Available online at www.sciencedirect.com

SCIENCE DIRECT®

Analytica Chimica Acta 539 (2005) 311–316

ANALYTICA
CHIMICA
ACTA

www.elsevier.com/locate/aca

A colorimetric method for fluoride determination in aqueous samples based on the hydroxyl deprotection reaction of a cyanine dye

Chang-Qing Zhu[a], Jin-Long Chen[b], Hong Zheng[a], Yu-Qin Wu[b], Jin-Gou Xu[a,*]

[a] The Key Laboratory of Analytical Science of MOE, Department of Chemistry, Xiamen University, Xiamen 361005, China
[b] College of Chemistry and Materials Science, Anhui Normal Unversity, Wuhu 241000, China

Received 6 January 2005; received in revised form 3 March 2005
Available online 30 March 2005

Abstract

A new highly sensitive and selective colorimetric method for fluoride determination in water is described. The novel reagent for this method is a cyanine dye (C_1) on which the hydroxyl group has been protected by reaction with *tert*-butyldimethylsilane (TBS) to form the silanated dye, C_2. C_2 is selectively attacked by fluoride ions to reform C_1. C_1 has an absorption maximum at 600 nm with a molar absorptivity of about 200,000. Under optimized conditions, absorbance at 600 nm is proportional to fluoride concentration up to about 1×10^{-4} mol/L with a detection limit of 1.0×10^{-7} mol/L. Because of the specific affinity of fluoride for the TBS functional group on C_2, there is little interference by other ions. The method has been successfully applied for fluoride determinations in local rainwater samples. Results determined by the proposed method agree favorably with those determined by a fluoride ion selective electrode method.

Keywords: Fluoride ion; Cyanine; Hydroxyl deprotection reaction; Colorimetric method

1. Introduction

The effect of fluoride on both humans and animals has a dual role as an essential element and at high levels as a toxic substance [1]. Excess fluoride ion results in fluorosis and renal, gastrointestinal and immunological toxicity [2]. Also, plants and fruits such as apricots, plums grapes, tulips, iris and sweet corn are sensitive to fluoride [3]. Hydrogen fluoride is often found in rainwater [4] as a result of various industrial processes, such as phosphate fertilizer production, aluminium production and metal smelting. Therefore, an accurate and rapid method for the determination of fluoride in rainwater samples is important for assessment of air and water quality.

Several analytical techniques have been developed and described for fluoride determinations in water including spectrophotometry [5–7], fluorometry [3,8–10], potentiometry (ion-selective electrodes (ISE) [11–13], ion chromatography (IC) [14], gas chromatography (GC) [15], capillary zone electrophoresis (CZE) [16] and radioanalysis [17]. Among these, ISE methods are most widely applied because they are easy to use, selective and provide a wide dynamic range [11]. Determination of low-concentration fluoride by ISE can be difficult due to long equilibration times, electrode drift and dissolution of the lanthanum fluoride membrane crystal [18,19]. Compared to ISE fluoride determination methods, chromatographic methods are time consuming [15] and require more expensive instrumentation. Several spectrometric methods [20–22] are widely accepted for the determination of trace fluoride in natural waters due to their simplicity, low cost and reliability. In most of these spectrometric methods, fluoride ions displace organic ligands from colored complexes of metal ions such as zirconium, thorium, titanium, aluminium and ferric iron [20–22]. Displacement of the metal ion or organic ligand by fluoride therefore causes the absorbance of the reaction mixture to decrease. Often, however, Beer's law is not obeyed in such methods

---

[*] Corresponding author. Tel.: +86 592 2180307; fax: +86 592 2188054.
E-mail address: jgxu@xmu.edu.cn (J.-G. Xu).

0003-2670/$ – see front matter
doi:10.1016/j.aca.2005.03.002

due to the diversity of co-existing complexes of fluoride with the metal ion in the solution. Furthermore, many anions or cations compete with fluoride or the central metal ion for coordination [7], which results in serious interference.

Recently, Descalzo et al. [23], Kim and Swager [24] reported a new reaction system for the selective detection of fluoride ion that exploits the unique chemical reactivity of fluoride ions with silicon. Long reaction times and organic solvent requirements of these reaction systems [24] greatly limited their utility for water analysis applications. In this paper, we describe using a new reagent for fluoride determination in aqueous solution, based on the selective attack of fluoride on the Si–O bond of the cyanine dye, C_2 (1-ethyl-4-(*p*-*tert*-butyldimethylsilane ether styryl) quinolinium iodide). C_2 is conveniently obtained in 98% yield by reaction of cyanine dye, C_1 (1-ethyl-4-(*p*-hydroxystyryl) quinolinium iodide) with *tert*-butyldimethylsilane (TBS) as shown in Fig. 1. The large molar absorptivity of C_1 ($\approx$200,000 L cm mol^{-1}) [25] makes it an excellent chromophoric reporter. When C_2 is incubated with fluoride ions in 7:3 v/v THF:water solutions, the characteristic absorption band of C_1 at 600 nm gradually appears. Under optimized conditions, a linear relationship between the absorbance at 600 nm and fluoride ion concentration is observed. This analytical approach provides a highly sensitive and selective colorimetric method for the determination of fluoride ion in aqueous solution that was applied to the detection of fluoride ion in local rainwater samples. Interference by foreign anions is negligible and results by the proposed method compare favorably with results by standard F^- ISE methods.

2. Experimental

2.1. Apparatus

A Hitachi U-3010 spectrophotometer (Tokyo, Japan) was used for recording absorption spectra and making absorption measurements. The pH was measured with a Model pHs-3c meter (Shanghai, China). A 201 fluoride Ion Selective Electrode (Jiangshu Electroanalysis Apparatus Factory, China) was used for the detection of fluoride in rainwater samples.

2.2. Reagents

The fluoride standard solutions were prepared by a serial dilution of a 10^{-2} mol/L sodium fluoride stock solution. Cyanine dye C_1 was synthesized and purified according to Blazsek-Bodo et al. [26,27] and silanated with TBS as described by Sartori et al. [28] (Fig. 1), to form the indicator, C_2 in 98% yield. C_2 was dissolved in chloroform solution to make a 1.7×10^{-3} mol/L stock solution. The purity of C_2 was confirmed by ^{1}H NMR and HRMS spectra. All chemicals were analytical reagent grade and used as received. Doubly deionized water was used for all experiments.

2.3. Pretreatment of samples

Two local rainwater samples were obtained after a pretreatment according to the literature [29]; two tap water samples were diluted by 10-fold with doubly deionized water for comparative experiment.

2.4. Standard procedure for the detection of fluoride

Add sequentially to 5.0 mL volumetric flasks containing 3.5 mL of THF solution, 0.1 mL of C_2 working solution, 1.3 mL of standard sodium fluoride solution or sample and 0.1 mL of NaH_2PO_4–NaOH buffer solution (pH 9.0). Mix the contents of the flask thoroughly. After 10 min, measure the absorbance at 600 nm using THF–water (7:3, v/v) solution as the reference. After determinations are complete, recycle THF by simple collection and distillation to reduce the possible pollution.

3. Results and discussion

3.1. Spectral characteristics

The visible absorption spectra of C_1 in pH 9.0 buffer displays two bands as shown in Fig. 2b. At low pH, however, the spectra of C_1 display only one visible band at 440 nm as shown in Fig. 3 that corrsesponds to the absorption of the

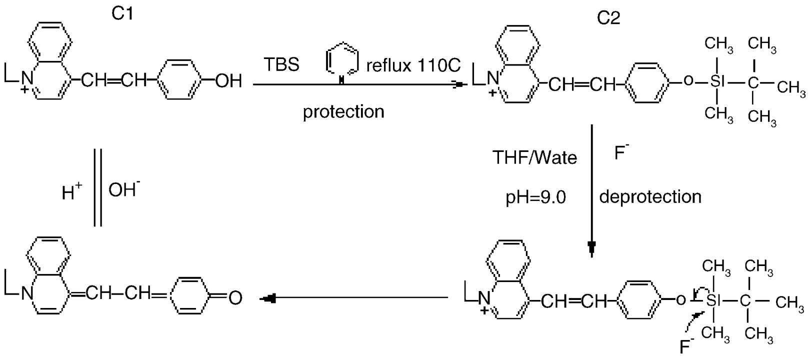

Fig. 1. Protection and deprotection of cyanine’s hydroxyl.