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ORIGINAL PAPER

Simple and Sensitive Synchronous- Fluorescence Method for the Determination of Trace Bisphenol S Based on its Inhibitory Effect on the Fluorescence Quenching Reaction of Rhodamine B

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Abstract An inhibitory kinetic fluorimetric method is reported for the determination of trace bisphenol S (BPS). The proposed method is based on the inhibitory effect of BPS on the fluorescence quenching of rhodamine B (RhB) caused by potassium bromate in a dilute phosphoric acid medium. Under the optimal conditions of the experiment, the detection limit for BPS was 0.021 mg/L, and the linear range of determination was from 0.035 mg/L to 0.750 mg/L. The relative standard deviations of 11 measurements for 0.20 mg/L and 0.40 mg/L BPS solutions were 2.74 % and 1.87 %, respectively. The method was successfully applied to the determination of bisphenol S derived from commercially available plastic film samples in hot water. A possible reaction mechanism of the inhibitory effect of BPS on the fluorescence quenching of RhB was proposed.

Keywords Bisphenol S · Inhibition · Rhodamine B · Synchronous fluorescence · Trace analysis

Introduction

Bisphenol S (BPS), 4, 4′-sulphonyl diphenol, has been widely used as a monomer in the production of epoxy resins [1], cyclic carbonates [2], and sulphonated poly-ether ketone or poly- ether sulphone [3]. BPS is similar to bisphenol A (BPA) in many of its properties and uses, especially in aggregation, and can also replace BPA in improving the mechanical properties and thermal stability of polymer products [4]. The development and application of BPS is gradually catching up to and even surpassing that of BPA [5]. However, the risk of human exposure to BPS is high because of the widespread application of this compound [6].

Phenolic compounds are toxic environmental pollutants that can seriously threaten human health [7, 8]. Different phenolic compounds possess distinct environmental behaviours and have varying ecological effects as well as toxicities [9]. BPS is one example of a phenolic compound with endocrine-disrupting effects [10, 11]. Animal experiments [12] have demonstrated that low BPS concentration can promote the lymphocytic proliferation whereas high BPS concentration can inhibit it. Thus, the detection and control of BPS concentration in the environment are particularly important and necessary.

To date, the major method for the determination of BPS that has already been reported is by gas chromatography–mass spectrometry (GC-MC) [13]. However, although HPLC [14] and GC-MC are highly accurate and widely used for estrogenic bisphenol quantification, these techniques involve either complex sample preparation or the use of toxic organic solvents. Aside from requiring trained technicians, these techniques are also time-consuming and expensive, making their widespread use quite challenging. Another BPS measurement method is ultraviolet spectrophotometry [15], which is a convenient process but also features low sensitivity. Therefore, there is a need to develop a sensitive, simple, quick, and inexpensive method to determine BPS concentration.

It is known that rhodamine B (RhB) can be oxidized by potassium bromate in acidic solutions. This oxidation reaction destroys the molecular structure of RhB, resulting in a markedly quenched fluorescence [16]. In the present work, the fluorescence quenching reaction was slowed down in the

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presence of trace BPS. Based on this inhibitory effect of BPS on the quenching of the RhB fluorescence, a novel kinetic spectrofluorimetric method has been proposed to detect the trace BPS. The proposed method is inexpensive, convenient, and does not require trained technicians to operate. The method has been successfully used to determine BPS derived from commercially available plastic film samples.

Experimental

Reagents

All chemicals were of analytical reagent grade, and double-distilled water was used throughout the present study. A BPS stock solution (100.0 mg/L) was prepared by dissolving 0.0100 g of BPS in an ultrasonic cleaner (KH-500B, Kunshan), diluting with water into a 100 mL volumetric flask and then storing in the dark at 4 °C. Working solutions were freshly prepared by diluting the stock solution with water before use. A 1.0×10^{-4} mol/L RhB stock solution was prepared by dissolving 0.0120 g of RhB in 250 mL of water. Working solutions of RhB were obtained by diluting the RhB stock solution with water. Other chemical solutions used in the study include 0.05 mol/L potassium bromate, 0.12 mol/L phosphoric acid, and 1.5 mol/L sodium acetate.

Instruments

The fluorescence spectra were measured with an FP-4600 fluorescence spectrophotometer (Shanghai Techcomp Instrument Ltd., Shanghai, China). The fluorescence intensity was obtained using 1 cm quartz cells. A model HH-601 thermostat bath (Jintan Ronghua Instrument Co., Ltd., Jintan, China) was used to keep the temperature of the system constant. Origin Professional version 5.0 software was used for data processing.

Procedure

The reagents were added to a 10.0 mL volumetric flask in the following sequence: 0.40 mL of 1.0×10^{-6} mol/L RhB solution, 0.40 mL of 0.12 mol/L phosphoric acid, and an appropriate amount of the BPS working solution. The flask was then diluted approximately to the scale with water. The mixture was quickly diluted to the mark as soon as 0.35 mL of 0.05 mol/L potassium bromate was added and then shaken until a homogeneous solution was obtained. The flask was placed in a thermostat water bath at 50±0.2 °C for 8 min, after which 1.0 mL of the 1.5 mol/L sodium acetate solution was added to it to terminate the reaction. The synchronous fluorescence intensity F of the sample was determined at 554.0 nm. Synchronous fluorescence spectra were obtained from 510 nm to 590 nm with an offset $\Delta\lambda$= 24 nm. The fluorescence value F_0 of the corresponding blank (without BPS) was obtained under the same conditions. The different value was calculated by $\Delta F=F - F_0$ and used for quantification.

Sample Preparation

The sample solution was prepared based on reference [17]. Three kinds of plastic film were washed with distilled water, solarized at room temperature, and cut into pieces of 2.0 cm^2. An appropriate amount of each sample was taken, and placed into a conical flask. Afterwards, 100 mL of distilled water was added in each conical flask. The solutions were heated in a water bath (70.0±0.2 °C) for 4 h, and then cooled to room temperature. Finally, a portion of the prepared sample was diluted with water directly or supplemented with BPS to test the recovery of the method.

Results and Discussion

Characteristics of Spectra

RhB can emit very strong yellowish-green fluorescence in aqueous solutions [18]. The excitation and emission spectra of RhB at different wavelengths are presented in Fig. 1. The maximal excitation and emission wavelengths are 553.0 nm and 577.0 nm, respectively. In this work, the measurements were performed using only synchronous fluorometry, which is based on the synchronous scanning of both the excitation and emission wavelengths at a constant wavelength interval (offset). The offset, $\Delta\lambda$, was derived from the difference between the characteristic wavelength maxima selected from the excitation and emission spectra [19, 20]. Therefore, the selected $\Delta\lambda$ of RhB was 24 nm, and the synchronous fluorescence spectrum of RhB was obtained at wavelength

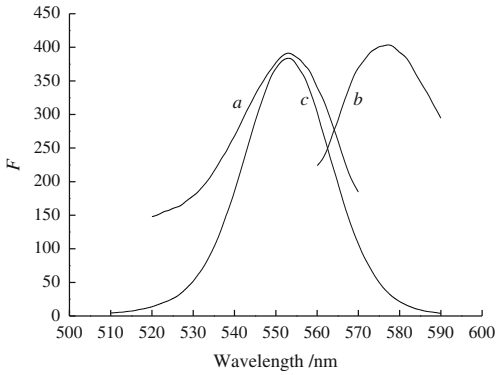


Fig. 1 Fluorescence spectra of RhB. *a*, Excitation spectrum; *b*, Emission spectrum; *c*, Synchronous spectrum

of 510 nm to 590 nm with $\Delta\lambda$=24 nm (Fig. 1c). Similar to rhodamine 6 G [21], the molecular structure of RhB was destroyed and RhB fluorescence disappeared when this compound was oxidized by oxidizers. Figure 2 shows that the synchronous fluorescence intensity of RhB decreased in the potassium bromate–phosphoric acid system; the presence of the trace BPS exhibited an evident inhibitory effect on the quenching of RhB fluorescence. The inhibition effect, which is reflected on the ΔF value, was remarkable. Furthermore, a linear relationship between ΔF and the concentration of added PBS was observed. Based on this observation, a new kinetic fluorimetric method was established to determine trace BPS concentrations. The determination wavelength of this method is 554.0 nm.

Optimization of the Experimental Variables

To take full advantages of the procedure, the reagent concentrations and reaction conditions should be optimized. Various experimental parameters were investigated in order to obtain an optimized system. Each parameter was optimized by setting all other parameters to be constant and optimizing the parameter of interest one at a time. The BPS concentration was kept to 0.40 mg/L in all reactions. Each experiment was replicated at least thrice.

Addition Sequence of Reagents

The addition sequence of reagents greatly affected the fluorescence quenching rate in this reaction system, which was manifested mainly when potassium bromate was added. When potassium bromate was added first to the reaction system followed by dilution, the fluorescence quenching rate in both the sample system and blank system increased rapidly, the ΔF value was small and the experimental reproducibility was poor. However, when the reaction system was diluted first followed by addition of potassium bromate, the fluorescence quenching of the sample system was relatively slow, indicating an obvious inhibitory effect, while the fluorescence quenching of the blank system was rather rapid. ΔF value was larger, and high experimental reproducibility was observed. The effects of the addition sequence of reagents depend largely on the reaction mechanism, which will be discussed at a later section.

Reaction Medium

Identical concentrations of the following media were tested in the present experiments: nitric acid, hydrochloric acid, acetic acid, and phosphoric acid. Nearly no inhibitory reaction in nitric acid was observed because of the strong oxidative effects of this acid. The reaction stability was poor in hydrochloric acid due to interferences from the chloride ion. The reaction sensitivity and speed were very low in acetic acid. The inhibition effect of BPS was significant only in phosphoric acid. Furthermore, a linear relationship between the ΔF and BPS concentration was observed. Therefore, phosphoric acid was selected as the reaction medium in the present study.

The rate of redox reactions is correlated with the redox potential, which is strongly dependent on pH. Therefore, the effect of the phosphoric acid concentration on the ΔF value was investigated in the range from 1.2×10^{-3} mol/L to 9.6×10^{-3} mol/L, the results of which are shown in Fig. 3. The maximum ΔF value appeared within the range from 3.6×10^{-3} mol/L to 6.0×10^{-3} mol/L. When the solution acidity is too low, the rate of the two reactions is slow and the BPS inhibitory effect is not obvious. In contrast, when the solution acidity is too high, the fluorescence intensities of both the sample reaction (F) and blank reaction (F_0) decrease rapidly, leading to a rapid reduction in ΔF. The experimental reproducibility was poor when 6.0×10^{-3} mol/L phosphoric acid was used; better reproducibility and good sensitivity were found at an acid concentration of 4.8×10^{-3} mol/L. Therefore, the optimal phosphoric acid concentration is 4.8×10^{-3} mol/L.

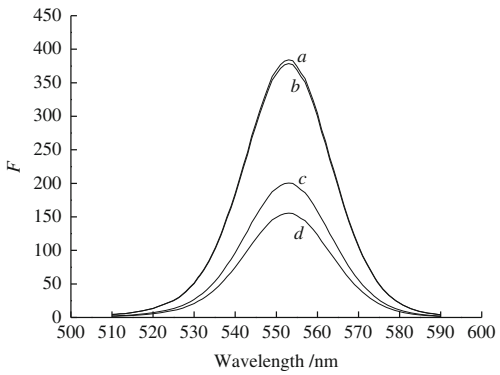


Fig. 2 Synchronous fluorescence spectra of RhB in the presence of different reagents: *a*, RhB+H_3PO_4; *b*, RhB+BPS; *c*, RhB+H_3PO_4+BPS+$KBrO_3$; *d*, RhB+H_3PO_4+ $KBrO_3$. RhB, 4.0×10^{-8} mol/L; H_3PO_4, 4.8×10^{-3} mol/L; BPS, 0.7 mg/L; $KBrO_3$, 1.75×10^{-3} mol/L

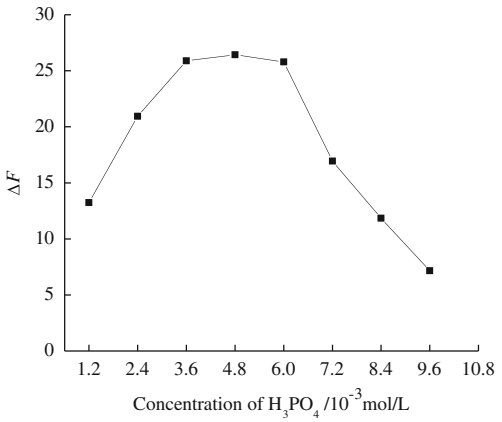


Fig. 3 Effect of phosphoric acid concentration on the ΔF value

Concentration of RhB

As the fluorescent indicator of the reaction, the effect of RhB concentration was studied in the range from 1.0×10^{-8} mol/L to 8.0×10^{-8}mol/L. An increase in RhB concentration caused an increase in the fluorescence intensity change in both the sample reaction (F) and the blank reaction (F_0); the intensities were very close to each other when the RhB concentration was above 7.0×10^{-8}mol/L. The graph of ΔF versus RhB concentration (Fig. 4) shows a constant maximum in the range from 3.0×10^{-8}mol/L to 5.0×10^{-8} mol/L. Therefore, a final concentration of 4.0×10^{-8}mol/L RhB is selected in the present study.

Concentration of Potassium Bromate

The effect of potassium bromate on ΔF was researched in the range from 5.0×10^{-4}mol/L to 3.0×10^{-3}mol/L. It was observed that the fluorescence intensity of the sample reaction (F) and the blank reaction (F_0) decreased simultaneously with increasing potassium bromate concentration. The graph of the difference between the fluorescence intensities of the sample and blank reactions ΔF versus the $KBrO_3$ concentration (Fig. 5) shows a maximum at 1.75×10^{-3} mol/L $KBrO_3$. Therefore, the optimal potassium bromate concentration in the present study is 1.75×10^{-3}mol/L.

Reaction Temperature

The effect of reaction temperature on ΔF was investigated in the range from 25 °C to 70 °C, the results of which are shown in Fig. 6. The fluorescence intensity of the sample reaction (F) increased gradually with the increase of reaction temperature and stabilized at ove 50 °C. In contrast, the fluorescence intensity of the blank reaction (F_0) kept constant within this temperature range. Therefore, the difference between the fluorescence intensities of the sample and blank reactions (ΔF) increased gradually

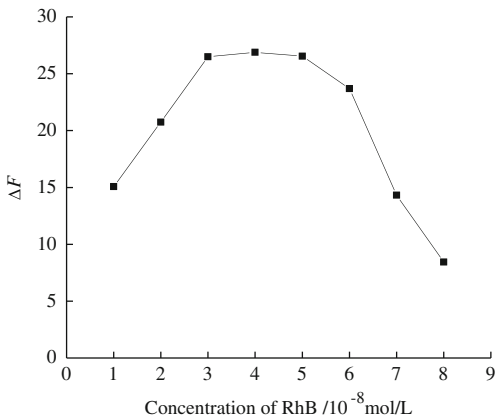


Fig. 4 Effect of RhB concentration on the ΔF value

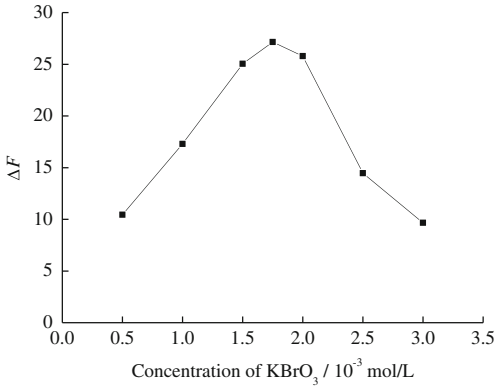


Fig. 5 Effect of potassium bromate concentration on the ΔF value

and reached a maximum at above 50 °C. When the reaction temperature is too high, the reaction speeds too quickly and the reaction process is difficult to control. Thus, 50 °C is the optimal reaction temperature in the present study. Thermodynamic analysis indicates that ln (ΔF) increased linearly with the reciprocal value of the thermodynamic temperature of the reaction ($1/T$) in the range from 25 °C to 50 °C. The relationships between the two parameters can be expressed as follows:

$$\ln(\Delta F) = 17.109 - 4.4625\times10^{3}/T \quad (1)$$

The regression coefficient of Eq. (1) is 0.9954, and the apparent reaction activation energy is E=37.1 kJ/mol.

Effect of Reaction Time

The effect of reaction time (t) was also examined in the present study. After t was prolonged to over 15 min, both the fluorescence intensities of the sample reaction (F) and the blank reaction (F_0) decreased rapidly. A plot of ΔF versus t over the range from 2 min to 12 min is shown in Fig. 7, which shows that the ($\Delta F - t$) curve is linear in the range from 2 min to 8 min. The linear relationship can be

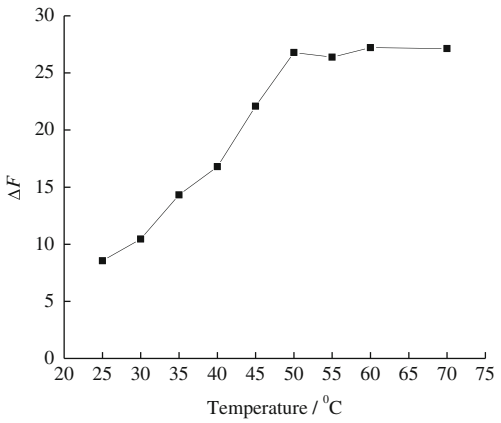


Fig. 6 Effect of temperature on the ΔF value

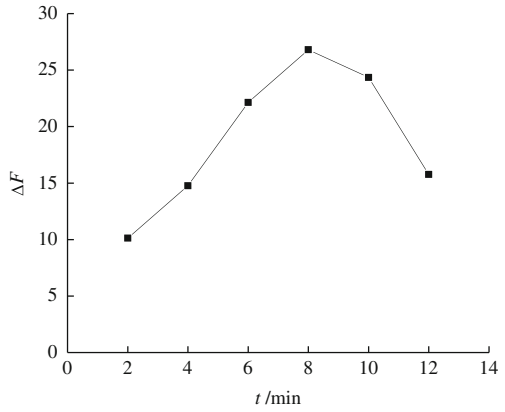


Fig. 7 Effect of reaction time on the ΔF value

described as follows:

$$\Delta F = 4.095 + 2.872t\,(\text{min}) \quad (2)$$

The regression coefficient of Eq. (2) is 0.9912. Therefore, the appropriate time by which to conduct the experiments in the present study is approximately 8.0 min. The apparent reaction rate constant is $k=\Delta F/t=4.64\times10^{-2}\,s^{-1}$.

Reaction Termination

Two reaction-terminating methods were investigated. One method involved cooling of the reaction to room temperature with running water while the other involved the addition of a reaction-terminating agent, in this case, 1.5 mol/L sodium acetate solution. The relationship between the fluorescence intensity F of the sample reaction and the storage time is shown in Fig. 8. F decreased slowly with an increase in the storage time by cooling with running water, while the F remained constant after addition of the reaction-terminating agent. The results indicate that the fluorescence-quenching reaction takes place in an acidic solution and cannot be stopped by cooling with running water only. This fluorescence-quenching reaction is effectively terminated by the addition of sodium acetate, which reduces the solution acidity to neutrality and even to alkalescence. Furthermore, the sodium acetate concentration

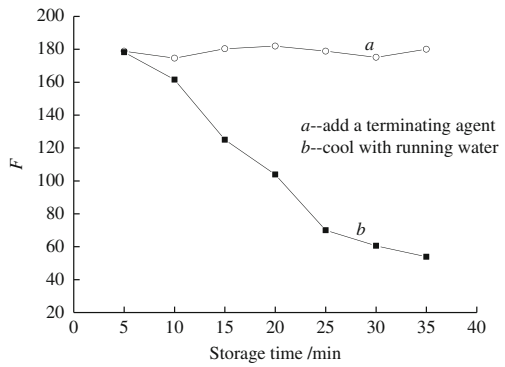


Fig. 8 Effect of reaction-terminating method on the F value

does not affect F, which remains unchanged for over 2 h. Therefore, 1.0 mL of 1.5 mol/L sodium acetate can be added into the reaction solution to terminate the reaction.

Analytical Characteristics

Under optimal conditions, the calibration graph for BPS was obtained using the fixed-time method. The linear relationship between ΔF and the BPS concentration was obtained in the range from 0.035 mg/L to 0.750 mg/L. The regression equation is:

$$\Delta F = 3.155 + 59.53C \quad (3)$$

where C represents the BPS concentration (mg/L), and the regression coefficient of Eq. (3) is 0.9993. The detection limit (C_L) was calculated using the following equation:

$$C_L = 3\,S_b/S \quad (4)$$

where S_b and S are the standard deviation of the blank reagent measurements (n=11) and the slope of the calibration graph, respectively. Thus, the limit of detection of BPS is 0.021 mg/L. The relative standard deviations are 2.74 % and 1.87 %, respectively, for 11 replicated determinations of 0.20 mg/L and 0.40 mg/L BPS.

Selectivity

To study the selectivity of the proposed method, the effect of a series of foreign substances on the determination of 0.60 mg/L BPS was tested under optimal conditions. Some ions commonly existing in water, as well as organic substances that could be used in HPLC and GC, were chosen for the selectivity test. When the effect of each foreign species on the peak height is less than 10.0 %, the species is assumed not to interfere in the determination of BPS. The results of selectivity testing are summarized in Table 1. Even>1000-fold concentrations of CH_3COO^-, EDTA, and ethanol exhibited no interference in the proposed method. No interference was also found when 400-fold concentrations of sodium citrate and

Table 1 Effects of foreign substances on the determination of 0.60 mg/L BPS

Foreign substance	Maximum tolerable ratio[a]
Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, PO_4^{3-}, CH_3COO^-, EDTA, ethanol	1000
F^-, SO_4^{2-}, sodium citrate, potassium sodium tartrate	400
Zn^{2+}, acetone, OP emulsifier, sodium dodecyl sulfate	100
Phenol, catechol, hydroquinone, resorcinol	8

[a] 1000 is the highest ratio tested

potassium sodium tartrate, 100-fold concentrations of acetone, OP emulsifier and sodium dodecyl sulfate, as well as 8-fold concentrations of phenol, catechol, hydroquinone, and resorcinol coexisted in the solution. The interference of some phenolic compounds can be eliminated when determining real samples by separation of these compounds through distillation [22].

Application

The proposed method was applied to determine BPS in samples and evaluate its applicability. The samples were prepared and treated based on the procedure previously described in "Sample preparation". The BPS content in samples was determined by inhibited fluorescence analysis, and the results are listed in Table 2. The experimental recoveries of 92.3 % to 107.0 % indicate that no serious interference occurs in the samples. Hence, the method is well applicable for real samples.

Table 2 Determination of BPS derived from plastic film samples

Sample	Added mg/L	Detected after added[a] mg/L	RSD (%)	Recovery[a] (%)
1	0.0	0.21	3.0	
	0.1	0.33	3.2	106.5
	0.3	0.48	2.8	94.1
2	0.0	0.16	4.6	
	0.1	0.24	2.4	92.3
	0.2	0.35	3.1	97.2
3	0.0	0.13	3.9	
	0.2	0.35	2.7	106.1
	0.3	0.46	1.1	107.0

[a] Average of three determinations

Proposed Reaction Mechanism

RhB emits very strong fluorescence in an acid medium. However, the fluorescence of RhB is quenched after the addition of potassium bromate. Combined with the data reported in the literature [23–25], a possible reaction mechanism among RhB, BPS and potassium bromate is as follows:

In the presence of a high H^+ concentration prior to dilution, several reactions could occur as follows:

$$BrO_3^- + RhB + H^+ \rightarrow RhB\,(Ox) + Br^- \quad (5)$$

$$BrO_3^- + BPS + H^+ \rightarrow CO_2 + H_2O + SO_4^{2-} + Br^- \quad (6)$$

Reaction (5) is an indicative reaction, and the oxidation of bromate in this reaction is enhanced by an increase in H^+ concentration. When the H^+ concentration is too high, BPS is also oxidized by bromate, as shown in reaction (6), which would greatly reduce the inhibitory effect of BPS. The sulfonyl group in BPS, a strong polar group, gives rise to sulfuric acid, which can further promote the oxidation of bromate. Sulfate ion can be detected with barium ions in high BPS concentrations.

In the presence of a low H^+ concentration after dilution, the following reactions may occur:

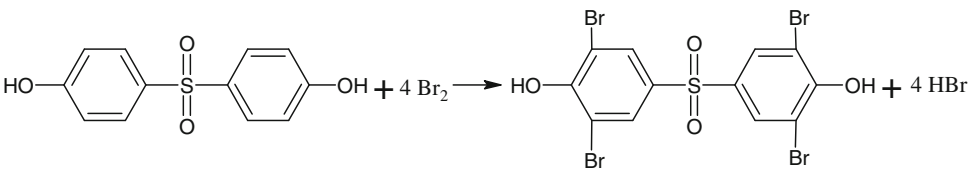
$$BrO_3^- + RhB + H^+ \rightarrow RhB\,(Ox) + Br^- \quad (5)$$

$$BrO_3^- + Br^- + H^+ \rightarrow Br_2 + 3H_2O \quad (7)$$

$$RhB + Br_2 \rightarrow RhB \cdot Br + Br^- \quad (8)$$

When the H^+ concentration is low, BPS cannot be oxidized by bromate. In contrast, the fluorescent dye RhB is not only oxidized [shown in reaction (5)], but also reacted with bromine produced from reaction (7). Both reactions result in the quenching of the RhB fluorescence. Bromine can be captured with carbon tetrachloride in high-concentration reagents.

According to the BPS property [26], BPS can react with bromine by bromination reaction on the benzene rings. The reaction is as follows:



(9)

When it is added, BPS could join in the series of reactions according to the experiment's results. Reaction (9) occurs more easily than reaction (8), thus slowing down the reaction rate of bromine with RhB. This reaction of bromine with BPS has an obvious inhibitory effect on the quenching reactions. BPS consumes some bromine during the reaction, thereby resulting in enhancements in the fluorescence intensity of the reaction system. Under specific conditions, the

concentration of added BPS has a linear relationship with the fluorescence recovery of the system.

Conclusions

A kinetic-synchronous fluorometric method for BPS determination has been established based on the strong inhibitory effect of BPS on the fluorescence quenching of RhB in a potassium bromate-phosphoric acid system. Applicability tests demonstrate that the proposed method is feasible for the quantitative analysis of BPS in actual samples. Compared with chromatographic approaches, the proposed fluorimetric method is rapid, inexpensive, and has a simpler operation. Thus, this method is easier to popularize.

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References

1. Rwei SP, Kao SC, Liou GS, Cheng KC, Guo W (2003) Curing and pyrolysis of epoxy resins containing 2-(6-oxido-6H-dibenz(c, e)(1,2) oxaphosphorin-6-yl)-1,4-naphthalenediol or bisphenol S. Colloid & Polymer Science 281(5):407–415
2. Kim MR, Kim HS, Park DW, Lee JK (2001) Synthesis of cyclic carbonates based on diglycidyl ether of bisphenol S by quaternary ammonium salts. React Kinet Catal Lett 72(2):373–381
3. Changkhamchom S, Sirivat A (2010) Synthesis and properties of sulfonated poly(ether ketone ether sulfone) (S-PEKES) via bisphenol S: effect of sulfonation. Polym Bull 65(3):265–281
4. Lotti N, Colonna M, Fiorini M (2011) Poly(butylene terephthalate) modified with ethoxylated bisphenol S with increased glass transition temperature and improved thermal stability. Polymer 52(4):904–911
5. Liao CY, Liu F, Kannan K (2012) Bisphenol S, a new bisphenol analogue, in paper products and currency bills and its association with Bisphenol A residues. Environ Sci Technol 46(12):6515–6522
6. Liao CY, Liu F, Alomirah H, Loi VD (2012) Bisphenol S in urine from the United States and seven Asian countries: occurrence and human exposures. Environ Sci Technol 46(12):6860–6866
7. Fan J, Zhang T, Sun J, Fan MH (2007) Kinetic fluorimetric measurement of trace resorcinol in phenol mixtures. J Fluoresc 17(1):113–118
8. Jiang XY, Zhang H, Chen XQ (2011) Determination of phenolic compounds in water samples by HPLC following ionic liquid dispersive liquid-liquid microextraction and cold-induced aggregation. Microchimica Acta 175(3–4):341–346
9. Shen G, Yu G, Cai ZX (2005) Development of an analytical method to determine phenolic endocrine disrupting chemicals in sewage and sludge by GC/MS. Chin Sci Bull 50(23):2681–2687
10. Ryoko KN, Ryushi N, Takashi M (2005) Estrogenic activity of alkylphenols, bisphenol S, and their chlorinated derivatives using a GFP expression system. Environ Toxicol Pharmacol 19(1):121–130
11. Grignard E, Lapenna S, Bremer S (2012) Weak estrogenic transcriptional activities of Bisphenol A and Bisphenol S. Toxicol Vitr 26(5):727–731
12. Li Y, Hu SQ, Yin DQ (2003) Primary screening and evaluation of endocrine disrupting activities of eleven substituted phenols. Environ Chem 22(4):385–389
13. Viñas P, Campillo N, Hernández-Córdoba M (2010) Comparison of two derivatization-based methods for solid-phase microextraction-gas chromatography–mass spectrometric determination of Bisphenol A, Bisphenol S and Biphenol migrated from food cans. Anal Bioanal Chem 397(1):115–125
14. Zhao RS, Wang X, Yuan JP (2009) Solid-phase extraction of bisphenol A, nonylphenol and 4-octylphenol from environmental water samples using microporous bamboo charcoal, and their determination by HPLC. Microchimica Acta 165 (3–4):443–447
15. Cao GP, Wang BB, Ding QC (2010) Determination of bisphenol S by ultraviolet spectrophotometric method. Chemistry & Bioengineering 27(10):86–88
16. Afkhami A, Afshar-E-Asl A (2000) Kinetic-spectophotometric determination of hydrazine by the inhibition of the bromate-hydrochloric acid reaction. Anal Chim Acta 419:101–106
17. Zhuang YF, Zhang JT, Cao GP (2008) Simple and sensitive electrochemiluminescence method for determination of bisphenol A based on its inhibitory effect on the electrochemiluminescence of luminol. J Chin Chem Soc 55:994–1000
18. Zhu J, Li JJ, Zhao JW (2009) Spectral characters of Rhodamine B as a multi-information fluorescence probe for bovine serum albumins. Sensors & Actuators: B Chemical 138(1):9–13
19. Algarra M, Radin C, Lamotte M (2000) Direct fluorometric analysis of PAHs in water and in Urine following liquid solid extraction. J Fluoresc 10(4):355–359
20. Liu XY, Wu X, Yang JH (2010) Protein determination using methylene blue in a synchronous fluorescence technique. Talanta 81(3):760–765
21. Feng S, Chen X, Fan J (1998) Kinetic determination of ultratrace amounts of ascorbic acid with spectrofluorimetric detection. Anal Lett 31:463–474
22. Pourreza N, Parham H, Attaran AM (2004) Reaction rate method for spectrophotometric determination of trace amounts of esorcinol. Instrum Sci Technol 32(2):167–173
23. Zhai QZ, Hu WH, Zhang Y (2010) Kinetic spectrophotometric determination of trace amount of europium based on its inhibitory effect of the oxidation of switzerland pigment by potassium bromate. Instrum Sci Technol 38(3):201–209
24. Zenovia M (2009) A novel kinetic-spectrophotometric method for determination of nitrites in water. Chem Pap 63(4):385–390
25. Saleem MD, Nirmala NH, Sharanappa TN (2002) Kinetics and mechanism of ruthenium(III)- catalysed oxidation of allyl alcohol by acid bromate-autocatalysis in catalysis. Transit Met Chem 27 (2):207–212
26. Wang KY, Qian D, Wang ZX (1995) Synthesis of tetrabromobisphenol S. Fine Chemicals 12:35–38