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Determination of Arsenic in Aqueous Samples by Kinetic Fluorescence

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A simple and selective method is described for the determination of arsenic(III) by kinetic fluorometry. The fluorescence intensity of pyronine B is decreased by adding some KIO_3. However, the fluorescence intensity of pyronine B is further decreased with the presence of arsenic(III), because the pyronine B oxidation by KIO_3 with arsenic(III) as catalyst was formulated in sulfuric acid medium. There is a good linearity between the fluorescence intensity of pyronine B and the concentration of arsenic(III). The method allows for the determination of arsenic(III) in the range from 2.0-300 μg/L and the limit of detection is 1.4 μg/L. It has been successfully applied to the determination of arsenic(III) in real samples and the RSD is 2.4 % at 100 μg/L arsenic(III) (n = 11).

Key Words: Kinetic fluorometry, Pyronine B, Arsenic(III).

INTRODUCTION

Arsenic naturally occurs in water, soil, ores and atmosphere has been widely studied due to its properties as a highly toxic poison in human and animal. Moreover, the trivalent arsenic compounds are more toxic than the pentavalent arsenic[1]. The contamination of arsenic mainly comes from the industrial processes, such as the mining, metallurgical, pesticide production, chemical, leather, pharmaceutical and glass[1]. In addition, some articles also reported that inorganic arsenic is more toxic than organic arsenic[2,3]. Therefore, developing a selective analytical methods is significant and it possesses some challenges in the trace determination of arsenic(III) in different materials.

In recent years, several analytical methods have been reported for the determination of arsenic, including atomic absorption spectrometric[4-6], tristimulus colorimetric[7,8], electrochemical[9-11], neutron activation analysis[12], inductively coupled plasma mass spectrometry[13-15], mass spectrometry[16], atomic fluorescence[17-19], spectrophotometric[20,21], flow injection hydride generation electrothermal atomic absorption spectrometric[22,23] and high performance liquid chromatography[24]. But, the above mentioned methods all have their disadvantage, such as high cost, robust sample handing and so on.

Kinetic analytical method is adopted to measure the reaction rate, from the results of the reaction rate, which can safely get the accurate data of the sample concentration. Surely, it has a good quantitative relationship between the reaction rate and the sample concentration. The kinetic method also has a general advantage of high sensitiveness combined with relatively simple procedures and instruments[25], such as Afkhami *et al.*, investigated a method of determination arsenic(III) in the range of 6-1000 μg/L, which is based on inhibitory effect on the redox reaction between bromate and hydrochloric acid[26]. Sicilia *et al.*[27], reported arsenic(III) in the range of 7-300 ng/mL, which is based on accelerating effect on the Os(III)-catalyzed reaction between iodide and bromate in micellar media.

Pyronine B has a strongly fluorescence which was used to determine other materials, such as artemisinin[28], manganese[29] and so on. The following step is to carry out our research of establishing a novel fluorescence analytical procedure. In this work, we investigated the factors that could affect the fluorescence intensity of pyronine B, such as the concentration of pyronine B, pH, oxidant, temperature and the reaction time. Moreover, under the optimum experimental conditions, there is a good linearity between the pyronine B fluorescence intensity and the concentration of arsenic in the range of 2.0-300 μg/L.

EXPERIMENTAL

Fluorescence spectra was performed with RF-5301 PC (Shimadzu, Japan). F96 (Lengguang Shanghai Technology Co. Ltd.) was utilized to measure the results of experiment conditions. The temperature controlled by Super CS501 thermostat (Chongqing Test Equipment Factory).

Standard solutions and reagent: All reagents were prepared using analytical grade and double distilled water. 1.0 mg/mL standard solution of arsenic(III) was prepared by

dissolving 0.1320 g of As_2O_3 (Shenyang Chemical Reagent Factory) in 10 mL of a 20 % (m/v) KOH solution, which was neutralized with 20 % (v/v) H_2SO_4 and diluted to 100 mL with double distilled water. The working solution diluted to 1.0 µg/mL with double distilled water. 0.01 mol/L KIO_3 solution was prepared by dissolving 0.5350 g of KIO_3 (Shanghai Reagent Factory) in 250 mL of double distilled water. A solution of 0.01 mol/L pyronine B was prepared by dissolving 0.3597 g of pyronine B (Sinopharm Chemical Reagent Co. Ltd.) and diluting to 100 mL with double distilled water, the working solution diluted to 1.0×10^{-5} mol/L. 1.0 mol/L sulfuric acid solution was prepared by appropriate dilution of concentrated sulfate acid.

Procedures: The basic analytical procedure of the reaction was to add 1.0 mL of 1.0×10^{-5} mol/L pyronine B, 0.4 mL 0.01 mol/L KIO_3, 0.75 mL 1.0 mol/L H_2SO_4 and to transfer a suitable arsenic(III) into 10 mL colorimetric tube and then to dilute to 10 mL with double distilled water. Finally, put them into cold water and after 5 min they were heated at 90 ºC for 12 min in super thermostat. The results of the experiment were performed with RF-5301 PC fluorescence spectrophotometer.

Sample preparation: We collected 100 mL of water samples and used quantitative filter and paper filter in order to remove suspended solids and 2.5 mL of 0.1 mol/L ascorbic acid was transferred into the filtrate solutions and then put it into boiling water about 7 min. In order to sustain a certain pH, a suitable H_2SO_4 was added into the samples. If the sample is difficult to handle, we should take some amount of the pretreatment solution through the ion exchange resin treatment[30]. The results of experiment showed in Table-2.

RESULTS AND DISCUSSION

Fluorescence spectra: A series of experimental conditions have been studied and optimized for maximum fluorescence intensity in this system. The fluorescence spectra of pyronine B recorded by RF-5301 PC and the maximum excitation wavelength and emission wavelength were 528 and 552 nm, respectively. Fig. 1 exhibited the fluorescence signals distribution of pyronine B. The strong fluorescence signals can be observed when pyronine B survived in H_2SO_4 solutions (curve 1). The curve 2 indicated that in presence of KIO_3 the fluorescence signals of pyronine B was weaken, but this phenomenon was not obvious, hence, it can be confirmed that KIO_3 has the oxidative capacity, which can oxidize the fluorescence reagent pyronine B. In fact, from the curve 3 to curve 6, the fluorescence signals continued to decrease when some amounts of arsenic(III) was added into the oxidative system, so it is concluded that arsenic(III) can catalyze the oxidative reaction in sulfuric acid medium. Additionally, we obtained a good relationship in real samples.

Influence of pyronine B: As we all know that fluorescence reagent plays a key role parameter for the determination of arsenic in the system. With the purpose of studying the effect of the fluorescence reagent on the performance of the kinetic fluorometry, we made a detail examination of different volume of pyronine B from 0.2-2.0 mL. It was evident that, with the results of experiment, the pyronine B is more than 1.0 mL and the ΔF value, on the contrary, was drop down. In order to obtain the optimum condition, 1.0 mL pyronine B was selected in the following work.

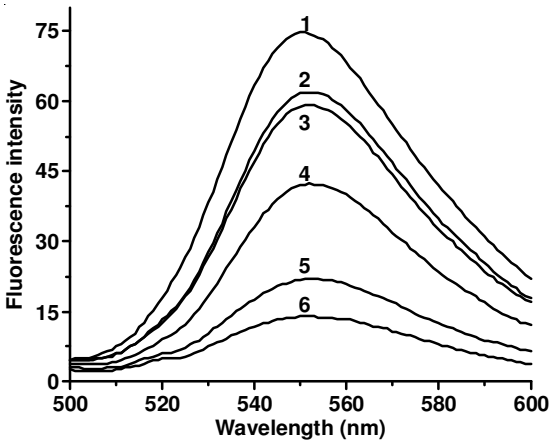

Fig. 1. Fluorescence emission spectrum

Influence of volume of H_2SO_4: Changing the pH value of the solution, the fluorescence intensity could make a big impact, so a suitable aliquot of acid is essentially surveyed in this system. Hence, we investigated the effect of hydrochloric acid and sulfuric acid mediums, respectively. Furthermore, the results testify that sulfuric acid is suitable for the pyronine B-KIO_3-arsenic(III) fluorescence system. The effect of the volume of sulfuric acid on the fluorescence signals of the pyronine B was studied in the range of 0.2-2.0 mL. When the volume was below 0.75 mL or beyond 1.0 mL, the ΔF value began to decrease (Fig. 2), therefore, 0.75 mL sulfuric acid was chosen for analytical purpose.

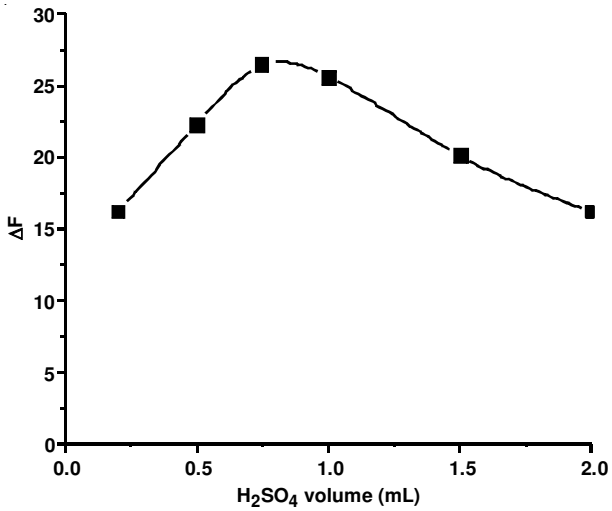

Fig. 2. Effect of sulfuric acid volume on the peak of fluorescence intensity

Influence of volume of KIO_3: In this article, the optimum volume of KIO_3 must be selected, so we carried out different amounts of KIO_3 under the fixed other reagents condition. The results showed that the peak of fluorescence intensity enhanced with the increase of the volume of KIO_3 (Fig. 3). When the volume of KIO_3 reached 0.4 mL, ΔF obtained a maximum value. On increasing the volume of KIO_3, the intensity of fluorescence signals was weakening. Hence, 0.4 mL of 0.01 mol/L KIO_3 was selected.

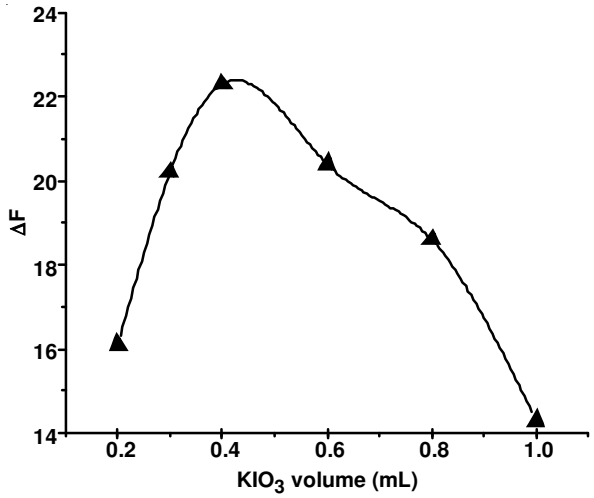

Fig. 3. Effect of KIO_3 volume on the peak of fluorescence intensity

Influence of temperature: The temperature is very important for kinetic fluorometry. The effect of temperature was investigated in detail. Fig. 4 revealed that the different temperature could affect the fluorescence signals. It is also evident that the reaction temperature was carried out at 90 °C, the fluorescence signals reached the maximum value.

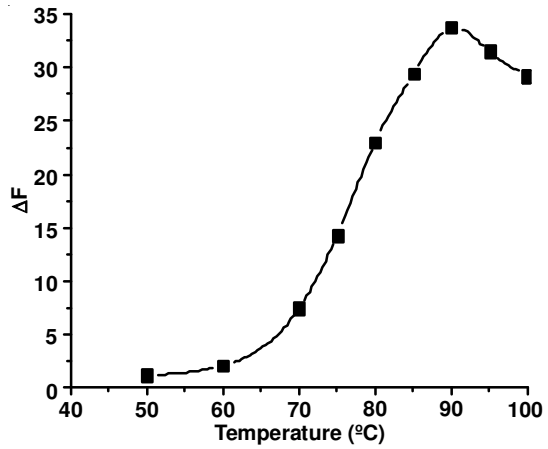

Fig. 4. Effect of temperature on the peak of fluorescence intensity

In addtion, it is surprised to find that the peak of fluorescence signals decreased when the temperature continued to increase. Thus, 90 ºC is selected as the optimum reaction temperature.

Influence of time: The influence of the reaction time on the fluorescence intensity of pyronine B was also examined. Under the different time circumstance, the reaction time from 4-16 min was observed. The reaction time in the range from 4-12 min, the fluorescence signals increased drastically and reached a maximum ΔF value. The results were showed in Fig. 5. So, the reaction time was standardized at 12 min for further experiments.

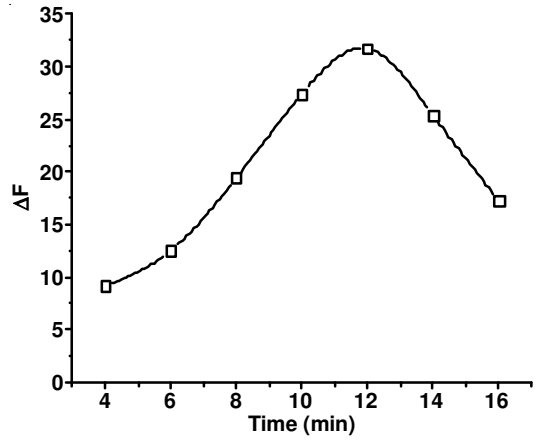

Fig. 5. Effect of time on the peak of fluorescence intensity

Calibration curve: Under the optimum experimental conditions chosen above, a linear calibration curve was obtained in the arsenic(III) concentration range of 2-300 μg/L. The correlation equation was ΔF = 3.918 + 0.1488m (μg/L), R = 0.9991. The detection limit is 1.4 μg/L, which was calculated in the ratio of three times the standard deviation of ΔF (n =11). The relative standard deviation (n = 11) was 2.4 % at 100 μg/L arsenic(III).

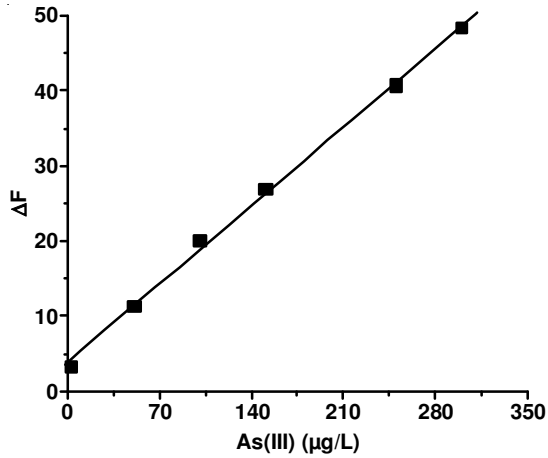

Fig. 6. Calibration curve

Effect of interference ions: Several ions have the potential to affect the pyronine B fluorescence emission. So a variety of ions had been chosen to investigate the influence on the fluorescence intensity of pyronine B in present work. Table-1 showed that Cr(IV), NO_2^- and BrO_3^- could strongly quench the fluorescence signals of pyronine B. Furthermore, the results also indicated that other ions slightly interfered with the sensitivity and selectivity of arsenic(III) determination.

Analytical application: The proposed method was applied to determine arsenic in real water samples, such as river water and well water. The determination procedure and samples pretreatment were performed as described earlier. Under the

TABLE-1
EFFECT OF FOREIGN IONS ON DETERMINATION OF ARSENIC

Interference folds	1500	1000	500	125	10
Ions	K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}, F^-, Br^-	Cu^{2+}, Mn^{2+}, Co^{2+}	As^{5+}, Ba^{2+}, Mg^2	Al^{3+}, Ca^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+}, Ni^{2+}	Cr^{6+}, NO_2^-, BrO_3^-

selected conditions, we measured the water samples by utilizing RF-5301 PC. Table-2 is the analytical results for the real water samples along with the recovery for samples. The recoveries of water samples were in the range of 98.7-104.6 %. For making sure present proposed method is feasible, we also attempt to survey and evaluate the real samples by inductively coupled plasma hydride method[31] and it is clear that the proposed method can be used to determine the arsenic(III) in real samples.

TABLE-2
DETERMINATION RESULTS OF WATER SAMPLE

Sample	Added (μg/L)	Obtained* (μg/L)	Recovery (%)	ICP (μg/L)
River water	0.00	8.6 ± 0.03	–	8.7 ± 0.05
	50	60.9 ± 0.05	104.6	60.5 ± 0.04
	100	111.6 ± 0.08	103.0	112.0 ± 0.06
	150	156.7 ± 0.05	98.7	156.3 ± 0.08
Well water	0.00	2.1 ± 0.02	–	2.2 ± 0.05
	50	53.7 ± 0.09	103.2	53.9 ± 0.02
	100	103.2 ± 0.03	101.1	103.5 ± 0.06
	150	153.1 ± 0.05	100.7	153.5 ± 0.03

*Mean ± average deviation (n = 5).

Conclusion

In this work, a new method for analysis of arsenic(III) by kinetic fluorometry is developed. The experimental conditions affecting the pyronine B-KIO_3-H_2SO_4 reaction were optimized and the analytical results were presented here. The obtained results proved that the quenching of fluorescence intensity of pyronine B was efficiently promoted by adding arsenic into system. The results also revealed that the established method had the advantage of being simple and selective and the method has been applied in the checking the samples obtained in an actual case.

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