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A Titrimetric Method for the Determination of Calcium

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Recently one of the authors described a titrimetric method for the determination of aluminum with a sodium fluoride solution using ferric thiocyanate as indicator [1]. The method is based on the fact that aluminum and ferric iron form complex ions with fluorides; as the aluminum complex is more stable than the iron complex the fluoride reagent reacts first with aluminum, and the red colour of ferric thiocyanate disappears at the equivalence point. The results obtained were quite satisfactory, and therefore we conducted experiments to determine whether the same indicator could be used also in precipitating calcium with a sodium fluoride solution.

Although the determination of calcium is a very common analysis it seems that a satisfactory volumetric method permitting its direct titration has not yet been found. From this point of view investigations of new titrimetric principles seemed desirable.

The titration of calcium with a sodium fluoride solution has formerly been performed employing physicochemical methods for the detection of the endpoint. Uri [2] recently described a potentiometric method, and in this issue one of the authors reports on an amperometric method [3].

The solubility product of calcium fluoride is 4×10^{-11}. Hence the calcium concentration in the equivalence point is 2×10^{-4}, and the fluoride concentration 4×10^{-4}, a value which is too high to permit a sharp jump in pF at the equivalence point. By adding alcohol the solubility can be decreased, and as a consequence the colour change becomes sharper. One or a few drops of 0.1 *M* ferric chloride will be enough, but a rather large excess of ammonium thiocyanate is necessary. The concentrations were the same as those used in titrating aluminum.

Procedure. Add to the solution — 10—20 ml in volume and containing if possible 50—100 mg Ca — 0.1 ml 0.1 *M* ferric chloride, 4 ml 60 % ammonium thiocyanate and

alcohol to double the volume. Titrate with 0.5 *M* sodium fluoride until the red colour disappears.

A correction due to the consumption of fluoride by the indicator should be made. For the reagent a 10 ml semi-micro burette has been found suitable.

The molarity of the sodium fluoride solution can be determined by titrating a solution of alum $KAl(SO_4)_2 12\ H_2O$, which is easily available very pure. This titration is performed as above, but the alcoholic solution should be saturated with solid sodium chloride. The purpose of the sodium chloride is to precipitate the sodium cryolite formed; the reaction will then be more complete and the colour change consequently sharper. In his study of the potentiometric determination of calcium Uri [2] prescribed that also in the precipitation of calcium fluoride the solution should be saturated with sodium chloride. According to our experience the addition of sodium chloride is not to be recommended, as neutral salts increase the solubility and thus make the potential curve less steep. Due to the fact that potassium alum is slightly soluble in alcohol high potassium concentrations should be avoided in titrating aluminum. For this reason sodium fluoride and ammonium thiocyanate ought not to be replaced by the corresponding potassium salts.

The results of some calcium titrations are given in Table 1.

Table 1. Titration of calcium with sodium fluoride.

ml 0.1 *M* $CaCl_2$	ml 0.5 *M* NaF calc.	found	% error
10	4.00	4.02	+ 0.5
10	4.00	4.00	± 0
10	4.00	4.01	+ 0.25
10	4.00	4.04	+ 1.0
10	4.00	4.02	+ 0.5
20	8.00	8.00	± 0
20	8.00	7.93	— 0.9
20	8.00	8.03	+ 0.4

The equivalence ratio in titrating calcium is not quite so advantageous as in titrating aluminum, and hence the accuracy is perhaps somewhat lower. With 0.5 *M* sodium fluoride the colour change can, however, be determined within 1—2 drops, if the volume is about 50 ml.

The optimum pH range is between about 2.5 and 3.5. At pH values above 3.5 the colour intensity of ferric thiocyanate decreases, and below 2.5 the calcium fluoride begins to dissolve.

SUMMARY

A rapid method for the direct titration of calcium is described. Sodium fluoride is used as reagent, a little ferric chloride and an excess of ammonium thiocyanate serve as indicator, and the solution should contain about 50 % alcohol. At the end-point the colour of the solution changes from red to colourless. A pH value between 2.5 and 3.5 is the most suitable.

REFERENCES

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