Determination of Aluminum, Cerium(III) and Lead with Fluoride by an Amperometric Indicator Method

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In a recent study in these laboratories, it has been shown that the amperometric indicator method with polarized electrodes can be applied with success for the determination of barium, lanthanum and thorium with fluoride involving precipitation reactions[1]. The field of application of this method is wide and the method is more general than conventional voltammetry. However, formation of complexes and neutralization, in general, had scarcely been made use of as titration reactions.

This paper reports the results of determination of aluminum, cerium and lead with fluoride involving both complex forming and precipitation reactions, using two identical polarized platinum electrodes at constant applied voltage in the presence of small amounts of ferric chloride as an indicator and the appropriate supporting electrolytes.

Various methods for the determination of aluminum[2-4], cerium[2,5] and lead[2,6-9] have been developed. Ringbom and Wilkman[3] titrated aluminum with fluoride amperometrically at the dropping mercury electrode versus saturated calomel electrode using trivalent iron as indicator whose reduction at the cathode produces diffusion current. So long as the ferric iron remains uncomplexed, it can be reduced at the dropping mercury cathode and the current passes through the cell; and excess fluoride complexes the ferric ions and stops the current. This method is much simpler in technique and has several advantages over conventional potentiometric or amperometric method.

Experimental and Results

Standard potassium fluoride solutions were prepared by accurate dilution of a more concentrated solution which has been standardized potentiometrically[10]. Stock solution of aluminum chloride was prepared by dissolving a weighed quantity of pure aluminum wire in dilute hydrochloric acid, which was transferred to 500 ml. standard volumetric flask. The amount of aluminum was determined potentiometrically by the Scott's method[4]. Cerium chloride solution was prepared by dissolving the weighed quantity of Merck's extrapure cerium carbonate in dilute hydrochloric acid in 250 ml. standard flask. Hydrogen peroxide was added to aliquot, a weakly ammoniacal solution of cerous chloride to oxidize it completely to ceric form, and the resulting solution was titrated by potentiometric method[11] and also amperometrically with two polarized electrodes[12] against standard ferrous ammonium sulfate solution. The stock solution of Merck's extrapure lead nitrate was standardized amperometrically with standard potassium dichromate solution[13]. Conductivity water was used for the preparation of all solutions, and test solutions were obtained after appropriate dilution of the stock solution with air-free water. All other chemicals used were of reagent grade.

Experimental arrangements for the amperometric titrations were essentially the same as described earlier[12,14]. Two platinum electrodes were immersed in the titration cell and a constant voltage of 0.04 V. was applied to these electrodes. Current through the cell was measured using a sensitive galvanometer, 0.5 μA with lamp and scale arrangements. The solution was stirred uniformly during the titration using a magnetic stirrer. Twenty milliliters of titration mixture in an appropriate buffer containing the suitable supporting electrolyte and a small amount of indicator was placed into the titration cell. Titrant (10^{-1} to 10^{-3}M)

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[1] D. Singh and A. Varma, *J. Sci. Res. BHU.*, in press.

[2] W. Wagner et al., "Advanced Analytical Chemistry", Reinhold Publishing Co., New York (1956), pp. 146—148, 152—153 and 172—174.

[3] A. Ringbom and W. Wilkman, *Acta. Chem. Scand.*, **3**, 22 (1949).

[4] A. H. Bushey, *Anal. Chem.*, **20**, 169 (1948).

[5] C. W. Leonard, H. J. Kelly and D. H. Hume, *Anal. Chim. Acta.*, **16**, 185 (1957).

[6] L. Farkas and N. Uri, *Anal. Chem.*, **20**, 236 (1948).

[7] J. Cihalik and E. Kuornovska-Pavlikova, *Chem. Listy.*, **49**, 1640 (1955); *Collection Czechoslov Chem. Communs.*, **21**, 718 (1956).

[8] F. R. Cropper, *Analyst*, **76**, 370 (1951).

[9] Yu I. Usatenko and M. A. Vitikina, *Zavodskya Lab.*, **23**, 427 (1957).

[10] S. T. Talipov and J. Z. Teodorovich, ibid., **15**, 529 (1949).

[11] N. H. Willard and P. Young, *J. Am. Chem. Soc.*, **50**, 1379 (1928).

[12] D. Singh, A. Varma and V. S. Agarwala, *Z. anal. Chem.*, in press.

[13] I. M. Kolthoff and Y. D. Pan, *J. Am. Chem. Soc.*, **61**, 3402 (1939).

[14] D. Singh and A. Varma, *J. Sci. Res. BHU*, **11**, 125 (1960).

TABLE I. TITRATION OF ALUMINUM BY FLUORIDE WITH TWO POLARIZED ELECTRODES AT 40 mV. USING 0.5 ml. OF 0.05 M FERRIC CHLORIDE AS AN AMPEROMETRIC INDICATOR

Volume of the titration mixture: 20 ml. Medium: 0.05 M NH_4Cl+Acetate buffer, pH 6.2.

Determinations made	Amount of aluminium, mg.		Experimental error, %	
	Taken	Found	Average	Maximum
3	4.568	4.568	0.00	0.00
4	2.284	2.291	+0.42	+0.64
4	0.3219	0.3233	+0.44	+0.86
5	0.1407	0.1396	−0.82	−0.96
3	0.0704	0.0698	−1.14	−1.56
5	0.0226	0.0221	−2.38	−2.60
6	0.0113	0.0116	+3.54	+5.32

TABLE II. TITRATION OF CERIUM(III) BY FLUORIDE WITH TWO POLARIZED ELECTRODES AT 40 mV. USING 1.0 ml. OF 0.05 M FERRIC CHLORIDE AS AN AMPEROMETRIC INDICATOR

Volume of titration mixture containing equal volume of 96% ethyl alcohol, 20 ml. Medium: 0.05 M NH_4Cl+Acetate buffer, pH 6.0 to 6.5; Temperature, 40±1.0°C

Determinations made	Amount of cerium(III), mg.		Experimental error, %	
	Taken	Found	Average	Maximum
4	16.114	16.103	−0.08	−0.16
5	3.223	3.223	+0.04	+0.12
5	1.612	1.608	−0.30	−0.55
3	0.8060	0.8093	+0.56	+0.72
4	0.3223	0.3233	+0.44	+0.68
6	0.0806	0.0810	+0.86	+1.12
5	0.0322	0.0314	−2.79	−5.09

TABLE III. TITRATION OF LEAD BY FLUORIDE WITH TWO POLARIZED ELECTRODES AT 40 mV. USING 1.0 ml. OF 0.05 M FERRIC CHLORIDE AS AN AMPEROMETRIC INDICATOR

Volume of titration mixture containing equal volume of 96% ethyl alcohol, 20 ml. Medium: 0.1 M KCl or KBr+Acetate buffer, pH 5.5 to 6.2

Determination made	Amount of lead, mg.		Experimental error, %	
	Taken	Found	Average	Maximum
5	20.655	20.655	+0.32	+0.64
3	10.355	10.361	+0.04	+0.08
4	2.788	2.785	−0.16	−0.25
5	2.066	2.059	−0.54	−0.96
6	1.033	1.030	−0.59	−0.84
5	0.8276	0.8289	+0.18	+0.25
4	0.2066	0.2072	+0.44	+0.68
4	0.1033	0.1029	−0.77	−1.00
6	0.0517	0.0528	+2.70	+3.10

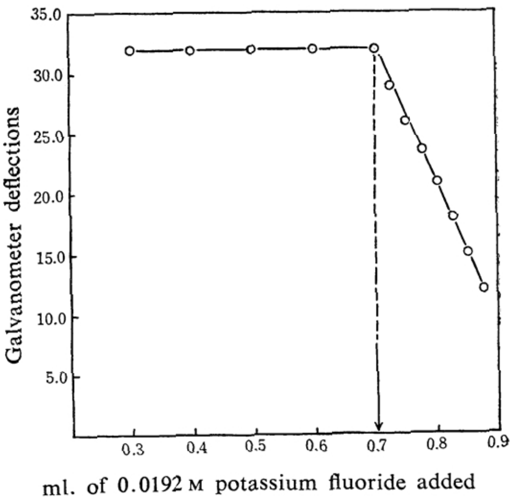

Fig. 1 Titration of 2.788 mg. lead with fluoride in 20 ml. acetate buffer, pH 5.5~6.5, containing 0.1 M KBr in equal volume of 96% ethyl alcohol, at 40 mV. with two polarized electrodes, indicator; $FeCl_3$.

was administered from 2 ml. semimicroburette with 0.01 ml. divisions. Readings were taken at uniform regular intervals, usually one minute, after each addition of the titrant. Equivalence points were found graphically by the usual plot of galvanometer deflections against the volume of titrant added. A typical titration curve is shown in Fig. 1. The end points were quite reproducible. A large number of experiments were carried and each determination was repeated several times for good and satisfactory results. Summarized results for the determination of aluminum, cerium(III) and lead are recorded in Tables I—III respectively. In column three is given the best experimental value observed for these estimations at the particular concentration.

Discussion

It has been observed that fluoride is an excellent titrant in precipitation and complex forming reactions. The fluoride ion is the smallest and the least deformable of the halide ions, and it should form the fewest complexes in accordance with the covalency rule, yet it forms far more complexes by electrostatic forces similar to those which hold "ion pairs" together[15,16]. This view is supported from the paramagnetism of such double salts as K_3FeF_6; the bonding is covalent and the electrons are paired and the molecules diamagnetic. Fluorine, having small size of the fluoride ion, brings

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[15] N. Bjerrum, *Kgl. Danske. Videnskb. Selskabs.*, 7, 9 (1926).

[16] R. M. Fuoss, *Chem. Revs.*, 17, 27 (1935).

out the highest coordination number of the atom with which it combines.

Fluoride ions have greater tendency to complex aluminum ions than trivalent iron ions and in neutral solution aluminum reacts with fluoride to form stable, AlF_6^{3-} ion; therefore on addition of potassium fluoride to the titration mixture, reaction shifts towards the formation of potassium cryolite:

$$AlCl_3+6\,KF \rightarrow AlF_3,\ 3\,KF\downarrow+3\,KCl$$

Aluminum first precipitates out as aluminum trifluoride, and this reacts with excess potassium fluoride forming the said stable complex.

Fluoride precipitates cerium trifluoride at pH 6.0 to 6.5, $CeCl_3+3\,KF \rightarrow CeF_3\downarrow+3\,KCl$; and the precipitate is insoluble in excess potassium fluoride. Lead is partially precipitated as lead chloride in presence of potassium chloride or as lead bromide in presence of potassium bromide in the titration mixture. On addition of potassium fluoride, the reaction proceeds towards completion yielding leadchlorofluoride or leadbromofluoride. These precipitation reactions are stoichiometric and quantitative especially in presence of equal volume of 96% ethyl alcohol, at pH 5.5 to 6.5.

In all these determinations, upto the equivalence point, corresponding to the stoichiometric completion of the reaction, current remains constant. After it, the excess fluoride ions complex the indicator ferric ions whose reduction constitutes the end point, and the current falls (cf., curve Fig. 1). The end point is sharp and quite reproducible.

Data recorded in Tables I–III show that the results are good and satisfactory with excellent accuracy upto 10^{-4} M. At lower concentrations, the maximum error is about ±5.0%.

Summary

Determinations of aluminum, cerium(III) and lead by fluoride involving complex formation, $KAlF_6$ and precipitations, CeF_3 and PbClF or PbBrF have been carried out successfully using amperometric indicator method at 0.04V. with two identical polarized platinum electrodes. A small amount of ferric chloride is used as an indicator, the reduction of which beyond end point constitutes the indicating system. Upto the equivalence point, current remains constant, and then it falls due to the reduction of the trivalent iron complex which is formed on addition of excess fluoride. The method is simpler in technique, sensitive and rapid, and the results obtained are good and satisfactory with accuracy of the right order of magnitude even at lower concentrations, as low as 10^{-4} M. At still higher dilutions the maximum error rises to about ±5.0%.

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