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Fluorometric determination of fluoride ion by reagent tablets containing 3-hydroxy-2′-sulfoflavone and zirconium(IV) ethylenediamine tetraacetate

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Abstract

A reagent tablet for determination of fluoride ion has been prepared using ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate complex of zirconium (Zr-EDTA), 3-hydroxy-2′-flavone (FS) and an appropriate pH buffer. Dissolving of the tablet into water exhibits an intense blue fluorescence (λ_{max} = 460 nm) upon excitation at 377 nm and the fluorescence intensity decreases with the presence of fluoride ion. Hence, a simple fluorescent detection procedure for fluoride ion in aqueous media was successfully constructed with this tablet. The principle of this detection system is the ligand exchange reaction of FS bound to Zr-EDTA with fluoride ion. The present system provides an easy, rapid and selective determination method of fluoride ion ranging from 5×10^{-6} to 1×10^{-3} mol dm^{-3}. The measurement of real samples with this tablet showed the similar results as those by the common method with the Alfusone reagent.

Keywords: Fluorometric determination; Fluoride ion; Reagent tablets; Simple method; Ligand exchange

1. Introduction

An upper limit of fluoride concentration in drinking water by the World Health Organization (WHO) is 1.5 μg/cm^3 because high levels of fluoride concentration in water causes serious health problems to human being. Since the increase in the use of fluoride has been continuing because of its great potential for industrial and biological applications, detection of fluoride ion in an aqueous media is essentially important for monitoring the pollution of various industrial, environmental and municipal waters [1,2]. In addition to a need for the detection method, simpler and easier methods are demanded for the frequent control and evaluation of the pollution by fluoride. Many kinds of methods such as ion selective electrodes [3], colorimetry [4–9], fluorescence [10–14] and capillary electrophoresis [15], have been so far reported for the determination of fluoride. Among these, naked-eye visual detection systems [5,7,15] can provide a simple and quick analysis for fluoride ion. However, most of these systems inevitably use organic solvent as the detection medium because these sensors rely on hydrogen bonding in addition to electrostatic interactions for the identification of analytes [16,17]. The application of these systems to practical water samples requires tedious solvent extraction procedures and phase transfer catalysts. Hence, detection of fluoride ion in aqueous media only is expected to overcome the above shortcoming.

A fluoride ion can form stable binary or ternary complexes with trivalent or tetravalent metal ions and also their complexes due to its high electronegativity. Thus, metal complexes of La(III), Ce(III) and Zr(IV) with dye compounds have been often applied for the colorimetric determination of fluoride [18–20]. However, these systems lack chemical stability and take some time for color development. It was previously demonstrated that Zr-EDTA complex can bind

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fluoride ion as well as oxo-anions like arsenate and selenate by ligand exchange with coordinated water molecules [17]. Based on this knowledge, it was shown that the combined use of Zr-EDTA as an anion receptor and flavonol as a probe molecule gave a fluorescence detection system of fluoride ion [11]. However, a drawback of the necessity of organic solvent was still present in this system.

In the present study we have found that 3-hydroxy-2′-sulfoflavone (FS) also shows an intense fluorescence in the presence of Zr-EDTA and a quenching of the fluorescence by the addition of fluoride ion. Since these reagents are available as a water-soluble solid and easily molded into tablets, a simple and easy fluoride detection method has been successfully constructed with this reagent tablet without using any organic solvents.

2. Experimental

2.1. Reagents and instruments

A stock solution of fluoride (1×10^{-2} M, M = mol dm^{-3}) was prepared by dissolving 99.9% NaF (Wako, Japan) in distilled water and standardized using the reported method [21]. The complex of $Zr(H_2O)_2EDTA \cdot 2H_2O$ was prepared as a white crystal according to the procedure [22] and 1×10^{-2} M stock solution was prepared by dissolving it into distilled water. Working solutions, as required, of the above reagents were prepared by appropriate dilution of the stock solutions. All other reagents used were of guaranteed reagent grade.

The fluorescence spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Absorption spectra were measured with a Hitachi UV-3150 UV–vis spectrophotometer with 1 cm quartz cells. The pH measurements were carried out using a Horiba digital pH meter with a glass electrode.

2.2. Preparation of reagent tablets

The reagent powders of 8.5 mg of FS, 25.0 mg of Zr-EDTA, 1.4 g of potassium hydrogen phthalate, 12.6 g of hexamethylenetetramine and 5.95 g of disodium ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate are thoroughly mixed by using an agate mortar and pestle. A 500 mg portion of the mixed reagent powders was shaped into a tablet by using an ordinary oil-pressure KBr pellets maker for the IR measurement. Each tablet contains 0.21 mg of FS, 0.625 mg of Zr-EDTA, 35 mg of potassium hydrogen phthalate, 315 mg of hexamethylenetetramine and 149 mg of disodium ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate, respectively.

2.3. Typical detection procedure

Twenty-five cubic centimeter of sample solution containing fluoride ion was taken into a glass bottle. One reagent tablet was added to this solution and the capped bottle is shaken vigorously for several minutes by hand until the tablet dissolves completely. The fluorescence intensity was measured at 460 nm by the excitation at 377 nm and compared with those of standard solutions containing known amount of fluoride ion.

3. Results and discussion

3.1. Ternary complex formation with FS

It is already known that EDTA forms a remarkably stable 1:1 complex with Zr(IV) with the formation constant of $\log K_{ML} = 29$ [23]. On the basis of the X-ray structural analysis, the $[Zr(H_2O)_2EDTA]$ complex has a mononuclear eight-coordinate structure in which Zr(IV) is surrounded by hexadentate EDTA and two water molecules [24]. Ternary complex formation has been demonstrated by replacement of the water molecules bound to Zr(IV) with various ligands [25–27]. In the previous paper on the development of a detection method for fluoride ion, flavonol was used as an exchangeable signal probe [11], because it shows a particularly intense fluorescence induced by metal complex formation [28]. However, the reaction needs organic solvents such as ethanol because of the low solubility of flavonol in water, In order to fabricate a reagent system without using any organic solvents, a search for water-soluble probe molecules has been mounted. As a result, we found that the similar ternary complex system could be obtained with FS and Zr-EDTA.

The absorption spectra of FS aqueous solution changes by the addition of Zr-EDTA solution as shown in Fig. 1. A mixture of Zr-EDTA and FS in an aqueous solution gives absorption spectra with peaks at 317 and 377 nm, whereas the solution of FS only shows a peak at 335 nm. In accord with the absorption spectral change, the aqueous solution

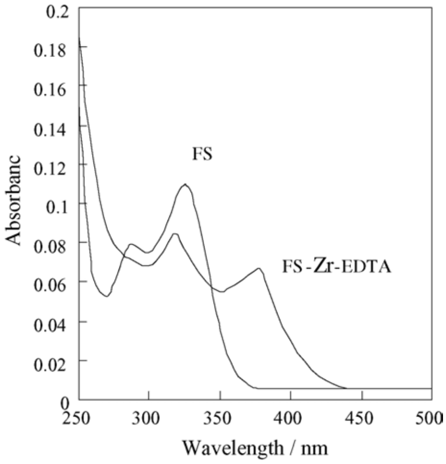

Fig. 1. The UV–vis absorption spectra of FS and FS–Zr-EDTA solutions. [FS] = 5×10^{-5} M, [Zr-EDTA] = 5×10^{-5} M, pH 5.8 (acetate buffer).

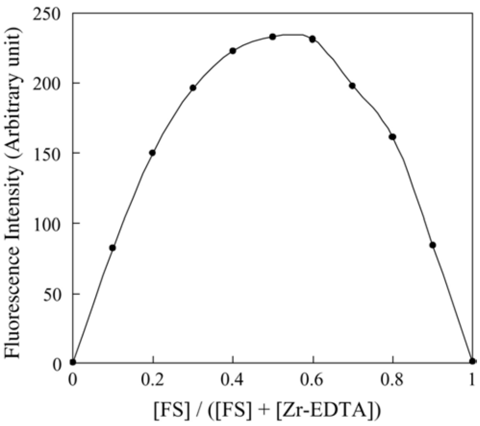

Fig. 2. A continuous variation plot for FS–Zr-EDTA system with respect to the fluorescence intensity. [FS] + [Zr-EDTA] = 5×10^{-5} M, pH 5.8 (acetate buffer), excitation wavelength 377 nm, emission wavelength 460 nm.

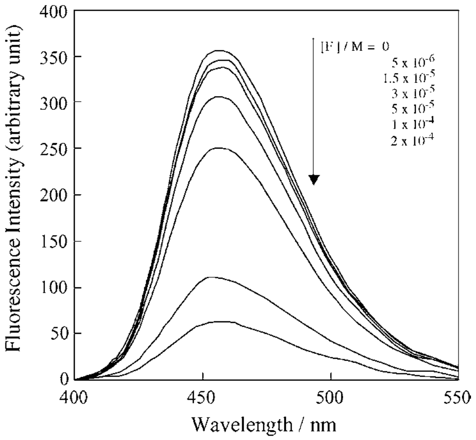

Fig. 4. A Change of emission spectra on the addition of fluoride ion. Excitation wavelength, 377 nm; emission wavelength, 460 nm $[Zr(H_2O)_2EDTA] = 1 \times 10^{-5}$ M; $[FS] = 1 \times 10^{-5}$ M; pH 5.8 (acetate buffer).

showed an intense blue fluorescence with a peak at 460 nm upon excitation at 377 nm. The observed spectral changes can be attributed to the complexation of FS to Zr-EDTA, since fluorescence of free FS at 460 nm is significantly small under the same conditions. A continuous variation method of fluorescence intensity in the FS–Zr-EDTA system indicated the 1:1 complex formation as given in Eq. (1), where FS presumably acts as a bidentate ligand and Zr-EDTA as a ligand receptor (Fig. 2). The conditional equilibrium constant of this reaction was determined to be $1.3 \times 10^5\ M^{-1}$ (pH 5.8, $I = 0.1$ ($NaClO_4$)) at 293 K by curve analysis of the molar ratio plots (Fig. 3). This value is a little smaller than $2.7 \times 10^5\ M^{-1}$ of flavonol complex [11]. The smaller formation constant of FS-complex than that of flavonol complex can be attributed to the presence of the electron-withdrawing sulphonic group in FS

$$FS + Zr(EDTA) \leftrightarrows Zr(FS)(EDTA) \qquad (1)$$

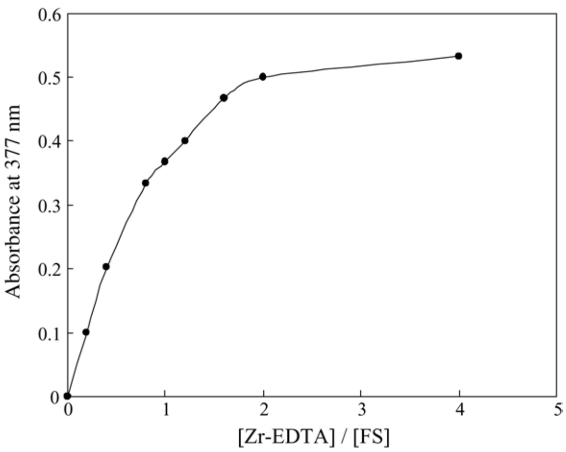

Fig. 3. A molar ratio plot for FS–Zr-EDTA system with respect to UV–vis absorbance. $[FS] = 5 \times 10^{-5}$ M, pH 5.8 (acetate buffer), $I = 0.1$ ($NaClO_4$), at 298 K.

3.2. Ligand exchange reaction with fluoride ion

The fluorescence peak at 460 nm was quenched upon addition of fluoride ion (Fig. 4). This change in fluorescence intensity depends on the concentration of fluoride ion added. The observed quenching of fluorescence by the addition of fluoride ion can be attributed to the replacement of FS by the strongly competing fluoride ion as expressed in Eq. (2). Direct binding of the fluoride ion to Zr-EDTA giving mono- and bis-fluoride complexes has been demonstrated by the shift of ^{19}F NMR peaks (122.38, 131.57 ppm) relative to the location of free fluoride upon addition of fluoride ion to aqueous Zr-EDTA solution [29]. Fig. 5 shows the plots of fluorescence intensity against pH in the absence and the presence of fluoride ion. Ternary complex formation with FS seems favorable at a pH ranging from 4 to 11. Obviously the signal intensity changes between pH 4 and 7, where ligand exchange between FS and fluoride ion takes place most effectively. Since the largest change in the intensity can be obtained between pH 5

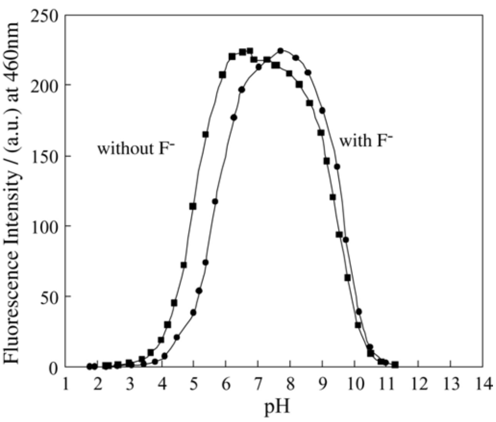

Fig. 5. Changes in fluorescence intensity of an equimolar mixture of [Zr-EDTA]–FS with and without F^- ion as a function of pH. $[Zr\text{-}EDTA] = [FS] = 1 \times 10^{-5}$ M, $[F^-] = 5 \times 10^{-5}$ M, $\lambda_{ex} = 377$ nm, $\lambda_{em} = 460$ nm.

Table 1
Influence of diverse ions on the determination of fluoride (5×10^{-5} M) with the reagent tablet

Ions	Concentration (M)	Recovery[a] (%)
None	Standard	100.0
Cl^-	5×10^{-3}	96.4
Br^-	5×10^{-3}	101.8
$NO_3{}^-$	5×10^{-3}	99.6
$SO_4{}^{2-}$	1×10^{-3}	98.8
$PO_4{}^{3-}$	5×10^{-4}	101.1
Ca(II)	2×10^{-4}	102.5
Mg(II)	2×10^{-3}	102.3
Al(III)	5×10^{-5}	98.4
Fe(III)	5×10^{-5}	101.6
Co(II)	2×10^{-4}	101.7
Ni(II)	8×10^{-4}	97.9
Zn(II)	8×10^{-4}	101.9

[a] Percentage of the fluorescence intensity decrease against that of standard.

and 6, the pH of the sample solution is preferably controlled to be in this range with an appropriate pH buffer. Time course experiments showed that the change of fluorescence intensity was rapid and terminated within 1 min upon addition of 5×10^{-5} M fluoride ion (pH 5.8) at 298 K

$$Zr(FS)(EDTA) + 2F \leftrightarrows ZrF_2(EDTA) + FS \qquad (2)$$

3.3. Interference of diverse ions

The effect of typical diverse ions on the detection of fluoride with the present system has been checked. As shown in Table 1, the presence of common anions such as Cl^-, Br^-, $NO_3{}^-$ and acetate did not interfere with the signal intensity up to at least 100 times concentration of the fluoride ion (5×10^{-5} M). The presence of $SO_4{}^{2-}$ is allowed up to 20 times. The coexistence of $H_2PO_4{}^-$ up to 10 times did not affect significantly. While metal cations including Al(III) and Fe(III) appreciably interfered due to the competing complexation of FS with these metal ions. However, it was found that the addition of EDTA masked these cations to some extent.

3.4. Preparation of a reagent tablet

Although the present determination system is successfully employed using the aqueous solutions of each necessary reagent, an attempt for the preparation of solid reagent system is a favorable option to fabricate simpler method from the practical point of view. Since the reagents required for fluorescence emission are available as easily water-soluble solid, the search for the appropriate solid buffer system is a key to prepare the reagent tablets for this detection method. Among the possible buffer systems, the combination of hexamethylenetetramine and potassium hydrogen phthalate was the best with respect to the solubility to water and stability of pH value. Mixing of the reagent powders was satisfactorily performed with an agate mortar and pestle. According to the results on the reaction characteristics of the system, the composition of the mixed reagents was set to be 8.5 mg of FS, 25.0 mg of Zr-EDTA, 1.4 g of potassium hydrogen phthalate, 12.6 g of hexamethylenetetramine and 5.95 g of disodium ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate. Dissolving of this set of reagents into deionized water makes the sample solution of pH 5.8, which is in the optimum range of pH. An excess amount of EDTA was added for the masking of possible coexisting metal ions. Reagent tablets are prepared by compressing a 500 mg portion of mixed reagents using an ordinary KBr pellets maker for IR measurement. It was confirmed that the tablet easily dissolves into water by hand-shaking of the solution for 1 min. The concentrations of FS, Zr-EDTA, EDTA and buffer should be 3×10^{-5}, 6×10^{-5}, 0.018 and about 0.01 M, respectively, when this tablet was dissolved into 25 cm^3 of water. It was also confirmed that the prepared tablet can be stored in a capped bottle without showing any deliquescence or deterioration at room temperature for at least 3 months.

Table 2
Measurement of fluoride ion in the real samples with the reagent tablet

Sample	This method ($\times 10^{-4}$ M)	Alfusone method ($\times 10^{-4}$ M)
A	3.4	3.4
B	3.8	4.3
C	4.2	4.7
D	4.7	4.9
E	4.0	4.4
F	1.1	1.7
G	3.0	3.9

3.5. Detection procedure of fluoride ion

The detection procedure of fluoride ion was simply constructed by dissolving of one tablet into each 25 cm^3 of sample solutions and standard solutions, respectively, followed by the measurement of fluorescence intensity at 460 nm upon excitation at 377 nm. The concentration of fluoride in the sample solutions were evaluated according to the intensities of standard samples. The detection range of fluoride ion by this method was from 5×10^{-6} to 1×10^{-3} M. Measurement of a 5×10^{-5} M fluoride sample showed a variation coefficient of 3.1% with 10 replicated samples. Fluoride concentrations of waste solutions from semi-conductor industries were measured by the present method and the results are well consistent with those by the reported method [21] with Alfusone reagent provided by Dojindo, Japan (Table 2).

4. Conclusion

The ligand exchange reaction between fluoride ion and FS coordinated to Zr-EDTA shows a rapid change in the fluorescence intensity. A new fluorometric determination method has been demonstrated using this reaction. Preparation of reagent tablets containing all of the necessary components successfully made the detection method easy and simple. The present system provides a rapid and selective detection method of fluoride ion in aqueous solutions ranging from 5×10^{-6} to 1×10^{-3} M. The measurement of fluoride concentration in the practical waste solution from a semiconductor industry has been successfully employed.

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