected during prolonged immersion by collodion, parafin, or spar varnish.

4) Wash bottles. For hot solutions, it was necessary to protect the mouth against steam by a bunsen valve inside the bottle (on the blowing tube). The stream was controlled by a third tube through the stopper of the bottle, which was so bent that it could be closed at will by the thumb. A short length of small rubber tube on the end of the glass tube protected the thumb from the steam, as it needed only to be bent sideways. Similar wash bottles must be used for ammoniacal solutions (even cold) as the ammonia fumes are very irritating to the mouth.

A small (250 ml.) wash bottle delivering a fine stream was found necessary.

5) A complete assortment of calibrated volumetric flasks. Any not within B. of S. tolerances were discarded. If kept full of water they held a film indefinitely.

A large number of breakages were avoided among the smaller sizes of volumetric flasks (100 ml. and less) by keeping at all times, even during use, in small beakers. A circle of filter paper in the bottom of the beaker prevented it from sticking to the flask by capillary attraction if any liquid dripped into it.

6) For the collection of small filtrates, a 50 ml. suction flask was handy. It was kept standing in a 100 ml. beaker with lead shot in the bottom, to prevent tipping over.

7) Several 250 ml. beakers were labeled with their weight to 1/10 g., and marked at 150 ml. Beakers with their ground glass spot at that level are best.

8) A triple-arm pan balance was used a lot, as mentioned later, to weigh solutions to 1/10 g. The one in the balance room at present has been calibrated twice; the accuracy is as follows: 0 to 50 g., 1/10 g.; 50 to 80 g., 3/10 g.; at 200 g., 4/10 g.

9) Four suberite rings, medium size (about 10 cm. diam.). These were excellent for holding 250 ml. beakers at an angle, so that the precipitate would settle in the lower corner, making decantation easier.

### C. Precipitation and Filtration of $\text{Fe}(\text{OH})_3$ .

1) Precipitation and Digestion. The procedure used by Victor (q.v.) has been modified to suit the determination of Magnesium directly rather than by difference. The volume of the solution during the precipitation was determined more accurately, as it is one of the important variables; and the filtration was speeded up greatly by using sintered glass crucibles with a cellulose mat, rather than paper and funnels (which are necessary in Victor's procedure).

It is desirable in comparing duplicate runs to have the volume of the solutions during the precipitation as uniform as possible, for the magnesium adsorbed depends on the magnesium concentration, which in turn depends on the volume. Therefore the 250 ml. beakers marked at 150 ml. are used, although the exact volume was determined by the relation:  $\text{volume} = \text{weight}/\text{density}$ ; this calculation is discussed later (p. 71).

It was found best to make the runs in sets of four at a time, either two pairs of duplicates or all the same. It will be assumed in the following that four runs were being carried through simultaneously.

The weighed and marked beakers were set up on tripods with asbestos-centered gauzes. Tirrel burners were set on 1 in. blocks beneath. A ringstand was set up beside them with a ring and plain wire gauze, a short-type Cenco Tirrel below, and a buret held in a buret-clamp high enough over the ring so that it will just clear a 250 ml. beaker. The buret was filled with filtered conc. ammonia.

(This assembly on the ringstand was the easiest means of measuring out a given excess of ammonia; if greater accuracy were desired in determining the excess, dilute ammonia could be used.) If a clamp-holder were clamped to the ring-stand up under the buret-holder, and the latter loosened so as to pivot around the stand, the buret could be swung out of the way with one hand while setting beakers on the ring.

A 7-8 mm. glass tubing manifold with six outlets to distribute gas to the five burners made a neater set-up.

The filtration set-up was made ready, with the mats prepared in the crucibles. The bunsen-valve wash bottle full of wash liquid was heated to boiling, with a 600 ml. beaker full heating on the steam bath. This last heated more quickly if all but the largest ring were taken out and the beaker set down in the bath; the large volume of wash liquid required made it necessary to have this beakerful heating all the time. (The above preparations could be made while the solutions below were heating to boiling.)

The amounts of Fe, Mg, and  $\text{NH}_4\text{Cl}$  desired were pipetted into the weighed beakers, diluted almost to the 150 ml. mark (leaving room for thermal expansion and rinsing), covered, and heated to boiling. The beaker was transferred with a beaker tongs to the ringstand, swinging the buret out of the way, the cover-glass and side of the beaker washed down, and water added just to the mark. The burner was placed under the beaker to bring again just to boiling, and removed. The buret was brought over the solution, and when boiling ceased, ammonia added slowly with constant stirring until the fresh

vapor, rising from the solution after blowing away the steam, had a distinct odor of ammonia. (Accurate control of the final pH might be obtained with indicators on a spot plate, if the effect of heat on the pH of the buffered solution were studied.)

Kolthoff and Sandell, p. 295, infer that the adsorptivity of  $\text{Fe}(\text{OH})_3$  is not altered significantly by the rate of addition of ammonia. This point should be studied, and the rate of addition governed accordingly.

The point at which the odor of  $\text{NH}_3$  is detectable is very soon after the Fe is all precipitated. Now,  $\text{Fe}(\text{OH})_3$  is all precipitated at a pH of around 5; furthermore, the high temperature and high ammonium ion concentration in the solution, will make the solubility of free ammonia very small. Considering these facts, it is likely (or at least possible) that the odor of  $\text{NH}_3$  will be detectable in slightly acid solution. As the adsorption behavior changes greatly in going from acid to basic solution (Kolthoff and Sandell, p. 296), the exact excess of ammonia is seen to be of great importance. The effect of adding various volumes of  $\text{NH}_4\text{OH}$  beyond the "odor point" should be investigated. The usual practise of adding a large excess of ammonia in the analysis of iron undoubtedly results in much more contamination of the precipitate than is necessary.

It is likely that variations in the final pH of the solutions were partly responsible for the lack of close agreement between the duplicate runs of both Victor and Chamberlin; in further work, great care should be taken in detecting the "odor point", and in measuring

any excess beyond it. (This implies, of course, a knowledge of the strength of the ammonia being used.)

When the requisite ammonia had been added, the temperature was taken (this datum was used later with the weight of solution in calculating the volume; and the temperature of an isotherm must be stated in any case). After several runs had been made, the procedure became quite uniform, and the temperatures were constant to within a degree or so, making necessary only occasional checks.

Next, the beaker and solution were weighed to 1/10 g. on the triple-arm balance, returned to the tripod and digested a minute or two at just below the boiling point. The flame had to be very small, as any ebullition would make the precipitate slimy and hard to filter (cf. Kolthoff and Sandell, p. 295), and also would retard settling.

The time of digestion may effect the amount of adsorption, a point which ought to be investigated.

After digestion, the beaker was removed from the flame, the precipitate let settle. If the precipitate tended to float on top of the solution instead of settling (due to bubbles of  $\text{NH}_3$  if any excess were added, or to some other cause), vigorous stirring would usually cause it to settle properly.

2) Filtration and Washing. When the precipitate had settled, the clear liquid was decanted through the sintered funnel, using just enough suction to cause a good rate of filtration. As little precipitate as possible was poured into the filter, as it would slow down the flow greatly.

If the filtrate were tinged with red, either the mat was thin or uneven, the suction too great, or the precipitate had not completely flocculated. Wash water which was not hot enough or which had too little electrolyte, would allow the precipitate to peptize. However, the loss of a minute amount of  $\text{Fe}(\text{OH})_3$  did little harm where Fe was not being determined.

In decanting, the stream was directed down a stirring rod on to the Witt plate, so that the mat was not disturbed, and the beaker held very steady, to avoid disturbing the precipitate. When the precipitate started to come over, the decantation was stopped.

The stirring rod and sides of the beaker were washed down with hot wash liquid, then the precipitate stirred up thoroughly with a strong stream, until, say 20-30 ml. had been added. The beaker was set in a suberite ring at a  $45^\circ$  angle to settle. After treating the other runs similarly, the first was decanted and washed again, repeating until washed sufficiently. When filtering after the last washing, the suction was reduced, and the precipitate transferred completely to the crucible (leaving in the beaker any precipitate which did not pour out).

Notes on Washing. The washing of the precipitate is the weakest point in this procedure. As shown below, so much washing is necessary to free the precipitate of the original Mg-rich solution, that for a period of about an hour it is soaking in wash liquid for low Mg concentration. If the Mg is truly adsorbed, it seems highly improbable that it would survive this long soaking unaffected. Unless

experiments are carried out as outlined on p. 10, which prove that desorption does not take place during this long washing, any methods requiring filtration of the precipitate must be discarded.

All this is in sharp contrast to the situation in method IV (p. 14), where the precipitate is never in contact with anything but the original solution, and is always under the same temperature conditions (use of a steam funnel will insure this).

To calculate the number of washings necessary, first we must figure the maximum fraction of the original Mg which may remain. The adsorbed Mg is about 1% of that present, under these experimental conditions; the unadsorbed Mg must be reduced to less than 1% of that adsorbed, to avoid error in determining the latter. Thus, we must wash out all but 0.0001 of the unadsorbed Mg.

Let us assume that 10 ml. are left in the beaker after each decantation, and that a washing is about 50% efficient. The first decantation (with 150 ml. originally) leaves  $1/15$  of the Mg, or 0.07. The last washing with a total volume of 30-40 ml. may be filtered nearly completely, leaving about 0.0025 of the Mg. To reduce it to the allowable value requires at least 5 or 6 intermediate washings as a minimum.

Naturally, everything which had been in contact with the original, comparatively concentrated, solution had to be rinsed carefully, e.g., the inside of the filter crucible.

#### D. Separation and Precipitation of Magnesium.

1) Separation of the Magnesium from the Precipitate. When the washing was finished, the bottom of the crucible was rinsed and the latter transferred to a smaller (250 ml.) suction flask. About 10 ml. of 1:3 HCl was added to the beaker, which was covered, and boiled gently until any precipitate on stirring rod or the sides of the beaker was dissolved by the acid vapor. Then the liquid was poured into the crucible (the suction being turned off), stirred until precipitate was all dissolved, then sucked through. The Witt plate was rinsed and removed; then crucible and mat washed until no yellow color remained. The adaptor was rinsed, and Fe solution transferred to original beaker, diluting to about 100 ml., and heated to boiling.

The 500 ml. suction flask and its adaptor were washed thoroughly (discarding the original solution and washings). The mat in the crucible was stirred up in water and sucked down evenly, and the Witt plate replaced. One cellulose mat could be used repeatedly until the sintered plate had to be cleaned out with nitrating mixture.

Enough  $\text{NH}_4\text{Cl}$  to keep magnesium in solution during the reprecipitation of the  $\text{Fe}(\text{OH})_3$  was formed by neutralization of the HCl.

The iron was precipitated as before, digested, let settle, and decanted through the sintered funnel, transferring the entire precipitate.

The author reprecipitated three times with several washings, but this appears to be time wasted; not more than 5% of the magnesium present would be coprecipitated, so two reprecipitations

would suffice to recover 99% plus, even with no washings, a great saving in time. Furthermore, the volume of the filtrates are only about 200 ml., if washings are omitted.

After the second reprecipitation and filtration, the ferric hydroxide was dissolved in hot 1:3 HCl and discarded. The ammoniacal filtrate containing the magnesium was put on the steam bath; any  $\text{Fe}(\text{OH})_3$  which may have passed through the filter would flocculate, and could be filtered out. When free of iron the filtrates were acidified slightly, to reduce the solubility of silica, and evaporated down.

Evaporations were much more rapid if the watch glasses, supported on hooks, were concave downwards, as vapor condensing on the under surface dripped outside the beaker instead of back in.

2) Removal of  $\text{NH}_4\text{Cl}$ . About 2.5 grams of  $\text{NH}_4\text{Cl}$  are in the filtrates with the magnesium from the neutralization of the dil. HCl with ammonia. This interferes in most of the micro-analyses for magnesium.

a) If more than 0.1 mg. of magnesium is present, it may be precipitated in the filtrates without evaporation. 5-10 g. more  $\text{NH}_4\text{Cl}$  should be added to bring the concentration up to that recommended by Berg (see p. 19, note). A gravimetric procedure is convenient for quantities between 0.1. and 10 mg.; for any procedure, a convenient filtration medium is a micro- or semi-micro-gooch filter.\*

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\*See, for instance, second note, p. 19; or Dunbar, Ind. Eng. Chem., Anal. Ed., 9, 355, (1937).

b) For less than 0.1 mg. of magnesium, most or all of the  $\text{NH}_4\text{Cl}$  must be removed. If Berg's micro-precipitation is used, 0.3 to 0.5 g. of  $\text{NH}_4\text{Cl}$  should be present; Brigg's ( $\text{MgNH}_4\text{PO}_4$ ) or Alten's procedures require the absence of  $\text{NH}_4$  ion. (Ref's, pp. 17-19).

Much time was spent (perhaps more than was necessary) finding the best way to remove  $\text{NH}_4\text{Cl}$ ; the following methods were tried, the solutions having been evaporated to dryness.

First the beakers were set in copper water-baths, which served as air-baths, to volatilize the salt by heat. This was a slow process (3-6 hours), and left on the bottom of the beaker a fluffy residue, probably partly silica, with some organic carbon, from which the magnesium could not be wholly extracted with decinormal  $\text{HCl}$ .

To burn off the carbon, the direct heating of the beakers was next tried. To prevent the escape of the heavy fumes, 200 ml. balloon flasks with water flowing through were set in the tops of the beakers (which were 400 ml.) as condensers. When a large amount of  $\text{NH}_4\text{Cl}$  had accumulated on the latter, they were momentarily removed, dipped in a large beaker of warm water to dissolve the salt, and wiped. This system would have been satisfactory, except that the strain set up in the thick glass caused them to break--either on cooling, or after a week or so. For small amounts of  $\text{NH}_4\text{Cl}$  and with smaller, thinner, beakers, the direct heating might be suitable.

The possibility of heating in porcelain was rejected solely because it would have been difficult to see whether the minute resi-

due after ignition were all dissolved or not.

The final solution of the problem was the easiest way of all: To the nearly dry salt were added 10-30 ml. of conc.  $\text{HNO}_3$ . The beaker was covered tightly until the initial rapid evolution of gases had ceased, then the cover glass was supported on hooks and the liquid evaporated to dryness. One such treatment removed almost all the  $\text{NH}_4$  salts. (Adding nitric acid to a solution was not nearly so effective as adding to it the nearly dry salt.)

When dry, a few ml. of hot decinormal  $\text{HCl}$  were added, and the residue loosened by rubbing well with a policeman. The mixture was let stand until certain that all the magnesium had dissolved, then filtered into the 50 ml. suction flask through a Gooch crucible fitted with a small circle of #42 Whatman's paper. The beaker was rubbed with the policeman, and rinsed well. The paper was washed thoroughly (using a fine stream to reduce the volume needed). The bottom of the Gooch crucible and the adaptor were then rinsed. With care, the volume could be kept to within 25 ml. If the precipitation was to be made in a centrifuge tube, the solution had to be evaporated to a small volume, transferred to the tube, and perhaps evaporated still further by supporting the tube in the steam bath in a cork. However, for large amounts of magnesium, above 25 gamma, it was necessary to dilute to known volume and take an aliquot for analysis, thus avoiding these last evaporations.

### 3) Precipitation of Magnesium.

a) A great many runs were made in which magnesium was precipitated as  $\text{MgNH}_4\text{PO}_4$ ; as stated previously, this seems to be un-

satisfactory. The precipitate was determined by the Bell-Doisy reaction (see p. 17). Every effort was made to avoid the presence of silica, which may interfere by forming silico-molybdic acid. The residue after removal of  $\text{NH}_4\text{Cl}$  was baked to render the silica insoluble, and the solutions were analyzed as rapidly as possible.

To determine the correction for losses or gains of magnesium through the process of separation and determination, several runs (denoted in the notebook by "st" after the number of the run) were made, in which the  $\text{Fe}(\text{OH})_3$  was precipitated and filtered as usual, but with no magnesium present. (The washings were omitted to save time.) After dissolving the precipitate in the usual manner, a known amount of magnesium was added (to simulate that usually coprecipitated), and the reprecipitations and subsequent treatment carried out in the usual manner. It is necessary to determine these corrections, if any, before the magnesium found can be assumed to equal that coprecipitated.

The results obtained were surprising. While the four check-runs in a given set often agreed to within a few percent, their divergence from the known values varied at random from plus 14% to plus 160%.\* To see if these errors were due to a mistake in preparing the dilute magnesium solutions, samples of the latter were analyzed by the same method, with the following results: Added 800 gamma, found 762, 771; added 40 gamma, found 31, 27. The first sample was ~~found~~ from one of the solutions previously checked gravi-

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\*A table of the results from the "st" runs will be found in Appendix III.

metrically (see p. 34), and found correct.

The results found here show, firstly, that the  $MgNH_4PO_4$  precipitation is not satisfactory for small amounts; and secondly, that the large positive errors found in the "st" runs are due either to magnesium picked up during the lengthy procedure, or to some foreign ion which precipitates as the phosphate in basic solution. The author could find no plausible source for the accidental introduction of amounts of magnesium as large as 100 gamma. There has been no time to decide this puzzling question either by making "st" runs with another method of determining the magnesium, or by making similar runs with no magnesium, to see whether the same effect would be found.

b) When the  $MgNH_4PO_4$  method had proved inaccurate, the oxine (8-quinolinol) precipitation was adopted. Two somewhat different procedures were found in the literature, that of Berg et al., and that of Alten et al. (ref's, pp. 18-19). Alten's method provides for the elimination of  $Fe^{+++}$ , Al, Ca, and  $PO_4$ , if present, while Berg's much shorter treatment assumes their absence.

It hardly seems possible that Fe or Al would be present, as both would be removed in the second reprecipitation. The purity of the reagents should ensure the absence of Ca or  $PO_4$ . Therefore, if qualitative tests do not demonstrate the presence of an interfering ion, Berg's precipitation should be used. (After the precipitation, the magnesium oxinate need not necessarily be determined by Berg's phenol reagent method, of course).

Berg's procedure for precipitation is as follows: In a 15 ml.

centrifuge tube, the magnesium solution is mixed with .3 to .5 g. of  $\text{NH}_4\text{Cl}$ , filled to 5 ml. with water, and heated to  $90^\circ$ . Add .2 ml. of freshly prepared 2% alcoholic solution of oxine, and 0.4 ml. of 25%  $\text{NH}_4\text{OH}$ . If very small amounts of magnesium are present, it will be necessary to induce precipitation by rubbing the walls of the tube gently with a stirring rod. Berg states that with quantities of magnesium under 15 gamma, a particular type of glass rod is necessary (consult the article for particulars),

The mixture is kept 10 minutes in the steam bath, then centrifuged at 2000 rpm. for 4 minutes. If the supernatant liquid is not orange, insufficient oxine has been added. Remove the clear liquid, wash three times with 2 ml. of hot 5%  $\text{NH}_4\text{Ac}$  made alkaline to phenolphthalein with  $\text{NH}_4\text{OH}$ . In each washing, mix the precipitate thoroughly with the hot wash liquid, centrifuge, and remove the liquid.

The author has made a few separations by this procedure, and it seems to be a good one. The following are a few remarks on the procedure.

1) Berg's precaution of using a quartz centrifuge tube, and making all solutions, including the phenol reagent, from water redistilled in quartz, seems unnecessary (unless, perhaps, for very minute amounts of magnesium). Even if errors were introduced from these sources, they are more easily rectified by carrying through a series of knowns, and determining the over-all corrections (if any) for the whole determination. This step is unavoidable in accurate work, in any case.

2) The alcoholic solution of oxine used by Berg slowly deteriorates,

whereas the solution in 1-2 N. HAc used by most other workers is good indefinitely. There is no apparent reason why the HAc solution could not be used here, possibly increasing the volume of dilute ammonia slightly to neutralize the HAc.

If an alcoholic solution is used, however, 50% alcohol must be used, as the oxine in the laboratory is in the form of 8-hydroxyquinoline sulfate.

The sulfate is sufficiently water-soluble to use an aqueous solution, adding a few ml. of conc.  $H_2SO_4$  per liter to prevent deterioration. This solution has been tried and found very satisfactory.

Remember that more of the sulfate is needed to make a solution of given strength. A 5 % solution of  $(C_9H_7ON)_2 \cdot H_2SO_4$  is 0.25 N.

3) As the precipitation was not tried with less than 20 gamma of magnesium, it was possible to start precipitation by vigorous stirring and rubbing the side of the tube with an ordinary soft glass stirring rod. Berg stresses the fact that with under 15 gamma of magnesium, a sharp point of a particular make of hard glass must be used to rub the quartz tubes used by him. Whether this is because of the quartz tube, or is a general requirement, is not known.

4) With small amounts of magnesium (20 gamma or less), a large excess of reagent is required to start precipitation; with larger quantities, precipitation takes place at once on adding the reagent. Since the principal source of error is occlusion of the reagent, it is best, when above 40 gamma of magnesium are present, to add the reagent drop-wise until the solution remains orange, then

a few drops in excess.

The presence of too large an excess results in the crystallization out of the reagent on cooling, making decantation and thorough washing difficult.

5) We are dealing here with a pure solution of magnesium (except for non-interfering ions). Hence, it should be permissible to decant the first wash liquid, and instead of further washing, dry and bake  $\frac{1}{2}$  to 1 hour at 130-140° to volatilize excess reagent. This would be a much easier and more effective procedure than washing, as the bulkiness of the precipitate prevents complete extraction of occluded oxine even with thorough shaking.

6) For amounts of magnesium above 50 gamma, the volume during precipitation may be as large as 15 ml., with no error. This permits aliquots of large volume to be taken.

7) The centrifuge available at this writing is unsatisfactory, being a small hand machine rated for 1000 to 1200 rpm. With some effort, a speed of 1500 turns can be maintained; this is a strain on the machine, the crank having broken in two places during a brief period of use. The centrifugal force produced by 1500 turns is only about half that at 2000, the speed specified by Berg. (Force  $\propto k \text{ times rpm}^2$ ). This is not enough to overcome the surface tension which holds some of the precipitate on the surface, the magnesium oxinate having a great tendency to creep. This is believed to be the main source of error in the author's trial analyses of knowns by Berg's method.

To overcome the tendency of the precipitate to creep, two possibilities are open:

a) To use a surface tension depressant such as Tergitol. To add a drop or so of this after the precipitation and digestion of the magnesium oxinate might solve the problem; but although no adverse effects can be foreseen, a thorough examination of the matter would have to be made.

b) To acquire a centrifuge capable of up to 3000 rpm. This would certainly overcome the surface tension and force the precipitate to the bottom; as an added advantage, it would pack the precipitate down much more tightly, decreasing the possibility of loss during removal of the liquid.

A hand centrifuge with a conical head might be turned fast enough, due to the reduction of air resistance. However, to maintain this speed for four minutes each centrifugation (a total of 16 minutes for each run) is hard work, and precludes the more efficient use of the time.

Therefore, a motor or water centrifuge is almost unavoidable if good results are to be obtained.

A conical cast aluminum centrifuge head\* permits heating while running, which would be desirable.

8) The removal of supernatant liquid from the centrifuged precipitates may be accomplished easily by a syphon tube.

A convenient arrangement is as follows: Provide a 6-inch side-arm test tube with a two-hole stopper. In one hole is a short glass tube which may be closed with the finger to control the suction, in

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\*MacNevin, Ind. Eng. Chem., Anal. Ed., 9 356 (1937).

the other is a tube bent down parallel to the test tube and drawn out into a rather fine capillary, long enough to reach the bottom of a centrifuge tube. This capillary should be fine enough to prevent a too-rapid flow if the suction is accidentally increased, which might disturb the precipitate.

To use, a small rubber tube from an aspirator is connected to the side-arm, the capillary is dipped into the liquid, and the vent in the test tube is closed with the finger. As the liquid is drawn from the centrifuge, the end of the capillary is lowered almost to the precipitate, using gentle suction. If some of the precipitate is drawn into the test tube, the liquid may be returned to the centrifuge tube and recentrifuged; therefore it is necessary to keep the test tube clean.

9) To heat the centrifuge tubes to  $90^{\circ}$ , the following arrangement is convenient. a 6-inch copper water bath full of water is set on a tripod with a burner underneath. A thermometer is inserted in the overflow spout of the bath by which to control the temperature. The rings are removed, and the bath is covered with a metal plate (preferably brass) in which several holes are bored to fit the centrifuge tubes. An aluminum plate used by the author corroded rapidly by electrochemical action unless insulated from the copper bath by rubber bands.

## Determination of Magnesium (after Precipitation).

The author has done work on two colorimetric micro-determinations of magnesium: the Bell-Doisy reaction, and Berg's Phenol Reagent reaction. (See pp. 17 et seq.) The following pages contain a discussion of the use of the colorimeter, and of these two procedures in particular.

### A. The Colorimeter.

The chapters in Yoe and Snell on the use and care of the colorimeter should be studied carefully. No analysis should be undertaken without first constructing a graph giving the corrections for deviations from Beer's law (see Yoe, p. 72). Besides the importance of knowing these corrections, their determination affords the opportunity of gaining experience with the colorimeter, and of learning the accuracy and limitations of the particular reaction being used.

The two main requirements for sustained accuracy of the observations are darkness and comfort. The room should be quite dark when taking readings, and as little light as possible used when filling cells and recording data. Before taking a reading, several minutes of darkness are required for the eyes to gain maximum sensitivity. Colors which are difficult to compare, such as yellow, require more resting of the eyes than others.

A good lamp for illuminating the notebook was a gooseneck lamp with a five-watt bulb; this was much too bright, but was easily dimmed down by fixing over it several sheets of heavy tinted bond

paper. The light was made just bright enough so that the page of the notebook was clearly legible when the eyes were accustomed to the darkness. The lamp was covered well enough so that no stray rays fell on the eyes, and was usually turned off while making the settings.

When filling the cells, the light used was as dim as was consistent with good visibility. A 7.5-watt bulb in a metal lampshade was satisfactory, if dimmed down a little with a sheet of heavy tinted paper. If the light is not too bright, the eyes do not lose their sensitivity during the filling of the cells.

A low table is desirable as a colorimeter stand for a verticle eyepiece instrument, so that readings may be made comfortably by leaning forward. The author used a large-sized packing box about 15 inches high, covered with dark instrument cloth. This box is beside a work table (for filling cells, etc.)

A few suggestions follow:

1) If the bottom of the cell and plunger are not perfectly clean, wipe off carefully with lens paper and alcohol. The windows of the light-box need frequent cleaning with a soft cloth.

2) Dust on the inner surface of the cell bottom may usually be washed out with a strong jet of water, while holding the cell inverted over a waste-beaker. As the cells must be rinsed out after every comparison, it is well to have a wash bottle with a tip directed upwards instead of downwards.

3) The cells should be removed from the instrument in the cell-holders, as these make a firm stand while filling and keep the

bottom clean.

4) If the cells have been filled too full, use a dropper to remove the excess. If the dropper is long enough to reach into the 25 ml. volumetric flasks, it may also be used to add a little more liquid to a cell.

5) When emptying the cells into the waste beaker, a drop of liquid always clings to the lip, often running down the side and dirtying the bottom of the cell; therefore, when emptying the cell, have a towel in the free hand to wipe off the lip before turning right-side-up. The same applies to pouring from the 25 ml. volumetric flasks.

6) As emphasized in the texts, the same cup, cup-holder, and plunger should always be used on the same side of the instrument. One set of parts in our instrument has been marked with a small scratch on the bottom of the cell-holder and on the metal part of the plunger, and a small nick on the rim of the cell; the other set has two scratches. In every comparison, the nick in the cell should face in the same direction (for instance, away from the observer). The singly marked set of parts has been used on the left side of the instrument. (When the terms "left" and "right" sides of the instrument are used in the following, they refer to the instrument when placed as in making readings, with the light-box away from the observer.) The above precautions will eliminate errors due to non-uniformities in the parts of the instrument.

7) When beginning a comparison, first rinse off the cell and plunger with the fresh liquid as follows: Pour about 3-4 cm. of the

liquid into the cell; then, holding it in the fingers, raise it up once or twice under the plunger until the liquid is forced up nearly to the top of the cell.

After thus washing off the previous liquid, empty the cell, refill with the fresh solution, and set in place in the colorimeter.

8) When the filled cell has been placed in the instrument, turn on the colorimeter lamp and watch carefully while raising the cell to the desired height, lest it overflow. When the plunger enters the liquid, the observer should look upwards through the side of the cell at the bottom of the plunger; if any air bubbles have been entrapped, they will stand out very plainly in the light. Such bubbles may usually be removed by rapidly moving the cell up and down while the plunger is in the liquid; if necessary, tip the instrument a little while doing this. Entrapped bubbles usually indicate that the plunger is dirty.

The cells are brought to a rough balance before the cover is replaced, to make sure that neither too much nor too little liquid has been put in them.

9) When through with a comparison, it is all right, unless working with corrosive solutions, to leave the liquid in the cells until ready for the next comparison. If this will be more than an hour or two, however, wash out the cell, using the wash bottle with the upward jet. Hold a 50 ml. beaker under the plunger, and wash down thoroughly with a wash bottle. Care must be taken that the bottom to the plunger is not scratched. Fill the cell with distilled water, place in the instrument, immerse the plunger, and leave until the next comparison.

10) The method of making the settings depends mainly on the preference of the observer. Some of the different ways are:

a) Raise and lower the cell about the point of balance, in the same way as a balance beam swings toward its rest point. This method seems to be the best for cases where a bad shade difference exists. In more favorable cases, where accurate results are desired, the method is not recommended, as the eye is very apt to become fatigued during the time required. (Snell states that the maximum sensitivity of the eye is obtained between 3 and 5 seconds after the start of an observation. Hence, settings should be made rapidly. If a good balance is not attained on the first try, look away from the instrument! Then try again.)

b) Yoe recommends moving the cell towards the point of balance, and stopping when the point is reached. Approach the point alternately from each side.

c) The method which the author prefers is similar to b) , except that the cell is moved each time until just beyond the point of balance, then moved back to exact balance. This may be done very rapidly, and gives results as consistent as, or more so than, the others.

11) Both eyes should be used for alternate pairs of readings, unless one eye is found to be less sensitive than the other; this is less tiring than using one eye alone, and may reduce errors of observation.

Such errors are indicated if the settings of one eye differ consistently from those of the other; and are due to such things as

not holding the eye exactly at the axis of the optical system, not focussing the eye on the exact center of the field, etc. If the same number of readings are made with each eye, such errors will probably average out.

It is sometimes difficult to make consistent readings while wearing glasses; however, the author has been able to make consistent readings without them, in spite of being quite near-sighted, since the sensitivity of the eye to color does not depend on sharpness of vision.

12) Enough settings should be made so that the probable error of the average is below  $\frac{1}{2}\%$  (for difficult comparisons,  $1\%$ ). If settings are made in the manner of 10) b) or c), above, not less than four should be made: two settings with each eye, approaching the balance from each direction.

Sometimes the first few readings are scattered, or show a drift. In case the next few readings straighten out, it is permissible to throw out the first ones, as the solutions sometimes have not reached chemical or thermal equilibrium if the comparison is made immediately after the mixing. Or the eyes may not have become fully adjusted to the darkness.

In calculating the probable error of  $\underline{n}$  readings, where  $\underline{a}$  is the average deviation from the mean, we have:

$$\text{Prob. error} = a / \sqrt{n}.$$

For example, if 16 readings are made, with an average deviation of  $1.2\%$ , the probable error is  $0.3\%$ . Eight to 12 readings are usually enough, except for difficult comparisons, when up to 20 may be neces-

sary for an accurate average; if the first four runs agree well, for most purposes no more need be made.

13) Checking the field. The zero points of the scales are assumed to have been adjusted. (See Yoe.) It is preferable when checking the fields to use a very stable solution of about the same color and intensity as those to be analyzed. As both the Bell-Doisy and Magnesium Oxinate-Phenol Reagent (Berg's) reactions result in a colloidal solution of Molybdenum Blue (presumably), a solution of cuprammonium ion is good for this purpose.

Fill both cells with the identical solution, set them at exactly the same reading, and adjust the fields until they are equal.

The light-box with which our colorimeter is provided has two fields, one bright and one dim. Too bright a field dazzles the eyes, while too dim a field strains them. The fields are changed by a lever at the bottom of the light-box; the bright field is obtained with the lever at the right, the dim field with it at the left. To adjust the former, the knob holding the bulb is loosened, and the bulb moved until the fields are equal. The dim field is adjusted by moving the lever. The latter field has been best for the two reactions studied.

When the fields seem equal, take a series of readings and calculate the ratio of the fields; this should be 1.000 plus or minus 0.003. If not, adjust again.

The fields should be checked periodically, especially whenever anyone else has handled the instrument. The accuracy of all the results depends on the equality of the fields. It is advisable to

determine the ratio at more than one depth; a variation would indicate some fault in the instrument.

14) In comparing an unknown with a standard solution, put the former in the lefthand cell and set exactly on some even cm. mark (e.g., 20.0 mm.). Put the standard in the right-hand cell and balance by moving this cell only, leaving the left cell stationary. The ratio:  $\text{Conc. of unknown} / \text{Conc of stand.}$ , which is equal to:  $\text{Reading of stand.} / \text{Reading of Unk.}$ , is found for each setting by an easy mental division.

If the unknown is considerably weaker than the standard, greater accuracy is obtained by setting the former at a higher reading (40 or 50 mm.). It must be remembered, however, that for any given ratio, the depth of the solutions must be the same as that used in determining the correction curve, as the corrections vary with the depths in most cases.

15) For accurately measuring out various volumes of standard, a small buret is convenient. A suitable one may be made by sealing a stopcock onto a 5 ml. graduated pipet. This pipet must be the type with 2 inches of free space between the graduated part and the tip. Before sealing on the stopcock, it is well to calibrate the pipet at several volumes, using a rubber tube, pinch clamp, and glass tip to control the delivery. If it is within the desired accuracy, cut off the tip, and seal on the stopcock, taking care that the graduated part is not heated very hot. After sealing, recalibrate.

The graduations on these pipets are rather far apart, hence, it is more accurate to adjust the volumes exactly to a given mark

than to attempt to estimate a reading. To allow proper drainage, run out the liquid to slightly above the desired mark, let drain at least 15 seconds, then adjust exactly to the mark. Do not neglect to touch the vessel to the buret tip to take off the last drop.

The calibration data for the author's buret will be found in Appendix IA. This buret was made from an Exax Blue-line 5 ml. pipet, and is accurate to 0.3% or better from 1 ml. to 5 ml.

16) To determine the Beer's law correction curve, make a series of comparisons in which the solution in the right cell contains the usual amount of standard (usually 5 ml.), and the solution in the left cell contains volumes (measured from the micro-buret) covering the range 0.5 ml. to 10 ml. in 0.5 ml. steps.

In most reactions, the upper limit is less than 10 ml., due to the exhaustion of a reagent.

Plot the ratios found against the corrections to be added.

17) Due to shade differences, instrumental errors, etc., when the solutions compared have far different concentrations (i.e., ratios outside the range 0.75 to 1.25), the Beer's law corrections are not so accurate. In that case, in making the check-run on an unknown solution, a volume of standard should be measured in the micro-buret nearly equivalent to the unknown, and more weight given to this second run, which will usually need no correction.

18) Explanation of page-layout in author's notebooks. The data from the colorimetric comparisons are recorded as follows: At the top of the page is the date (month and day), with the symbol "A", "P", or "E", meaning morning, afternoon, or evening, re-

spectively.

On the first two lines (sometimes on the opposite page) will be, for example:

$$\begin{array}{l} \#1 = 2.00 \text{ cc. unk.} \\ \#2 = 5.00 \text{ cc. st.} \end{array} \left. \vphantom{\begin{array}{l} \#1 \\ \#2 \end{array}} \right\} 3:14$$

meaning that the colorimetric reaction was carried out in 25 ml. volumetric flask #1 using 2.00 ml. of unknown, and in volumetric flask #2 using 5.00 ml. of standard, the reaction being completed at 3:14 o'clock.

The rest of the page consists of four columns. The first and second are the scale readings of the left and right cells, respectively; the third and fourth are the calculated ratios, and the deviations from the average, respectively, both with their averages at the bottom. At the top of the first two columns are the numbers of the volumetric flasks used to fill the corresponding cells. The time at which readings began is also noted.

## B. Colorimetric Reactions.

The Beer's Law correction curves determined for the Bell-Doisy and Oxinate-Phenol Reagent reactions are not reproduced here, as they should not be used by another worker. (Yoe, p. 70.) Furthermore, these curves would be of little value, since the Bell-Doisy reaction is advised against in future analyses for magnesium, and since certain changes are recommended in the procedure used for the other reaction.

A very thorough discussion of the Bell-Doisy and related reactions will be found in Snell (Chap. on Analysis of  $PO_4$ ). Although the author has done considerable work on it, it does not seem useful for future work, and will not be taken up here.

The Magnesium Oxinate-Phenol Reagent reaction of Berg is carried out as follows\*:

Dissolve the oxinate in  $\frac{1}{2}$  ml. of N. HCl and transfer to a 25 ml. volumetric flask with a few ml. of water. After addition of 5 ml. of  $Na_2CO_3$  and 1 ml. of Phenol reagent, immerse in a boiling water bath for 30 seconds, cool to room temperature; dilute to mark, mix, and compare with a solution similarly prepared from 5 ml. standard magnesium solution.

Phenol Reagent: Snell and Berg differ somewhat in their directions for preparing this. The author has tried both ways, and found Berg's easier.

Mix 100 g. Na tungstate, 20 g. phosphomolybdic acid, and 50

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\*Snell, p. 471; this differs in some minor points from Berg.

ml. 85%  $H_3PO_4$  with enough water to dissolve completely, boil two hours, cool, and fill to a liter with water. (Berg recommends using water redistilled in quartz for all solutions. See p. 52, 1.)

**Standard Magnesium Solution:** Berg recommends comparing with a known amount of magnesium precipitated and reacted simultaneously with the unknown. Snell uses for the colorimetric reaction a standard solution of the magnesium complex in HCl, prepared as follows: Dissolve 10 g.  $NH_4Cl$  in 100 ml. of 1%  $MgSO_4$  solution ( = 0.1 mg. magnesium), add ammonia until basic to phenolphthalein. Heat slowly to boiling, and add 10 ml. of a 3% solution of oxine. Boil for 10 minutes and filter in sintered crucible. Wash precipitate with hot 1:40  $NH_4OH$  until filtrate is colorless. Dry at  $105^\circ$ . As a standard, dissolve 0.1433 g. in 20 ml. of 0.5 N. HCl; dilute to a liter. Each ml. = 0.01 mg. magnesium. (The foregoing directions differ slightly from Snell's.)

Carrying through a known amount of magnesium along with the unknown, from the precipitation of magnesium oxinate, is preferable to using a standard solution for the colorimetric reaction, but entails much more work. A compromise between these two methods is to make up a standard, then run a series of known quantities of magnesium through the precipitation, and compare with the standard. (Use aliquots of the HCl solution for large amounts of precipitate.) A graph of over-all corrections for the whole range can thus be found. Errors in preparing the standard are corrected by this process. If a new standard must be made, it should be carefully compared with the previous one, and adjusted to the same strength.

The following are some observations on the Phenol reaction:

1) It is more convenient to use a 6 inch copper water bath than the large one in the hood for heating the flasks. Shake the flasks vigorously during the 30-second heating.

2) To cool more rapidly, immerse in a large beaker full of ice-water and shake. Cooling to room temperature can be accomplished in less than a minute.

3) Too long heating will cause the colloidal Molybdenum Blue to flocculate, causing loss of color.

4) The solutions are quite stable, so time may be saved by making up two unknowns and one standard together. Both unknowns may be compared in turn with the same standard, using a fresh portion of the latter for the second comparison.

5) On long standing (2 hours) the colored colloid begins to flocculate, causing marked fading of the color.

6) One ml. of the Phenol reagent will not take care of more than 30 gamma of magnesium (as oxinate). Berg used not more than 15 gamma magnesium in a comparison.

The author, having been used to the similar Bell-Doisy reaction, where the standard amount of magnesium is 50 gamma, doubled the volume of Phenol reagent to permit the use of the same amount of standard. This gave rise to the difficulty that below 25 gamma, a turbidity (and subsequent white precipitate) would form, probably due to the slight solubility of some constituent of the unreacted reagent. To avoid this, the Beer's law corrections were found using only 1 ml. of Phenol reagent in the respective flask when less than

25 gamma of magnesium were present.

This is clumsy, and it is recommended that in any further work, the standard be equivalent to 15 gamma of magnesium, and that aliquots be so chosen that the magnesium present falls between 5 and 20 gamma.

Due to the large amounts of phenol present for each ion of magnesium, the color produced is much darker than in the Bell-Doisy reaction (for the same amount of magnesium). Amounts as high as 50 gamma give colors deeper than is desirable, another reason for using a lower range for comparison.

7) The method of Alten et al. for determining the magnesium oxinate by formation of a dye (see p. 21), should not be overlooked. This method probably has a far larger range than Berg's, is probably as accurate, and as easy, if not more so. Less than 10 gamma cannot be determined, however. A disadvantage is the red-orange color, which may be difficult to compare accurately. (Of course, this should be remediable by making more settings, or by the use of a suitable color filter.) The solutions are probably very stable.

## Miscellaneous.

1) Calculation of volume of solution in the precipitation of  $\text{Fe}(\text{OH})_3$ . (P. 43.)

$$\text{Volume} = \text{Weight} / \text{Density.}$$

That concentration of magnesium left after the addition of the ammonia is presumably the concentration in equilibrium with the adsorbed magnesium; hence, the volume after addition of  $\text{NH}_3$  is the volume to be found. As most of the ammonia added is required to neutralize the acid present and raise the pH of the solution against the  $\text{NH}_4\text{Cl}$  buffer, the volume will change but slightly after precipitation starts. (In calculating the concentration of magnesium, the amount carried down must be deducted from the total added.)

The weight of solution is found by weighing the beaker, both empty and with the solution.

The density of a solution near  $100^\circ$  is a more difficult problem, but the following approximate equation is probably sufficiently accurate:

$$D. = 0.960 + 0.0007 \times (100 - T) + 0.010$$

In this equation, the first two terms give with sufficient accuracy the density of water at the temperature  $T$ , near  $100^\circ$ , while the last term is a correction for the presence of salts.

It was assumed that the effect of salts on the density at  $100^\circ$  is about the same as at  $20^\circ$ ; at this temperature 4% of  $\text{NH}_4\text{Cl}$  (part added as such, and part formed by neutralization of  $\text{HCl}$  by  $\text{NH}_4\text{OH}$ ) will raise the density by about 0.010. For different salt concentrations, as when much magnesium is present, the last term would have

to be changed. (Densities of salt solutions may be found in any handbook, for room temperature.) This term is admittedly a rough approximation, but an error of 50% in it will cause an error in the magnesium concentration of only  $\frac{1}{2}\%$ .

In the second term, it takes a variation of several degrees to change the density by  $\frac{1}{2}\%$ ; therefore, when the temperature after precipitation has once been determined, this term may be calculated once for all. The author found this temperature to be  $92^{\circ}$  plus or minus  $2^{\circ}$ , making the term 0.005.

It would be desirable to measure one or more specimen densities directly, as a check on the calculation, keeping, of course, the same temperature.

This method of determining the density of the solution (and from this the concentration of magnesium) is more accurate than those of Victor and Chamberlin. The former estimated a volume of 150 ml. in a 250 ml. beaker, which could hardly be accurate to better than 5-8%; the latter added up the volumes of all the solutions used, but did not allow for expansion on heating to boiling, which amounts to around 4%.

The importance of accurately determining the volume of the solution (and from this the concentration of magnesium) is obvious, as the concentration of magnesium is one of the two variables from which the curve is plotted.

2) Numbering of runs. As the runs were usually made in sets of four, they were numbered with the number of the run in the set, followed by the number of the set; as, for instance, "3-18" means the third run of the 18th set.

Runs made as on pp. 40 et seq., have only the two numbers.

Runs made similarly, but with magnesium added after precipitation (p. 13, II, b) should be identified by a suitable symbol.

Control runs made as on p. 50, have "-st" after the numbers.

Runs in which a known amount of magnesium is precipitated and compared against a standard (by Berg's procedure) to determine the over-all corrections for the process, are denoted by "-Mg" after the numbers.

### 3) Checking of Chamberlin's results.

Chamberlin left several of his  $\text{Fe}_2\text{O}_3$  residues, dissolved from the crucibles with conc. HCl. The magnesium can be separated out just as on p. 46, et seq., and determined to see if the results checked his gravimetric ones. Whether the results would justify the work involved (see p. 12, I), is open to question, although they would be of genuine interest.

## DISCUSSION OF RESULTS

Although the author's work has not as yet yielded any reliable results, those of Victor and Chamberlin warrant some discussion even though their method is open to certain criticisms. (See I, p. 12.)

A graph showing their results will be found in Appendix II.

The most striking fact about the two curves is that Victor's levels off (at Mg = 1 g./liter) to a maximum (slightly under 8 mg. Mg/gm. Fe) which is very constant up to the highest Mg concentration used, while Chamberlin's has an inflection at the point where the former reached its maximum, and increases rapidly from there on.

Although pointing out the apparent conflict between these data, Chamberlin offers no explanation for it. After comparing the procedures used by these two authors, however, the writer feels that their results are not necessarily contradictory.

It was pointed out on p. 42 that the final pH of the solutions after precipitation of the  $\text{Fe}(\text{OH})_3$  is of great importance. To elaborate on this point, let us calculate the solubility of  $\text{Mg}(\text{OH})_2$  at various values of the pH. The solubility product at  $18^\circ$  is about  $1 \times 10^{-11}$ , therefore the Mg ion concentrations in a saturated solution for different pH's will be:

pH	Mg <sup>++</sup> (in a sat. sol'n of $\text{Mg}(\text{OH})_2$ )
7	1000 Molar (i.e., cannot be precipitated)
8	10 "
9	0.1 "
10	0.001 "
11	0.00001 " (i.e., insoluble)

It is seen that at a pH of 7,  $Mg(OH)_2$  will have little or no tendency to precipitate. With each unit increase in pH, this tendency (with a given amount of Mg present) will increase 100-fold, and at a pH of 9 or 10, its solubility will be slight enough so that precipitation will be promoted to a marked extent on a hydrous oxide. While the solubility product may be changed greatly at 100°, these figures will still retain their qualitative significance.

Now Victor added ammonia to the hot solutions until its odor was just detectable, which is probably at a pH of about 6 or 7 (see p. 42), whereas Chamberlin merely poured in an arbitrary volume of ammonia which he knew would give an excess. His final pH may well have been one or two units higher than Victor's.

In view of these facts, it is possible, or even probable, that in Victor's solutions the  $Mg(OH)_2$  was so far from the point of precipitation that it was solely a case of true adsorption. Such a situation would result in a fixed maximum when the entire surface was covered with a monomolecular layer.

On the other hand, in Chamberlin's solutions the  $Mg(OH)_2$  would have been much nearer the saturation point, which would be expected to lead (in the case of the higher Mg. concentrations) to a promoted precipitation on the surface of the hydrous oxide.

This explanation seems to conciliate the results obtained by these two workers, and emphasizes the importance of rigidly controlling the pH in this sort of work.

In considering the maximum obtained by Victor, the author has made the following estimation of the maximum to be expected.

Kolthoff and MacNevin (see V, p. 15, and footnotes) have determined the surface of various  $\text{BaSO}_4$  precipitates by the dye-adsorption method. For the most finely divided precipitate which they could make, they found the specific surface to be  $54 \times 10^{18}$  Ba ions/gm.  $\text{BaSO}_4$ ; this equals  $1 \times 10^{20}$  Ba plus  $\text{SO}_4$  ions/gm.  $\text{BaSO}_4$ . As the molecular weight of  $\text{Fe}(\text{OH})_3$  is  $\frac{1}{2}$  that of  $\text{BaSO}_4$ , and as it has twice the number of ions per mole, there will be in the same size particle  $4 \times 10^{20}$  Fe plus OH ions/gm.  $\text{Fe}(\text{OH})_3$ , or  $3 \times 10^{20}$  OH ions/gm.  $\text{Fe}(\text{OH})_3$ , or  $1.5 \times 10^{20}$  OH ions per gm. Fe.

Now, as the  $\text{BaSO}_4$  in question consisted of almost colloidal particles, the non-crystalline aggregates of freshly precipitated  $\text{Fe}(\text{OH})_3$  cannot be of much smaller size. Let us assume that the surface of the latter is twice that of the former, i.e., that the particles have about  $1/3$  the volume. The last figure above becomes  $3 \times 10^{20}$  OH ions/gm. Fe.

If the surface is saturated with Mg ions, there will be one for each two OH ions, giving  $1.5 \times 10^{20}$  Mg ions/gm. Fe. Dividing by Avogadro's number to get the moles, we have  $2.5 \times 10^{-4}$  moles Mg/gm. Fe, or about 6 mg. Mg/gm. Fe.

This close agreement to the value 7.7 mg/gm. Fe obtained by Victor must not be taken too seriously, based as it is on a mere guess as to the relative particle sizes of the two precipitates. It should, nevertheless, encourage similar investigations of the spe-

cific surface of  $\text{Fe}(\text{OH})_3$  formed under various conditions; such data would be invaluable in interpreting the adsorption curves.

Other suggested lines of investigation are the effect of adding the magnesium after, as well as before, the precipitation, with various times of digestion before the addition; the speed of desorption, which should be measurable if a true adsorption is at hand; the dependence of adsorption on temperature; etc.

If we hope to show that the adsorption obeys one of the well-known adsorption laws (see p. 2), we must obtain accurate data in the range of Mg concentrations from 10 to 100 mg. Mg per liter, where only a fraction of the total surface is covered; when a large part of the surface is covered, as is the case with most of Victor's and Chamberlin's data, the equations break down.

## ABSTRACT OF THESIS

Victor and Chamberlin have studied the coprecipitation of Magnesium on Hydrous Ferric Oxide with the results discussed in the preceding section. Their method was to determine the increase in weight of the ignited ferric oxide precipitated in the presence of known amounts of magnesium.

As it seemed desirable to investigate the amount of true adsorption of Magnesium taking place under various conditions, this was chosen as the subject of the present work. In an adsorption study, the most significant results are usually those obtained at low concentrations of adsorbed substance, where only a small part of the adsorbing surface is covered. At these low concentrations (of magnesium) the amount adsorbed is very small compared to the weight of ferric oxide; in the studies of Victor and Chamberlin the experimental error in weighing the oxide was as large as the weight of MgO adsorbed when the concentration of magnesium was still rather large. Therefore, the author decided to determine the adsorbed magnesium itself after separating it from the hydrous ferric oxide precipitate.

This separation is accomplished by dissolving the filtered and washed precipitate, and reprecipitating at least twice, which leaves the adsorbed magnesium in the filtrates. The principal difficulty involved here is the washing of the original precipitate, which must be sufficient to remove completely all magnesium not adsorbed.

However, the prolonged washing necessary for this might easily cause a loss of part of the adsorbed magnesium by desorption into the wash liquid.

In a future study of this (or a similar) adsorption it might be preferable to add the adsorbed ion immediately after, rather than before, the precipitation. With this modification, the penetration of the magnesium into the pores of the precipitate would be small, and the amount of washing required would be reduced greatly.

For the determination of the adsorbed magnesium after its separation from the precipitate, a colorimetric method seemed preferable. As the Briggs method had been used by many workers with success, it was the one first chosen for the present work. The magnesium is precipitated as  $MgNH_4PO_4$ ; this precipitate is then dissolved, and the phosphate determined colorimetrically by the Bell-Doisy reaction:

Phospho-molybdate + hydroquinone  $\rightarrow$  molybdenum blue.

The large amounts of  $NH_4Cl$  present interfered with the  $MgNH_4PO_4$  precipitation and must be removed. Volatilization of the  $NH_4Cl$  by heat was first tried, but was very tedious. The best method was to evaporate the solution to dryness and add from one to three 20 ml. portions of conc.  $HNO_3$ , evaporating to dryness after each addition.

Rack blanks were run, in which known amounts of magnesium were added to the pure  $Fe(OH)_3$  precipitate and carried through the separation, removal of  $NH_4Cl$ , and determination of magnesium. The results

(Appendix III) were very high. The agreement between the runs of a given set was generally fair, but the results of different sets ranged at random from 15 to 150% high. Tests with pure magnesium solutions indicated that the  $MgNH_4PO_4$  precipitation gives results low by a few percent with small quantities of magnesium; therefore the high results mentioned above were ascribed to the presence of some foreign ion. Since no source could be found for any such ion in quantities equivalent to 0.1 to 0.2 mg. of magnesium, the Briggs method was abandoned.

Work was next started on the 8-hydroxyquinoline micro-determination of magnesium. It appeared that this method would be very satisfactory if a suitable centrifuge were available.

At this time, however, it seemed to the author that the indirect determination of the adsorbed magnesium by measurement of the loss from the supernatant liquid would be far preferable to the direct determination as outlined above. For theoretical reasons presented on pp. 14-15 et ante, the indirect method measures only the true adsorption; and in practice, its rapidity and simplicity are in very favorable contrast to the tedious and difficult direct procedure.

The indirect method offers the added advantage of requiring a macro-, rather than a micro-, determination of magnesium. The results of work now in progress indicate that magnesium may be weighed as the anhydrous 8-hydroxyquinolate with the following accuracies: 5% for 0.4 mg. Mg, 2% for 1.0 mg. Mg, 0.3% for 10 m. Mg, and 0.2% above 10 mg. Mg. The precision seems to be slightly greater, which

which is of importance in the indirect procedure, where the difference between two concentrations is being found.

Work is now in progress at this writing (May 22, 1938) on the indirect procedure, and results are expected in a few days.

#### Suggestions for Future Study

(At several places in this thesis, points which should be investigated in future work on the subject were suggested. It was recommended that these points be listed in this abstract. The author makes no claim to either originality or completeness in this list, but hopes that it may make a starting-point for future investigations.)

1) Effect of adding the adsorbed ion after, instead of before, the precipitation.

2) Effect of temperature, pH, and ionic strength of solution. This latter point includes the presence of "inert" electrolytes (e.g., NaCl,  $K_2SO_4$ ) as well as various concentrations of ammonium salts.

3) Effect of physical state and perfection of crystal structure of precipitate. These properties may be varied by the temperature and speed of precipitation, time of digestion (ageing), and other factors. It would be important to find out whether less adsorption occurs on  $Fe(OH)_3$  precipitated by urea, or by standing in a desiccator over aqua ammonia.

4) Effect of change of solvent; for instance, the addition of alcohol to the solution.

5) The rate of desorption when the contaminated precipitate is let stand in various wash liquids. This study would best be made on precipitates to which the adsorbed ion is added after precipitation, as practically all the adsorbed ions would then be on surfaces exposed to the solution.

6) The specific area of precipitates formed under various conditions could probably be found by a dye adsorption method (see p. 15), and correlated with the amount of adsorbed cation.

7) Determine the mechanical inclusion of solution by the precipitate, using the procedure described in III, p. 14.

8) It would be desirable to control the pH closely at all times with a glass electrode. It must be emphasized that ordinary pH indicators cannot be used without due consideration of the following facts: a) the salts present will affect indicators markedly, b) the end-points of the indicators will be different in hot solutions than at room temperature, and c) if samples of the hot solutions are cooled to 20° and their pH determined, the results will be well-nigh worthless, as the temperature will affect the pH of the buffered solutions markedly. Of course, uniformity in the pH of cooled samples would show uniformity in the hot solutions, and variations in pH would be shown qualitatively.

## SUMMARY

Reasons for the importance of the question of coprecipitation of magnesium on hydrous ferric oxide are given. Various methods of attack on the problem are discussed, as well as certain theoretical considerations which seem to have been overlooked in previous studies, e.g., the matter of desorption during washing of the  $\text{Fe}(\text{OH})_3$ . Suggestions have been made which it is hoped will lead to greater accuracy in further work on the problem.

A rather comprehensive list of the various macro- and micro-determinations of magnesium is given, and a selection made of those best suited to the study of this problem.

The experimental methods used by the author have been given in detail, and numerous suggestions made concerning apparatus and procedures which it is hoped will be of assistance in continuing the work.

The author has unfortunately arrived at no final results, but the results of Victor and Chamberlin have been discussed, and an explanation offered for the apparent contradiction in these results, viz., that the procedures used resulted in a difference in the final pH of the solution, which was sufficient to make the amount of adsorption very different in the two cases.

## APPENDIX I

Calibration of Volumetric Ware

A. Micro-Buret, made by sealing stopcock on Exax Blue-Line graduated pipet, 5 ml.

Initial Reading	Final Reading	Volume Found (ml.)
0.000	1.000	0.998
0.000	2.500	2.507
0.000	5.000	5.012

B. Graduated Pipet, 2 ml., marked "Hydroquinone".

When running out liquid to tip of pipet, the remaining drop should be blown out gently (after draining) while touching the tip on the side of the vessel. Large errors result from failure to do so.

Readings			
Initial	Final	Volume Read	Volume Found
0.000	2.000 (tip)	2.000	1.994
1.000	2.000	1.000	0.997
1.500	2.000	0.500	0.495

## APPENDIX I (continued)

## C. Volumetric Flask Calibrations. 20° C.

Volumes (ml.)		Identifying Mark, and Type
Stated	Found	
1000	999.9	#8 Exax--not Blue-Line
500	500.09	Exax--not Blue-Line
250	250.20	B&L (in circle), marked 15°C
250	250.05	No identification
100	100.04	B&L (in circle), marked 15°C
100	100.02	A.H.T.Co. #916 (neck broken)
50	49.93	One scratch on neck
50	49.85	Two " " "
50	49.99	Three " " "
25	25.01	#26 Exax Blue-Line, label #1
25	24.97	#20 " " " #2
25	25.02	#37 " " " #3
25	25.01	#34 " " " #4
25	25.00	#21 " " " #6
25	24.99	#81 " " " #5

## APPENDIX I (continued)

## D. Pipet Calibrations (Transfer Pipets).

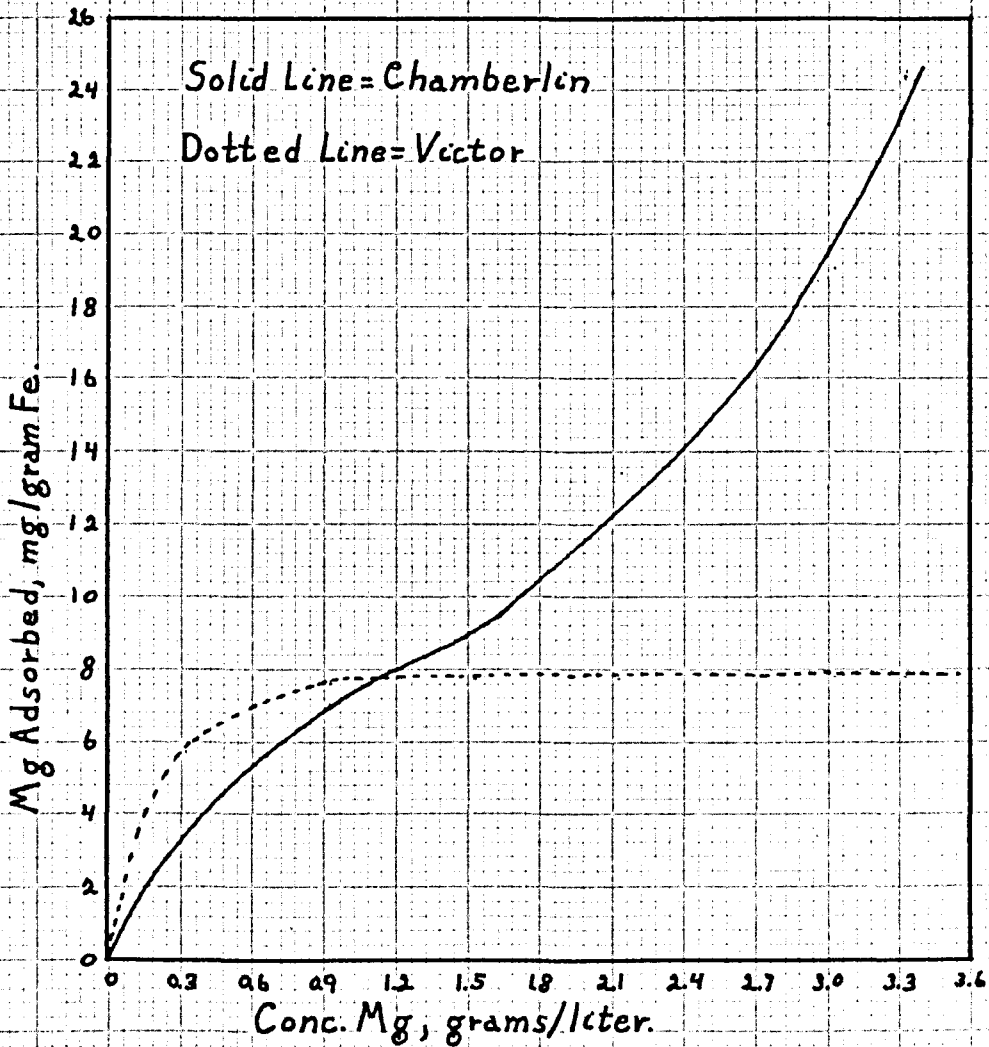
All pipets are Exax Blue-Line unless otherwise stated.

Volumes (ml.)		
Stated	Found	Identifying Mark, Etched
100	99.95	(Labeled with true volume)
50	49.93	D.S.T.
25	24.98	Fe
25	24.99	NH <sub>4</sub> Cl
25	24.97	Mg
10	9.98	Unk
5*	5.00	Unk
5**	5.02	Mg

\*This pipet is an Exax, but not Blue-Line.

\*\*Make not known.

Note: Considering that the Exax Blue-Line pipets are all low by a few hundredths of a ml., it is possible that the last drop should have been blown out; this was not done.



## APPENDIX III

Results of rack blanks (see p. 50). From Notebook II.

No. of Run	Mg added	Mg found
3-1-st	2.00 mg	2.04 mg
4-1-st		1.91 mg
1-2-st	0.400 mg	0.439 mg
2-2-st		0.410 mg
3-2-st		0.638 mg
4-2-st		0.518 mg
1-3-st	0.100 mg	0.156 mg
2-3-st		0.164 mg
3-3-st		0.204 mg
4-3-st		0.163 mg
1-5-st	0.040 mg	0.096 mg
3-5-st		0.094 mg
*1-6-st	0.400 mg	0.515 mg
2-6-st		0.483 mg
3-6-st		0.455 mg
4-6-st		0.498 mg
1-7-st	1.000 mg	1.14 mg
2-7-st		(1.10 mg) Loss
3-7-st		1.13 mg
4-7-st		1.14 mg
1-8-st	0.100 mg	0.273 mg
2-8-st		0.260 mg
3-8-st		0.260 mg
4-8-st		0.284 mg

\*In sets 1 to 5, the  $\text{NH}_4\text{Cl}$  was volatilized by heat. The missing runs are due to cracking of the beakers from heat strain. In sets 6 to 8, the  $\text{NH}_4\text{Cl}$  was removed by treating the evaporated residue with one or more portions of conc.  $\text{HNO}_3$  and evaporating to dryness. Although the latter three sets are more uniform, note that the largest gain occurs when the added magnesium is the least!

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**ACKNOWLEDGEMENT**

The author is grateful for  
the aid and encouragement  
of Professor C. M. Alter.