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Rapid and environmentally friendly determination of trace nitrite in water under combined effects of cetyltrimethyl ammonium bromide and β-cyclodextrin

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ABSTRACT

Nitrite is a characteristic pollutant in natural water. A simple, rapid and highly selective spectrofluorimetric method for determination of trace nitrite has been developed. It was based on the fact that nitrite reacted rapidly with iodide at room temperature and led to the fluorescence quenching of 4′,5′-dibromofluorescein (DBF) under the combined effects of cetyltrimethyl ammonium bromide (CTAB) and β-cyclodextrin (β-CD). The fluorescence intensity of the above reaction system was measured with excitation and emission wavelengths of 532 and 551 nm, respectively. Optimal values of the main factors involving volumes of CTAB, β-CD and sulfuric acid were explored by a Box–Behnken design. Under the optimized experimental conditions, the fluorescence quenching intensity was good linear over a nitrite concentration range of 0.2–46.0 μg/L with a correlation coefficient better than 0.998. The detection limit of 0.16 μg/L was obtained for the determination of nitrite by the proposed method. The general coexisting ions did not interfere to the reactions of nitrite with iodide and DBF. The relative standard deviation of the method for the determination of nitrite in water samples was below 2.7%, and the corresponding recoveries were between 92.1% and 107.9%. The proposed method is environmentally friendly and suitable for water monitoring.

Keywords: Nitrite; 4′,5′-Dibromofluorescein; Cetyltrimethyl ammonium bromide; β-Cyclodextrin; Combined effects

1. Introduction

Nitrite is an important water pollutant and commonly monitored for environmental protection purposes. Excessive concentration of nitrite in drinking water is hazardous to health. Nitrite may lead to the production of carcinogenic nitrosamines when it reacts with secondary amines in the stomach [1]. Nitrite can oxidize the iron(II) in hemoglobin of red blood cells to form methemoglobin, which makes the blood lose its ability to carry oxygen [2]. Besides, nitrite is also an important intermediate formed during the biodegradation of nitrogenous organic matter, and the amounts of nitrite can provide an index of organic pollution in water [3]. In view of the increasing interest in the quality of natural and sewage waters, a rapid, sensitive and specific determination of nitrite with non-toxic chemicals is highly desirable.

Environmental analytical chemistry contributes significantly to the growth of environmental sustainability through environmental monitoring. However, a lot of analytical methods employed to investigate environmental problems generate new chemical wastes, which contribute to environmental pollution [4]. Even some of the chemicals used are more toxic than the species being monitored. Consequently,

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in the development of a new analytical method, the amount and toxicity of the reagents used and of the wastes produced are as important as any other analytical feature [5].

A lot of spectrophotometric methods for determination of nitrite are based on the diazotization of various aromatic amines by nitrite under special conditions to form a diazonium salt. This is coupled with a selected aromatic compound to produce a highly colored azo dye which is subsequently determined colorimetrically. However, these methods have drawbacks such as pH dependence, low diazotization temperature and long coupling time. Toxicity of certain amines is also an important point for chemist [6]. Aydin et al. [7] has listed more than 12 aromatic amines used for this purpose. However, many of the aromatic amines are carcinogens and the procedure affects the health of the operators [8]. Some kinetic spectrophotometric methods are based on the catalytic effect of nitrite on the decolorization of pyrogallol red [9], brilliant cresyl blue [10], malachite green [11], methyl red [12], perphenazine [13], and tropaeolin OO [14] with bromate as an oxidant. These catalytic spectrophotometric methods are characterized by high sensitivity but often suffer from the strict reaction conditions.

Fluorescence quenching is highly useful in developing spectrofluorimetric methods. Many fluorescence quenching methods for the determination of nitrite are based on the diazotization of some amino-containing compounds such as indole [15], rhodamine 110 [16], 6-amino-1,3-naphthalenedisulfonic acid (ANDSA) [17] and 4-amino-3-hydroxynaphthalene-1-sulfonic acid (AHNSA) [18]. These fluorescent reagents react with nitrite in an acidic medium to form non-fluorescent products. Coupling agents are not used in these methods, which weakens the impact of analytical methods on environment. Besides, some new fluorescent probes have been developed for the determination of nitrite, such as mono[6-*N*(2-carboxy-phenyl)]-β-cyclodextrin (OACCD) [19], 1,3,5,7-tetramethyl-2,6-dicarbethoxy-8-(3′,4′-diaminophenyl)-difluoroboradiaza-s-indacene (TMDCDABODIPY) [20], and 2-amino-5,7-dimethyl-1,8-naphthyridine (ADMND) [21]. These fluorescent probes are sensitive and selective for nitrite determination.

4',5'-Dibromofluorescein (DBF) is an acid xanthene dye which is commercially available [22]. Xanthene dyes are used as colorants for foods, drugs and cosmetics in Japan and North America. They have also been developed for use as an insecticide against crop pests given their rapid photodegradation and low mammalian toxicity [23]. With suggestions of lessened environmental impacts, we selected DBF as a fluorescent probe for the determination of nitrite in this study. The novel spectrofluorimetric method has been developed depending on the oxidation of nitrite. The fluorescence intensity of DBF is quenched under the combined effects of cetyltrimethyl ammonium bromide (CTAB) and β-cyclodextrin (β-CD). CTAB and β-CD, which are commonly used as sensitizers in analytical chemistry [24,25], play especially important roles in the fluorescence quenching of DBF. The procedure occurs rapidly at room temperature and does not need heating, which is needed in other fluorometric methods [26–28]. This method has some advantages such as easy and fast operation, high sensitivity, good selectivity and easily obtained and environment-friendly reagents.

2. Materials and methods

2.1. Apparatus

Fluorescence measurements were performed with a Hitachi (Japan) F-4600 fluorescence spectrometer equipped with a 150-W Xenon arc lamp as the light source. Excitation and emission slit widths were kept at 5.0 nm. Scanning rate of monochromators was maintained at 1,200 nm/min. The photomultiplier tube voltage was set at 700 V. A 1-cm quartz cell was used. For best resolution and smoothing, a smoothing order of 3 and 50 points were used for the fluorescence spectra. A UV-1102 spectrophotometer (Techcomp, China) was used to obtain UV–Vis absorption spectra of DBF and its derivative.

2.2. Reagents

DBF was purchased from Tianjin Heowns Biochemical Technology Co. Ltd. (China). CTAB and β-CD were obtained from Shanghai Xinfan Biotechnology Co. Ltd. (China). Sodium nitrite ($NaNO_2$), potassium iodide (KI) and sulfuric acid (H_2SO_4) were purchased form Sinopharm Chemical Reagent Co. Ltd. (China). Sodium nitrite was used to provide the nitrite, NO_2^-. All of the chemicals used were of analytical grade or chemically pure grade. Double-distilled water was used throughout the experiment.

A standard stock solution of 100.0 mg/L NO_2^- was prepared by dissolution of 0.0375 g sodium nitrite in water and dilution in a 250-mL standard flask. Working standards of NO_2^- were prepared from standard stock solution by appropriate dilution before use. A stock solution of 1.0×10^{-3} mol/L DBF was prepared by dissolution of 0.1226 g DBF with 100 mL of ethanol and dilution in a 250 mL standard flask with water. A working solution of 1.0×10^{-5} mol/L DBF was prepared by transfer of 2.5 mL of DBF stock solution into a 250 mL standard flask and dilution to the mark with water before use. All stock solutions were preserved in a refrigerator at 4°C. A 0.5 g/L KI solution was prepared by dissolution of 0.1251 g potassium iodide and dilution to 250 mL with water. The other chemical solutions used in the study included 1.0 g/L CTAB, 1.0 g/L β-CD and 0.03 mol/L H_2SO_4.

2.3. Determination of nitrite

Volumes of 2.0 mL of 0.5 g/L KI, 3.1 mL of 1.0 g/L CTAB, and 3.0 mL of 1.0 g/L β-CD were successively transferred into a 25-mL standard flask, and the solution should be shaken and mixed well before the next reagent was added. Subsequently, 1.0 mL of 1.0×10^{-5} mol/L DBF working solution, 2.0 mL of 0.03 mol/L H_2SO_4, and appropriate amounts of NO_2^- standard solution or water samples (in the working concentration range) were added to the above solution, and the whole solution was diluted to the mark with water. The resulting solution was allowed to stand for 5 min at room temperature. Then, the fluorescence signal of the reaction solution was measured.

The fluorescence emission spectra of the reaction solution were recorded by scanning in the wavelength of 535–700 nm at an excitation wavelength of 532 nm. The fluorescence intensity F of the sample solution was determined at the emission wavelength of 551 nm, and the fluorescence

intensity F_0 of the blank solution without nitrite was obtained under the same conditions. Finally, the fluorescence quenching intensity ΔF was calculated by $\Delta F = F_0 - F$ and used for quantification.

3. Results and discussion

3.1. Spectral characteristics of DBF

The excitation and emission spectra of 4.0×10^{-7} mol/L DBF under different pH conditions are shown in Fig. 1. The excitation and emission maxima of DBF in pH 9.0 and 7.0 were at 506 and 530 nm, respectively. However, the excitation and emission maxima of DBF in pH 5.0 appeared at 516 and 539 nm, respectively. Furthermore, the fluorescence intensity of DBF with the same concentration in pH 5.0 was much lower than that in pH 7.0 or 9.0.

DBF did not react with nitrite in an acidic solution, viz. nitrite did not quench the fluorescence of DBF when there was not I^- in the solution. Meanwhile, the I^- present in acidic, neutral or alkaline solutions could not cause fluorescence quenching of DBF. However, I_2 significantly reduced the fluorescence intensity of DBF in acidic and neutral solutions. The I_2 could also be generated by the reaction between nitrite and I^-. Based on these findings, a new, rapid and highly selective fluorescence quenching method for the determination of nitrite with low detection limit was developed.

3.2. Fluorescence spectra of reaction system

However, the fluorescence quenching phenomenon did not occur in the KI-DBF-H_2SO_4-NO_2^- system. At a certain H_2SO_4 concentration, nitrite reacted rapidly with I^- as follows:

$$2NO_2^- + 2I^- + 4H^+ = I_2 + 2NO + 2H_2O \quad (1)$$

$$I_2 + I^- = I_3^- \quad (2)$$

The I_3^- formed in this reaction system could not quench the fluorescence intensity of DBF. The resulting I_3^- has been applied to resonance scattering by forming association particles [29,30], but it is useless in this system. Therefore, new agents should be added into the system to prevent I^- from reacting with I_2. CTAB and β-CD were selected to achieve this function.

CTAB and β-CD did not emit fluorescent light (Fig. 2 curve 3′). The fluorescence properties of DBF changed as DBF was modified by CTAB and β-CD. The excitation peak of DBF shifted from 516 to 532 nm (Fig. 1 curve 3; Fig. 2 curve 1), and the emission peak shifted from 539 to 551 nm (Fig. 1 curve 3′; Fig. 2 curve 1′). The fluorescence intensity of DBF in the presence of CTAB and β-CD was about eight times higher than that in the absence of them. The fluorescence intensity was greatly enhanced due to the sensitization of CTAB and β-CD. Most importantly, the fluorescence intensity located in 551 nm decreased when appropriate amounts of nitrite were added to the reaction system (Fig. 2 curves 1′and 2′). The alteration of fluorescence intensity indicated that CTAB and β-CD effectively prevented

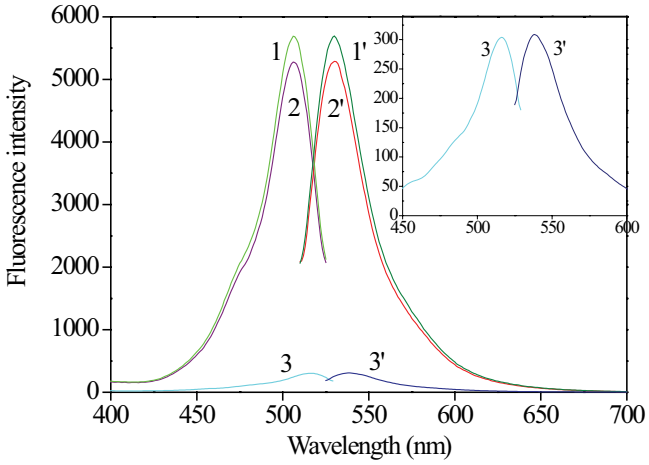

Fig. 1. Fluorescence spectra of DBF in different pH: 1 excitation spectrum in pH 9.0 with emission at 530 nm, 1′ emission spectrum in pH 9.0 excited at 506 nm, 2 excitation spectrum in pH 7.0 with emission at 530 nm, 2′ emission spectrum in pH 7.0 excited at 506 nm, 3 excitation spectrum in pH 5.0 with emission at 539 nm, 3′ emission spectrum in pH 5.0 excited at 516 nm. Experimental condition: 1.0 mL of 1.0×10^{-5} mol/L DBF and 25 mL total volume.

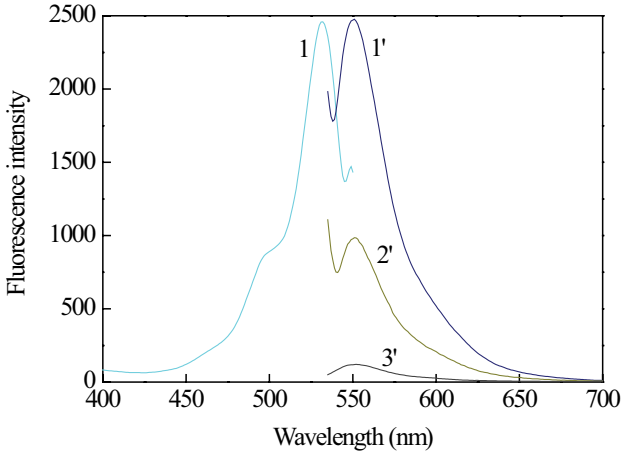

Fig. 2. Fluorescence spectra of the reaction system under different conditions. Curve 1 shows excitation spectrum with emission at 551 nm; Curves 1′, 2′ and 3′ show emission spectra excited at 532 nm. 1, 1′: KI-CTAB-β-CD-DBF-H_2SO_4; 2′: KI-CTAB-β-CD-DBF-H_2SO_4-NO_2^-; 3′: CTAB-β-CD. Experimental condition: 2.0 mL of 0.5 g/L KI, 3.1 mL of 1.0 g/L CTAB, 3.0 mL of 1.0 g/L β-CD, 1.0 mL of 1.0×10^{-5} mol/L DBF, 2.0 mL of 0.03 mol/L H_2SO_4, 0.8 mL of 1.0 mg/L NO_2^- and 25 mL total volume.

the formation of I_3^- in this system. Therefore, the fluorescence quenching phenomenon appeared obviously in the KI-CTAB-β-CD-DBF-H_2SO_4-NO_2^- system. Excitation 532 nm and emission 551 nm were chosen as operating wavelengths for this experiment.

3.3. Optimization of the determination conditions

The redox reaction between nitrite and I^- and fluorescence quenching of DBF occurred quickly at room temperature and

the fluorescent signal remained stable for more than 30 min. The fluorescence quenching intensity ΔF did not change significantly in the temperature range from 10°C to 50°C. So, the determination of fluorescence intensity was carried out after all the reagents had been reacted for 5 min at room temperature. However, some reagent concentrations, such as those of DBF, potassium iodide, CTAB, β-CD, and sulfuric acid, affected the performance of the proposed method. These parameters were carefully investigated and optimized.

3.3.1. DBF concentration

DBF was a fluorescent probe in this reaction system. Appropriate DBF concentration was studied in the range from 1.0×10^{-7} to 6.0×10^{-7} mol/L. Fig. 3 indicates that an increase in DBF concentration caused an increase in the fluorescence intensity change in F_0 and F. The ΔF began to keep stable when the DBF concentration was above 4.0×10^{-7} mol/L. Therefore, 4.0×10^{-7} mol/L DBF was chosen as an optimum concentration for further studies, which was realized by adding 1.0 mL of 1.0×10^{-5} mol/L DBF working solution to a 25-mL flask.

3.3.2. KI concentration

KI provided I^- required for the redox reaction. The concentration of KI should be sufficient to ensure that all nitrite in the solution were reacted. Fig. 4 indicates that nitrite was not completely reduced by KI with a concentration below 0.03 g/L and the fluorescence intensity F decreased with the increase of KI concentration. The ΔF values did not increase when the concentration of KI solution exceeded 0.04 g/L. In order to reduce the cost of determination method, a concentration of 0.04 g/L KI was selected in the present study, which was realized by adding 2.0 mL of 0.5 g/L KI solution to a 25-mL flask.

3.3.3. Volumes of CTAB, β-CD and H_2SO_4

According to the above study, CTAB and β-CD played important roles in the fluorescence quenching process. In this system, the reaction of nitrite with I^- proceeded in an acidic medium. Proper H_2SO_4 volume should be selected to provide the appropriate concentration of H^+ required for the redox reaction.

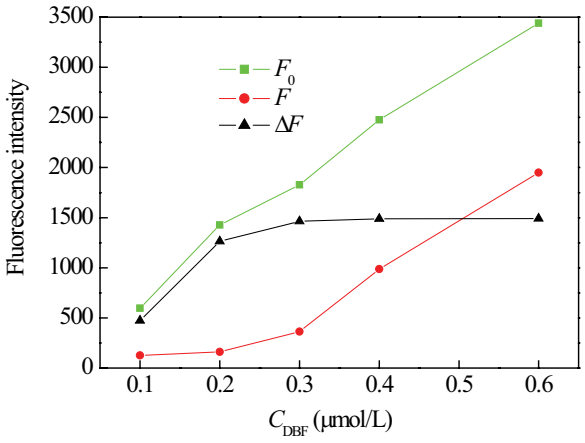

Fig. 3. Effect of DBF concentration on fluorescence intensity of the reaction system. Experimental condition: 2.0 mL of 0.5 g/L KI, 3.1 mL of 1.0 g/L CTAB, 3.0 mL of 1.0 g/L β-CD, 2.0 mL of 0.03 mol/L H_2SO_4, 0.8 mL of 1.0 mg/L NO_2^- and 25 mL total volume.

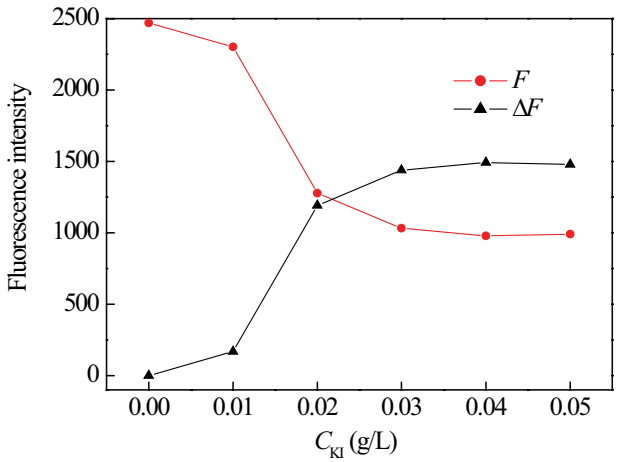

Fig. 4. Effect of KI concentration on fluorescence intensity of the reaction system. Experimental condition: 3.1 mL of 1.0 g/L CTAB, 3.0 mL of 1.0 g/L β-CD, 1.0 mL of 1.0×10^{-5} mol/L DBF, 2.0 mL of 0.03 mol/L H_2SO_4, 0.8 mL of 1.0 mg/L NO_2^- and 25 mL total volume.

We optimized the volumes of CTAB, β-CD and H_2SO_4 using a Box–Behnken design (BBD). The disadvantages of the optimization processes based on the independent study of variables are well known because the number of experiments is large and they do not give information about the possible interaction between variables [31]. In contrast, the Box–Behnken designs are all spherical designs and require factors to be run at three levels [32]. By spacing all the points at an equal distance from the center, this type of design allows the main factors and their interactions to be understood and optimal values for parameters to be deduced, while reducing the number of experiments compared with a sequential design [33]. Each of the independent variables investigated for this study was consecutively coded as A, B and C at three levels: –1 (low level), 0 (central level) and +1 (high level). The experimental domain and levels of studied variables are presented in Table 1.

The BBD matrix is shown in Table 2. The design involved 17 batch experiments. The chronological listing of the BBD represented the statistically randomized order in which the experiments were undertaken. Replicates (n = 5) of the central points were performed to estimate the experimental error [34]. The F_0 and F were determined under each condition, after which the corresponding ΔF was calculated and used for further evaluation.

It was found that the F_0 increased with the increase of CTAB volume, which showed that CTAB had a sensitization effect on this system. Furthermore, the fluorescence intensity of the system decreased from F_0 to F when the CTAB was added. This indicated that CTAB, as a cationic surfactant, orientationally bound I^- through electrostatic attraction [35] and prevented the combination of I^- and I_2. However, when the amount of CTAB was too much, the fluorescence quenching did not occur in the system, which might be that the powerful

Table 1
Factor codes and their levels applied to optimize the fluorescence quenching conditions of DBF by nitrite

Factors	Code	Variable levels		
		–1	0	+1
CTAB volume (mL)	*A*	1.5	3.0	4.5
β-CD volume (mL)	*B*	2.0	3.0	4.0
H_2SO_4 volume (mL)	*C*	0.5	2.0	3.5

electrostatic force generated by excessive CTAB prevented the reaction of nitrite with I^-. β-CD had little effect on the F_0 and did not cause the fluorescence quenching of DBF in the reaction system. The β-CD coexisting with CTAB was helpful to smooth the drastic change of the fluorescence quenching value in the system and improve the accuracy and precision of the proposed method. Cyclodextrins are cyclic oligosaccharides constituted by six or more D-glucopyranose units that present an almost conical hydrophobic cavity being able to form inclusion complexes with a large variety of molecules [36]. The β-CD does usually possess a good complexation efficiency with organic compounds. The binding effect of CTAB on I^- was further improved by complexation into β-CD molecules.

To analyze the data and the design of the experiment, the software package Design-Expert 8.0.6 was employed. The analysis of variance (ANOVA) summary (Table 3) shows that the model was very significant, with a *p*-value less than 0.0001. A lack-of-fit *p*-value of 0.1246 implied that the lack-of-fit was not significantly associated to the pure error. The parameters of CTAB volume (*A*), β-CD volume (*B*) and H_2SO_4 volume (*C*) had very significant effects on the response, and the order of their effects was $A > B > C$. The higher the *F*-value, the more significant the effect of this factor. The interactive effects of *AB* term and *AC* term were significant.

Table 2
Box–Behnken design matrix with three independent variables expressed in code value and the response values[a]

Run	*A*	*B*	*C*	F_0	*F*	$\Delta F = F_0 - F$
1	–1	0	+1	842	416	426
2	0	+1	–1	1,938	1,114	824
3	0	0	0	2,474	989	1,485
4	0	0	0	2,472	983	1,489
5	0	+1	+1	1,425	563	862
6	–1	–1	0	1,264	1,081	183
7	0	0	0	2,476	992	1,484
8	0	–1	–1	2,592	1,834	758
9	+1	–1	0	2,971	2,604	367
10	–1	+1	0	973	747	226
11	0	–1	+1	2,136	1,331	805
12	+1	0	+1	2,413	1,784	629
13	0	0	0	2,475	987	1,488
14	+1	+1	0	2,060	1,613	447
15	–1	0	–1	1,117	746	371
16	+1	0	–1	3,009	2,419	590
17	0	0	0	2,472	986	1,486

[a]Experimental condition: 2.0 mL of 0.5 g/L KI, 1.0 mL of 1.0×10^{-5} mol/L DBF, 0.8 mL of 1.0 mg/L NO_2^- and 25 mL total volume.

In order to gain insight about the effect of each factor, the three-dimensional (3D) response surface graphs for the measured responses were plotted to analyze the variation of the response surface as shown in Fig. 5. These 3D figures show the relationship between two factors and response ΔF at the center level of the other factor. The curvatures of the plots indicate the interaction between the factors [37]. Fig. 5a depicts the response surface obtained by plotting CTAB volume vs. β-CD volume with the volume of aqueous

Table 3
Analysis of variance (ANOVA) for the response surface quadratic model

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model	3.78E + 6	9	4.20E + 5	4.63E + 4	<0.0001
A	8.55E + 4	1	8.55E + 4	9431.64	<0.0001
B	7,564.50	1	7,564.50	834.54	<0.0001
C	4,005.13	1	4,005.13	441.86	<0.0001
AB	342.25	1	342.25	37.76	0.0005
AC	64.00	1	64.00	7.06	0.0326
BC	20.25	1	20.25	2.23	0.1786
A^2	2.33E + 6	1	2.33E + 6	2.57E + 5	<0.0001
B^2	8.01E + 5	1	8.01E + 5	8.84E + 4	<0.0001
C^2	2.38E + 5	1	2.38E + 5	2.63E + 4	<0.0001
Residual	63.45	7	9.06		
Lack of fit	46.25	3	15.42	3.59	0.1246
Pure error	17.20	4	4.3		
Cor total	3.78E + 6	16			

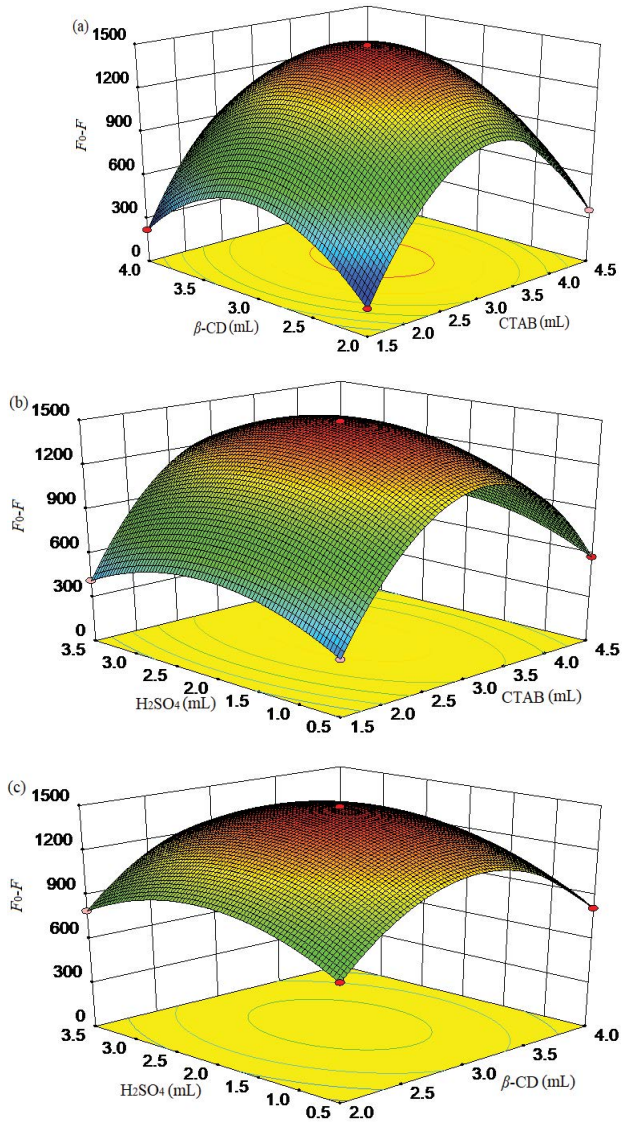

Fig. 5. 3D response surface diagrams showing the effects of the mutual interactions between two independent variables: (a) CTAB volume vs. β-CD volume, (b) CTAB volume vs. H_2SO_4 volume, (c) β-CD volume vs. H_2SO_4 volume. Experimental condition: 2.0 mL of 0.5 g/L KI, 1.0 mL of 1.0×10^{-5} mol/L DBF, 0.8 mL of 1.0 mg/L NO_2^- and 25 mL total volume.

sample fixed at 25 mL. The ΔF improved with the increase of CTAB volume while increasing the β-CD volume until it reached 3.0 mL. Excessive volume of CTAB and β-CD caused a rapid decrease in the ΔF values. The interaction of CTAB and β-CD was significant. The maximum response was obtained at 3.1 mL CTAB and 3.0 mL β-CD. When fixing the β-CD volume at 3.0 mL, the effects of CTAB volume and H_2SO_4 volume on the ΔF values are shown in Fig. 5b. With increasing CTAB volume from 1.5 to 3.1 mL and H_2SO_4 volume from 0.5 to 2.0 mL, the 3D response surface for the ΔF values reached their highest point. Fig. 5c shows that 3.0 mL β-CD and 2.0 mL H_2SO_4 were the inflection point for increasing average ΔF values. The interaction of β-CD and H_2SO_4 was not significant. In general, the operating conditions that allowed us to reach the best results for the analysis of nitrite were 3.1 mL CTAB, 3.0 mL β-CD, and 2.0 mL H_2SO_4.

3.4. Analytical characteristics

Under the optimized conditions, the fluorescence spectra changes during the reactions between 0.4 μmol/L DBF and nitrite with different concentrations are shown in Fig. 6. The fluorescence intensity of the reaction system at 551 nm decreased with the increase in nitrite concentration. The calibration curve for nitrite was obtained by plotting the fluorescence quenching intensity ΔF vs. nitrite concentration, as shown in Fig. 6 inset. Clearly, the ΔF was proportional to the nitrite concentration in the range from 0.2 to 46.0 μg/L. The statistical data of the calibration curve are reported in Table 4. The detection limit was calculated with the signal to noise ratio (S/N) value of 3 (n = 11) [38]. The precision of the present method was evaluated by determining the fixed concentration of 17.0 and 40.0 μg/L nitrite. The low relative standard deviation indicates that this method is highly precise and reproducible [7].

Table 4
Analytical data of the constructed calibration curve

Parameters	Results
Linear range (μg/L)	0.2–46.0
Slope (b) (L/μg)	42.49
Intercept	131.02
Correlation coefficient (R)	0.998
Detection limit (μg/L)	0.16
Reproducibility (RSD, %) (NO_2^- = 17.0 and 40.0 μg/L, n = 11)	2.25 and 1.78

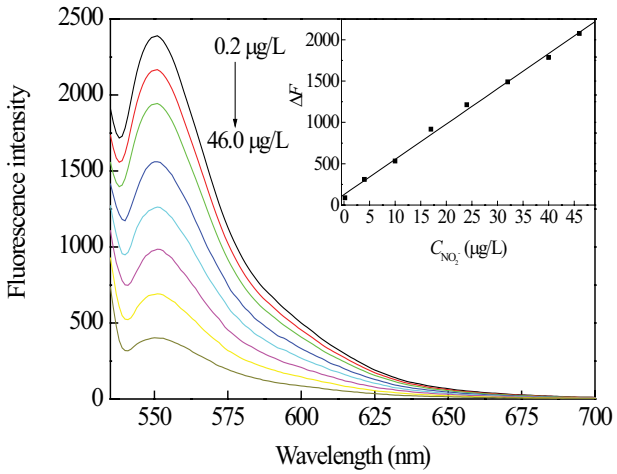

Fig. 6. Fluorescence spectra of DBF reacted with different concentrations of nitrite. Inset: plots of fluorescence quenching value vs. nitrite concentration. Experimental condition: 2.0 mL of 0.5 g/L KI, 3.1 mL of 1.0 g/L CTAB, 3.0 mL of 1.0 g/L β-CD, 1.0 mL of 1.0×10^{-5} mol/L DBF, 2.0 mL of 0.03 mol/L H_2SO_4 and 25 mL total volume.

3.5. Selectivity

To obtain the selectivity of the proposed method, we selected foreign ions commonly present in water samples (i.e., F^-, Cl^-, CH_3COO^-, NO_3^-, HCO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}) and checked their effects on the ΔF of the reaction solution containing 32.0 μg/L NO_2^-. When the effect of foreign species on the ΔF was less than ±5.0% [29], the species was assumed not to interfere in the determination of nitrite. In the presence of each one of the above-mentioned ions, the ΔF stayed mostly unchanged, thus suggesting high selectivity of the proposed method (Fig. 7). The interference of some oxidising anions, such as OCl^- and MnO_4^-, was also checked. OCl^- and MnO_4^- interfered the determination when their concentration was more than 1.0 μmol/L.

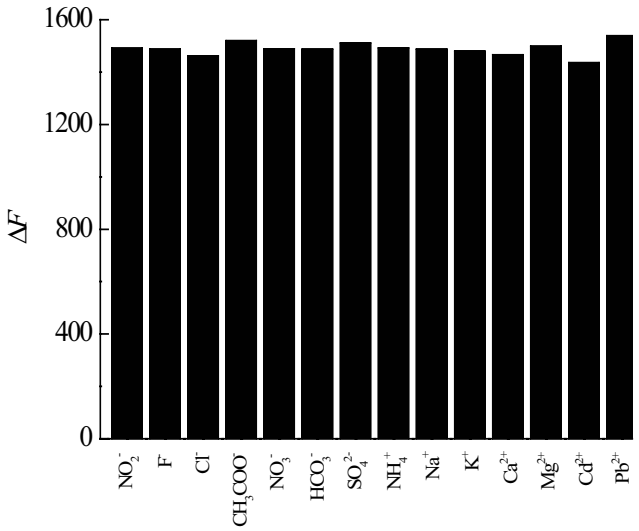

Fig. 7. ΔF values at 551 nm of reaction solution containing 0.70 μmol/L NO_2^- in the presence of NaF, NaCl, CH_3COONa, $NaNO_3$, $NaHCO_3$, Na_2SO_4, NH_4Cl, KCl, $CaCl_2$, $MgCl_2$, $Pb(NO_3)_2$ or $CdCl_2$ (each 140 μmol/L) in aqueous solution. Experimental condition: 2.0 mL of 0.5 g/L KI, 3.1 mL of 1.0 g/L CTAB, 3.0 mL of 1.0 g/L β-CD, 1.0 mL of 1.0×10^{-5} mol/L DBF, 2.0 mL of 0.03 mol/L H_2SO_4, 0.8 mL of 1.0 mg/L NO_2^- and 25 mL total volume.

However, they usually do not coexist with nitrite in water. The method has good selectivity.

3.6. Application

The proposed method was applied for the determination of nitrite in water samples. The water samples were collected from different sources, and were filtered before analysis. Samples with high concentrations were diluted appropriately with water before measurement so that the nitrite concentration was in its linear range. Recovery tests were performed by the standard addition method with known amounts of NO_2^- standard solution at two levels added to a fixed amount of real water sample, and then the mixture was analyzed according to the proposed procedure. The results are reported in Table 5. The relative standard deviation was 2.64% or less, thereby indicating the precision of the proposed method was good. The experimental recoveries between 92.1% and 107.9% revealed that no interference from commonly encountered constituents was present in the real sample. Hence, the proposed method is well applicable for real samples.

3.7. Mechanism of fluorescence quenching

DBF has intrinsic fluorescence. The fluorescence quenching of DBF in the determination of nitrite was not a dynamic quenching, which resulted from the molecular diffusion and collision. It was caused by a static quenching process resulting from the new component produced between molecules. UV–Vis measurements were carried out to reveal the fluorescence quenching mechanism of DBF toward nitrite. Fig. 8 shows the UV–Vis spectra of DBF and DBF/NO_2^- against reagent blank. It is clear that absorption peaks located in 507, 293 and 250 nm (Fig. 8 curve a) shifted to 531, 341 and 286 nm (Fig. 8 curve b), respectively. It is well known that -I group is an auxochrome which can move the absorption wavelength of organic compounds to the longer wavelength region. The red shift of the absorption spectra in Fig. 8 indicates that DBF reacted with I_2 under the experimental conditions and yielded a new derivative having the -I group. As an electron-attracting group, the attached -I

Table 5
Determination of nitrite in different water samples based on the proposed method

Sample	Added (μg/L)	Found[a] (μg/L)	RSD (%)	Recovery (%)
Rainwater	0.0	1.32	1.06	–
	3.0	3.98	0.58	92.1
	6.0	7.74	1.01	105.7
Surface water	0.0	3.65	1.92	–
	5.0	8.83	0.97	102.1
	10.0	13.55	1.26	99.3
Wastewater	0.0	16.41	2.64	–
	10.0	28.50	1.47	107.9
	20.0	34.16	1.83	93.8

RSD, relative standard deviation.
[a]Average of three determinations.

Table 6
Comparison of published results for the spectrofluorimetric determination of nitrite

Reagent	Linear range (μg/L)	Detection limit (μg/L)	Reaction time (min)	Reference
Indole	10.0–600	2.5	10	[15]
Rhodamine 110	0.5–14.0	0.03	60	[16]
ANDSA	6.0–75.0	2.1	35	[17]
AHNSA	5.0–500	13.6	40	[18]
OACCD	0.9–78.0	0.01	5	[19]
TMDCDABODIPY	0.4–14.0	0.01	15	[20]
ADMND	5.0–115	1.9	20	[21]
DBF	0.2–46.0	0.16	5	This method

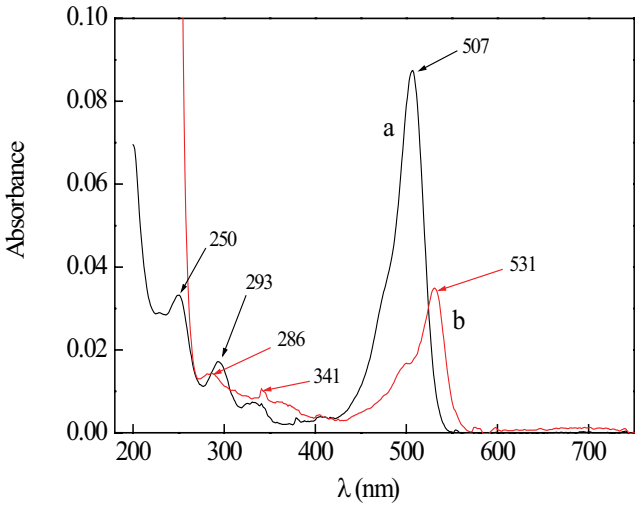

Fig. 8. UV–Vis spectra of (a) DBF (0.4 μmol/L) and (b) DBF (0.4 μmol/L)/NO_2^- (46.0 μg/L) against reagent blank. Experimental condition: 2.0 mL of 0.5 g/L KI, 3.1 mL of 1.0 g/L CTAB, 3.0 mL of 1.0 g/L β-CD, 1.0 mL of 1.0 × 10^{-5} mol/L DBF, 2.0 mL of 0.03 mol/L H_2SO_4, 1.15 mL of 1.0 mg/L NO_2^- and 25 mL total volume.

group quenched the fluorescence of the resulting derivative. Moreover, the fluorescence quenching of DBF in the system was not correlated with the increase of reaction temperature. Therefore, the quenching mechanism of DBF with nitrite was mainly a static quenching.

3.8. Comparison of reported methods with the proposed method

Some of the published spectrofluorimetric methods for the determination of nitrite are collected in Table 6. The methods have been compared based on the linear range, detection limit and time of the analysis. A few reagents, such as indole, rhodamine 110, ANDSA and AHNSA, are easily available on the market. The methods with these probes often suffer from poor sensitivity, some inherent interference, a long response time and even toxicity. The detection limits of some methods reported in Table 6 are relatively low compared with that of our method. However, the reagents used, such as OACCD, TMDCDABODIPY and ADMND, are synthesized in the laboratory with complicated steps. In the study by Gao et al. [19], the reaction step of the analysis requires 5 min; however, the synthesis of OACCD may take more than 12 h. The dynamic linear range of the present method is wide, which is convenient for routine environmental analysis. Considering the linear range and the lower detection limit, the proposed method is very sensitive. DBF is commercially available and reacts quickly with nitrite at room temperature. The method is easy to popularize.

4. Conclusions

An environmentally friendly and highly selective fluorescence quenching method for the determination of trace nitrite has been established based on its oxidation of iodide with DBF as a fluorescent probe. The reactions among nitrite, iodide and DBF were carried out rapidly at room temperature. The CTAB and β-CD added to the system not only enhanced the fluorescence intensity of DBF but also restrained the formation of I_3^- by binding I^-. Applicability tests demonstrate that the proposed method is feasible for the trace analysis of nitrite in actual samples. The new method is simple, inexpensive and environmentally friendly, and thus easy to popularize.

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