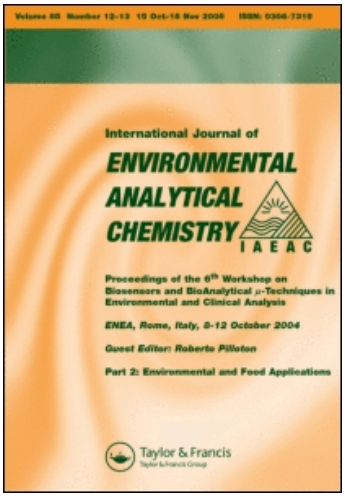

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FLUORIMETRIC DETERMINATION OF ARSENITE AND ARSENATE IN WATER USING FLUORESCEIN AND IODINE

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A rapid, simple and sensitive fluorimetric method has been developed for the determination of inorganic arsenic. The method is based on the competitive reaction of arsenite and 2′,7′-dichlorofluorescein (DCF) as fluoregenic reagent ($\lambda_{ex} = 510$ nm, $\lambda_{em} = 528$ nm) at pH 6.5–7.5 with iodine (I_2) to cause the increasing fluorescence intensity of the solution. Arsenate and other ions do not react with iodine. After reduction to the trivalent state by using L-cysteine, total arsenic is determined by spectrofluorimetry. Arsenate concentration can be calculated by difference. The calibration graph is linear over the range 4–180 ng/mL arsenite. The linear regression equation is $\Delta F = 7.82C + 0.76$ and the relative coefficient is 0.9991. The detection limit is 0.6 ng/mL arsenite. The recovery of this method for detecting arsenite is 96–105%. The method has been applied successfully to the determination of arsenite in tap and pool water.

Keywords: Fluorimetry; 2′,7′-dichlorofluoresce; Arsenite; Arsenate; Water sample

INTRODUCTION

Arsenic has increasing application in a variety of industries and is used, for instance, in building materials, chemical industries and pharmaceutical syntheses. However, in recent years arsenic has attracted a great deal of attention because it is a high toxic pollutant in the environment. Regarding inorganic arsenic, trivalent species are considered to be more toxic[1, 2] and generally are found at trace levels. However, in surface water, the predominant arsenic species is usually arsenate, as it is important that sensitive and accurate methods be available for determination of arsenite and arsenate.

Several hyphenated techniques have been used for separation and determination of arsenic. For example, ion-exchange chromatography or a flow injection procedure has been used for separating inorganic arsenic compounds. In a subsequent step, atomic absorption spectrometry[3, 4], atomic fluorescence spectrometry[5], hydride generation[6, 7], inductively coupled plasma mass spectrometry[8] or emission spectrometry[9] are usually used as detection techniques.

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In this work, a new fluorimetric method is developed to determine arsenate and arsenite without any separation step. Iodine reacts with fluorescein to produce a non-fluorescent species. If arsenite was present, the following reaction happened: $AsO_3^{3-} + I_2 + 2OH^- \rightarrow AsO_4^{3-} + I^- + H_2O$. Hence, the fluorescence intensity of the solution increased with the increasing concentration of arsenite when appropriate amounts of iodine and fluorescein were added, which can be made use of determining arsenite. Arsenate is pre-reduced by L-cysteine to arsenite and then the total arsenic is determined. Arsenate concentration can be calculated by difference. A linear calibration curve was obtained in a certain range. The method possesses distinct advantages over other fluorimetric methods with respect to sensitivity, interference, simplicity and rapidity. The method has been applied to the determination of arsenite and arsenate in water and standard reference material successfully.

EXPERIMENTAL

Apparatus

A Hitachi 650-10s spectrofluorimeter and 960 spectrofluorimeter (Shanghai, China) were used for recording spectra and making fluorescence measurements. RF UV-240 spectrophotometer (Shimadzu, Kyoto) was used to record absorption spectra. pH measurements were made with a model PHS-301 digital pH meter 631 (Xiamen, China).

Reagents

All chemicals were of analytical-reagent grade. All aqueous solutions were made up in deionized, distilled water.

Sodium arsenite solution: a 0.1 mg/mL stock solution of arsenite was prepared by dissolving 0.0782 g of sodium arsenite, in distilled water and diluting to 500 mL. Diluted solutions should be prepared fresh daily.

Sodium arsenate solution: a 0.1 mg/mL stock solution of arsenate was prepared by dissolving 0.2082 g of $Na_2HAsO_4 \cdot 7H_2O$, in distilled water and diluting to 500 mL. Working solutions were freshly prepared by appropriate dilution with 0.02 mol/L HCl.

2′,7′-Dichlorofluorescein (DCF) solution: a stock solution (4×10^{-5} mol/L) was prepared by dissolving 0.0160 g 2′,7′-dichlorofluorescein (Shanghai, China) in water and diluting to volume in a 100 mL standard flask. The solution was diluted to 1×10^{-6} mol/L with water as working solution.

Iodine solution: a stock solution (1.000 mg/mL) was prepared by dissolving 0.1000 g iodine in 100% ethanol and diluting to volume in 100 mL standard flask. The solution was diluted to 10 μg/mL with 100% ethanol as working solution. Iodine solution (10 μg/mL) must be prepared before use.

Buffer solution: a pH 7.0 buffer solution was prepared by mixing two volumes of 0.3 mol/L sodium phosphate dibasic with one volume of 0.3 mol/L potassium phosphate monobasic.

Tap water was collected at SKLEAC, Research Center for Eco-environmental Sciences. This water was used without previous treatment. The standard reference material from the National Institute of Standards and Technology (SRM 1643d) with a certified value of total arsenic was used.

Procedure

An appropriate amount of arsenite standard solution was taken in a 25.00 mL volumetric flask, to which 2.50 mL of buffer solution, 1.50 mL of 10 μg/mL iodine solution and 1.50 mL of 1×10^{-6} mol/L DCF solution was added, diluted to the mark and mixed. The fluorescence intensity at 528 nm (with excitation at 510 nm) was measured against a reagent blank within 6 h.

The pentavalent arsenic analytical solutions were prepared before use by adding 50 mL arsenate solution and 0.5% L-cysteine. After 30 min, an appropriate amount of analytical solution was taken into a 25.00 mL volumetric flask, and 0.80 mL 1 mol/L NaOH was added. The sequent experimental step followed the procedure described above.

RESULTS AND DISCUSSION

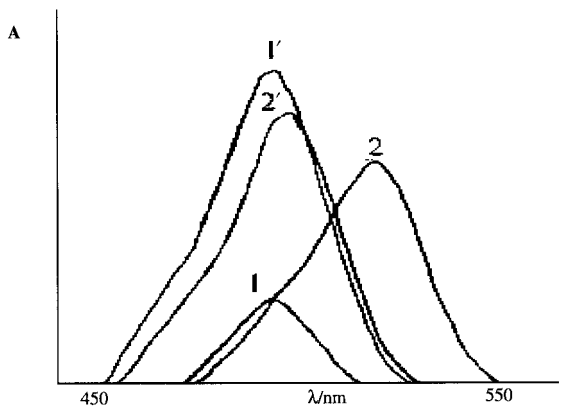
Spectral characteristics

The absorption spectra of DCF–I_2–AsO_3^{3-}, DCF–I_2, DCF and erythrosine are shown in Fig. 1. The maximum absorption wavelength of DCF–I_2–AsO_3^{3-}, and DCF are all at 495 nm. However, the maximum absorption wavelength of DCF–I_2 shifts to red area and finally is 505 nm. Correspondingly, the maximum of erythrosine is 520 nm, so it may be concluded that iodine reacts with fluorescein to produce iodic replacers.

The fluorescence spectra of the system are shown in Fig. 2. The fluorescent species have excitation and emission maximum wavelengths at 510 nm and 528 nm, respectively.

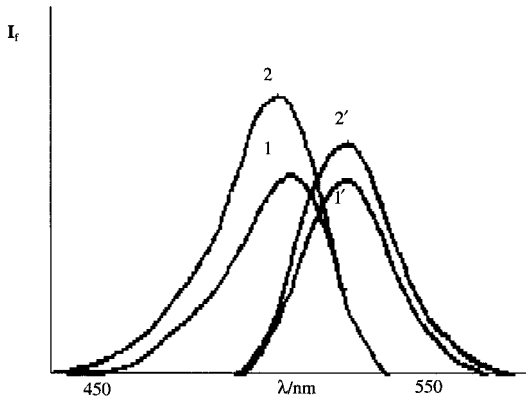
Optimum conditions for fluorimetric determination

The experimental results indicated that the maximum fluorescence intensity was achieved when 1.50 mL of 1×10^{-6} mol/L DCF solution and 1.50 mL 10 μg/mL iodine solution were employed.



1 DCF; 1′ DCF–I_2– AsO_3^{3-}; 2 Erythrosine; 2′ DCF–I_2

FIGURE 1 Absorption of spectra.



1,1′ DCF–I_2; 2,2′ DCF-I_2– AsO_3^{3-}

FIGURE 2 Excitation and emission spectra.

TABLE I Tolerance of foreign ions in the determination of 1 μg arsenite

Foreign ions	*Ratio to arsenite (w/w)*
Na^+, K^+, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, HPO_4^-, HCO_3^-	1000
Mg^{2+}, Ca^{2+}, Al^{3+}, Cu^{2+}, Ba^{2+}, Co^{2+}, Hg^{2+}, Cr^{6+}, SCN^-	500
W(VI), Ni^{2+}, As(V)	250
Pb^{2+}	150
Mn^{2+}, Cr^{3+}	100
Zn^{2+}, Cd^{2+}	50
Fe^{3+}	15

The maximum fluorescence intensity occurs over the pH range 6.5–7.5. A pH of 7.0 is recommended for use, achieved via addition of 2.50 mL of buffer solution per 25 mL of final solution.

The influence of setting time was investigated. The results indicated that the reaction was finished immediately in room temperature and the difference in fluorescence intensity between the DCF–I_2–AsO_3^{3-} and DCF–I_2 blank remains constant within 6 h.

Comparing with KI and KI–ascorbic acid, the optimum reducing agent was L-cysteine. The experimental results showed that the pre-reduction of As(V)–As(III) could be completed in 30 min by adding 0.5% L-cysteine and at low acidity (0.02 mol/L HCl).

Interference of other ions

The effect of foreign ions on the determination of arsenite is shown in Table I. An error of ± 5% in the intensity values was considered tolerable. Table I indicates that most foreign ions have no effect.

Calibration graph

A linear calibration graph of fluorescence intensity of the system vs. arsenite concentration was obtained, covering the range 4–180 ng/mL. The detection limit is 0.6 ng/mL (for S/N value of 3). The regression line and correlation coefficient found by the least-squares method is: $\Delta F = 312.8C + 0.76$, $r = 0.9991$ (the unit of C is ng/mL), where ΔF

is the fluorescence quenching and C the arsenite concentration. The proposal is a novel and rapid method for determining total arsenic and also inorganic arsenic species.

Determination of arsenite in tap and pool water

The appropriate amount of water is transferred into a 25 mL volumetric flask. The determination of arsenite is completed by the procedure described above. To determine arsenate, the pre-reduction step is adapted following the experimental procedure and the difference of total arsenite and arsenite is arsenate. The possibility of using this method for analysis of the samples was tested by determining the recovery of known amount of AsO_3^{3-} added to the sample. The results in Table II and Table III show that the recoveries of AsO_3^{3-} for the tap and pool water tested are 96–105% and the total arsenic concentration is in agreement with the certified value of the reference material at 96% confidence level. The reproducibility of the determination was good.

Mechanism of the reaction

The reaction between iodine and 2′,7′-dichlorofluorescein probably is: iodine replaces hydrogen on the ring of benzene to produce an iodo-fluorescein which is a non-fluorescence substance (shown in Fig. 3).

TABLE II Determination of arsenite in tap water and in a certified water

Sample	*Added* (μg/L, $n=6$)		*Found* (μg/L, $n=6$)		*Certified value* (μg/L)
	As(III)	*As(V)*	*As(III)*	*As(V)*	
1	2.50	1.50	2.54 ± 0.11	1.68 ± 0.08	–
2	1.50	2.50	1.55 ± 0.06	2.61 ± 0.13	–
3	0.00	4.00	0.00 ± 0.04	4.13 ± 0.11	–
SRM	–	–	13.24 ± 1.21	40.36 ± 1.86	56.02 ± 0.73

TABLE III Determination of arsenic in pool water

No.	*Water* (mL)	*As(III)* (μg, $n=6$)	*As(V)* (μg, $n=6$)	*As(III) added* (μg, $n=6$)	*As(V) added* (μg, $n=6$)	*Recovery* (%, $n=6$)
1	10.00	0.58	0.45	1.00	0.00	103.4
2	10.00	0.63	0.41	2.00	0.00	102.1
3	10.00	0.67	0.49	0.00	1.00	101.6
4	10.00	0.59	0.44	0.00	2.00	98.8

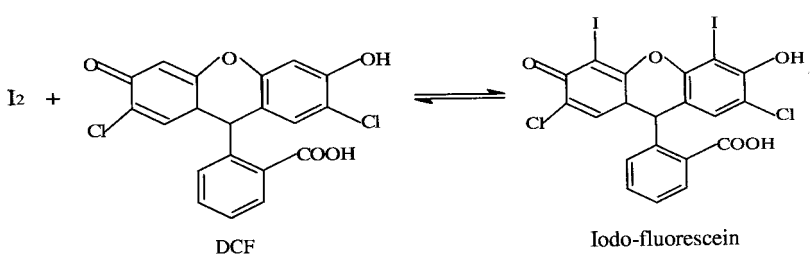


FIGURE 3 A plausible mechanism from DCF to Iodo-fluorescein.

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