

The electrolysis of a solution of *chromium chloride* gave a green precipitate. The solution from the latter showed no chromium. When the current of 0.9 ampere and 5 volts had fallen to 0.05 ampere a colloidal body seemed to form, because on filtering out the precipitate at this point there remained a solution green in color from which common salt precipitated chromium hydroxide. If the current was allowed to fall to 0.03 ampere, and the precipitate was then removed, its filtrate did not show the presence of chromium.

These represent our experiences in electrolyzing the chlorides of sesquioxides.

Turning for a moment to *chlorides of protoxides* it may be noted that if cobaltous chloride yields a colloidal hydroxide it is very unstable. Colloidal bodies were not observed with manganese and glucinum. In the case of cadmium chloride, the hydroxide of the metal alone was produced. Stannous chloride gave, at first an amalgam, with the separation of some hydroxide, but on filtering this out, the filtrate while clear, was brown in color and gave a brown precipitate upon the addition of a salt solution. Ammonium hydroxide was without effect. The colloidal solution became darker in color on heating, separating eventually a dark precipitate. The solution showed no reducing action with potassium permanganate. Iodine did not separate when it was treated with hydrochloric acid and potassium iodide.

Colloidal solutions were not obtained with zinc, nickel or copper. The chloride of the latter gives at first white cuprous chloride.

Stannic chloride gave an abundance of stannic hydroxide almost immediately. There was no evidence of colloidal formation. There seemed to be a slight colloidal production with *thorium chloride*, but it soon separated from its solution, while with *zirconium* and *titanium* there was complete absence of anything like a colloidal state. *Uranium chloride* gave rise to an unstable colloidal hydroxide from which uranic hydroxide soon separated.

It may then be concluded that in electrolyzing metallic chlorides as outlined in the preceding paragraphs, stable colloidal hydroxide solutions will be found with those of the sesquioxide type, while with chlorides of the dioxide and protoxide types such formation will not arise, or if it does, it will be extremely unstable.

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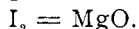
NOTES ON VOLUMETRIC DETERMINATION OF MAGNESIUM IN WATER.

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A rapid method for the determination of magnesium in water must necessarily be of great importance to the water analyst. The writers,

while in search for a satisfactory method, were led to try the arsenic method as given by Stolba (Chem. Centr. 1876, p. 727). It was soon found, however, that this method was hardly a satisfactory method for water analysis on account of the difficulty of obtaining concordant results and on account of the difficulty experienced in carefully washing the ammonium magnesium arsenate. After a number of trials without obtaining satisfactory results, and in fact without reducing the time required materially over the old phosphate method, we were led to try the modified arsenic method as mentioned by R. K. Meade. In following out this method (J. Am. Chem. Soc., 1899, 746; Chem. News, 1899, 275-8; Sutton's Volumetric Analysis), difficulties were soon encountered, as the results obtained did not check with gravimetric results. On looking more carefully into the matter, it was found that a mistake had been made in the calculations of the original paper, and copied in the Chemical News and in Sutton's Volumetric Analysis. A glance at these calculations will show that magnesium and not oxide of magnesium is intended. As stated by Meade, arsenic acid was titrated with standard iodine solution prepared by dissolving 52.24 g. of pure resublimed iodine in a solution of 75 g. of potassium iodide in 200 cc. of water, and the whole diluted to 1 l. It was further stated that each cc. of this solution should be equivalent to 0.005 g. of magnesium oxide, according to the equation:



It will be seen that according to this equation the proportional weights will be as follows :

$$253.94 : 40.36 :: \frac{52.24}{1000} : X.$$

Therefore, X is equivalent to 0.0082 g. of MgO and not to 0.005. On the contrary, if we substitute the atomic weight of magnesium instead of the molecular weight of magnesium oxide, we get the following :

$$253 : 94 : 24.36 :: \frac{52.24}{1000} : X.$$

X in this equation is equivalent to 0.005 g. of magnesium, which was unquestionably intended in Meade's calculation.

Having made corrections for this error, a number of determinations were made, but with only a moderate degree of satisfaction and accuracy. The chief difficulty was experienced with the starch indicator. This difficulty is apparently caused by the action of the strong hydrochloric acid on the starch solution. The acid seems to hydrolyze the starch so that instead of obtaining a blue starch iodide, a brownish color is formed which apparently does not disappear until long after the free iodine has been used up, thus resulting in a very unsatisfactory endpoint. We were unable in the presence of the stated amount of hydrochloric acid to obtain a good characteristic blue starch iodide.

After numerous attempts to use starch as an indicator, we were led to try the titration without the use of starch, and were surprised to find a very much sharper end-point than by using the starch paste. The last drop of thio-sulphate solution changes the straw-colored solution to a perfectly colorless one, with wonderful accuracy, so that all the determinations which have been made and which appear in this paper, have been made by titration without using starch. After making a number of determinations, we were led to modify the manipulation somewhat, believing that the method is improved by this modification, especially in the determination of magnesium in water. We would recommend the following as giving best results.

Measure out 500 cc. of water to be examined, precipitate out the iron group, and calcium by the ordinary methods. Acidify and evaporate until the salts start to crystallize out. Make up to 100 cc., transfer to an Erlenmeyer flask, add one-third of the volume of concentrated ammonia and 25 cc. of a 10 per cent. solution of sodium arsenate, cork and shake vigorously for ten minutes.

The matter of precipitation during the first determination was carefully studied. A number of experiments indicated that vigorously shaking for 2 minutes is sufficient to precipitate all of the magnesium. Exactly the same results were obtained by shaking 2 minutes, and by allowing to stand before filtering, for 12 hours. After the precipitate has settled, filter and wash with dilute ammonia until the washings are free from arsenic, using as small a quantity of ammonia as possible. Now dissolve the precipitate in 50 cc. of dilute sulphuric acid (1 to 4), and allow it to run into the flask in which the precipitation was made. Wash the filter paper with hot water until the total solution measures about 100 cc. Now add 10 cc. of sulphuric acid (1 to 1), cool and add from 3.5 g. of pure potassium iodide. Allow the solution to stand for 5 minutes, and titrate with thiosulphate to straw color. Then add **cautiously drop by drop**, until the yellow solution becomes colorless. From the amount of thiosulphate solution used, the per cent. of magnesium may be immediately calculated.

The following analyses give comparative results of the gravimetric, of Stolba and of the Meade methods :

Sample No.	Mg—Parts per million	Gravimetric.	Stolba.	Volumetric.
1.	58.	66.	60.
2.	57.22	62.	58.9
3.	55.5	60.	58.1
4.	91.	96.	92.1
5.	90.4	94.	92.
6.	90.	94.	91.
7.	154.6	168.	160.
8.	153.	169.	166.
9.	160.1	170.	162.

It will be seen that the results obtained by the volumetric method coincide very well with those obtained by the gravimetric method. It will therefore appear that this method is perfectly safe to use for rapid accurate work.

Note.—Owing to a number of errors in bibliography, the following corrections are given below :

Stolba, Zur quantitativen Bestimmung der Magnesia, Phosphor und Arsen durch Alkalimetrie. Chem. Zentr., 1876, 727 instead of 1866.

R. K. Meade, A New Volumetric Method for Magnesium. J. Am. Chem. Soc., 1899, p. 146, instead of 1889. (See Sutton's Volumetric Analysis).

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THE DETERMINATION OF CHLORIDES OR BROMIDES IN THE PRESENCE OF SULPHOCYANATES.¹

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§ I. Introductory.

In the course of a research undertaken in this laboratory it became necessary to analyze a number of solutions containing mixtures of chlorides and sulphocyanates. Investigation of the literature of the subject showed that no method exists by which such mixtures can be analyzed quickly and accurately; it was found that those methods which can be relied upon for accuracy of results require such expenditure of time as prohibits their use where large numbers of analyses must be performed. In like manner search revealed no suitable method for the analysis of bromide-sulphocyanate mixtures.

To remedy this lack, the following volumetric method is proposed. It permits of an accuracy within the limits of the usual errors of measurement with pipettes and burettes, and requires less time than any of the existing methods; a single complete determination has been found to require about one and one-half hours, while two determinations can be performed without difficulty in two hours. By proper organization of the work eight to ten analyses can easily be made within a working day.

The sum of chloride and sulphocyanate, or of bromide and sulphocyanate, is established by precipitation with excess of standardized silver nitrate and determination of the excess by titration with standardized ammonium sulphocyanate, according to the method of Volhard.² Precipitates containing silver chloride must be filtered off before the excess of silver nitrate is determined, while in the case of the bromide filtration is unnecessary.³ The new method has for its object, the determination of the chloride or bromide in a fresh sample of the solution, by oxidizing

¹ Presented before the New York Section of the Am. Chem. Soc., May 10, 1907.

² J. pr. Chem., 9, 217 (1874); Z. anal. Chem., 13, 171, (1874).

³ Rosanoff and Hill. This Journal, 29, 269, (1907); Chem. Zentr., 1907, I, 1596.