

Conductometric Titration of Iron, Aluminum, and Magnesium

E. W. KANNING and E. H. LEWIS, Indiana University

Conductometric methods of analysis have been applied to a number of determinations involving precipitation reactions. I. M. Kolthoff¹ reports, in his monograph on conductometric titrations, successful results of titrations involving the determination of the following constituents:

1. Chloride, bromide, iodide, cyanide, thiocyanate, and chromate, using silver nitrate as reagent.

2. Chloride, bromide, iodide, cyanide, thiocyanate, formate, acetate, and its homologues, using mercuric perchlorate as reagent.

3. Iodide, ferrocyanide, ferricyanide, sulfate, pyrophosphate, sulfite, thiosulfate, oxalate, tartrate, succinate and benzoate, using lead nitrate as reagent.

4. Sulfate, chromate, carbonate, pyrophosphate, oxalate, tartrate, and citrate, using barium acetate or chloride as reagent.

5. Potassium at 0°C., using sodium perchlorate as reagent. In addition to the determination of these common constituents, many others have been reported in the literature.

Since the hydroxides of ferric iron, aluminum, and magnesium are quite insoluble, it is logical that solutions of salts of these metals can be titrated conductometrically with sodium hydroxide solution to a definite end point. The purpose of this investigation was to determine the adaptability of conductance methods to the titration of these three metal ions by precipitation as hydroxides from neutral solutions of the chlorides.

Procedure

The titrations were carried out using a conductance cell of the dip type, the platinum electrodes having surfaces of 1.5 sq. cm. each, placed 3.5 cm. apart. It was found unnecessary to platinize the electrodes, as the bright platinum seemed to give somewhat better results. The solutions during the titrations were kept agitated by means of a mechanical stirrer and also maintained at a constant temperature in a water bath.

The resistance of the solution after each addition of the reagent was measured by means of a Leeds and Northrup 60 cycle A.C. galvanometer, No. 19123, and a resistance box, No. 75928.

Stock solutions of magnesium, aluminum, and ferric chlorides were prepared from the hydrated salts using carbon dioxide-free water. These solutions were standardized by gravimetric methods for the metal ion content. The sodium hydroxide solutions used in the titrations were prepared from carbon dioxide free-water.

Various volumes of the stock solutions, measured by means of pipets, were made up to 125 ml. and titrated with sodium hydroxide solution. With the exception of a few experiments, the titrations were carried out at 25°C.

The investigation was divided into four series of titrations: (1) titrations of magnesium chloride, (2) titrations of aluminum chloride,

¹Kolthoff, I. M., *Konduktometrische Titrationem*. Dresden, 1923.

(3) titrations of ferric chloride, and (4) titrations of mixtures of two or more of the metal chlorides.

In all cases the end points in the titrations were determined graphically by plotting the resistance of the solution as ordinates and the volume of reagent as abscissa.

Results

The data in Table I show the results obtained in the first series of experiments involving the conductometric titration of neutral solutions of magnesium chloride with sodium hydroxide as reagent.

TABLE I. TITRATION OF MAGNESIUM CHLORIDE

Expt.	Magnesium Present Grams	Vol. of NaOH Theoretically Required ml.	Vol. of NaOH Actually Used ml.	Error ¹ %
2 ²	0.0602	41.4	41.7	+0.33
16 ³	0.0481	29.2	29.5	+0.74
17 ³	0.0481	29.2	29.2	0 00
20 ³	0.0842	51.1	51.2	+0 05
21 ³	0.0842	51.1	52.0	+1.50
22 ³	0.1205	73.0	73.0	0 00
23 ⁴	0.1205	76.4	76.5	+0.33
24 ⁴	0 0602	38.2	39.0	+1.61
25 ⁴	0.0602	38.2	38.5	+0.33

¹Error = Grams magnesium present minus grams magnesium found from the titration, divided by the grams magnesium present times 100.

²0.1192 N NaOH used.

³0.8353 N NaOH used.

⁴0.1292 N NaOH used.

In general it was found that the determination of magnesium by the precipitation of the hydroxide with sodium hydroxide can be carried out very successfully and accurately by the conductance method. The error involved in all the experiments cited is quite low and in some cases negligible. The end points of the titrations were clearly defined and easily determined from the conductance curves, an example of which is shown in Figure 1, which is typical of all the titrations in this series.

The effect of increased temperature on the titrations was determined by carrying out a few experiments at temperatures of 40°C., 50°C., 60°C., and 70°C. The elevated temperature decreased the accuracy of the determination of magnesium because of the difficulty in locating the end points of the titrations on the graphs, due to the fact that the curves flattened out in the neighborhood of the end points.

The results obtained in the experiments involving the titrations of solutions of aluminum chloride with sodium hydroxide indicate quite conclusively, as in the case of the titration of magnesium chloride, that the conductometric method is satisfactory in the volumetric determination

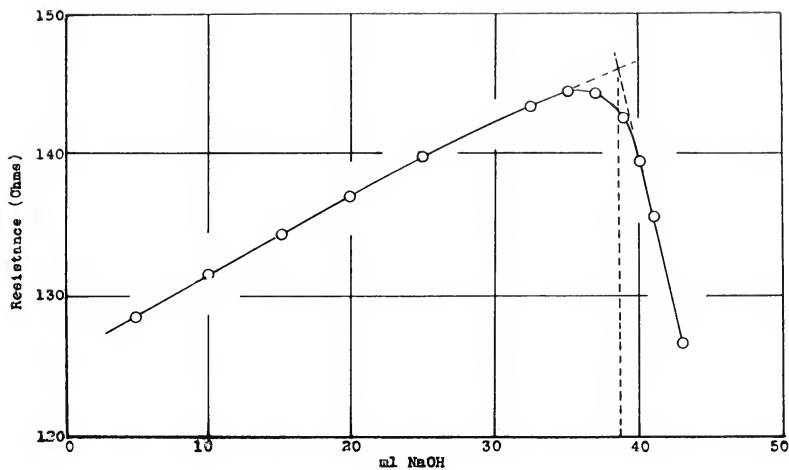


Fig. 1.

of aluminum by the precipitation as the hydroxide. The data for this series of experiments are shown in Table II.

The equivalence points for the quantitative separation of aluminum hydroxide are very clearly defined in the curves. A typical example is given in Figure 2. The formation of the aluminate is shown by a slight change in direction of the conductance curve. The greater the concentration of aluminum chloride in the original solution, the more distinctly

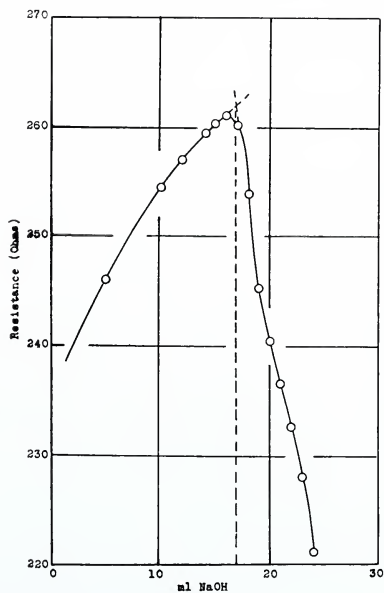


Fig. 2.

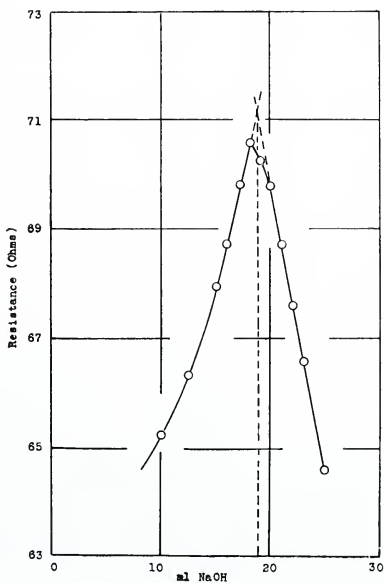


Fig. 3.

TABLE II. TITRATION OF ALUMINUM CHLORIDE

Expt.	Aluminum Present Grams	Vol. of NaOH ¹ Theoretically Required ml.	Vol. of NaOH ¹ Actually Used ml.	Error %
41	0.0101	8.50	8.50	0.00
42	0.0202	17.00	17.00	0.00
43	0.0253	21.20	21.00	-1.42
46	0.0354	29.70	29.70	0.00
47	0.0506	42.50	42.50	0.00
48 ²	0.0253	25.50	25.50	0.00

¹0.1321 N NaOH was used.²0.1095 N NaOH was used.

the aluminate formation was shown by the curves. In no case was the quantitative determination of the aluminate equivalence point possible.

The third series of experiments involved the titration of solutions of ferric chloride with sodium hydroxide. The error involved in these titrations was considerably greater than in the two previous series. In all cases the error was found to be a negative one. It may be possible that the colloidal nature of the ferric hydroxide precipitate effected the conductance of the solutions in such a manner as to interfere with the accurate indication of the equivalence points of the titrations. The addition of various salts to effect a precipitation of the colloid seemed to bear out this contention, since the accuracy of the determinations was greatly increased by the addition of sodium chloride to the solutions to be

TABLE III. TITRATION OF FERRIC CHLORIDE

Expt.	Ferric Ion Present Grams	Vol. of NaOH ¹ Theoretically Required ml.	Vol. of NaOH ¹ Actually Used ml.	Error %
60	0.0215	10.00	9.70	-3.02
61	0.0215	10.00	9.70	-3.02
62	0.0430	20.00	19.50	-2.20
63	0.0430	20.00	19.50	-2.20
64	0.0537	25.00	24.00	-3.82
65	0.0537	25.00	23.80	-4.63
66 ²	0.0753	34.40	33.00	-5.70
67 ²	0.0753	34.40	33.00	-5.70
68 ²	0.1076	49.10	48.00	-3.90
69 ²	0.1076	49.10	47.50	-4.08

¹0.1156 N NaOH was used.²0.1175 N NaOH was used.

titrated. The data for the ferric chloride series are shown in Table III. The conductance curves in this series are typified in Figure 3.

As far as this investigation has gone, the determination of ferric iron by titration of solutions of the chloride with sodium hydroxide is found to be only approximate, the error involved in the titrations preventing an accurate quantitative estimation.

The titration of mixtures of magnesium, aluminum, and ferric chloride with sodium hydroxide should, theoretically at least, give successive breaks in the conductance curves. With this in mind, definite mixtures of each of the three possible pairs and also mixtures of all three of the metal chlorides were titrated with sodium hydroxide for the purpose of a quantitative determination of each ion in the presence of one or more of the others.

The titration of mixtures of magnesium and aluminum chlorides yielded a large positive error in the equivalence point for the aluminum and a smaller positive error for the magnesium. The first break in the conductance curves was quite indistinct, in this case showing the precipitation of aluminum hydroxide. The second break, indicating the complete separation of magnesium hydroxide, was quite clear and yielded an accurate detection of the end point. From twelve titrations involving mixtures of magnesium and aluminum chlorides an average error in the estimation of aluminum was found to be +3.76%, and in the determination of magnesium, +0.31%. This series of experiments indicates a very accurate determination of magnesium in the presence of aluminum and a somewhat less accurate estimation of aluminum.

The conductometric titration of solutions of mixtures of ferric and magnesium chlorides with sodium hydroxide yields a large negative error for the estimation of ferric iron and a very small, nearly negligible, error for the determination of magnesium. The error in the case of the iron was due entirely to the difficulty in determining the point of inflection of the conductance curve which represented the equivalence point, since two distinct breaks in the curve occurred in the neighborhood of the iron end point.

From the experiments, the average error found in the determination of the ferric ion was -4.00%, and, for the determination of magnesium, +0.20%. From the data, it can be seen that a very accurate determination of magnesium in the presence of ferric iron can be carried out by a conductometric titration of the neutral chlorides with sodium hydroxide. However, the estimation of the ferric ion is only fairly accurate.

The titration of mixtures of ferric and aluminum chlorides gave results quite similar to the titration of mixtures of ferric and magnesium chlorides. The greater error was found at the first end point (ferric ion). From approximately ten experiments, the average error in the determination of the ferric ion was -2.72% and in the determination of the aluminum, -1.46%. From the data obtained, the determination of ferric iron and aluminum in the presence of each other by the conductance titration of solutions of the neutral chlorides with sodium hydroxide yields quite accurate results, the slight difficulty in locating the exact end point for the ferric ion preventing an exact determination of each ion involved.

The titration of solutions containing mixtures of the three ions yields results to be expected. The determination of aluminum and of magnesium is quite accurate, while the determination of the ferric iron end point involves considerable error. From an average of ten experiments, the error for the determination of each of the three ions was found to be: ferric, -6.13% , aluminum, $+0.56\%$, and, magnesium, -0.94% .

As a conclusion, it is evident from the data given that the conductometric titration of solutions of magnesium, aluminum, and ferric chlorides with sodium hydroxide yields (1) accurate results for the following determinations:

- a. Aluminum in solutions of aluminum chloride,
- b. Magnesium in solutions of magnesium chloride,
- c. Magnesium in solutions of magnesium and aluminum chlorides,
- d. Magnesium in solutions of magnesium and ferric chlorides,
- e. Aluminum in solutions of aluminum and ferric chlorides,
- f. Magnesium and aluminum in solutions of magnesium, aluminum, and ferric chlorides,

and (2) fairly accurate results in the determination of:

- a. Ferric iron in solutions of ferric chlorides,
- b. Aluminum in solutions of magnesium and aluminum chlorides,
- c. Ferric iron in solutions of magnesium and ferric chlorides,
- d. Ferric iron in solutions of aluminum and ferric chlorides.