

Electrometrical Determination of Magnesium by the Use of Antimony Electrode.

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[March 9, 1934.]

The applicability of antimony electrode for the determination of magnesium was investigated. The method was proposed by MALVEA and WITHEROW¹⁾ who made the use of antimony electrode in place of the hydrogen electrode which was used by HILDERBRAND and HARNED²⁾ and found to be too sensitive as well as complicated.

First it was reported that HILDERBRAND and his co-worker²⁾ determined the magnesium in dolomite and limestone by using the hydrogen electrode and reported that the method enabled the determination quickly with a comparative accuracy. However the method is rather complicated and too sensitive, so that MALVEA and his co-worker¹⁾ substituted the antimony electrode and obtained very satisfactory results where magnesium alone is present but in the presence of calcium, the quantity of magnesium should be more than 0.1 g.

Since the authors were interested in the method, the applicability was investigated under various conditions.

Experimental :

As to the use of antimony electrode in determination of hydrogen ion concentration has been investigated and reported already³⁾. It was found that the good results could be obtained in case of hydrogen ion determination by shaking the electrode, so that in this investigation the electrode was used by both shaking and otherwise. The equipment used is the same as in case of the hydrogen ion determination. As the test solutions, the standard magnesium chloride and calcium chloride which were standardized gravimetrically, were used.

The determination of magnesium was carried out as follows :

A known amount of MgCl solution which is equivalent to a certain amount of MgO is taken alone or mixed with a known quantity of CaCl₂ solution, and placed in a beaker (200 cc. volume); the solution is made slightly acid to methyl orange by adding dilute hydrochloric acid, and titrated by adding a small amount of standard sodium hydroxide, 0.5 to 2.0 cc., at a time and immediately the potential is determined by the antimony electrode. When the

titration is completed, the data are plotted on a graph so that a curve with two turning points is obtained. The first point indicates the end of neutralization of hydrochloric acid originally present, and the amount of sodium hydroxide to reach the second point correspond to the amount of magnesium which is precipitated as magnesium hydroxide. By using this method, the following experiments were carried out.

Experimental:

1. Influence of time on the change of potential.

MALVEA and WITHROW¹⁾ noted that it takes 2—10 minutes to reach the equilibrium after sodium hydroxide is added, and it was investigated as to this aspect, as noted in Table I, by taking a sample which contained 0.0464 g. of magnesium oxide and 0.0268 g. of calcium oxide in 100 cc.

Table I.
Influence of Time on the Change of Potential.

Time in minutes.	Potential.	
	Shaken.	Unshaken.
Initial.	(volt.) 0.5540	(volt.) 0.5757
2.	0.5528	0.5735
3.	0.5524	0.5732
5.	0.5517	0.5726
10.	0.5510	0.5723
15.	0.5506	0.5721

The above results indicate that when the quantity of magnesium and calcium as well as the amount of magnesium hydroxide precipitate is small, no appreciable change of potential is observed with the time so long as tried in this experiment, and also the difference between shaken and unshaken cases, is very small.

Next a larger amount of magnesium oxide, 0.116 g. and calcium oxide, 0.8232 g. in 100 cc. sample was titrated by adding 0.1265 g. of sodium hydroxide (29 cc. in volume), and obtained the following results as shown in Table II.

(See Table II on next page.)

Table II indicates that as the concentration of magnesium and calcium together with the amount of magnesium hydroxide precipitate increases, the potential varies greater and a longer time is required to reach the equilibrium, and the shaking method seems to be better than unshaken.

Table II.
Influence of Time on the Change of Potential where
a comparatively Large Amount
of MgO present.

Time in minutes.	Potential.	
	Shaken.	Unshaken.
Initial.	(volt.) 0.5625	(volt.) 0.5597
2.	0.5592	0.5560
3.	0.5583	0.5535
5.	0.5555	0.5520
10.	0.5514	0.5482
15.	0.5484	0.5437

2. *Influence of different concentration of sodium hydroxide used in the titration.*

It was investigated as to the influence of different concentration of sodium hydroxide and also that of the sample on the velocity of reaction.

Hundred cc. of sample containing 0.0464 g. MgO were taken and titrated with 0.1265/N and 1.1007/N NaOH solution and obtained the following results.

Table III.
Influence of Different Concentration of Sodium Hydroxide
used in the Titration.

No. of tests.	Concentration of NaOH.			
	0.1265/N		1.1007/N	
	0.0464 g. MgO	% Error.	0.0464 g. MgO	% Error.
1.	(g.) 0.0471	1.5	(g.) 0.0468	0.8
2.	0.0471	1.5	0.0477	2.8

As these results shown in Table III, no appreciable difference was found among these different concentration. Consequently it is advisable to use the less concentrated NaOH when the amount of Mg is not very large.

3. *Interrelation of different concentration of MgO and CaO present in the system.*

The interrelation of different concentration of MgO and CaO present in the system was investigated by using 0.1265/N NaOH, by both methods, shaken and unshaken, as to the results of titration and obtained the following results:

Table IV.
Interrelation of Different Concentration of MgO
and CaO Present in the System.

Amount used.		Shaken.			Unshaken.
MgO	CaO	NaOH used.	MgO found.	% Error.	MgO found.
(g.)	(g.)	(mg.)	(g.)		(g.)
0.1180	—	45.5	0.1180	—	0.1180
0.1180	—	45.5	0.1180	—	0.1180
0.1180	0.0134	45.5	0.1180	—	—
0.1180	0.0470	45.5	0.1180	—	—
0.1180	0.0823	46.5	0.1185	2.1	0.1185
0.1180	0.4116	46.5	0.1185	2.1	—
0.1180	0.8232	47.5	0.1212	4.4	0.1212
0.0464	—	18.5	0.0471	1.5	0.0478
0.0464	—	18.5	0.0471	1.5	0.0471
0.0464	0.0470	18.7	0.0478	2.5	—
0.0464	0.0823	18.5	0.0471	1.5	—
0.0464	0.1646	19.0	0.0484	4.3	—
0.0464	0.4115	20.0	0.0510	9.9	—
0.0464	0.8232	—	—	—	—
0.0106	—	4.5	0.0115	8.5	0.0121
0.0106	—	4.25	0.0108	2.3	0.0108
0.0106	0.0067	4.75	0.0121	14.5	—
0.0106	0.0134	5.00	0.0128	21.5	—
0.0053	—	2.25	0.0057	8.4	0.0064
0.0053	—	2.25	0.0057	8.4	0.0064
0.0053	0.0067	2.50	0.0064	20.5	—

Table IV indicates that the accurate results were obtained when the concentration of MgO was 0.116 g., and a slight error was caused by the presence of CaO to an extent that 4—5% error was obtained in the presence of eight times as much CaO as MgO. As the amount of MgO decreases viz. 0.0464 g. the value becomes larger. In the presence of a larger amount of CaO, the error becomes larger and no accurate end-point was reached when seventeen times as much CaO was present as that of MgO. By the unshaken method, the same results were obtained when MgO was present alone but no titration was possible even when the equal amount of CaO was present. An appreciable error was obtained where

the concentration of CaO was less than 0.01 g. and it became greater by the presence of CaO. Again in less concentrated MgO than 0.01 g., even a small amount of NaOH was used, no accurate end-point was reached.

Summary :

The applicability of antimony electrode for the determination of magnesium was investigated by using 0.1265 N. KOH in presence of various amount of Ca, and found that comparatively accurate determination can be made when the concentration of Mg is above 0.0464 gm. An addition of Ca increases the error but as far as the amount of Ca remains within four times as much of Mg, the determination is made within 4—5% error. Mg concentration below 0.01 gm., the error becomes much larger. Further investigation is necessary before this method could be put in practice.

Literature :

- 1.) B. B. MALVEA and JAMES R. WITHROW, J. Amer. Chem. Soc. 54, 1932.
 - 2.) HILDEBRAND and HARNED, Proc. 8th Intern. Congr. App. Chem. 1, 1912.
 - 3.) ITANO, A. and S. ARAKAWA, J. Science of Soil and Manure, Japan. IV, 29—46, 1930.
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