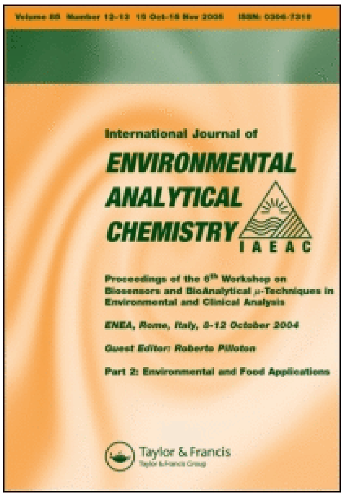

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF FLUORIDE USING N-PHENYLBENZOHYDROXAMIC ACID

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Fluoride gives a very stable complex with scandium and, hence, by determining the unreacted scandium, the fluoride content can be calculated. Excess scandium is reacted with an ethanolic solution of N-benzoylphenylhydroxylamine (BPHA) at pH 6.0, and the scandium-BPHA complex is extracted into isoamyl alcohol. Scandium is determined spectrophotometrically after adding xylenol orange. Beer's law for fluoride is obeyed in the range of 0.05–1.5 ppm; the molar absorptivity is $1.94 \times 10^4 \, l \, mol^{-1}$ at 565 nm. The procedure is applicable for the determination of fluoride in various types of samples.

KEY WORDS: Fluoride determination, solvent extraction, spectrophotometry.

INTRODUCTION

The methods reported so far for the spectrophotometric determination of fluoride are indirect, i.e. the decolouring or quenching effect of F^- on coloured metal-chromogenic reagent complexes is utilised. However, these methods have a lack of selectivity, due to the effect of various cations and anions either on the selected metal ion or on the chromogenic reagent. Moreover, since most of these methods are in aqueous medium, their selectivity will be less good than those of extraction methods.

In the present investigation a method is proposed adopting a solvent extraction technique. The hydroxamic acids are versatile reagents for solvent extraction of metals and they are used in organic, inorganic and pharmaceutical analysis.[1–4] The extraction and determination of unreacted metal ion after treating with the anion under investigation has also been utilised for the quantitative determination of anions.[5,6]

In the present work, complexation of fluoride with scandium is used. The excess of scandium is extracted with N-benzoylphenylhydroxylamine (BPHA) into isoamyl alcohol as a Sc-BPHA complex. Sc-BPHA gives a colourless binary complex and, hence, the chromogenic reagent xylenol orange (XO) has been used. The ternary Sc-BPHA-XO complex exhibits maximum absorbance at 565 nm.

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EXPERIMENTAL

Reagents and Chemicals

All the chemicals used were of AnalaR or G.R. grades of BDH and E. Merck, respectively, unless otherwise specified.

N-benzoylphenylhydroxylamine (BPHA) was synthesised by the method of Agrawal and Tandon,[7] and its purity was checked by its melting point and its UV and IR spectra. A 0.4% (w/v) BPHA solution and a saturated xylenol orange solution were prepared in ethanol.

Fluoride and Scandium Solutions

Standard 1000 ppm solutions of scandium and fluoride were prepared by dissolving the proper amount of scandium oxide and sodium fluoride, respectively, in doubly distilled water. Final concentrations of scandium and fluoride were determined volumetrically[8] and spectrophotometrically,[9] respectively. The solutions were diluted as and when required.

Apparatus

The spectral measurements were made on a Spectronic-20 (Bausch and Lomb) spectrophotometer with matched cells. A Systronic pH meter, Model-324 with combined glass and calomel electrodes, was used for the pH measurements.

Extraction Procedure

An aliquot of a fluoride (1.25 – 37.5 ppm) solution was transferred to a 60-ml separatory funnel containing 37.5 ppm of scandium; 5 ml of acetate buffer (pH 6.0) were added and the contents shaken vigorously for 1 min. Then 5 ml of 0.4% (w/v) BPHA in ethanol were added and the scandium-BPHA complex was extracted with 10 ml of isoamyl alcohol. The organic extract was separated, dried over anhydrous sodium sulphate and transferred to a 25-ml volumetric flask. Two millilitres of a saturated ethanolic solution of xylenol orange were added and the contents diluted to the mark with isoamyl alcohol. The absorbance of the scandium-BPHA-XO complex in isoamyl alcohol was measured at 565 nm against the reagent solution as blank.

RESULTS AND DISCUSSION

Effect of pH

Fluoride forms a very stable complex with scandium at pH 3.0–6.0. The maximum extraction of the scandium-BPHA complex is observed in the same pH range, hence pH 6.0 was chosen for the extraction and determination of fluoride (Table 1).

Table 1 Effect of pH on the extraction of scandium

pH	*Absorbance*	*% E*
1.0	—	0.00
2.0	0.04	0.06
3.0	0.66	100
3.5	0.66	100
4.0	0.66	100
4.5	0.66	100
5.0	0.66	100
6.0	0.66	100
8.0	0.53	80.4
9.0	0.23	34.9

Scandium, 1.5 ppm; BPHA, 5 ml 0.4% in ethanol; XO, 2 ml saturated solution in ethanol; λ_{max}, 565 nm.

Reagent Concentration

For a fixed amount of 1.5 ppm of scandium, 5 ml of 0.4% BPHA in ethanol are sufficient for complete extraction of scandium. Two millilitres of a saturated solution of xylenol orange in ethanol give maximum colour intensity.

Extractions

The scandium-BPHA complex was extracted into various solvents, viz. chloroform, tetrachloromethane, benzene, hexane, isoamyl alcohol, methyl-isobutyl ketone and octanol. The extraction was found to be quantitative with isoamyl alcohol.

Equilibration Time and Stability

The shaking time for the extraction was varied from 5 to 30 min. The results showed that extraction is quantitative within 10 min. The reaction time for the complexation between scandium and fluoride was varied from 2 to 30 min; stoichiometric complexation was found within 2 min. The scandium-BPHA complex extracted under the optimum condition is stable for 24 h.

Validity of Beer's Law

Beer's law is obeyed in the range of 0.05–1.5 ppm of fluoride for a fixed amount of scandium (1.5 ppm). The molar absorptivity is $1.94 \times 10^4 \, \mathrm{l\,mol^{-1}\,cm^{-1}}$ at 565 nm.

Regression analysis gave as a result:

$$\text{Absorbance} = 0.3468 \times \text{concentration} + 0.6591 \qquad (1)$$

with a correlation coefficient of 1.000.

Table 2 Interferences from cations and anions in the scandium-BPHA determination of fluoride

Ions	*Added as*	*Amount (ppm)*	*Absorbance measured*
Ca(II)	$Ca(NO_3)_2.4H_2O$	100	0.49
Ba(II)	$BaCl_2.2H_2O$	100	0.49
V(V)	NH_4VO_3	50	0.49
Ti(IV)	TiO_2	50	0.49
MoO_4^{2-}	$(NH_4)_6Mo_7O_{24}.4H_2O$	50	0.49
Ce(IV)	$(NH_4)_4Ce(SO_4)_4.2H_2O$	50	0.50
Zr(IV)	$ZrOCl_2.8H_2O$	50	0.50
La(III)	$LaCl_3.7H_2O$	50	0.49
Th(IV)	$Th(NO_3)_4.6H_2O$	25	0.48
Pb(II)	$Pb(NO_3)_2$	75	0.49
Sn(II)	$SnCl_2$	75	0.50
Ni(II)	$NiCl_2.6H_2O$	75	0.50
Cd(II)	$3CdSO_4.8H_2O$	75	0.50
Al(III)	$AlCl_3.7H_2O$	50	0.49
Fe(III)	$Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$	50	0.49
S^{2-}	Na_2S	100	0.49
NO_3^-	KNO_3	100	0.49
PO_4^{3-}	NaH_2PO_4	100	0.49
Cl^-	NaCl	1000	0.49
SO_4^{2-}	Na_2SO_4	1000	0.49

Scandium, 1.5 ppm; fluoride, 0.5 ppm; BPHA, 5 ml 0.4% in ethanol; XO, 2 ml saturated solution in ethanol; pH, m6.0; λ_{max}, 565 nm; absorbance, 0.49.

Effect of Diverse Ions

The effect of various cations and anions on the determination of fluoride as well as scandium was studied by following the recommended procedure (Table 2). Only a few cations, like Fe(III), Th(IV), V(V) interfere. The interference of Fe(III) and V(V) can be removed by a preliminary extraction with the same reagent in acidic medium; Th(IV) can be masked using citrate. Lanthanides do not interfere because their complex with BPHA can only be extracted in alkaline medium. Phosphate interferes and can be removed by reacting it with Ca(II). Interfering cations can also be removed by increasing the pH using NaOH, and filtering off the metal hydroxides. Boron interferes seriously as it forms a complex with fluoride and cannot be removed.

Applicability of the Method

The procedure has been applied for the determination of fluoride in various samples after proper dissolution and pretreatment steps. The water samples were used as such for the determination of fluoride. The results show good agreement with those obtained by means of literature methods.[11] (Table 3).

Table 3 Determination of fluoride in standard samples

Samples	*ppm F found by*[a]		*C.V.*[b]
	Standard methods	*Present method*	
Glass sample 91—opal U.S. NBS	1.0	1.05	0.34
Rock sample 56b—Tennessee brown U.S. NBS	1.0	0.95	0.29
Pharmaceutical sample fluorouracil (Inj.)	1.0	1.02	0.18
Tap water	0.05	0.05	0.23
Wastewater a	0.10	0.095	0.14
Wastewater b	0.50	0.50	0.13

[a] Average of seven determinations.
[b] Coefficient of variation.

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