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Spectrophotometric Method for Determination of Fluoride Ion in Water Samples Based on its Bleaching Effect on Aluminium-SPADNS Lake

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A simple and rapid spectrophotometric method for determining fluoride in potable water has been developed. The factors which effect the bleaching effect of fluoride on the aluminium-SPADNS lake to adopt it as a spectrophotometric method for estimation of fluoride in water were studied. Beer's law is obeyed from 0.0 to 4.0 ppm of fluoride ion buffered at pH 4.9 ± 0.03 at 590 nm. This method can be used over a wide concentration range of fluoride which is not possible in other spectrophotometric methods.

Key Words: Aluminium, SPADNS, Fluoride, Spectrophotometric determination.

INTRODUCTION

Fluoride can be estimated by titrimetric[1, 2], spectrophotometric[3–24], complexometric[25], gravimetric[26] and potentiometric[27, 28] methods. Spectrophotometric methods for fluoride generally utilize coloured metal-dye complexes or lakes. Aluminium with eriochromecyanin[12–14], hematoxylin[15–18], chromeazurol-S[19], sodium quinalizarin sulphonate[20], pyrocatechol violet[21] were used for spectrophotometric estimation of fluoride. These methods either require long hours for development of the complex or heating for few minutes for formation of the complex and precise control of pH and temperature. The present method being proposed neither requires long hours for development of the complex nor heating. Aluminium and SPADNS reagent form a purple coloured complex within 5 min which will be bleached by fluoride proportionately to its concentration. Moreover, as no extraction process[30] is involved in the procedure, this method is simple, sensitive and rapid.

EXPERIMENTAL

The absorbance measurements were made with a Shimadzu UV-240 spectrophotometer using 1 cm quartz cells. Systronics digital pH-meter 802 was used for pH measurements.

Analytical-reagent grade chemicals and doubly distilled water were used throughout. SPADNS solution (0.2%) was prepared by dissolving 2.0 g of SPADNS reagent in distilled water and made up to 1 L with distilled water.

Standard aluminium solution was prepared by dissolving 0.3357 g of aluminium ammonium sulphate ($AlNH_4(SO_4)_2 \cdot 12H_2O$) in distilled water and finally made up the volume to 100 mL with distilled water, this solution was prepared daily (1 mL = 200 μg Al). For use 16 mL of the above solution was made up to 100 mL (1 mL = 32 μg Al).

Stock fluoride solution: 0.221 g of sodium fluoride was dissolved in water and made up to 1 L with distilled water (1 mL = 100 μg F.).

Standard fluoride solution: 100 mL of stock fluoride solution was then made up to 1 L (1 mL = 10 μg F).

Buffer solution (pH 4.9 ± 0.03): 400 mL of 0.2 M acetic acid solution was added to 600 mL 0.2 M sodium acetate solution.

Aluminium-SPADNS colour reagent: To 200 mL of buffer solution 100 mL of 0.2% SPADNS solution and 100 mL of std. aluminium solution were added and mixed thoroughly and allowed to stand for 5 min before using to allow complete development of colour.

Reference solution: To 6 mL of 0.2% SPADNS taken in a 50 mL std. flask 10 mL of buffer was added and made up to the mark.

Preparation of standard curve: Into a 50 mL calibrated flask, enough fluoride standard solution was pippetted in to give final fluoride concentrations between 0.0 and 4.0 ppm followed by the addition of 20 mL of Al-SPADNS colour reagent and made up to volume with doubly distilled water and the absorbance was measured at 590 nm against reference after 5 min.

RESULTS AND DISCUSSION

The reaction conditions investigated were the optimum wavelength for use, best ratio of dye to aluminium, optimum pH and time of development of colour of complex and for bleaching of colour by fluoride, composition of the colour complex formed and interference from other ions.

Absorption Curves: Fig. 1 illustrates the absorption curves of the colour developed by the aluminium-SPADNS reagent. Curve 1 is the absorption curve

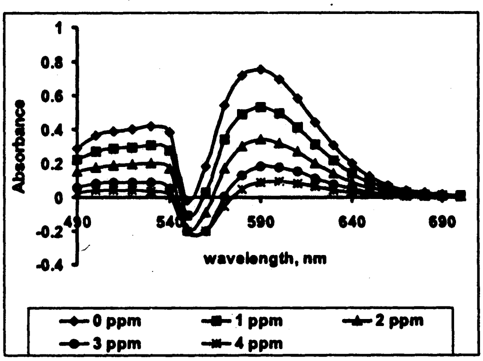

Fig. 1. The absorption curves of 0, 1, 2, 3, and 4 ppm fluoride against blank

of aluminium-SPADNS which has no fluoride while Curves 2, 3, 4, 5 are the absorption curves of solutions in which the reagent has been bleached by 1.00, 2.00, 3.00, 4.00 mg per L of fluoride. These curves were run against reference. The maximum differential occurs at 590 m; therefore, this wavelength was chosen for further studies.

For selecting the best ratio of colour producing reagents, the experiments were restricted to ratio so as to produce a coloured solution which will be sensitive to small amounts of fluoride, and not to be bleached completely within the 4 ppm concentration of fluoride. A molar ratio of 1 aluminium to 3 of SPADNS dye was found to be satisfactory for rapid colour development and for a calibration curve up to 4 ppm of fluoride.

At a pH of 4.9 ± 0.03 the time required for the complete development of colour of the aluminium-SPADNS complex was less compared to that at other pH values. At pH values lower than 4.9 ± 0.03 the colour development of the lake took longer time. As the pH is increased beyond 4.9 ± 0.3 the stability of the lake formed decreased. Acetic acid and sodium acetate buffer was used to maintain the desired pH.

The colour development of the aluminium-SPADNS complex was 99% complete within 5 min. The bleaching of the lake by fluoride was also 99% complete within 5 min. The calibration curve for 0.0 to 4.0 ppm of fluoride is given in Fig. 2. The molar absorptivity for fluoride was found to be 10.6×10^3 lit mol^{-1} cm^{-1}.

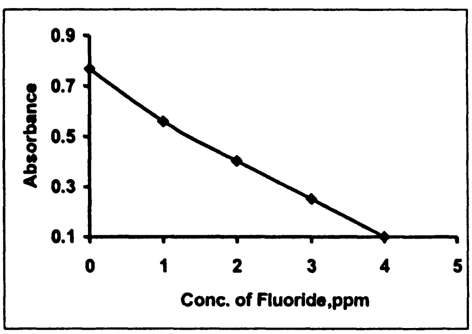

Fig. 2. Calibration curve of fluoride with aluminium-SPADNS

Composition of the coloured complex of aluminium-Spadns lake

The empirical formula of the coloured complex of aluminium and SPADNS was determined by adopting the slope ratio method given by Harvey and Manning[29].

For the study of the complex, two series of solutions were prepared. In one series, the concentration of aluminium was varied in the presence of constant excess of SPADNS; in the other, SPADNS was variable and aluminium was a constant component. The pH of the solutions was adjusted to 4.9 by using sodium acetate-acetic acid buffer.

Optical density measurements at the wavelength of maximum absorption for aluminium complex were made within 10 min after preparing the solutions. The values obtained were plotted and are shown in Figs. 3 and 4. The slope ratio was found to be 1 : 1 for aluminium-SPADNS which suggests the formation of a 1 : 1 complex of aluminium with SPADNS.

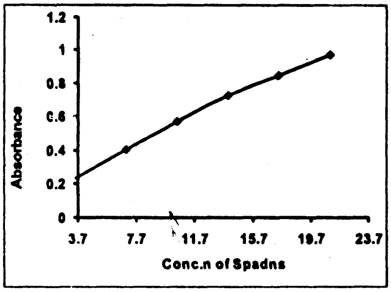

Fig. 3. Composition of coloured complex; variation of SPADNS conc., n × 10^{-5} M

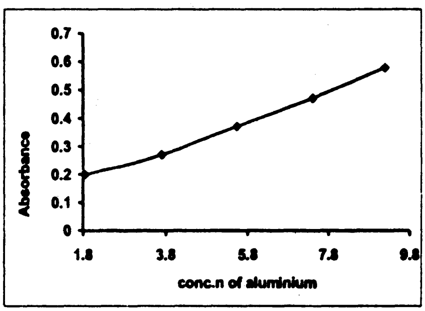

Fig. 4. Composition of coloured complex; variation of aluminium conc., n × 10^{-5} M

Interferences: The study on the effect of interferences (Table-1) indicates that copper and thorium interfere seriously which may be due to complex formation with SPADNS. The interfering cations can be removed by pretreating the water by passing through cation exchange resin. Most of the anions did not interfere except for phosphate.

Water samples subjected to distillation can be analyzed directly by this procedure, with no neutralization or concentration. For water samples which have interfering ions within the limits, this method has a standard deviation of 0.1 and an accuracy of ±1%.

Comparison with other analytical methods

The zirconium-alizarin method[30] is probably the most satisfactory for determining fluoride in natural waters. This method covers less than the range covered by the present method, requires 1 h for bleaching by fluoride ion and extraction into pentanol. The details are given in Table-2. Hence, the proposed method can be used for rapid and precise estimation in water supplies that naturally contain fluorides as well as those that have been fluoridated.

TABLE-1
INFLUENCE OF FOREIGN IONS ON DETERMINATION OF 100.0 μG OF FLUORIDE

Ions and salts	Molar concentration ratio to fluoride	F^- found, (μg)	Relative error, (%)
Ca(II)	4.7	98.0	–2.0
Cd(II)	1.7	99.0	–1.0
Co(II)	3.2	97.0	–3.0
Cu(II)	3.0	60.0	–40.0
Mg(II)	7.8	98.5	–1.5
Ni(II)	3.2	97.0	–3.0
Pb(II)	0.92	97.0	–3.0
Th(IV)	0.82	40.0	–60.0
Zn(II)	2.9	96.5	–3.5
Br^-	2.4	99.5	–0.5
I^-	1.5	100.0	0.0
PO_4^{3-}	0.8	104.0	4.0
KNO_3	95	101.5	1.5
$NaClO_4$	95	103.5	3.5
KCl	95	102.0	2.0
NH_4NO_3	95	103.5	3.5
CH_3COONa	95	105.0	5.0
Na_2SO_4	20	103.5	3.5

TABLE-2
COMPARISON WITH OTHER METHODS

Method	λ_{max}, nm	Time required for colour development of the complex (min)	Time required for bleaching of fluoride (min)	Time required for extraction (min)	Fluoride linear range (ppm)	Molar absorptivity (lit^{-1} mol^{-1} cm^{-1})	Reference
Zirconium-alizarin method	430	—	60	30	0.0–1.5	7.3×10^3	30
Aluminium-SPADNS method	590	5	5	—	0.0–4.0	10.6×10^3	This method

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