

Determination of microquantities of fluoride by ion-exchange spectrophotometry

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Amberlite IRA 400 in the thiocyanate form is used for the estimation of fluoride by ion exchange spectrophotometry. Various reaction conditions have been optimised and interferences due to other anions have been removed. The method is used for the estimation of fluoride in drinking water.

Numerous methods have been proposed for the determination of fluoride because of its ecological importance in natural and waste waters. They are mainly spectrochemical and electrochemical in nature. Most of the existing spectrophotometric methods are based on the bleaching action of fluoride either on aqueous metal complexes^{1,2} or on complexes in micellar medium³. Some other direct spectrophotometric methods^{4,5} are based on the formation of ternary metal complexes of fluoride. Atomic absorption, molecular absorption and emission methods are also used in the determination of microquantities of fluoride. However, all these methods are either complex or require specialised instruments. In the present note we are reporting a very simple and economical method for the estimation of fluoride. The method is reproducible, sensitive and allows fluoride estimation in the presence of halides, sulphide and sulphate.

Experimental

AR grade chemicals and doubly deionised water were used throughout the course of the work. Absorbance was measured on a Spectronic 20, Baush and Lomb photometer.

In a glass column of 18 cm in length and 1.2 cm int. dia slurry of the Amberlite-IRA 400 resin in the thiocyanate form was poured to achieve a uniform packing. Excess water was drained and air gaps were avoided to overcome the eddy diffusion. The length of the resin bed was maintained at 10 cm. A resin pre-column of 5 cm length was prepared as described earlier using Dowex 50W-XB (mesh 20-50) cation exchange resin in silver ion form.

Stock solutions (10^{-2} M) of the anions required

for the study were prepared by dissolving appropriate amounts of AR grade sodium salts in deionised water.

Determination of fluoride

Sodium fluoride solution (10 ml, 10^{-3} M) was passed through the SCN^- form column at the flow rate of 1 ml min^{-1} . The column was washed with 10 ml of deionised water. The column effluents were collected alongwith the washings and diluted to 25 ml with deionised water. The iron-thiocyanate complex was developed at pH 1.5-1.8 by using appropriate quantity of 10^{-2} M ferric solution and the column effluent. The absorbance was measured at 480 nm against reagent blank. Operational conditions were optimised by varying column length, ferric ion concentration and flow rate. A calibration curve was plotted by using 10^{-4} - 10^{-5} M fluoride solution.

Results and discussion

The method is based on the displacement of equimolar quantity of SCN^- by fluoride. The displaced thiocyanate when treated with ferric ion at pH 1.5-1.8 forms iron-thiocyanate complex which absorbs at 480 nm. Fluoride was estimated at preoptimised conditions using calibration plot constructed for complexes formed from 10^{-4} - 10^{-3} M KCNS solutions and 10^{-2} M iron(III) solution. A linear plot with the correlation coefficient 0.9998 and least square equation, $A = 1031 [\text{SCN}^- \text{ M}] - 0.013$, was obtained. In the study of effect of resin bed length (2-10 cm) on fluoride estimation it was observed that resin bed of 2 cm length was sufficient for the quantitative displacement of thiocyanate by fluoride. It was also observed that flow rate of column effluents from 1 ml to 8 ml min^{-1} does not influence the displacement of thiocyanate from the column by fluoride. It was observed that a linear plot (correlation coefficient = 0.9998) was obtained from the 10^{-3} to 10^{-5} M sodium fluoride concentration and displaced thiocyanate in terms of iron-thiocyanate complex. Fluoride concentration as low as 10^{-6} M also displaced SCN^- from the column, but the absorbance developed was not accurately measurable. By developing a flow manifold with a microcolumn of resin (4×0.2 cm), determination of fluoride upto 10^{-7} M was possible. The least square equation obtained for these results was, $A = 958 [M \text{ conc. of } \text{F}^-] - 0.013$. In the study of interference due to displacement by other anions it was observed that equimolar solutions of the ions thiosulphate, chloride,

Table 1—Analysis of drinking water

Water source at Tavadia	pH	Fluoride ($\mu\text{g ml}^{-1}$) (mean of 5 determinations)	
		proposed method	SPADNS method
Water works (bore well)	7.45	3.85	3.7
Municipal (tube well)	7.4	5.05	4.9
Water works (tube well)	8.1	4.0	4.0
Private (tube well)	7.9	4.35	4.30

bromide, iodide, nitrate, sulphate, hydrogen phosphate and sulphide do not displace thiocyanate to the same extent. The displacement of SCN^- by equimolar solutions depends upon the charge present on the anion indicating the relationship between the absorbance and the concentration of anions in terms of normality. The interference due to chloride, bromide, iodide and sulphide was eliminated by introducing a precolumn in Ag^+ form. For the removal of sulphate along with earlier mentioned interfering ions a precolumn made up of Ag^+ and Ba^{2+} form resin was efficient and effective.

In the estimation of fluoride in the presence of chloride, bromide, iodide, sulphide and sulphate, thiocyanate column coupled with precolumn in the form of Ag^+ and Ba^{2+} was used. It was observed that all these interfering ions are quantitatively masked by the precolumn and displacement of

SCN^- is only due to fluoride in the solution. Proportionate increase in the displacement of thiocyanate was observed when only thiocyanate column was used. It was further confirmed by passing the fluoride, chloride, iodide, bromide, sulphide and sulphate solutions separately through combined column. It was observed that displacement of SCN^- by fluoride remains unchanged whereas for all other anions combined column suppresses the displacement of thiocyanate from the column quantitatively.

Analysis of drinking water

In Gujarat (India) fluoride content in drinking water is in the range of 3.8 to $4.2 \mu\text{g ml}^{-1}$ particularly in Mehsana district. This value is much higher than the US public health drinking water standards ($1.5 \mu\text{g ml}^{-1}$). It is even higher than the permissible values given by Indian Standards Institution⁶ ($3.0 \mu\text{g ml}^{-1}$). The analysis of samples collected from various sources used for drinking water at Tavadia is given in Table 1. From the results in Table 1, it is observed that the results obtained by the proposed method are in good agreement with those obtained by SPADNS method.

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