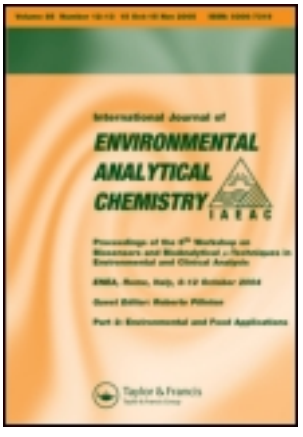

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

Highly sensitive inhibitory kinetics fluorescence method for determination of arsenic

Guirong Li [a] & Yunfu Liu [a]
[a] College of Public Health, University of South China, Hengyang 421001, China

Available online: 06 Jul 2011

To cite this article: Guirong Li & Yunfu Liu (2011): Highly sensitive inhibitory kinetics fluorescence method for determination of arsenic, International Journal of Environmental Analytical Chemistry, 91:9, 866-875

To link to this article: http://dx.doi.org/10.1080/03067310903207618

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 9, 10 August 2011, 866–875

Taylor & Francis
Taylor & Francis Group

Highly sensitive inhibitory kinetics fluorescence method for determination of arsenic

Guirong Li* and Yunfu Liu

College of Public Health, University of South China, Hengyang 421001, China

(*Received 18 February 2009; final version received 11 July 2009*)

A new and highly sensitive inhibitory kinetic fluorescence method for the determination of arsenic (III) has been established based on its inhibitory effect on the oxidation reaction of Acridine red (ADR) by $KBrO_3$ in sulphuric acid medium. The reaction has been followed by measuring the enhancement of fluorescence at 550 nm. It relies on the linear relationship where the change in the fluorescence (ΔF) versus added As(III) amounts in the range of 0–0.450 $\mu g\,mL^{-1}$ is plotted, under the optimum conditions. The sensitivity of the proposed method, i.e. the limit of detection, is $2.1 \times 10^{-2}\,ng\,mL^{-1}$. The method is featured with good accuracy and reproducibility for arsenic (III) determination. This method was successfully applied for the quantitative determination of arsenic (III) in food products samples, and the relative standard deviations and the recoveries were in ranges of 2.31–2.83% and 90.0–107.2%, respectively. A review of recently published catalytic or inhibiting kinetic methods for the determination of arsenic (III) has also been presented for comparison. The mechanism of reaction was studied.

Keywords: arsenic; inhibitory kinetics fluorescence; Acridine red; food products

1. Introduction

Arsenic in the environment or food products has attracted widespread attention because of its own some hazardous characteristics [1,2] such as carcinogenesis, teratogenesis and mutagenesis. Therefore, it is significant of determining arsenic in food samples. At present, the analytical methods for arsenic are mainly chromatography [3,4], ICP-MS [5], electrochemical analysis [6,7], atomic absorption spectrometry [8,9], atomic fluorescence spectrometry [10–12], chemiluminescence analysis [13], Raman and infrared spectra method [14,15] and spectrophotometry [16]. Although these methods are valuable and each method has its own advantages, there are still some disadvantages in these methods. For example, Heitland *et al.* [17] had reported a fast determination of arsenic in urine by a HPLC-ICP-MS. It was expensive and a large amount of the organic solvents being used were toxic. Vincent *et al.* [18] had reported a collision cell technology ICP-MS system for the determination of arsenic. This method had high sensitivity. Nevertheless, there was the formation of polyatomic interferences within the collision cell. Zhu *et al.* [19] had reported a hydride generation atomic fluorescence system for the determination of arsenic using a dielectric barrier discharge atomiser. The detection limit of As(III) was 0.04 $ng\,L^{-1}$. But the temperature had a large effect on this method. Therefore, it is necessary to develop new method for the determination of arsenic.

*Corresponding author. Email: liguirong525@126.com

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903207618
http://www.informaworld.com

Table 1. A comparison of the proposed method for the determination of arsenic with the published kinetic methods.

IRS	DL ug mL^{-1}	DRC ug mL^{-1}	MT	Ref.
Victoria blue 4R + $KBrO_3$	5.0×10^{-2}	8.0×10^{-2}–3.5×10^{-1}	IKM[1] SPM[2]	[20]
Xylene cyanol FF + H_2O_2 + KIO_4	9.8×10^{-5}	0–4.0×10^{-3}	CKM[3] SPM	[21]
Rhodamine 6G + KIO_3	2.6×10^{-4}	4.1×10^{-3}–8.2×10^{-2}	CKM FLM[4]	[22]
Red pigment of Hibiscu Sabariffa Linn + Sn^{2+} + PVA	5.0×10^{-6}	0–1.20×10^{-3}	IKM SPM	[23]
m-Sulfonyl-chlorophosphonazo + Cr(VI) + KIO_4	4.0×10^{-4}	0–16×10^{-3}	CKM SPM	[16]
2-Hydroxy-5-methylazobenzene-4′-sulfonic acid sodium + $KBrO_3$ + KBr	3.6×10^{-5}	0–0.04	IKM SPM	[24]
$Fe(Phen)_3^{2+}$ + Cr(VI)	1.0×10^{-2}	0–3.0	RKM[5] SPM	[25]
Acridine red + $KBrO_3$	2.1×10^{-5}	0 – 0.450	IKM FLM	present

Notes: [1]inhibitory kinetic method; [2]spectrophotometric monitoring; [3]catalytic kinetic method; [4]fluorescence monitoring; [5]revulsive kinetic method.

On the other hand, kinetic methods of analysis are very simple, inexpensive and alternatives for arsenic determination. A review of the published kinetic methods involving monitoring technique (MT) along with the indicator reaction system (IRS), detection ranges of concentration (DRC) and detection limits (DL) of these methods are provided in Table 1. However, many of these methods require the use of additional chemicals as activator.

In continuation of our efforts [26,27] to develop methods for arsenic (III) determination, the present investigation reports a new, highly sensitive and selective inhibitory kinetic fluorescence method for the determination of As(III) based on its inhibitory activity on the oxidation of ADR by $KBrO_3$ in acid medium. The method permits the determination of arsenic (III) concentration down to 2.1×10^{-2} ng mL^{-1} with very good accuracy and reproducibility.

Acridine red (ADR) is an organic dye that is widely used in analytic chemistry [28]. In the present study, we found that ADR itself has a strong fluorescence in sulphuric acid medium. This fluorescence was employed for the first time to determine As(III) based on a sensitive inhibitory effect of As(III) on the redox reaction of ADR with $KBrO_3$ in sulphuric acid medium. The oxidation of ADR resulted in the decrease of the fluorescence intensity. At the optimum conditions, the enhancement of fluorescence intensity was proportional to the concentration of As(III) in the range of 0–0.450 μg mL^{-1}, and a novel inhibitory kinetic fluorescence method of determining trace As(III) was developed. In our method, the instruments used are simple, and the operations are rapid and convenient. The method is easy to use widely for the analysis of trace As(III) in foods with high sensitivity and good selectivity.

2. Experimental

2.1 *Apparatus*

The fluorescence spectra and the intensities of fluorescence were measured with a Hitachi F–4500 Spectrofluorometer (Japan) equipped with a 1 cm quartz cell. The slit widths of

both excitation and emission light were kept at 10 nm. All absorption spectra were measured on a UV–8500 Spectrophotometer (Shanghai Trianmei Instrument Factory, China). A tri-function thermostat water bath was used to control the reaction temperature. A stopwatch was used for recording the reaction time.

2.2 *Reagents and solutions*

All chemicals used were of analytical reagent grade, and redistilled water was used for dilution of reagents and samples.

As(III) stock solution ($1.00\,mg\,mL^{-1}$) was prepared by dissolving 0.3301 g of As_2O_3 (Beijing Chemical Reagent Company) with 10 mL of $1.0\,mol\,L^{-1}$ sodium hydroxide. It was diluted to 250 mL with redistilled water in a volumetric flask. Working standard of $1.00\,\mu g\,mL^{-1}$ was prepared by appropriate dilution of stock solution.

ADR solution ($1.00 \times 10^{-4}\,mol\,L^{-1}$) was prepared by dissolving ADR (Beijing Chemical Reagent Company) in redistilled water. A sulphuric acid solution ($0.20\,mol\,L^{-1}$) was prepared by diluting 2.80 mL of 96% H_2SO_4 (Qingzhou Zhenhua Chemical Company) in 250 mL with redistilled water. Potassium bromate solution ($0.20\,mol\,L^{-1}$) was prepared by dissolving $KBrO_3$ (Qingzhou Zhenhua Chemical Company) with redistilled water.

2.3 *General procedures*

Into a 10 mL colorimeter tube, several solutions were added in the following order: 0.80 mL of ADR solution, 1.0 mL of H_2SO_4 solution, 0.60 mL of $KBrO_3$ solution and an appropriate amount of Ar (III) or the sample solutions. The mixture was diluted to 10 mL with redistilled water. After being shaken well, the mixture was placed in a water bath for heating at 50°C for 13 min. Then it was rapidly taken out and cooled under ice water to stop the reaction. The fluorescence spectra was obtained by scanning with $\lambda_{ex} = 529$ nm from 500 to 700 nm in a 1 cm quartz cell with slit width at 10 nm for the excitation and emission. The intensity of fluorescence was measured at the maximum fluorescence wavelength of 550 nm. The enhanced fluorescence intensity of the reaction system was represented as $\Delta F = F - F_0$; here F and F_0 were the fluorescence intensities of the reaction system with and without As(III), respectively.

3. Results and discussion

3.1 *Spectral analysis*

The fluorescence spectra of the reaction system obtained from the experiments are shown in Figure 1. Figure 1 shows ADR itself has strong fluorescence in dilute sulphuric acid medium in the wavelength range of 510–610 nm, and the maximum fluorescence wavelength is located at 550 nm (curve 1). A visible decrease of the fluorescence intensity can be observed while the oxidising agent $KBrO_3$ was added into the solution of ADR + H_2SO_4 (curve 2), because $KBrO_3$ can oxidise ADR. But after adding 0.020 and $0.40\,\mu g\,mL^{-1}$ of As(III) into the solution of ADR + $KBrO_3$ + H_2SO_4, a visible enhancement of the fluorescence intensity of ADR can be observed (curves 3 and 4), which indicated that As(III) has an inhibitory effect on the oxidation reaction of ADR by potassium bromate in sulphuric acid medium. At 550 nm, the enhanced fluorescence

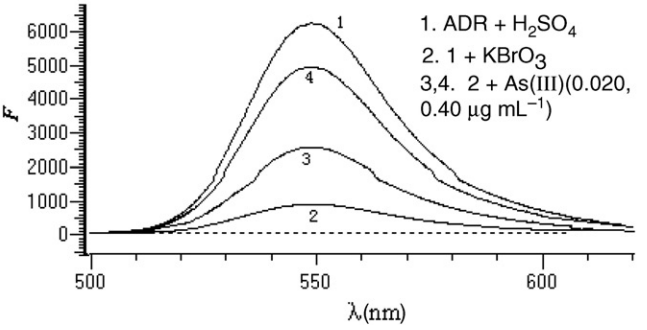

Figure 1. The fluorescence spectra of the ADR.

intensity was in proportion to the concentration of As(III), which suggested that a new assay method for As(III) should be established.

3.2 *Reaction mechanism analysis*

As show in Figure 1, the $KBrO_3$ could rapidly oxidise ADR_{red} to a non-fluorescence compound (ADR_{ox}) without As(III). When trace As(III) was added, the oxidation-reduction reaction could hardly take place, because the reaction speed is very slow. This resulted in the increase of fluorescence intensity of $ADR + KBrO_3 + H_2SO_4$ system. Without As(III), the experimental results showed the indication reaction was very slow before 5 min (without Br^- or Br_2); after 5 min, it becomes very rapid as the Br^- or Br_2 was produced. Additionally, our experiments also testified that the reaction between As(III) and BrO_3^- could not take place without Br^-. Considering the above experimental results and literature about the inhibitory action of As(III) as reducer [24], one can assume the following probable reaction scheme:

$$BrO_3^- + Br^- + H^+ \xrightarrow{k_1} Br_2 + H_2O \tag{1}$$

$$ADR_{Rd} + Br_2 \xrightarrow{k_2} ADR_{Ox} + Br^- \tag{2}$$

$$As(III) + Br_2 \xrightarrow{k_3} As(V) + Br^-. \tag{3}$$

Here k_1, k_2 and k_3 are the reaction speed constants. Because $k_3 > k_2$, the indication reaction becomes very slow after adding As(III). The total reaction can be shown as follows:

$$BrO_3^- + ADR_{Rd} + H^+ \xrightarrow{\text{As(III)inhibitory}} Br^- + ADR_{Ox} + H_2O$$

Experiments have shown that the larger the concentration of As(III) was, the slower the reaction was. The rate equation for the reaction studied could be expressed as follows:

$$-\frac{dC_{ADR}}{dt} = k_0 \cdot C_{ADR}^{\alpha} \cdot C_{KBrO}^{\beta} \cdot C_{As}^{\gamma}.$$

Here k_0 is the rate constants of the reactions. Assuming that the concentrations of ADR and $KBrO_3$ are much greater than those of As(III), and because $F = K\ C_{ADR}$, the rate equation can be written as

$$-\frac{dF}{dt} = k \cdot C_{As}^{\gamma}.$$

Here k is the conditional rate constant. This rate equation was the quantitative basis for the determination of As(III) by the proposed method. When the reaction time was kept the same, the enhancement of fluorescence intensity of the system was in proportion to the concentration of As(III): $\Delta F \propto c_{As}$.

3.3 *Influence of the quantity of addition of H_2SO_4, ADR and $KBrO_3$*

Because the reaction took place in acidic medium, the effects of various acid types such as sulphuric, phosphoric, hydrochloric and nitric acid on ΔF were studied. The results showed that the maximum ΔF was observed in H_2SO_4 medium. Therefore, we chose H_2SO_4 medium for the determination. Experiments indicated that the acidity had a large effect on ΔF. The effect of H_2SO_4 ($0.10\,mol\,L^{-1}$) volume was examined in the range of 0.40–1.40 mL, and the results are shown in Figure 2. It can be seen that the maximum ΔF was obtained in the H_2SO_4 volume range of 0.90–1.10 mL (concentration range of 9.0×10^{-3} – $1.1 \times 10^{-2}\,mol\,L^{-1}$). So 1.00 mL of the H_2SO_4 solution (concentration of $1.0 \times 10^{-2}\,mol\,L^{-1}$) was chosen to be added for the determination.

The concentration of ADR influenced on the fluorescence intensity of the system remarkably. The effect of ADR ($1.00 \times 10^{-4}\,mol\,L^{-1}$) volume on ΔF was tested in the range of 0.40–1.40 mL and the results are shown in Figure 2. The tests showed that the ΔF increased with increasing volume of ADR when the ADR volume was less than 0.60 mL, whereas the ADR volume was more than 0.90 mL, the lower ΔF may result from the bigger reagent blank. The ΔF reached a maximum with increasing ADR volume at 0.80 mL (concentration of $8.0 \times 10^{-6}\,mol\,L^{-1}$).

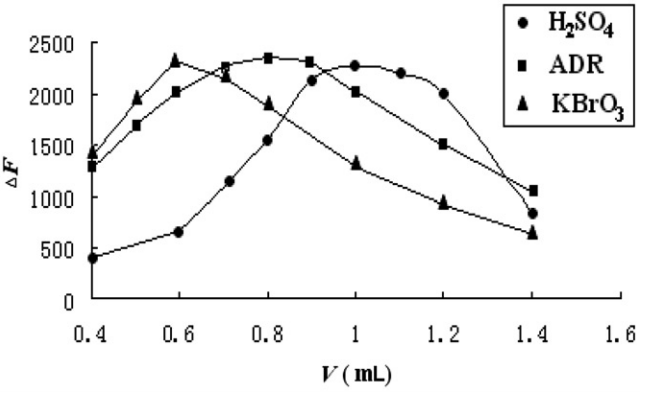

Figure 2. The influence of reagents dosage on ΔF.

The effect of $KBrO_3$ ($0.10\,mol\,L^{-1}$) volume on ΔF was examined in the range of 0.4–1.40 mL and the results are shown in Figure 2. The biggest ΔF was observed when the amount of $KBrO_3$ volume added was 0.60 mL (concentration of $6.0 \times 10^{-3}\,mol\,L^{-1}$).

3.4 *Effect of temperature and time*

After we had prepared the solutions according to the empirical method and controlled the temperature of the solution from 20°C to 65°C, the ΔF values were detected every 5°C. The experimental results (shown in Figure 3) indicated that the ΔF reached the maximum at 50°C. When the reaction temperature was lower than 45°C, the non-inhibitory reaction was very slow, whereas at higher than 65°C, the reaction was very rapid and the As(III) do not have any inhibitory action.

The influences of reaction time on ΔF were tested in range of 5–23 min, and the results are shown in Figure 4. There was a linear relationship between the ΔF and the reaction time in range of 5–13 min, which indicated that this indication reaction was first order reaction. The linear regression rate equation was $\Delta F = -432.8 + 202.1\,t$ (min), $R = 0.9993$. The conditional reaction velocity constant was $k = 0.0419\,min^{-1}$, which was calculated

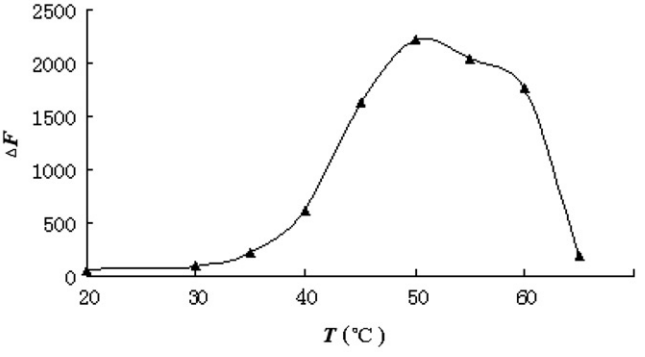

Figure 3. The influence of reaction temperature on ΔF.

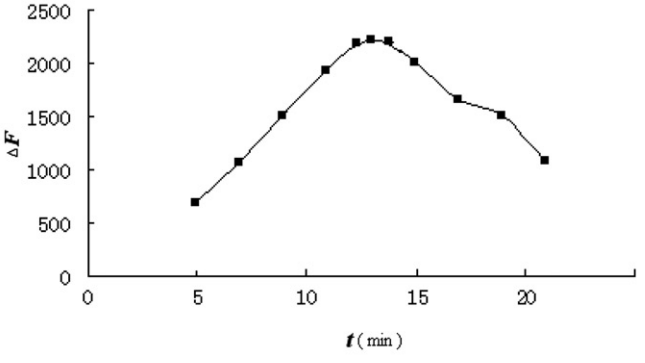

Figure 4. The influence of reaction time on ΔF.

according to the rate equation. The fluorescence intensity remained stable for at least 1 h after cooling; thus, this system exhibits good stability in the experiment. The heating time selected was 13 min and the cooling time chosen was 5 min.

3.5 *Analytical parameters*

The calibration graph for the determination of As(III) was described at the optimum conditions. The results showed that there was a linear relationship between the ΔF and the concentration of As(III) in the range of 0–0.45 $\mu g\,mL^{-1}$. The linear regression equation was $\Delta F = 622.2 + 15.66\,c$ ($\mu g\ ml^{-1)}$ for As(III) with a correlation coefficient of $R = 0.9990$. The detection limit was $2.1 \times 10^{-2}\,ng\,mL^{-1}$ for As(III), which was calculated according to $3S_0/S$, where S_0 is the standard deviation of the blank measurements ($n = 11$), and S is the slope of the calibration graph. The relative standard deviations for the seven determinations of 0.05 and 0.15 $\mu g\,mL^{-1}$ of As(III) were 2.83% and 2.31%, respectively. The results indicated that the precision of the method was good.

3.6 *Effects of interfering species*

The effects of some interfering species on the determination of 0.050 $\mu g\,mL^{-1}$ As(III) were investigated. The results are shown in Table 2. We can observe that common metal cations, inorganic anions and some organics may be tolerated at high concentration. However, Cu^{2+}, Ag^{+}, and I^{-} had lower tolerable amounts. Trace I^{-} can be removed by silver salt precipitation, and these inorganic cations can be sheltered by adding citric acid. Therefore, the proposed method had good applicability.

3.7 *Analytical application to samples*

Samples were pre-treated using an appropriate modification of the method of Xu *et al.* [29]. Four seafood samples and two tea samples were collected from the market. The food samples (5.0 g) were placed in a glass beaker and 50 mL of HNO_3–$HC10_4$ (4:1) acid were added, leaving to react for 12 h. Then, the mixture was heated at 105°C for smoking until the yellow vapour became achromaticity. Finally, the residue solution (about 1 mL) was diluted to 50.0 mL by redistilled water in a volumetric flask.

A 5.0 mL of the samples digested solution in a crucible was evaporated to dryness, 10 mL concentrated HCl were added for dissolution. After shaking well, 0.5 mL 30% KI solution was added and left to react for 10 min. Then the sample solution was transferred into a separatory funnel and was extracted twice by 2 mL of benzene each time to seperate As(III) from P(V) and other interfering substances. The organic phase collected was extracted contrarily twice by 2 mL of water each time. The water phase collected was evaporated to near dryness after adjusting to pH 6–7 with 0.1 $mol\,L^{-1}$ NaOH solution. At length, the residue (about 1 mL) was redissolved and diluted to 10.0 mL with redistilled water.

Under the experimental condition, the proposed method was applied to the determination of arsenic in samples solutions. Recovery tests of arsenic were carried out by adding a known amount of arsenic to the samples. Simultaneously, the comparison tests were conducted in accordance with the current standard method-atomic fluorescence spectrometry (AFS) [30]. Experimental data were handled by statistics and the results are

Table 2. Tolerance levels of foreign species in the determination of $0.05\,\mu g\,mL^{-1}$ arsenic.

Foreign species	Concentration/$\mu g\,mL^{-1}$	Change of ΔF/%
K^+	≥390.0	1.5
Na^+	≥230.0	1.9
NO_3^-	620.0	2.0
Zn^{2+}	391.8	−2.4
Mg^{2+}	145.8	0.7
F^-	114.0	−1.2
Ca^{2+}	96.0	0.9
Ni^{2+}	140.9	1.9
Cd^{2+}	134.9	1.2
PO_4^{3-}	114.0	−3.1
Al^{3+}	16.2	−3.6
Co^{2+}	35.3	2.7
NH_4^+	10.8	0.7
Ba^{2+}	41.1	3.3
Mn^{2+}	55.2	−1.3
Cl^-	177.5	−2.5
Fe^{3+}	1.7	3.0
I^-	0.8	7.2
Ag^+	0.6	−5.9
Cu^{2+}	0.4	6.6
Sb(III)	12.2	2.7
Acetoacetate	6.5	2.2
Propanol	3.0	1.8
Oxalic acid	70.6	2.9
Citric acid	336.2	−2.7
Phenol	28.2	3.0
2,4,6-Trinitrylphenol	13.7	−2.1
Acetic acid	12.0	−1.9

listed in Table 3. Table 3 shows that $t_{0.05,\,(8)} = 2.306$, and $t < t_{0.05,\,(8)}$; to sum up, there was no significant difference for the determination result of the two methods.

3.8 *The apparent activation energy of inhibition reaction*

While all reagents dosage and the reaction time were kept the same, the rate equation can be written as

$$\ln\left(-\frac{dF}{dt}\right) = \ln(k \cdot C_{As}^{\gamma}) = \ln k + \ln C_{As}^{\gamma} = \ln k + \text{constant}.$$

According to Arrhenius equation: $\ln k = -\frac{E_a}{RT} + B$, the above equation can be written:

$$\ln\left(-\frac{dF}{dt}\right) = -\frac{E_a}{R}\cdot\frac{1}{T} + B' \text{ or } \log\left(-\frac{\Delta F}{\Delta t}\right) = -\frac{2.303E_a}{R}\cdot\frac{1}{T} + B'.$$

Here R is the gas constant, T is the experimental temperature, E_a is the apparent activation energy and B' is the constant. Meanwhile the reaction time was kept the same: $t_1 = 4.0$ min, $t_2 = 4.5$ min, $\Delta t = 0.5$ min and $\Delta F = F_{t_1} - F_{t_2}$. After control of the temperature of the

Table 3. Analytical results for samples ($n = 5$).

Samples	Original ($\mu g\,g^{-1}$)	RSD (%)	Added ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	Recovery (%)	AFS ($\mu g\,g^{-1}$)	t
shrimp	0.340	3.60	0.300	0.622	94.0	0.332	1.05
cuttlefish	0.300	4.32	0.300	0.590	96.7	0.285	1.83
laver	19.7	2.76	15.0	35.7	106.7	20.4	2.03
sea tangle kelp	18.1	3.14	15.0	32.8	98.0	17.3	2.22
green tea	0.281	4.68	0.300	0.590	103.0	0.300	2.28
black tea	0.330	3.93	0.300	0.602	90.7	0.347	2.07

solution from 20 to 65°C, the linear correlation between $\log(-\Delta\bar{F}/\Delta t)$ and $1/T$ was assessed for the inhibitory reaction and the non-inhibitory reaction. The results were shown as follows:

$$\log\left(-\frac{\Delta\bar{F}_1}{\Delta t}\right) = -7.40 \times 10^3 \times \frac{1}{T} + 16.85 \quad (r = 0.9985)$$

$$\log\left(-\frac{\Delta\bar{F}_2}{\Delta t}\right) = -3.85 \times 10^3 \times \frac{1}{T} + 16.88 \quad (r = 0.9939).$$

The apparent activation energy of the inhibitory reaction and the non-inhibitory reaction were calculated: $E_{a1} = 7.40 \times 8.314 \times 2.303 = 141.68$ ($kJ\,mo1^{-1}$) and $E_{a2} = 3.85 \times 8.314 \times 2.303 = 73.72$ ($kJ\,mo1^{-1}$), respectively.

4. Conclusion

An inhibitory kinetic fluorometry method for trace As(III) determination with the detection limit at nanogram level was proposed based on the inhibitory effect of As(III) on the reaction of ADR with $HBrO_3$ and the enhancement of fluorescence of ADR. The method is simple, highly sensitive, and indicates good stability and tolerance towards most coexisting substances. In this paper, the experimental results showed that the inhibitory kinetic fluorescence was a successful technique for determination of As(III) in food samples with satisfactory recoveries. It has been verified that the inhibitory kinetic fluorescence technique can be further developed and widened to allow application in more extensive scopes and domains.

Acknowledgements

The authors gratefully acknowledge the support of the Science Foundation of Hengyang, China (No. 2005KS01-018).

References

[1] M.F. Hughes, Toxicol. Lett. **133**, 1 (2002).
[2] R.B. Georgieva, P.K. Petrov, P.S. Dimitrov, and D.L. Tsalev, Int. J. Environ. Anal. Chem. **87**, 673 (2007).

[3] A.L. Lindberg, W. Goessler, M. Grander, B. Nermell, and M. Vahter, Toxicol. Lett. **168**, 310 (2007).
[4] Y.C. Yip, H.S. Chu, C.F. Yuen, and W.C. Sham, J. AOAC Int. **90**, 284 (2007).
[5] V. Dufailly, L. Noel, and T. Guerin, Anal. Chim. Acta. **611**, 134 (2008).
[6] A. Lolic, S. Nikolic, and J. Mutic, Sci. **24**, 877 (2008).
[7] J. Long and Y. Nagaosa, Int. J. Environ. Anal. Chem. **88**, 51 (2008).
[8] J. Michon, V. Deluchat, R.A. Shukry, C. Dagot, and J.C. Bollinger, Talanta **71**, 479 (2007).
[9] C.G. Bruhn, C.J. Bustos, K.L. Saez, J.Y. Neira, and S.E. Alvarez, Talanta **71**, 81 (2007).
[10] X. Li, Y. Su, and K. Xu, Talanta **72**, 1728 (2007).
[11] A.R. Kumar and P. Riyazuddin, Int. J. Environ. Anal. Chem. **88**, 255 (2008).
[12] J.M. Bundaleska, T. Stafilov, and S. Arpadjan, Int. J. Environ. Anal. Chem. **85**, 199 (2005).
[13] A.U. Rehman, M. Yaqoob, A. Waseem, and A. Nabi, Int. J. Environ. Anal. Chem **88**, 603 (2008).
[14] C. Ludwig, H.J. Gotze, and M. Dolny, Spectrochim. Acta A **56**, 547 (2000).
[15] C. Ludwig, M. Dolny, and H.J. Gotze, Spectrochim. Acta A **53**, 2363 (1997).
[16] X. Peng and G.S. Chen, Chin. J. Anal. Chem. **31**, 38 (2003).
[17] P. Heitland and H.D. Koster, J. Anal. Toxicol. **32**, 308 (2008).
[18] D. Vincent, N. Laurent, and G. Thierry, Anal. Chim. Acta **611**, 134 (2008).
[19] Z.L. Zhu, J. Liu, and S.H. Zhang, Anal. Chim. Acta **607**, 136 (2008).
[20] V.D. Mitic, S.D. Nikolic, and V.P. Stankov-Jovanovic, Croatica Chem. Acta **79**, 195 (2006).
[21] G.S. Chen, W. Li, and X. Peng, J. Anal. Sci. **19**, 221 (2003).
[22] D.X. Cheng and H.W. Zhong, Chin. J. Anal. Lab. **21**, 67 (2002).
[23] J.M. Liu, Chin. J. Anal. Chem. **26**, 579 (1998).
[24] G.S. Chen and H.S. Yang, Envion. Chem. **16**, 478 (1997).
[25] R.H. He and J.H. Wang, Chin. J. Enviro. Sci. **4**, 78 (1993).
[26] G. Li, Y. Liu, Y. Wang, and L. Liao, Spectrochim. Acta A **72**, 811 (2009).
[27] G. Li, Y. Liu, and Y. Wang, Anal. Lett. **42**, 94 (2009).
[28] M. Wang, X. Wu, F. Huang, and J.H. Yang, Anal. Chim. Acta **422**, 151 (2000).
[29] J.H. Xu, M. Chen, and W.H. Wang, Chin. J. Heal. Lab. Tech. **14**, 8 (2004).
[30] C.J. Sun, *Physical Testing and Chemical Analysis for Biological Material*, 1st ed. (People's Medical Publishing House, Beijing, 2006), pp. 66–67.