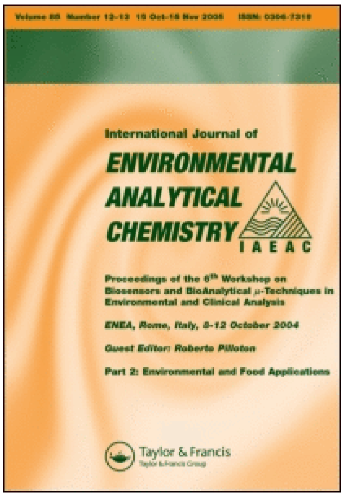

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Direct Determination of Fluoride in Saudi Arabian Water Samples

Fatma Basyoni Salem[a]; Sheikha Mohammed Al-gannam[a]
[a] Department of Chemistry, College of Science, Girls Colleges, Dammam, Kingdom of Saudi Arabia

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ANALYTICAL DATA

DIRECT DETERMINATION OF FLUORIDE IN SAUDI ARABIAN WATER SAMPLES

FATMA BASYONI SALEM and SHEIKHA MOHAMMED AL-GANNAM

Department of Chemistry, College of Science, Girls Colleges, Dammam, Kingdom of Saudi Arabia.

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Fluoride is determined in Saudi Arabian water samples. Fluoride is precipitated as lead chlorofluoride and the excess lead is determined potentiometrically using molybdate in the presence of a lead-ion selective electrode. Fluoride ions can be determined in the concentration range of 1.9 g to 190 μg per liter. The results are compared with those of the colorimetric procedure using eriochrome cyanine R in the presence of Ce(III).

INTRODUCTION

The determination of fluoride in water has considerable interest for marine chemists. Currently two major approaches are employed: (i) the spectrophotometric method of Greenhalgh and Riley[1] which is based on the colour of the lanthanum-alizarin complex with xyenol orange,[2] and (ii) the potentiometric methods described by Brewer *et al.*,[3] Warner,[4] and Cragg *et al.*[5]

EXPERIMENTAL

Apparatus

An Orion research microprocessor pH/millivolt meter 811 equipped with an Orion model 94-82 Lead-ion electrode and a model 90-02 double-junction reference electrode were used.

Reagents

All solutions are prepared with analytical reagent grade chemicals (BDH) using bidistilled water.

— 0.01 M stock solutions are prepared of sodium fluoride; lead nitrate is standardized against standard EDTA solution; ammonium molybdate is standardized potentiometrically with a lead nitrate solution as titrant. Serial dilutions of these solutions are made to get concentrations down to 1×10^{-5} M.

— A 0.02 M cerous nitrate solution, 10% w/v sodium chloride and 0.2% w/v eriochrome in water are used.[6,7]

Procedures

Titrimetric determination of fluoride in authentic samples of fluoride: Pipette 10 ml of a standard fluoride solution into a 250 ml beaker, add 2 drops of bromophenol blue indicator, 3 ml of 10% sodium chloride and dilute the mixture to 50 ml. Add dilute nitric acid until the colour just changes to yellow, and then add dilute sodium hydroxide solution until the colour just changes to blue. Treat with 1 ml of concentrated hydrochloric acid, then add 50 ml of lead nitrate in the range of 1×10^{-1} to 1×10^{-5} M as required in the experiment and heat on the steam bath. Stir gently and then immediately add 5.0 g of crystallised sodium acetate and stir vigorously. Digest on the steam bath for 30 min, with occasional stirring, and allow to stand overnight to allow precipitation of lead chlorofluoride. The excess lead nitrate is determined potentiometrically by titration with 1×10^{-1} to 1×10^{-5} M standard solution of ammonium molybdate as required in the presence of the lead-selective electrode. A blank run is carried out under the same conditions. The end point is determined graphically from the maximum slope or from the second derivative.

Colorimetric determination of authentic samples of fluoride Introduce an accurately measured amount of fluoride of up to 114 μg into a 10-ml volumetric flask. Add 0.5 ml Ce(III) solution, 5 ml of concentrated sulphuric acid, 0.5 ml of an aqueous eriochrome cyanine R solution and complete to volume with 4 M sulphuric acid; then mix well. Measure the absorbance of the solution at 525 nm against a reagent blank. The fluoride concentration is calculated using a calibration curve in the range of 9.5 to 115 μg of fluoride ion.

RESULTS AND DISCUSSION

The described procedure is based on the precipitation of lead chlorofluoride, the excess lead being determined potentiometrically with standard ammonium molybdate in the presence of a lead-selective electrode.[8] The method can be carried out at pH = 3.6–5.6, so that phosphates, sulphates, chromates, carbonates and silicate do not interfere. Working at this pH prevents interference by silicate and phosphate because the optimal condition for molybdosilicic acid formation is an acidic solution of pH 1.5. At higher acidity (pH 0.5), molybdophosphoric acid is formed, while at higher pH phosphate passes into solution.[9]

Water samples of Saudi Arabia are characterized as hard water, but no interference occur from the elements naturally associated with the hardness, i.e., calcium, magnesium, barium, strontium, copper or zinc. The only interferences in water are caused by aluminium and iron, which form strong fluoride complexes. These could be eliminated by complexation with sodium citrate after oxidation of iron by hydrogen peroxide in an acidic medium. The method has been checked against the zirconium-eriochrome R method of Megregian[10] as the spectrophotometric method of choice. The use of Ce(III) improves this procedure, because no preliminary water treatment is now required. The only interference in the Ce(III)-eriochrome cyanine R method are aluminium and iron, if present above 50 and 3000 ppm, respectively.

In our study no water treatment is required as the selected samples contain iron and aluminium in concentrations of not more than 0.6 and 0.02 ppm, respectively. The presence of concentrated sulphuric instead of hydrochloric acid increases the colour intensity of the complex.

The method could be used in the range of 0.95 to 11.4 μg of fluoride ion per ml, in the presence of 2 to 25 μg per ml of zirconyl chloride, with molar absorptivities of 22,663 and 10,268 L mol^{-1} cm^{1} with the Ce(III) and zirconyl chloride-cyanine R methods, respectively.

The potentimetric technique is a more reliable method for determining higher amounts of up to 1.9 g per liter. It is moreover simple and rapid and no loss of the precipitate occurs as in the gravimetric technique. Neither the potentiometric nor the spectrophotometric method requires a preliminary separation of fluoride by distillation. Abdel Fattah *et al.*[11] used a fluoride electrode for determining fluoride in Saudi Arabian water samples. They concluded that the method suffered from interferences by several other ions being, in addition, time consuming and involving more steps than the present method.

Table 1 Determination of fluoride ion in water samples (in mg/l) of Kingdom of Saudi Arabia

Water Samples	*Method Used*[a]	
	Colorimetric	*Potentiometric*
Eastern Province		
a) Dammam City		
Houses tap	1.33 ± 0.05	1.33 ± 0.01
	1.60 ± 0.06	1.52 ± 0.06
Colleges tap	11.14 ± 0.11	10.45 ± 0.02
Tanker alone	1.10 ± 0.08	6.27 ± 0.01
b) Rahimah City		
Houses tap	0.95 ± 0.02	1.14 ± 0.02
Northern Province		
Houses tap	14.85 ± 0.03	15.20 ± 0.03
Western Province		
a) Jeddah City		
Houses tap	1.71 ± 0.08	2.57 ± 0.04
b) Zamzam well	2.81 ± 0.10	3.42 ± 0.02

[a] Each result is the mean of three experiments ± standard deviation

The potentiometric and spectrophotometric methods show no mutual differences when using statistical analysis, student's t test at the 95% significance level or 10 degrees of freedom (t calculated, 0.016; tabulated, 1.812). The methods have been used to determine fluoride ion in water samples from the Eastern, Western and Northern provinces of Saudi Arabia.

Table 1 summarizes the data: the fluoride ion contents range from 0.95 to 14.85 and 0.95 to 15.2 ppm with the spectrophotometric and potentiometric methods, respectively. Fluorine does not seem to be a necessary element for metabolism but may be added to drinking water to assist in the control of dental caries. According to the literature, 0.8–1.7 ppm of fluoride[12] is the permissible concentration level because above 2 ppm people suffer from mottling of teeth, while at 10 ppm skeletal fluorosis may occur.[13] Obviously, some of the present results are relatively high, especially those. for tap water from the Northern province.

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