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Kinetic Fluorimetric Measurement of Trace Resorcinol in Phenol Mixtures

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Abstract A kinetic spectrofluorimetric method was studied to measure the concentration of trace resorcinol. The proposed method is based on the inhibitory effect of resorcinol on the oxidation of rhodamine B by potassium bromate in the medium of dilute sulfuric acid. The detection limit and linear range of the proposed resorcinol measurement method are 12 μg L^{-1} and 24 ~ 280 μg L^{-1}, respectively. Relative standard derivations of eleven measurements for 80 μg L^{-1} and 200 μg L^{-1} resorcinol solutions are 2.12% and 1.08%, respectively. The trace of resorcinol can be determined directly by the proposed method without any pre-separation process when phenol and many other phenolic compounds are present.

Keywords Kinetic spectrofluorimetric · Resorcinol · Rhodamine B · Waste water

Introduction

Phenolic compounds are highly toxic environmental pollutants, and seriously threaten human's health. Phenolic compounds in environment come from different sources, including industrial wastewater, solid castoff of coal tar, coking factory, gasworks, paper mill, chemical plants, pharmaceutical industry. Because of their toxicities, some of phenolic compounds have been listed as control targets in many countries. Phenolic compounds are also poisonous organic pollutants. Therefore, many governments have spent a lot of effort in their detection and control.

The currently used methods for determination of the phenolic compounds include 4-aminoantipyrine (4-AAP) [1] and gas chromatograph [2]. 4-AAP method can only be used to measure the total concentration of phenolic compounds and is not able to measure concentration of individual phenolic compound in a mixture, consequently, the toxicity of the mixture can not be exactly evaluated. Gas chromatograph can only be used to determine monohydric phenols and chlorophenols [3–5].

Different phenolic compound possesses different environmental behavior and has different ecological effect and toxicity. The real waste samples typically contain several phenolic compounds, therefore, determination of concentration of individual phenolic compound is particularly important and useful especially when a pre-separation is not necessary.

Resorcinol is one kind of phenolic compounds with high toxicity. It can be easily absorbed through the gastric tract and human skin, which can cause dermatitis, catarrh, convulsion, cyanopathy, and even death [6]. The major methods for the determination of resorcinol that have already been reported are high-performance liquid chromatography [7–11] and gas chromatography [12, 13]. The separations of these methods are efficient, but require expensive instrument and therefore are expensive. Another resorcinol measurement method is ultraviolet-visible spectrophotometry [14, 15]. This method is convenient but its sensitivity is low. Therefore, there is a need for development of a sensitive, simple, quick and inexpensive method for determination of resorcinol.

It is known that rhodamine B can be oxidized by potassium bromate in acidic media. This oxidation reaction destroyed

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the molecular structure of rhodamine B, and therefore its fluorescence was quenched greatly [16]. In this work, we found that in the presence of resorcinol, the oxidation reaction was slow down because of the competing reaction of resorcinol. Based on this inhibitory effect of resorcinol on the oxidation of rhodamine B by potassium bromate, a kinetic spectrofluorimetric method is proposed for the determination of trace of resorcinol. It is anticipated that the proposed method can overcome the disadvantages of traditional resorcinol method.

Experimental

Reagents and apparatus

All chemicals were of analytical reagent grade and redistilled water was used throughout the study. Resorcinol (Res) stock solution (1.0 g L^{-1}) was prepared freshly before each measurement by dissolving 0.1000 g of resorcinol in 100 mL of water. Working solutions were prepared by diluting the stock solution according to needs. Rhodamine B(RhB) stock solution (1.0×10^{-3} M) was prepared by dissolving 0.0479 g of RhB in 100 mL of water. Working solutions of Rhodamine B were obtained by diluting its stock solution with water. Other chemical solutions used during the study include: 0.05 mol L^{-1} Potassium bromate, 1.0 M Sulfuric acid, 1.0 g L^{-1} *o*-Cresol (OCR), 1.0 g L^{-1} Phenol (Phe), 1.0 g L^{-1} m-Cresol (MCR), 1.0 g L^{-1} *o*-Nitrophenol (ONP), 1.0 g L^{-1} *p*-Nitrophenol (PNP), 1.0 g L^{-1} m-Nitrophenol (MNP), 1.0 g L^{-1} catechol (Cat), 1.0 g L^{-1} Hydroquinone (Hyd).

Fluorescence spectra were obtained with an FP-6200 spectrofluorimeter (JASCO, Japan) and a 930A fluorophotometer (Shanghai, China) were used for measuring fluorescence values of solutions. A Model 501 thermostat bath (Chongqing, China) was used to control experimental temperatures.

Procedure

To start the tests, 0.3 mL of 1.0×10^{-4} M rhodamine B solution, an appropriate amount of resorcinol working solution, 0.65 mL of 1.0 M sulfuric acid solution, and 2.8 mL of 0.025 M potassium bromate were mixed in a 25 mL flask, quickly diluted to the 25 mL mark of the flask and shaken for a moment. Then the flask was placed in a thermostat water bath with its temperature 55 ± 0.2°C for 5 min and taken out to cool to room temperature by running water. The final step was to measure the fluorescence value (F) and blank value ($F_\circ$) at an excitation wavelength of 556.0 nm and an emission wavelength of 576.0 nm. Values of ΔF were the differences between F and $F_\circ$.

Results and discussion

Spectral characteristics

Rhodamine B can emit strong fluorescence. Its excitation and emission spectra at different wavelengths were presented in Fig. 1 with additions of different agents. Fig. 1 shows that when rhodamine B was oxidized by oxidizers, its molecular structure was destroyed and fluorescence disappeared. In this research, rhodamine B was oxidized by potassium bromate. When trace of resorcinol was added, this oxidation reaction was inhibited. The inhibition effect, reflected by ΔF value, is maximum. Furthermore, at an excitation wavelength of

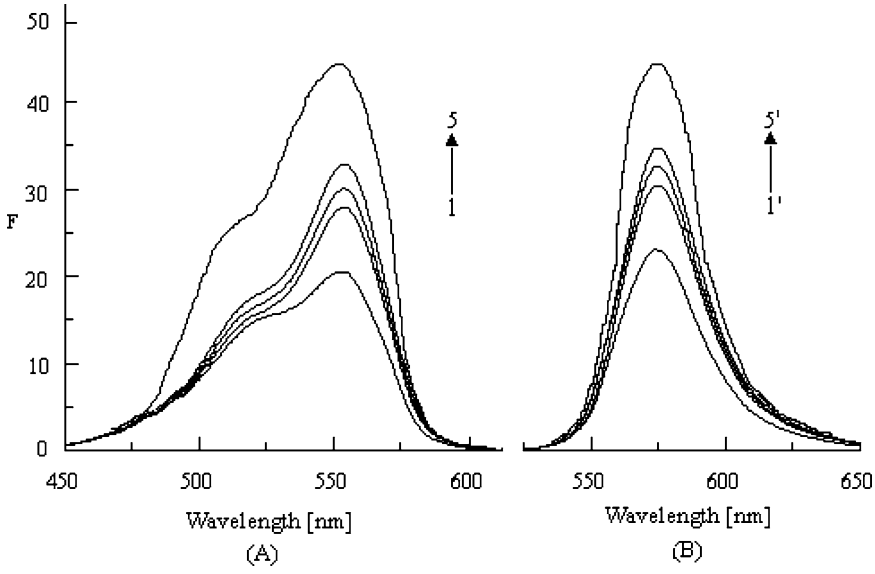

Fig. 1 Excitation (A) and emission (B) spectra of RhB in presence of different reagents. RhB, 1.2×10^{-6} mol L^{-1}; sulfuric acid, 2.6×10^{-2} mol L^{-1}; potassium bromate, 2.8×10^{-3} mol $L^{-1;}$ Temperature, 55°C; Reaction Time, 5 min. (1-1′), $RhB + H_2SO_4 + KBrO_3$; (2-2′), $RhB + H_2SO_4 + KBrO_3 + Res$ (80 μg L^{-1}); (3-3′), $RhB + H_2SO_4 + KBrO_3 + Res$ (110 μg L^{-1}); (4-4′), $RhB + H_2SO_4 + KBrO_3 + Res$ (140 μg L^{-1}); (5-5′), $RhB + H_2SO_4$

556 nm and an emission wavelength of 576 nm, it is noted that there is a linear relationship between ΔF and the concentration of resorcinol added. Based on this observation, a new kinetic fluorimetric method was established to determine the concentration of trace resorcinol.

Establishment of experimental conditions

Reaction medium

The following media have been tried in the present experiments: sulfuric acid, hydrochloric acid, perchloric acid and periodic acid. It was found that ΔF values of the solutions were very small when hydrochloric acid, perchloric acid and periodic acid were present; ΔF values were high in the medium of sulfuric acid and a linear relationship between ΔF values and resorcinol concentration existed. Therefore, sulfuric acid was selected as the reaction medium for the study.

The effect of concentration of sulfuric acid solution on ΔF has been investigated in the range of $8.0 \times 10^{-3} \sim 3.6 \times 10^{-2}$ M. The results indicate that the ΔF values increased with the increase of concentration of sulfuric acid, the highest ΔF value appeared at the concentration of 2.8×10^{-2} M. Then the ΔF values decreased with the increase of concentration of sulfuric acid, however, experimental reproducibility was poor when 2.8×10^{-2} M sulfuric acid was used. Through trial and error, better reproducibility and good sensitivity were found at the concentration of 2.6×10^{-2} M.

Concentration of rhodamine B

The effect of concentration of rhodamine B was examined in the range $6.0 \times 10^{-7} \sim 2.8 \times 10^{-6}$ M. The results showed that the ΔF values changed only slightly when the concentration of rhodamine B was in the range of $1.0 \times 10^{-6} \sim 1.6 \times 10^{-6}$ M. The ΔF values decreased significantly with the increase of concentration of rhodamine B when the concentration of rhodamine B was higher than 2.0×10^{-6} M. Therefore 1.2×10^{-6} M of rhodamine B was selected for further studies.

Concentration of potassium bromate

When the concentration of potassium bromate was in the range of $1.6 \times 10^{-3} \sim 3.6 \times 10^{-3}$ M, the ΔF value first increased with the increase of potassium bromate and reached the highest point at the potassium bromate concentration of 2.8×10^{-3} M, and then decreased with the increase of the concentration of potassium bromate, so 2.8×10^{-3} M of potassium bromate was adopted.

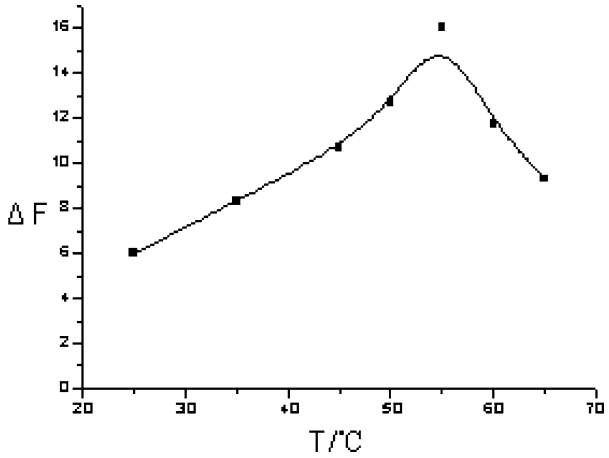

Fig. 2 Influence of temperature on ΔF. rhodamine B, 1.2×10^{-6} mol L^{-1}; sulfuric acid, 2.6×10^{-2} mol L^{-1}; potassium bromate, 2.8×10^{-3} mol L^{-1}; resorcinol, 0.16 mg L^{-1}; reaction time, 5.0 min

Effect of reaction time

The effect of reaction time (t) was investigated in the range of $2.0 \sim 7.0$ min. The results showed that the ΔF -t curve is linear in the range $t = 2 \sim 5$ min. The linear relationship can be described as follows:

$$\Delta F = -3.67 + 3.82t \text{ (min)} \quad (1)$$

The regression coefficient of Eq. (1) is 0.9918. Therefore, 5.0 min is chosen as the preferable reaction time to conduct the other part of the study. The apparent reaction rate constant $k = \Delta F/t = 6.37 \times 10^{-2}$ S^{-1}.

Reaction temperature

The effect of the reaction temperature on ΔF was studied in the range of $25.0 \sim 65.0$°C, Fig. 2 shows that reaction temperature considerably affects the oxidation of rhodamine B. 55.0°C was chosen in this study. Thermodynamic analysis indicates that ln (ΔF) increases linearly with the reciprocal value of the thermodynamic temperature of the reaction (1/T)

Table 1 The influence of matrix components.

Matrix components	Ratio	Matrix components	Ratio
K^+, Cl	2.9×10^3	MCR, Zn^{2+}	1.3×10^2
ClO_3^-, PNP	2.1×10^3	Hyd	40
Ca^{2+}, Na^+	1.8×10^3	OCR	35
Mg^{2+}	1.38×10^3	Pb^{2+}	25
ONP	1.0×10^3	F^-	19
NO_3^-, MNP	6.2×10^2	Cat	10
Phe	4.5×10^2	Fe^{3+}	0.5
Mn^{2+}, Cu^{2+}	2.7×10^2		

Table 2 The linear calibration equations for different phenols in different concentration ranges.

Phenol	Linear calibration equation	Correlation coefficient R	Linear range C(mgL^{-1})
Res	$\Delta F = 3.51 + 70.31C$	0.9993	$0.024 \sim 0.28$
Cat	$\Delta F = 5.80 + 135C$	0.9959	$0.04 \sim 0.1$
OCR	$\Delta F = 1.15 + 20.63C$	0.9973	$0.08 \sim 0.56$
Hyd	$\Delta F = 2.40 + 8.99C$	0.9973	$0.08 \sim 1.1$
Phe	$\Delta F = -0.20 + 0.04C$	0.9975	$80 \sim 400$
MNP	$\Delta F = 2.15 + 0.01C$	0.9966	$80 \sim 800$
PNP	$\Delta F = -4.7 + 0.02C$	0.9986	$400 \sim 1000$
ONP	$\Delta F = -13.70 + 0.02C$	0.9990	$800 \sim 1400$

in the rang of $25.0^{\circ}C \sim 55.0^{\circ}C$. Their relationships can be expressed as follows:

$$\ln(\Delta F) = 12.11 - 3.101 \times 10^3/T \quad (2)$$

The regression coefficient of Eq. (2) is 0.9940. The apparent reaction activation energy $E = 25.8$ kJ mol^{-1}.

Calibration equation

The oxidation conditions chosen above were used to establish the calibration equation for measuring the concentration of resorcinol. The linear relationship between ΔF and resorcinol concentration was obtained in the range of $24 \sim 280$ $\mu g\ L^{-1}$. The regression equation is:

$$\Delta F = 3.51 + 70.31C \quad (3)$$

where C represents the concentration of resorcinol (mg L^{-1}) and the regression coefficient of Eq. (3) is 0.9993. The detection limit (C_L) can be calculated using

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

where S_b and S are respectively, the standard deviation of reagent blank measurements ($n = 11$) and the slope of the calibration graph, with a correlation coefficient of 0.9993. Thus, the limit of detection is found to be 12 $\mu g\ L^{-1}$. The relative standard derivations are 2.12% and 1.08%, respectively, for 11 replicated determinations of 80 $\mu g\ L^{-1}$ and 200 $\mu g\ L^{-1}$ of resorcinol.

Interference of matrix components

The influences of common ions and organic compounds on the determination of 160 $\mu g\ L^{-1}$ resorcinol were investigated assuming that the allowable relative deviation from the ΔF value is $\pm 5\%$. The results are summarized in Table 1. It can be seen that Fe^{3+} interferes the determination seriously. The interfering ions have been separated by distillation when determining real samples [17].

Responses to different phenolic compounds

Eight phenolic compounds have been used to evaluate their responses to the proposed resorcinol method. The calibration equations for these phenolic compounds are presented in Table 2 and four calibration curves obtained by the method are plotted in Fig. 3. Combination of the results of Table 2 and Fig. 3 indicate that only four phenolic compounds can be determined with the proposed method in the range of $0 \sim 1.2$ mg L^{-1}. Among them is resorcinol.

Sample analysis and applications to real samples

Analysis of synthetic samples by the present method

It is common multiphenolic compounds that coexist in environment. In order to show that the selectivity of the present method is satisfactory, eleven samples synthesized with (Phenol, resorcinol, Hydroquinone, catechol, *o*-Cresol, *p*-Nitrophenol, *m*-Nitrophenol, *o*-Nitrophenol) were prepared and the concentrations of resorcinol were measured using the proposed method. The measurement results are listed in Table 3. It can be seen that the measured resorcinol concentrations for synthetic samples *B*, *F*, *H* and *I* are closer to the actual concentration. It shows that resorcinol can be

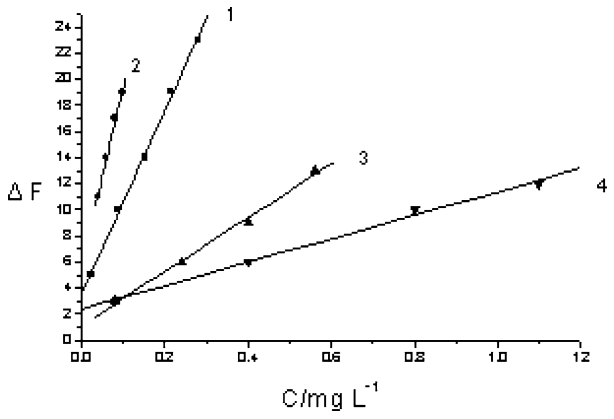

Fig. 3 The linear calibration graphs of different phenol. 1, Resorcinol; 2, Catechol; 3, *o*-Cresol; 4, Hydroquinone

Table 3 The results for the determination of resorcinol in synthetic samples ($n = 4$).

Sample	Composition of synthetic samples (mg L^{-1})								C_{total}	$C_{res,\ measured}$	Relative error (%)
	Phe	Res	Hyd	Cat	OCR	PNP	MNP	ONP			
A	–	0.2000	–	–	–	–	–	–	0.2000	0.1989	0.60
B	40.00	0.2000	–	–	–	–	–	–	40.20	0.2015	0.75
C	40.00	0.2000	1.000	1.000	–	–	–	–	42.20	0.2163	8.15
D	40.00	0.2000	–	–	3.000	–	–	–	43.20	0.2073	3.65
E	40.00	0.2000	1.000	1.000	3.000	–	–	–	45.20	0.2121	6.05
F	40.00	0.2000	–	–	–	40.00	–	–	80.20	0.2011	0.55
G	40.00	0.2000	1.000	1.000	–	40.00	–	–	82.20	0.1974	1.30
H	40.00	0.2000	–	–	–	40.00	40.00	–	120.2	0.2057	2.85
I	40.00	0.2000	–	–	–	40.00	40.00	40.00	160.2	0.2081	4.05
J	40.00	0.2000	1.000	1.000	–	40.00	40.00	40.00	162.2	0.1945	2.75
K	40.00	0.2000	1.000	1.000	3.000	40.00	40.00	40.00	165.2	0.2077	3.85

determined solely without a pre-separation process in the presence of a large amount of phenol and nitrophenol. In real samples isomeric compounds of resorcinol are present together with resorcinol, so synthetic samples *C*, *E*, *G* and *J* were determined with satisfactory results. The analytical concentrations obtained suggest that the sensitivity of the present method is higher.

Application in analyzing actual samples

The proposed method was used to determine the concentrations of resorcinol in actual tap water and wastewater samples collected from laboratory and industry. The real samples were treated by using a standard distillation method [17–18]. Moreover, addition-recovery tests were carried out to evaluate the accuracy of the proposed measurement method. All the results are shown in Table 4. It can be seen that the recoveries are close to 100%, indicating that there is no serious interference in such water samples.

Conclusions

The trace resorcinol in phenol mixtures can be detected and its concentration can be measured directly without any pre-separation process even when high concentrations of other phenols coexist in solutions. Applicability tests demonstrate that the proposed method is feasible for quantitative analysis of resorcinol in wastewater samples. Compared with the high-performance liquid chromatography and gas chromatography approaches, which need carry-gas and organic solvents during measurements, the proposed method is simpler, cheaper and less harmful.

Table 4. The results for the determination of resorcinol in some real samples ($n = 4$).

Sample	Found (μg L^{-1})	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Industrial waste water 1	19.7	233	262.9	104.4
Industrial waste water 2	21.2	233	249.5	98.0
Waste water in the lab	40	233	279.3	102.7
Tap water	–	233	229.5	98.5

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