Amperometric Titrations with Indicators

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During the last few years amperometric titrations have proved to have a very wide field of applicability. Compared with conductometric and potentiometric titrations they offer many advantages, yet they have also certain limitations. Thus it is not possible according to principles adopted hitherto to determine a reducible (or oxidizable) substance in the presence of large amounts of more easily reducible (oxidizable) substances. Generally speaking it is difficult to use polarographic methods in the analysis of metals with high negative half-wave potentials. Magnesium, for instance, can not be determined polarographically, and the determination of calcium is influenced by even small amounts of the alkali metals.

A new principle in amperometric titrations, the use of *indicator substances*, will be described in this paper *. This principle makes it possible to determine certain metals not analyzed polarographically before, and the disturbing influence of many metals with low half-wave potentials can be eliminated by its application. The diffusion current measured is due to a suitable indicator, which is added to the solution. If the indicator is reducible at a sufficiently low potential neither the polarographic behaviour of the original sample nor that of the reagent added by the titration has any significance. Some examples will elucidate this principle.

I. TITRATION OF ALUMINUM WITH FLUORIDE SOLUTION

Aluminum forms with fluorides the complex ion AlF_6^{3-}. It might therefore be expected that the amperometric determination of aluminum could be carried out with a sodium fluoride solution. The half-wave potential of alu-

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* A preliminary report of the methods here described was given at the 6th Scandinavian Chemist Congress in August 1947.

Fig. 1. Titration of aluminum with sodium fluoride.

5 ml 0.1 M Al^{3+}
0.4 ml 0.1 M Fe^{3+}
25 ml alcohol
Excess of solid NaCl
Water to 50 ml
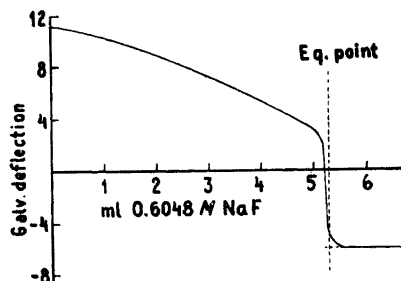
minum is, however, so high (—1.75 V) that the titration offers some difficulties, especially if large amounts of other salts are present. We have added a few drops of a ferric salt as indicator. Ferric iron is reduced by mercury without requiring the application of any potential to the dropping mercury electrode. If the saturated calomel electrode (SCE) is used as an external anode, the diffusion current of the ferric ion is obtained right at the start of the polarogram when the applied e. m. f. is zero. Both aluminum and iron form complex ions with fluorides, but the aluminum complex is more stable than that of iron. If, therefore, a sample containing both aluminum and iron is titrated with a sodium fluoride solution, the reaction between fluoride and aluminum will precede the reaction between fluoride and iron. In the presence of 50 % of alcohol the bulk of the iron will not react with fluoride until nearly all the aluminum has been converted into AlF_6^{3-} ions. The reduction of the ferric fluoride complex requires a potential of about — 1.4 V. If no potential is applied, the diffusion current, therefore, will change during the titration as shown in Fig. 1. The negative values observed after the end-point are due to the fact that the residual current corresponding to the potential $\pm$ 0 (SCE) is negative.

In order to make the equivalence point more distinct it is advantageous to saturate the solution with sodium chloride, which promotes the precipitation of Na_3AlF_6.

The optimum pH range is between about 2.5 and 3.5.

The apparatus employed was extremly simple. As no external potential is needed, the circuit consists of the sample solution, a calomel electrode, and the dropping electrode connected through a galvanometer (sensitivity = 5.7×10^{-8} A/unit of deflection).

Procedure. Add 0.5 ml 0.1 *M* ferric chloride, 25 ml alcohol, and an excess of solid sodium chloride to a 20—25 ml sample containing 10—40 mg aluminum. Remove dissolved oxygen by passing nitrogen or carbon dioxide through the sample, introduce

into the solution a calomel electrode and the mercury dropping electrode, and then titrate with 0.6 M sodium fluoride solution. The end-point of the titration is determined in the way indicated in Fig. 1. A volume of fluoride solution equivalent to the added ferric salt is subtracted from the total volume of fluoride solution consumed.

For the reagent a 10 ml semi-micro burette may be used.

The results of a few titrations are given in Table 1.

Table 1. Titration of aluminum with sodium fluoride. Volume = 50 ml.

ml 0.1 M Al-sol.	ml 0.635 M NaF		% error
	calc.	found	
5.00	4.72	4.70	— 0.4
8.00	7.56	7.56	± 0
8.00	7.56	7.57	+ 0.1
8.00	7.56	7.54	— 0.3
10.00	9.45	9.46	+ 0.1
10.00	9.45	9.40	— 0.5

The agreement is fairly satisfactory. The molarity of the sodium fluoride solution can be determined by titrating a solution of alum $KAl(SO_4)_2 \cdot 12\ H_2O$.

It may be mentioned that the reaction between aluminum and fluoride takes place in steps and is not complete at the equivalence point unless alcohol and sodium chloride are added. The equilibrium constants of aluminum fluoride in water solution have been determined by Brosset [1].

The error caused by interaction of the mercury on the bottom of the cell and the ferric ions is usually negligibly small. If necessary, the error can be minimized by collecting the falling drops in a narrow cavity in the bottom of the cell.

II. TITRATION OF MAGNESIUM WITH FLUORIDE SOLUTION

Magnesium also forms with fluoride ions a complex ion MgF_3^-, which is more stable than the FeF_6^{3-} ion. It might therefore be expected that the determination of magnesium should be possible by a method quite analogous to that described for aluminum.

Experiments conducted in order to investigate this possibility gave, however, no satisfactory results. The values were too low and varied considerably. It is likely that these observations are due to the fact that magnesium fluoride is temporarily precipitated during the titration and reacts but slowly with further amounts of fluoride ions to form complex MgF_3^- ions. Somewhat better results were obtained when the titration was carried out very slowly.

The difficulties mentioned can be avoided if the magnesium solution is added to an excess of sodium fluoride, the solution warmed and titrated back with a standard solution of an aluminum salt. The best results were obtained if also the aluminum solution was added in excess, and the final titration conducted with standard fluoride solution.

Procedure: Take a measured excess of 0.6 M sodium fluoride and add the sample solution containing magnesium. Heat the solution to boiling, cool, and add a measured excess of standard aluminum sulfate solution, 0.5 ml 0.1 M ferric chloride, and alcohol until it forms about 50 % of the solution. Add an excess of solid sodium chloride and titrate with sodium fluoride as described above.

The accuracy was not quite so good as in the titration of aluminum. The error was about $\pm$ 1 %.

III. TITRATION OF CALCIUM WITH FLUORIDE SOLUTION

Not only titrations involving complex formation but also precipitation titrations can be carried out by amperometric methods using indicator substances. As an example the titration of calcium with fluoride may be described.

Calcium fluoride is a rather slightly soluble salt — the solubility product in water is 4×10^{-11} — and consequently the possibility of using a ferric salt as an indicator seemed to exist. On adding sodium fluoride solution calcium fluoride will precipitate, and the diffusion current due to ferric ions will not reach its minimum until most of the calcium has been precipitated.

The titration is performed in a manner similar to that described above for the determination of aluminum. However, no sodium chloride should be added as the solubility of calcium fluoride is increased in the presence of large amounts of salts. As before, about 50 % alcohol is necessary to obtain a sharp end-point.

Procedure: Add to the sample solution 0.5 ml 0.1 M ferric chloride and alcohol to double the volume. Introduce into the solution a calomel electrode and the mercury drop electrode, and titrate with 0.6 M sodium fluoride after removing the air from the solution. The shape of the titration curve is seen in Fig. 2.

The weight ratio in the determination of calcium is not so advantageous as it is in the determination of aluminum. One millimole of fluoride corresponds to only 1/6 millimole of aluminum = 4.5 mg, but corresponds to $\frac{1}{2}$ millimole of calcium = 20 mg. Hence the accuracy attainable in titrating very dilute calcium solutions is not very great. Highly concentrated solutions are not
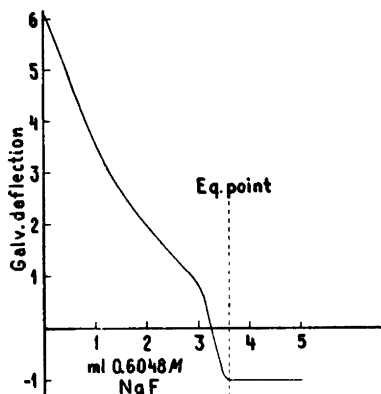
Fig. 2. Titration of calcium with sodium fluoride.

10 ml 0.1 M Ca^{2+}
0.4 ml 0.1 M Fe^{3+}
25 ml alcohol
Water to 50 ml

suitable either. In the latter case the precipitate is not quite pure, and the diffusion current may be influenced by very large precipitates. Thus the accuracy in the titration of calcium was less than in the titration of aluminum. By titrating amounts from 40—100 mg in a volume of about 50 ml the maximum error was about 1 %.

## IV. TITRATION OF CALCIUM WITH SODIUM OXALATE SOLUTION

It is possible to titrate calcium amperometrically not only with a fluoride but also with an oxalate. The indicator must in this case be the salt of a metal forming a slightly soluble oxalate, although it must be more soluble than calcium oxalate. The half-wave potential of this metal must not be too high. Various experiments revealed that a cadmium salt was the most suitable for this purpose. In order to decrease the solubilities of the precipitated salts it was necessary to titrate in the presence of alcohol as in the methods presented above.

As the difference between the solubility of calcium oxalate and that of cadmium oxalate is small ($L_{CaC_2O_4} = 2 \times 10^{-9}$, $L_{CdC_2O_4} = 1.5 \times 10^{-8}$) a coprecipitation of the two oxalates can scarcely be avoided. It is advantageous to add a rather large amount of cadmium and to subtract from the result the amount of oxalate corresponding to the added cadmium. Fig. 3 shows the shape of the titration curve.

Procedure: Add to the calcium solution 2 ml of a 0.02 M cadmium chloride solution and an amount of alcohol corresponding to about 50 %. Remove the oxygen by passing nitrogen through the solution. Titrate in the usual way with 0.1 M sodium oxalate solution applying an emf. of — 0.8 V (SCE). The equivalence point is obtained from the titration curve as shown in Fig. 3.

Fig. 3. Titration of calcium with sodium
oxalate.

5 ml 0.1 M Ca^{2+}
2 ml 0.02 M Cd^{2+}
25 ml alcohol
Water to 50 ml
Potential = — 0.8 V
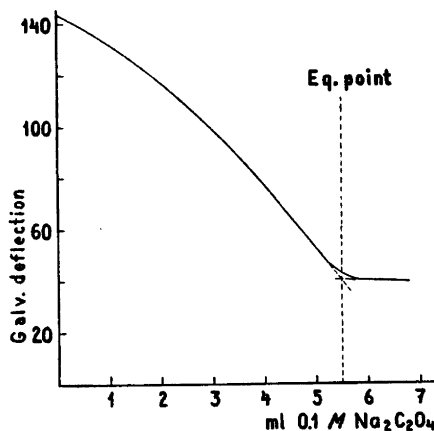
The results were about as accurate as when titrating with fluoride. A correction for the small amounts of cadmium remaining in the solution at the equivalence point can, if necessary, be applied.

It may finally be mentioned that the direct titration of aluminum, calcium and magnesium with a fluoride solution is also possible *visually*. Ferric thiocyanate formed by adding one drop of ferric chloride and an excess of ammoniumthiocyanate was used as indicator; the red colour disappears at the endpoint of the titration. The determination of aluminum has been described elsewhere by one of the authors [2], and the determination of calcium is reported in the following paper in this issue [3]. In the literature Treadwell and Bernasconi [4], and Uri [5] previously have described potentiometric methods in which fluoride has been used as reagent.

SUMMARY

A new principle in amperometric titrations — the use of indicator substances — is described. The diffusion current is due to an indicator, which reacts with the reagent at the equivalence point. The following titrations are considered:

1. Titration of aluminum with sodium fluoride using ferric chloride as indicator.

2. Titration of magnesium with sodium fluoride using ferric chloride as indicator.

3. Titration of calcium with sodium fluoride using ferric chloride as indicator.

4. Titration of calcium with sodium oxalate using cadmium chloride as indicator.

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