IV.—*The Effect of Dilution in Electro-titrimetric Analyses.*

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THE first application of conductivity measurements to analysis is that due to Küster and Grütters (*Zeitsch. anorg. Chem.*, 1903, **35**, 454), who showed that acids could be titrated accurately by these means. Later, Küster, Grütters, and Geibel (*ibid.*, 1904, **42**, 225) proved the accuracy of the method even when such substances as potassium dichromate and potassium permanganate were present in the acid solution. The estimation of acetic acid in vinegar, of total acid in red wine, of magnesia, and of various alkaloids was also shown to be possible.

Further work has demonstrated that the method is capable of very varied application. Amongst the uses to which it has been put may be noticed the analysis of wines by Duboux (*Chem. Zeit.*, 1913, **37**, 879) and by Duboux and Dutoit (*Compt. rend.*, 1908,

147, 134), the preparation of neutral ammonium citrate solutions by Hall (*J. Ind. Eng. Chem.*, 1911, **3**, 559), and the analysis of soil solutions by Van Suchtelen and Itano (52nd Ann. Rep. Mich. Board of Agric., 1913, 49). The last-named workers have also published (*J. Amer. Chem. Soc.*, 1914, **36**, 1793) the results of experiments on the estimation of chlorides, sulphates, nitrates, phosphates, potassium, calcium, ferrous iron, strong and weak acids, and of chlorides and phosphates in urine. Quite recently, Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252) has shown that certain bivalent metals in the form of their sulphates can be determined accurately by the conductivity method by titration with barium hydroxide. Meerburg (*Versl. v. h. Centr. Lab. t. b. h. v. h. Staatsoez. o. d. Volksgehoondh.*, 44-54, 1917; *Chem. Weekblad*, 1917, **14**, 1054) has reported adversely on the method as applied to the estimation of sulphates by barium acetate and of calcium by oxalic acid, but mentions that good results may be obtained in the determination of alkalinity in potable waters.

It is noteworthy that, although the method has been applied to so many reactions, no attention has been paid to the lower limit of concentration at which accuracy may still be obtained. Most of the experiments have been carried out on relatively concentrated solutions (seldom weaker than 0.1*N*), the only reference to results with very dilute solutions being one by Van Suchtelen and Itano (*loc. cit.*), who state that the titration of as little as 5 c.c. of 0.001*N*-sulphuric acid with 0.01*N*-sodium hydroxide can be performed accurately. In those titrations involving the precipitation of a salt, the solubility of which would be expected to limit the sensitiveness of the method, this point has not been touched upon.

It appears, therefore, to the author that an investigation of this nature was desirable. If the method is capable of yielding accurate results at very low concentrations, many estimations, for example, those carried out in the analysis of potable waters, could be made without previous concentration of the solutions. The present communication is concerned with the limits of the method as applied to the estimation of sulphates, chlorides, calcium, and magnesium. Rigid accuracy was not aimed at, the object being to find to what extent the method could compete with ordinary gravimetric or volumetric processes without the introduction of troublesome precautions. To that end, beyond the use of standardised measuring vessels and of "purest" commercial reagents, no special precautions were taken. No attempt was made to keep the temperature of the solutions constant during the titrations, the duration of which was usually fifteen to twenty minutes.

EXPERIMENTAL.

Except for the use of a double receiver telephone, which proved very convenient in minimising the interference of external noises, the apparatus employed was of the usual nature and therefore calls for no special comment.

The liquid to be titrated was placed in a beaker of such a size that thorough mixing could be effected by giving the vessel a rotatory motion, the stationary electrodes serving as a stirrer. The reagent was delivered from a burette capable of being read to 0.01 c.c. The curves were plotted with conductivity as ordinates and volume

FIG. 1.

of reagent as abscissæ, and in order to eliminate experimental errors at least three, and usually more, readings were taken on each limb of the curve.

Estimation of Sulphates.

A stock solution of Merck's purest potassium sulphate was prepared and the SO_4 estimated gravimetrically in duplicate as barium sulphate. From this solution weaker solutions were prepared by dilution. For the titration of these, two solutions of barium chloride, approximately $N/10$ and $N/25$ respectively, were prepared and similarly standardised.

Table I shows that the results are accurate only down to a concentration of about 200 milligrams of SO_4 per litre, a typical curve being shown in Fig. 1. When the concentration of SO_4 is 100 milli-

grams or less per litre, the precipitation of barium sulphate is so incomplete that the resulting curve changes entirely in character, exhibiting irregularity, but no definite break such as appears in Fig. 1.

Van Suchtelen and Itano (*loc. cit.*) added to their solutions a certain amount of the salt that was to be precipitated with the object of avoiding errors due to solubility. In order to test this procedure, a suspension of fine precipitated barium sulphate in distilled water was added to the sulphate solution in the beaker some little time prior to titration. The results are given in Table II.

TABLE I.

Concentration of SO_4 , mg. per litre.	Strength of BaCl_2 .	SO_4 found. Per cent.
990	$N/10$	100.0, 100.4, 99.4
198	"	99.2, 99.2, 99.2
99	} $N/25$	No end-point.
49.5		

TABLE II.

Concentration of SO_4 , mg. per litre.	Strength of BaCl_2 .	SO_4 found. Per cent.
99	$N/10$	99.7, 99.7
49.5	$N/25$	99.5, 99.2, 99.6
24.7	} "	End-point indefinite.
9.9		

Reference to table II will show that this method succeeded to a certain extent as, by means of it, good results were obtained down to a concentration of about 50 milligrams of SO_4 per litre. However, it was not effective when only 25 milligrams of SO_4 per litre were present, giving curves with an indefinite end-point of the type shown in Fig. 2. Titration at boiling temperature did not alter the character of this curve. In such cases it is possible, by taking only those points well remote from the curved portion, to arrive at an approximate value for the end-point (see dotted lines). For instance, figures derived in this manner from experiments on solutions containing 25 milligrams of SO_4 per litre were about 5 per cent. in excess of the correct value.

Estimation of Chlorides.

The salt chosen for this purpose was a sample of Merck's purest fused sodium chloride. A stock solution of this, together with the approximately $N/10$ - and $N/25$ -silver nitrate solutions used for titration, was standardised by duplicate gravimetric estimations as silver chloride.

The results obtained with varying concentration of chlorine are shown in table III.

TABLE III.

Concentration of Cl, mg. per litre.	Strength of AgNO ₃ .	Cl found. Per cent.
1000	N/10	99.7, 99.3
200	"	100.1, 99.3, 100.8
50	N/25	100.2, 100.9
10	"	100.6, 100.8
5	"	End-point indefinite.

As in the case of sulphates, a limit of concentration is reached at which the method fails, the figure in this instance being 10 milli-

FIG. 2.

grams of chlorine per litre. The addition of precipitated silver chloride before titration did not render the end-point sharp at lower concentrations.

The type of curve obtained in this estimation is similar to that shown in Fig. 1.

Estimation of Calcium.

A stock solution of calcium chloride was prepared by dissolving pure calcite in hydrochloric acid and eliminating the excess of acid by repeated evaporations on the water-bath. Both this solution and the approximately N/10-ammonium oxalate solution employed

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in the titrations were standardised by means of potassium permanganate.

Table IV shows the results obtained.

TABLE IV.

Concentration of Ca, mg. per litre.	Ca found. Per cent.
500	100.0, 100.4, 99.2, 100.4
200	99.1, 100.6, 99.1
100	End-point indefinite.

As in the case of the determination of chlorides, previous addition of the precipitated salt did not lead to sharp end-points at the last-mentioned concentration. In three such experiments, figures given by producing the straight portions of the curves gave 97.0, 97.6, and 95.8 per cent. respectively of the amounts taken.

Estimation of Magnesium.

A solution of Merck's purest magnesium sulphate was employed, standardisation being effected by duplicate estimations as magnesium pyrophosphate. An approximately *N*/10-sodium hydroxide solution, standardised by means of sulphuric acid and pure sodium carbonate, was used for titration.

Variation of the concentration of magnesium gave results shown in table V. The typical curves for these cases have no minimum, but exhibit a definite break.

TABLE V.

Concentration of Mg, mg. per litre.	Mg. found. Per cent.
539	99.2, 99.7, 99.7
269.5	99.7, 100.1, 100.4, 100.1
202	100.8, 99.9, 100.8, 100.6
134.5	End-point indefinite.

Addition of magnesium hydroxide prior to titration lead to no improvement at the last-mentioned concentration.

In connexion with the estimation of magnesium by this method it is interesting to note that Harned (*loc. cit.*) says, "This titration gives only a fairly easily detectable end-point for the change in direction of the plot before and after the end-point is not great. A reagent must, therefore, be sought which will increase the difference in the slopes at the end-point." For this reason he employed barium hydroxide to titrate solutions containing magnesium sulphate. Apart from the fact that the use of this reagent, to be

effective, demands that the magnesium shall be present as sulphate and the total elimination of carbon dioxide from the solution, comparison of Harned's figures with those recorded above shows that the use of barium hydroxide does not present any definite advantage. It appears that errors from other sources are of greater magnitude than that derived from difficulty in reading the intersection of the two limbs of the curve.

Summary of Results.

(1) The determination, by means of conductivity measurements, of sulphates, chlorides, calcium, and magnesium has been studied at low concentrations.

(2) It has been shown that, in relatively weak solutions, very small quantities of each of the above mentioned may be estimated, without any attempt at temperature control, with an error not exceeding ± 1 per cent.

(3) In each case a limit of dilution is reached at which the results cease to be accurate, smooth conductivity curves being obtained. With the exception of the case of sulphate estimations, saturation of the solution with the salt to be precipitated does not lead to an improvement in this respect.

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