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Spectrofluorimetric Determination of Arsenic(III) in Water Samples

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A novel analytical method for determination of trace arsenic(III) is established by kinetic spectrofluorimetric. The method is based on quenching of the fluorescence, Rhodamine B, by the action of iodine, which is released by the reaction between arsenic(III) and potassium iodate in acidic medium. Under the optimized conditions, the detection limit was 0.5 μg L^{-1}, the relative standard deviation was 3.2 % for arsenic(III) (c = 40 μg L^{-1}, n = 6). The recovery of real arsenic(III) samples were in the range of 95.6-104.1 %. This method has been applied for the trace of arsenic(III) detection in real water samples. The results indicated that there was a good linearity between the fluorescence intensity of Rhodamine B and the concentration of arsenic(III).

Key Words: Kinetic spectrofluorimetric, Arsenic(III), Rhodamine B, Potassium iodate.

INTRODUCTION

Arsenic mostly occurs in water, soil, ore and atmosphere, which was widely investigated due to its compound properties as a highly toxic in human and animal. In general, the arsenic is basic nontoxic element, but which compounds have different toxicity, such as the trivalent arsenic compounds are more toxic than the pentavalent arsenic. In addition, the arsenic can cause acute or chronic poison in human[1]. So it is necessary to develop a simple and accurate method for the detection of arsenic.

In previous report, several analytical methods have been reported the arsenic detection. Boadu *et al.*[2] reported a new method for the determination of arsenic in the water samples by neutron activation analysis, but the range of average arsenic levels is too high, which the range between 0.04 and 12.2 mg L^{-1}. Ševaljevic *et al.*[3] described a novel method for the arsenic determination based on electrolytic arsine generation and atomic absorption spectroscopy detection, the detection range was 0.002-0.02 mg L^{-1}. Other researcher also illustrated the detection of arsenic by atomic absorption spectroscopy[4,5]. Though the ICP-MS method is too expensive, moreover, the combination of instruments makes the determined procedure more complex, Entwisle *et al.*[6] still used this method to determine the arsenic, due to their newly developed procedure overcomes these issues by complete mineralization of the matrix leaving insignificant amounts of residual carbon and by removal of chlorine by evaporation. Because of the high performance liquid chromatograph with excellent separation for species in aqueous samples, many researchers reported HPLC to connect with ICP-MS, which can separate and detect arsenic for speciation analysis[7-10].

Recently, many workers also described atomic fluorescence spectrometry, which has been applied for the determination of arsenic in real samples. For example, Le *et al.*[11] demonstrated that analyses of arsenic speciation were carried out using ion pair chromatographic separation with hydride generation atomic fluorescence detection in urine samples, Yin *et al.*[12] also developed a new hyphenated technique for speciation analysis of four environmentally significant and toxic forms of arsenic by on-line coupling of capillary electrophoresis to atomic fluorescence spectrometry, electrothermal atomization laser-excited atomic fluorescence spectrometry was reported to determine arsenic by Swart *et al.*[13]. In addition, electrochemical method also attracted many chemists[14-16].

Recently, determination of arsenic also reported using spectrophotometer. Morita and Kaneko[17] developed for the low ppb levels of arsenic detection in water samples, they used a nanoparticle of ethyl violet with a molybdate iodine tetrachloride complex as a probe for molybdoarsenate and obtained good results. Karayünlü and Ay[18] found a cost effective spectrophotometer method for the determination of arsenic at trace level using hexamethylene ammonium hexamethylene dithiocarbamate, however, the linearity range is too narrow and the detection limit is too high.

The aim of this study is to establish a kinetic spectrofluorimetric method for analysis of arsenic(III) in real samples and it has been successfully applied for the trace arsenic(III) determination in real samples and obtained satisfactory result.

EXPERIMENTAL

All reagents used were analytical grade and the double distilled water used throughout the experiment. Arsenic(III) was purchased from Shenyang Chemical Reagent factory and the stock standard solution (1 mg mL^{-1}) was prepared by dissolving 0.1320 g of As_2O_3 in 10 mL of 20 % (m/v) KOH solution, which was neutralized with 20 % (v/v) H_2SO_4 and diluted to 100 mL. In addition, the arsenic(III) working solution diluted to 1.0 mg mL^{-1} with double distilled water. 0.5350 g KIO_3 (0.01 M) dissolved in 250 mL with double distilled water, which obtained from Shanghai Reagent factory. 0.01 M rhodamine B (Shanghai Reagent three factories) was prepared by dissolving 0.3597 g and diluted to 100 mL with double distilled water, the working solution diluted to 5.0×10^{-5} M. 0.1 M Hydrochloric acid solution was prepared by appropriate dilution of concentrated hydrochloric acid.

Using F96 (LengGuang Technology Co. Ltd, Shanghai) optimize the experiment conditions, using RF-5301 PC (Shimadzu, Japan) scan the fluorescence spectra of rhodamine B and detect arsenic(III). The temperature controls by Super CS-501 thermostat (Chongqing Test Equipment Factory).

Experimental procedure: The basic analysis procedure of this system was respectively to add 1 mL 5.0×10^{-5} M rhodamine B, 0.8 mL of 0.1 M HCl, 1.2 mL 0.01 M KIO_3 and an appropriate arsenic(III) into 10 mL colourimetric tube, the another tube is a blank reagent, then dilute to scale line with double distilled water. Finally, after heating for 12 min at 100 ºC, the solutions cool to room temperature about 4 min. The results of the experiment were determined through RF-5301 PC fluorescence spectrophotometer and obtained the fluorescence value of containing arsenic(III) (F) solution and blank reagent (F_0) solution. At last, calculate the ΔF ($\Delta F = F_0 - F$) value of the corresponding amount of arsenic(III).

Sample preparation: First, in order to remove suspension solids, 100 mL clear water samples carry on the quantitative filter paper and then put the filtrate into 200 mL beaker. Second, 10 mL concentrated nitric acid join into the beaker and steam the solution to near half at low temperature, continuing to join 8 mL 30 % H_2O_2 and heat to nearly dry at low temperature. Third, the crystallization salts dissolve in beaker and shift to 50 mL measuring flask, adjust the pH near neutrality and dilute to 50 mL with double distilled water. At last, the solutions carry on through the ion exchange resin[19].

RESULTS AND DISCUSSION

Fluorescence spectra: Using RF-5301 PC scanned the fluorescence spectra features of rhodamine B. Fig.1 shows the maximum excitation wavelength and emission wavelength of this system at 562 and 579 nm, respectively. The curve 1-1' was rhodamine B fluorescence spectra in hydrochloric acidic medium. It was evident that, from the curve 2-2' imply, the fluorescence intensity was weaken when the potassium iodate was added, but this phenomenon was not obvious, there upon it can safely concluded that potassium iodate can oxidize rhodamine B in strong acidic solution. It is interesting to note that the fluorescence of rhodamine B was quenched obviously when some arsenic(III) joined into the oxidation system (curve 3-3'). For further study and refer some previous works[20,21], we confirm that the rhodamine B was quenched by the reaction of iodine, which was generated by the reaction between potassium iodate and arsenic in strong acidic solution.

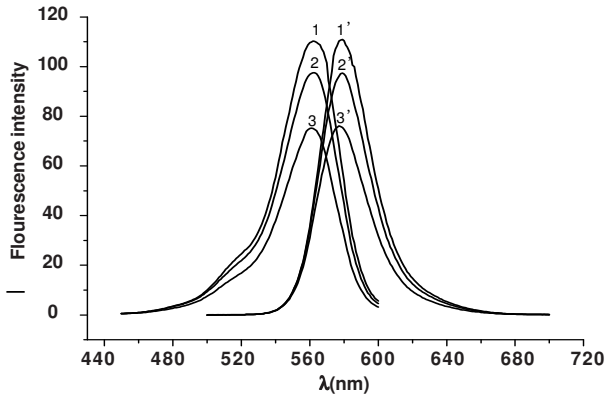

Fig. 1. Excitation and emission spectra

Effect of rhodamine B: When other reagents were fixed, the effect of rhodamine B concentration on the fluorescence intensity of the solution was evaluated. Results show that the fluorescence intensity increased gradually since the volume of rhodamine B increased from 0.2 to 1.0 mL. While the volume of rhodamine B increased to 1 mL, ΔF reached a maximum value. Continuing to increase the volume of rhodamine B, on the contrary, the value of ΔF decreased. Then a 1 mL of 5.0×10^{-5} M of rhodamine B solution was used as optimal for which the highest sensitivity was obtained.

Effect of HCl: The volume of HCl in this system also influences the signals for arsenic(III) determination. For this investigation, of which the results are shown in Fig. 2, solution of 0.1 M HCl was used and all other operating parameters were reported when studying the effect of the volume of rhodamine B. In the present work, HCl was chosen to obtain an acidic medium and its effect on the fluorescence signal was evaluated in the range from 0.2 to 2.0 mL. It was evident that, with the results of experiment, a plateau for ΔF value when HCl volume was in the range of 0.8-1.2 mL. Hence, 0.8 mL of 0.1 M HCl was chosen for the following experiments.

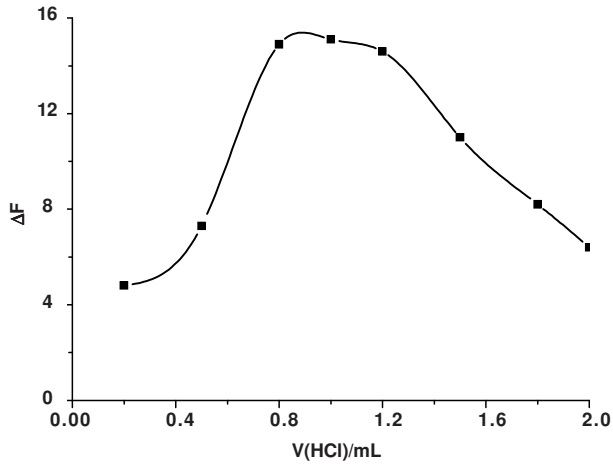

Fig. 2. Effect of the concentration of HCl on ΔF value of arsenic(III)

Effect of KIO_3 concentration: To check the effect of KIO_3 of the proposed method, the volume of KIO_3 was examined in the range of 0.2-2.0 mL. Fig. 3 shows the maximum

ΔF value when the volume of KIO_3 was 1.2 mL. Higher or lower volume of KIO_3 cause the ΔF value to decrease. Finally, 1.2 mL of 0.01 M KIO_3 was selected.

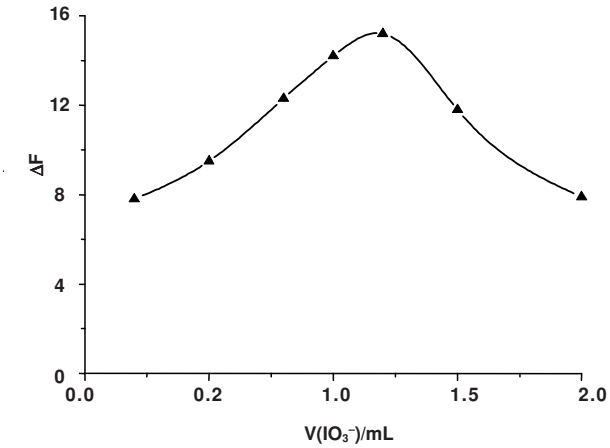

Fig. 3. Effect of KIO_3 on ΔF value of arsenic(III)

Effect of temperature: The effect of temperature is very important for kinetic fluorescence and investigated in detail. From the Fig. 4, the reaction had no obvious change below 70 ºC. However, the experiment results demonstrated that the ΔF value increased when still rose the temperature. While the reaction carried out at 100 ºC, ΔF reached a maximum value. So the reaction temperature 100 ºC was used.

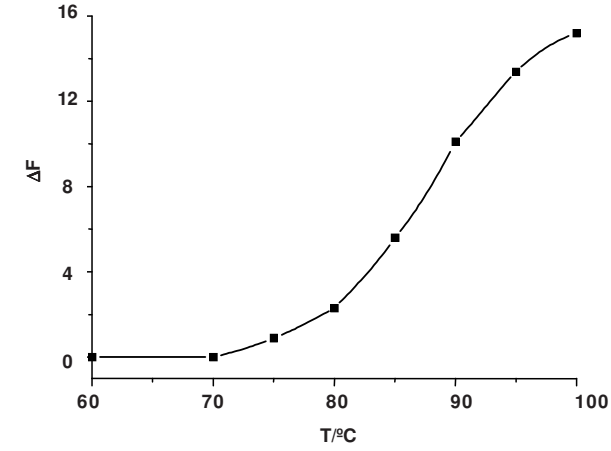

Fig. 4. Effect of temperature on ΔF value of arsenic(III)

Effect of reaction time: In order to investigate the effect of reaction time, it was studied from 4 to 14 min in this study. Fig. 5 revealed that ΔF value drastically increased in the range of 4-10 min. ΔF obtained a maximum value when the reaction time was 10 min, however, with the time increased the value of ΔF gradually decreased. Thus, the reaction time of 10 min was chosen for further experiment.

Effect of interference ions: To investigate the selectivity of this proposed method, the effect of interference ions on the determination of arsenic(III) also investigated by adding known quantities of the interference ions to a fixed amount of arsenic(III) and determining arsenic(III). Tolerance defined as the amount of interference ions that produced an error not

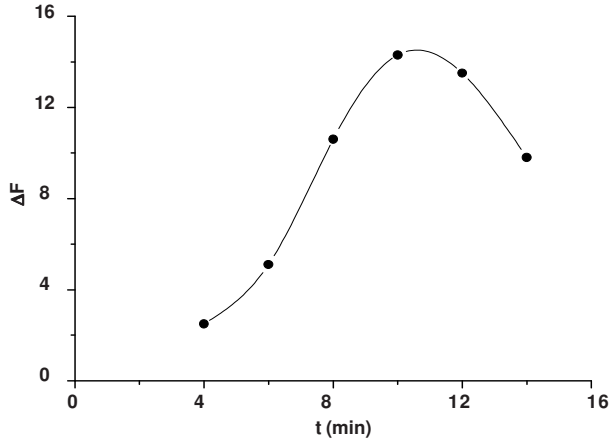

Fig. 5. Effect of reaction time on ΔF value of arsenic(III)

exceeding ± 5 % in the determination of 200 μg L^{-1} arsenic(III) was evaluated. The determination was not interfered by X-fold excesses of: K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}, F^-, Br^-(1500), Mn^{2+}, Co^{2+}(750), As(V), Ba^{2+}, Mg^{2+} (200), Al^{3+}, Ca^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} (100), Cu^{2+}, Fe^{3+} (50), Cr(VI), NO_2^-, BrO_3^-(15). The results indicated that this method could apply to determine arsenic(III) in real samples.

Calibration curve: Under the optimum experimental conditions, the linear calibration curve was obtained in the arsenic(III) concentration range from 1 to 600 mg L^{-1} with correlation coefficient R as 0.9991, the correlation equation was ΔF = 1.3974 + 0.0802c (μg L^{-1}). We also studied the range from 1 to 100 μg L^{-1} in detail, the correlation equation was ΔF = 1.0964 + 0.0851c (mg L^{-1}) and the coefficient R is 0.9974. From the two calibration equation, there has some deviation but it is tolerance limit. The method detection limit is 0.5 μg L^{-1}, which was calculated in the ratio of three times the standard deviation of ΔF (n = 12). The relative standard deviation (n = 6) was 3.2 % at 40 μg L^{-1} arsenic(III).

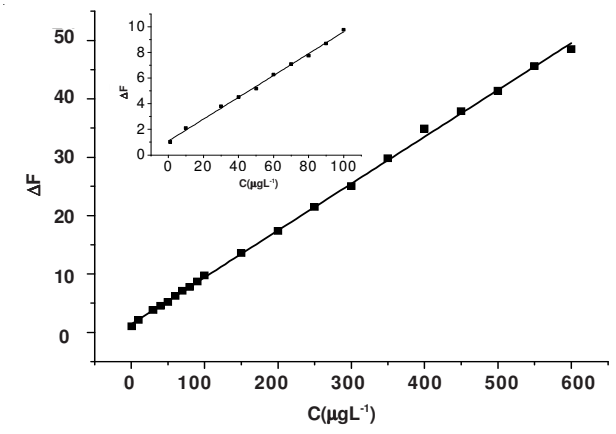

Fig. 6. Calibration curve

Samples analysis: According to the experimental procedure, we took 3 mL treated sample to determine and calculate the arsenic(III) concentration in water sample. The recoveries were investigated and the results are given in Table-1. Meanwhile, in order to examine the accuracy of this method, the water samples were also measured by atomic absorption spectrophotometry (AAS)[22].

TABLE-1
RESULTS OF RECOVERY TEST FOR THE DETERMINATION OF SAMPLES (n = 6)

Sample	Added (μg L^{-1})	Found (μg L^{-1})	RSD (%)	Recovery (%)	AAS (μg L^{-1})
River water	0.00	6.57	3.01	—	6.89
	25	32.59	2.1	104.1	—
	50	57.17	3.64	101.2	—
	75	79.32	4.02	97	—
	100	108.8	2.38	102.2	—
Well water	0.00	2.84	4.26	—	3.19
	25	28.64	2.39	103.2	—
	50	52.14	3.97	98.6	—
	75	74.54	4.27	95.6	—
	100	101.5	2.61	98.7	—
Lake water	0.00	10.12	2.35	—	9.87
	25	34.45	2.67	97.3	—
	50	61.67	3.58	103.1	—
	75	86.25	4.36	101.5	—
	100	107.6	3.9	97.5	—

Conclusion

In this manuscript, rhodamine B oxidized by potassium iodate in strong acidic medium, when the arsenic(III) was added, the reaction was activate between potassium iodate and arsenic(III) and released iodine and then the iodine cause the rhodamine B quenching. Hence, depending on these researches, we can safely conclude that a novel method is established for arsenic(III) determination by kinetic spectrofluorimetric. The obtained results revealed that this technology could use for this purpose, which was detected arsenic(III) in natural water and obtained satisfactory results and the method was more sensitive than other methods (Table-2).

TABLE-2
FIGURES OF PARAMETERS OF METHODS FOR DETERMINATION OF ARSENIC(III)

Method used	Analytical ranges (μg L^{-1})	Detection limit (μg L^{-1})	Reference
Spectrophotometer method	40-400	----	20
Spectrophotometer method	0-20	0.50	17
Spectrophotometer method	200-1000	60.0	18
Spectrophotometer method	0-40	2.10	23
Fluorescence method	4.12-82.4	0.26	24
Fluorescence method	16-320	5.70	25
Fluorescence method	1-600	0.50	This paper

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