Kinetic-spectrophotometric method for the determination of trace amounts of bromide in seawater

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Kinetic-Spectrophotometric Method for the Determination of Trace Amounts of Bromide in Seawater

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Abstract

A novel simple, sensitive and rapid kinetic-spectrophotometric method is proposed for the determination of trace amounts of bromide. The method is based on its catalytic effect on the oxidation of methylene blue (MB) by hydrogen peroxide in strongly acidic solution. The oxidation reaction is activated by large amounts of chloride and can be monitored spectrophotometrically by measuring the decrease in the absorbance of MB at 746 nm. The determination of bromide is performed by a fixed-time method at the first 100 s from the initiation of the reaction. Unlike other kinetic-spectrophotometric methods for the determination of bromide, the proposed method does not require heating the solution. Bromide can be determined in the range from 80 to 960 μg l^{-1} with the detection limit of 35 μg l^{-1}. The relative standard deviation of ten replicate determination of 480 μg l^{-1} bromide was 1.4%. The influence of potential interfering ions was studied. The proposed method was satisfactorily applied to the determination of bromide in seawater without interfering effect from chloride ion.

Keywords: kinetic-spectrophotometry, methylene blue, bromide, seawater

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1. Introduction

The determination of bromide is increasingly interested in a variety of fields such as food, contraction material and environmental samples. Bromide ion is one of the trace constituents of seawater, and its average concentration in seawater is approximately 60 – 70 mg l^{-1} [1]. At trace concentrations, it is also found in many waste waters, ground waters and surface waters. Intrusion of seawater can significantly elevate the levels of bromide ion in the surface and ground waters near the sea. Furthermore, bromide can be converted to reactive gas species, bromine (Br_2) and hypobromous acid (HOBr), which can affect to ozone chemistry. Moreover, bromide can combine with many kinds of organic pollutants, which may present in natural waters, to form toxic compounds that can cause serious harm to human health and the environment.

A number of analytical techniques to determine bromide in environmental samples have been reported so far. Some of the most commonly used methods are high performance liquid chromatography [2, 3], ion chromatography [4-6], gas chromatography [7] and capillary electrophoresis [8-10]. However, such methods require expensive instruments and can suffer from time-consuming for sample preparation and long analysis time. Highly sensitive and selective methods are still required for the determination of trace amounts of bromide in environmental samples.

Kinetic-spectrophotometric methods are attractive alternative method for bromide determination, because they have advantages of high sensitivity, sufficient accuracy, simple procedures and the necessity of less expensive apparatus. Some kinetic-spectrophotometric methods for bromide determination have been reported. They use several types of indicator reaction [11-18]; for example, the reaction systems with pyrocatechol violet in the presence of H_2O_2 [12] and 4,4'-bis-(dimethylamino)-diphenylmethane (Tetrabase) in the presence of chloramine T [16] were applied to the determination of bromide. However, these methods are severely interfered from iodide, and some of the kinetic methods must be carried out at elevated temperatures for improving sensitivity [18]. Moreover, chloride in millimolar levels can interfere with these kinetic reactions, which leads to the difficulty to apply such kinetic reactions to the determination of bromide in the presence of chloride. In order to overcome such interference problems, we aimed at developing a new kinetic-spectrophotometric reaction for the selective determination of bromide without any extraction and separation steps.

Methylene blue (MB) is one of cationic thiazine dyes, and has been widely used for biological-stain application in bioanalytical chemistry [19, 20]. There were only a few reports on the application of MB to the catalytic analysis of some elements [21, 22]. However, all of them have been used for the determination of metal ions, and there was no analytical application for halide determination.

In this study, we propose a new kinetic-spectrophotometric method for the determination of bromide in the presence of high chloride matrix, which is based on its catalytic effect on the oxidation of methylene blue with hydrogen peroxide. Large amounts of chloride as an activator was found to enhance the sensitivity of the method.

The proposed method could determine bromide in the range from 80 to 960 μg l^{-1}, and be successfully applied to the determination of bromide in seawater samples.

2. Experimental

2.1 Reagents

All chemicals used were of analytical regent grade. Deionized-distilled water was used for the preparation of reagent solutions. A stock solution of standard bromide (1000 mg l^{-1}) was prepared by dissolving 0.1488 g of KBr crystals (Wako Pure Chemicals, Osaka) in 100.0 ml water. Working solutions of bromide were subsequently prepared by appropriate dilution of the stock solution with water. A $5.2x10^{-4}$ mol l^{-1} methylene blue (MB) solution was prepared by dissolving 0.0166 g of MB crystalline (Tokyo Kasei, Tokyo) in water in a 100 ml volumetric flask. A commercially available solution of 30% (10 mol l^{-1}) hydrogen peroxide (Kanto Chemical Co. Inc., Tokyo) was directly used for the procedure without any dilution. The solution of 2 mol l^{-1} sodium chloride was prepared by dissolving 11.7 g of NaCl (Wako Pure Chemicals) in 100 ml of water. A 5 mol l^{-1} sulfuric acid solution was prepared by diluting 28 ml of 98% H_2SO_4 (Wako Pure Chemicals) to 100 ml with water.

Seawater samples were collected at the Seaside of Okayama and Okinawa prefecture. Filtration with a filter paper (Advantec, No. 5B) and proper dilution with deionized-distilled water was only pretreatment steps.

2.2 Apparatus

A UV-2400 PC double beam spectrophotometer (Shimadzu, Japan) equipped with 1.0 cm path length glass cells was used to get absorbance spectra and absorbance-time curves at fixed wavelength. The temperature was controlled by a model Thermominder Mini-80 thermostat water bath (Taiyo, Japan). A stop-watch was used for measuring the reaction time.

2.3 Recommended procedure

All of the reagent solutions were brought to the required temperature before mixing. An aliquot of the standard or sample solutions containing 0.2 to 2.4 µg of bromide was directly pipetted into a glass cuvette, followed by the addition of 250 µl of 2 mol l^{-1} NaCl (0.2 mol l^{-1}), 125 µl of 5.2×10^{-4} mol l^{-1} methylene blue (2.6×10^{-5} mol l^{-1}) and 625 µl of 5 mol l^{-1} H_2SO_4 (1.25 mol l^{-1}). Deionized-distilled water was added to make the volume to 2.25 ml as soon as 250 µl of 10 mol l^{-1} H_2O_2 was added. Then, the cuvette was cover with cuvette lid after that the solution was quickly shaken and placed in the spectrophotometer cell holder using exactly time 15 s. The reaction was traced spectrophotometrically by monitoring the decrease in absorbance of MB with time from 15 s to 135 s at 746 nm. A blank experiment was also performed by adding deionized-distilled water instead of the standard bromide solutions. A calibration graph was constructed by plotting the difference in the absorbance between the reactions in the absence and in the presence of bromide at the fixed time of 100 s ($\Delta A_{15\text{-}115s}$).

2.4 Titration for the determination of bromide

The titration was performed according to the method recommended in “Handbook of Anion Determination” [23]. A 10.0 ml of seawater was transferred into 250 ml conical flask followed by the addition of 5 ml of 1 mol l^{-1} KH_2PO_4, 5 ml of 2 mol l^{-1} NaCl and 2.5 ml of 0.35 mol l^{-1} NaOCl. Then the mixture was heated just to boiling and then add 5 ml of 50 %(w/v) HCOONa. The solution was then cooled and diluted to approximately 100 ml with water. A 15 ml of 10 %(w/v) KI, 15 ml of 3 mol l^{-1} H_2SO_4 and 1 ml of 0.1 mol l^{-1} ammonium molybdate were added. The mixture was titrated against a standardized $Na_2S_2O_3$ solution (about $2.7x10^{-3}$ mol l^{-1}), using 1 %(w/v) starch as an indicator.

3. Results and discussion

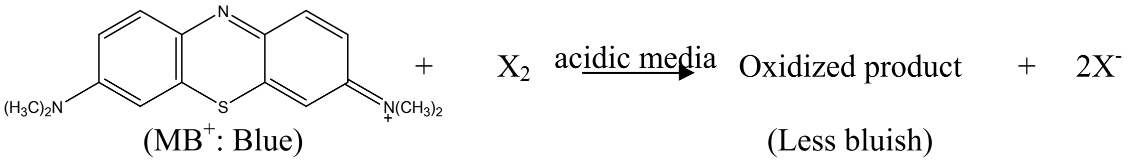
3.1 Preliminary investigations

We, for the first time, observed that halogen ions can act as a catalyst on the decolorization of MB in the presence of H_2O_2. The mechanism of the decolorization of MB is seemed to be as follows.

(1) Halide ions can be oxidized by H_2O_2 to halogen as the following reaction:

$$2X^- \quad + \quad H_2O_2 \quad + \quad 2H^+ \longrightarrow X_2 \quad + \quad 2H_2O \qquad (X=Cl^-, Br^-, I^-)$$

(2) The halogen formed can react with MB to form an oxidized product, and this reaction cause the decolorization of the blue color of MB as follows:



$$\text{MB}^+ + X_2 \xrightarrow{\text{acidic media}} \text{Oxidized product} + 2X^-$$

(MB^+: Blue) (Less bluish)

We examined the change in the absorption spectra, which were determined by scanning the spectrum of a reaction solution over the range of 500-800 nm. MB is a blue-colored reagent and has two maximum absorption wavelengths at 672 and 746 nm in strong acidic medium, and can be oxidized by H_2O_2 at an extremely slow reaction rate to give a reddish product. Fig. 1 shows the absorption spectra of MB-H_2O_2 system (curve 1), MB-H_2O_2-Br^- system (curve 2), MB-H_2O_2-Cl^- system (curve 3), MB-H_2O_2-

Cl^--Br^- system (curve 4), MB-H_2O_2-Cl^--I^- system (curve 5) and MB-H_2O_2-Cl^--Br^--I^- system (curve 6). The results shows that trace amounts of bromide can slightly catalyze the oxidation of MB in the presence of H_2O_2 (curve 2) in the strongly acid solution. However, the effect of bromide is considerably activated in the presence of large amounts of chloride (curve 4), whereas trace amounts of iodide can catalyze slightly the reaction even when chloride is present in the reaction system (curve 5): the catalytic effect of iodide shows a slower reaction rate than that of bromide. As is also demonstrated in Fig. 1, in the reaction system of MB-H_2O_2-Cl^--Br^--I^-, the catalytic behavior is mainly due to bromide; that is, there was no change on the absorption spectra between the reactions in the absence of I^- (curve 4) and in the presence of I^- (curve 6). This means that at equimolar concentration of iodide and bromide, the latter showed superior effect on the decolorization of MB. Such results indicate the possibility that, the determination of trace amounts of bromide is achieved in the presence of large amounts of chloride without the interference from equimolar amounts of iodide. By using this criterion, the catalytic reaction proposed here can be applied to the selective and sensitive determination of bromide in the presence of high concentrations of chloride in such samples as seawater.

3.2 Effect of reaction variables

3.2.1 Effect of sodium chloride on the catalytic reaction

As can be seen in Fig. 1, large amounts of chloride can catalyze the reaction between MB and H_2O_2 (curve 3) even when bromide was absent and the catalytic effect of bromide is appreciable when chloride is present (curve 4). Therefore, in this work, the reaction mixture containing a large amount of chloride and no bromide was used as a reagent blank mixture. The time courses of the absorbance of MB at 746 nm at various concentrations of chloride are shown in Fig. 2: the effect of chloride was investigated in the concentration range from 0 to 0.4 mol l^{-1}. As can be seen from Fig. 2, 15 s before the absorbance measurement started was necessary for the preparation of the solution; that is the mixing of the solutions was started at point A, and the absorbance measurement was started at point B. The results show that the absorbance are initially decreased linearly, and those at the time of 15 s decrease with increasing chloride concentrations. The extrapolated points of the initial straight lines are merged at the identical point, which corresponds to the starting point of mixing the solutions. Moreover, the rate of the decolorization of the absorbance at the beginning after the preparation of the solutions was very fast, and after that the rate becomes slower. The absorbance changes for the reaction in the absence of bromide (blank) and the reaction in the presence of 480 μg l^{-1} of bromide (bromide effect) at a fixed time of 100 s as a function of NaCl concentration were investigated; the results are shown in Fig. 3. The absorbance for both reactions decreased with increasing the NaCl concentrations. As can be seen from Fig. 3, the difference between the blank and the bromide effect (ΔA) increased up to about 0.1 mol l^{-1} of NaCl, and ΔA remained almost indentical between 0.1 and 0.35 mol l^{-1}, and decreased at higher NaCl concentration. Therefore, 0.2 mol l^{-1} of NaCl was selected as the optimum concentration for the reagent blank. Such results indicate that large amounts of chloride can act as an activator for enhancing the sensitivity of the method.

3.2.2 Effect of acids and acidity on the decolorization of MB

From the preliminary examination, it was found that kinetic reaction did not occurred in the acidic medium of acetic acid, whereas the kinetic reaction occurred when sulfuric acid, nitric acid and hydrochloric acid was used; with respect of the decolorization of MB, sulfuric acid was the most effective of all the acids tested because it provide the highest acidity (1 mole of acid equal to 2 mole of proton). Hence, sulfuric acid was selected as the acidic medium in this work.

The effect of sulfuric acid concentration was examined over the ranges from 0.25 to 1.75 mol l^{-1}. Fig. 4 shows that the absorbance of blank mixture and ΔA value increase rapidly with increasing in the sulfuric acid concentration up to 1 mol l^{-1}, and at the concentrations of more than 1 mol l^{-1} they become almost identical. Therefore, the sulfuric acid concentration of 1.25 mol l^{-1} was used for the method.

3.2.3 Effect of hydrogen peroxide concentration on the decolorization of MB

The effect of H_2O_2 concentration on the sensitivity was investigated in the ranges from 0.25 to 2.5 mol l^{-1}. The results are shown in Fig. 5. The absorbance changes for both reactions with and without the addition of bromide show the same trend. The absorbance decrease with increasing H_2O_2 concentrations, and then are almost constant at the H_2O_2 concentrations above 0.75 mol l^{-1}. A 1 mol l^{-1} H_2O_2 concentration was chosen for the further experiments.

3.2.4 Effect of methylene blue concentration on the sensitivity

The MB concentration was optimized by varying the concentrations from $2x10^{-5}$ to $3.2x10^{-5}$ mol l^{-1}. The effect of MB concentration on the linear range of the calibration graph for bromide was also investigated as is shown in Table 1. There were no significant differences in the slopes of the calibration graphs. The absorbance range was not appropriate when the concentration of MB was $2x10^{-5}$ mol l^{-1}, while the absorbance range obtained at the concentrations of $2.6x10^{-5}$ and $3.2x10^{-5}$ mol l^{-1} of MB were both applicable. However, the linear range obtained at the concentration of $2.6x10^{-5}$ mol l^{-1} is recommended with respect of the application to real samples.

3.2.5 Effect of temperature on the sensitivity

The effect of temperature on the sensitivity was examined in the range of 20 to 50 °C. At high temperatures, the decrease of the absorbance differences (ΔA) occurred, which is probably due to the degeneration of MB. At the temperature from 20 °C to 25 °C, the highest absorbance difference (ΔA) was obtained; 25 °C was selected for further experiments.

3.3 Analytical characteristics

Under the optimized conditions given above, the calibration graph was prepared using standard bromide solutions, whose concentrations were between 80 to 960 µg l^{-1}: the equation of the calibration graph was $\Delta A_{15\text{-}115s} = (5.29\underline{+}0.07)x10^{-4}\ C_{Br-} + (2.58\underline{+}0.44)x10^{-2}$, $R^2 = 0.999$, where C_{Br-} is the concentration of bromide in µg l^{-1}. Each point in the calibration graph was the average of three determinations. The precision was evaluated by ten replicate determination of 480 µg l^{-1} of standard bromide: the relative standard deviation was 1.4%, and the detection limit was 35 µg l^{-1}, which was calculated as three times of the standard deviation of the blank value (3σ of blank).

3.4 Interference study

The criteria for the interference from coexisting substances were considered to be within a relative error less than ±5% of the average ΔA for the 480 μg l^{-1} of bromide. A number of foreign ions may present in seawater, and the effects of such interferences were examined using the proposed method for the determination of bromide. The maximum tolerable molar ratios of the interfering ions in the determination of 480 μg l^{-1} of bromide are summarized in Table 2. Most of metal ions show less interference. Such ions as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} are present in seawater at high concentration [1], and may interfere with the determination of bromide. Also, Fe(II), NO_2^-, ClO^- and I^- can interfere with the determination of bromide in seawater. Normally, bromide content in seawater was approximately 60-70 mg l^{-1}. Dilution of seawater to 25 folds should be done prior to the measurement of bromide by proposed method. Therefore, such interferences can be suppressed, and the effect of these ions can be negligible.

3.5 Application of the proposed method to seawater samples

Recovery test of bromide in seawater samples was studied by the addition of 2.4 mg l^{-1} standard bromide into 25 folds diluted samples. As shown in Table 3, the recoveries were ranging from 95.2 to 106% (n=8). These results indicated that the components in the seawater samples do not interfere with the determination of bromide. Eight kinds of seawater samples were analyzed for bromide content, the results were compared with the titrimetric method [23]. Table 3 shows the analytical results obtain by the proposed kinetic-spectrophotometric method and the titrimetric method for the determination of bromide in seawater. The results obtained by both methods are in good agreement with each other. Paired *t*-test [24] was employed to compare the difference in the results. No significant difference was found ($t_{observed} = 0.45$, $t_{critical} = 2.36$ at $P = 0.05$). These results demonstrate that the proposed method is suitable as an alternative method for the determination of bromide in seawater.

4. Conclusion

A new kinetic-spectrophotometric method for the determination of bromide in seawater was accomplished. In the proposed reaction system, high concentrations of chloride can act as an effective activator for the catalysis of bromide. Therefore, using chloride has an interesting advantage over other kinetic reactions in which chloride may interfere with the kinetics of reactions. The method was successfully applied to the analysis of bromide in seawater.

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Figures' and Tables' Caption

Fig. 1. Absorption spectra of (1) MB-H_2O_2; (2) MB-H_2O_2-Br^-; (3) MB-H_2O_2-Cl^-; (4) MB-H_2O_2-Cl^--Br^-; (5) MB-H_2O_2-Cl^--I^-; (6) MB-H_2O_2-Cl^--Br^--I^-. Conditions: MB $2.6x10^{-5}$ mol l^{-1}, H_2O_2 1 mol l^{-1}, H_2SO_4 1.25 mol l^{-1}, Cl^- 0.2 mol l^{-1}, Br^- $6x10^{-6}$ mol l^{-1}, I^- $6x10^{-6}$ mol l^{-1}, temperature 25°C, reaction time 2 min.

Fig. 2. Kinetic profiles for the various concentrations of chloride. [Cl^-]: (1) 0 mol l^{-1}, (2) 0.1 mol l^{-1}, (3) 0.2 mol l^{-1}, (4) 0.3 mol l^{-1}, (5) 0.4 mol l^{-1}. Conditions: MB $2.6x10^{-5}$ mol l^{-1}, H_2O_2 1 mol l^{-1}, H_2SO_4 1.25 mol l^{-1}, Br^- 480 µg l^{-1}, temperature 25°C. Points A: mixing of the solutions was started, B: absorbance measurement was started.

Fig. 3. Effect of NaCl concentration on the decolorization of MB. Absorbance changes: (♦) in the absence of bromide (blank); (■) in the presence of bromide (Br effect); and (▲) the difference between the blank and the Br effect difference (ΔA). Conditions: MB $2.6x10^{-5}$ mol l^{-1}, H_2O_2 1 mol l^{-1}, H_2SO_4 1.25 mol l^{-1}, Br^- 480 µg l^{-1}, temperature 25°C, reaction time 100 s.

Fig. 4. Effect of H_2SO_4 concentration on the decolorization of MB. Absorbance changes: (♦) the reaction in the absence of bromide (blank); (■) in the presence of bromide (Br effect); and (▲) the difference between the blank and the Br effect difference (ΔA). Conditions: MB $2.6x10^{-5}$ mol l^{-1}, H_2O_2 1 mol l^{-1}, NaCl 0.2 mol l^{-1}, Br^- 480 µg l^{-1}, temperature 25°C, reaction time 100 s.

Fig. 5. Effect of H_2O_2 concentration on the decolorization of MB. Absorbance changes: (♦) the reaction in the absence of bromide (blank); (■) in the presence of bromide (Br effect); and (▲) the difference between the blank and the Br effect difference (ΔA). Conditions: MB 2.6x10^{-5} mol l^{-1}, H_2SO_4 1.25 mol l^{-1}, NaCl 0.2 mol l^{-1}, Br^- 480 µg l^{-1}, temperature 25°C, reaction time 100 s.

Table 1

Results obtained by using of different concentrations of methylene blue

Table 2

The maximum tolerance value of various foreign ions for the measurement of 480 µg l^{-1} (6x10^{-6} mol l^{-1}) bromide by the proposed method

Table 3

The results for the determination of bromide in seawater samples

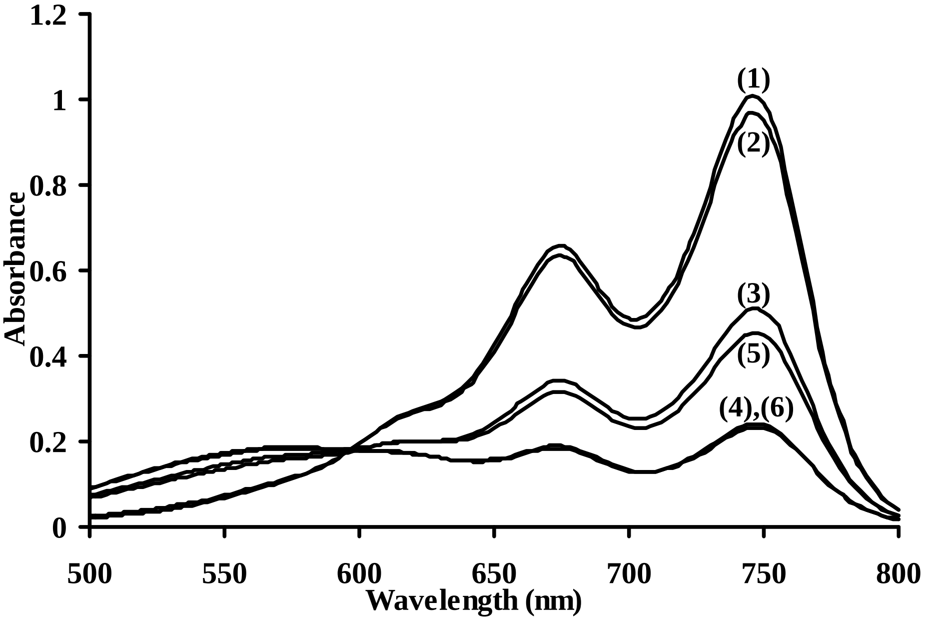
1.2
1
0.8
0.6
0.4
0.2
0
Absorbance
500
550
600
650
700
750
800
Wavelength (nm)
(1)
(2)
(3)
(5)
(4),(6)

Fig. 1.

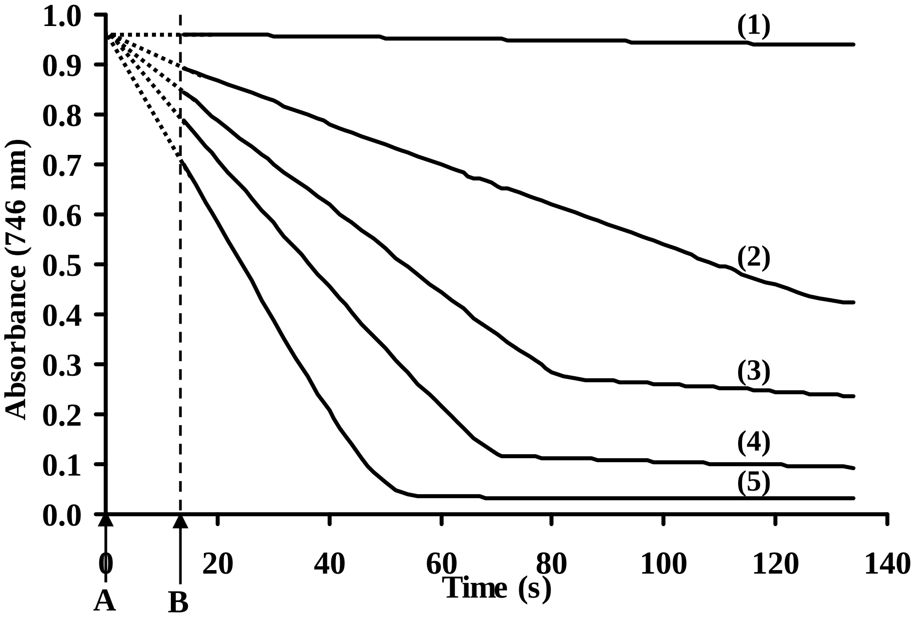
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Absorbance (746 nm)
(1)
(2)
(3)
(4)
(5)
0
20
40
60
80
100
120
140
Time (s)
A
B

Fig. 2.

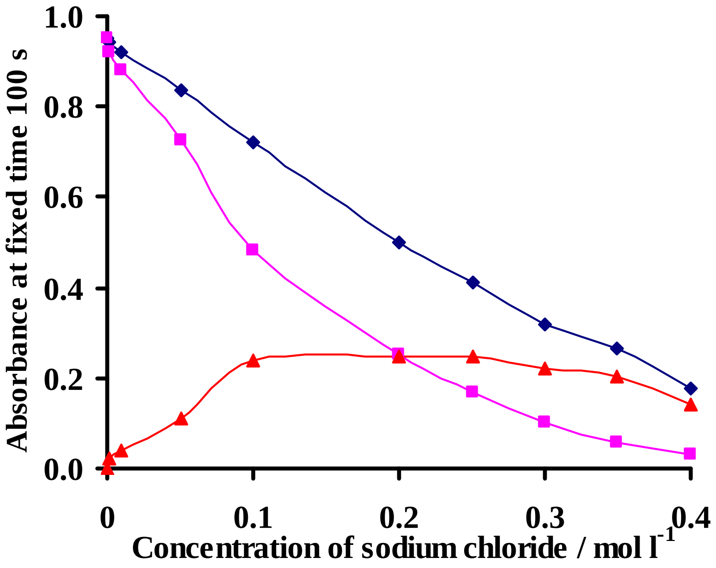
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance at fixed time 100 s
0
0.1
0.2
0.3
0.4
Concentration of sodium chloride / mol l-1

Fig. 3.

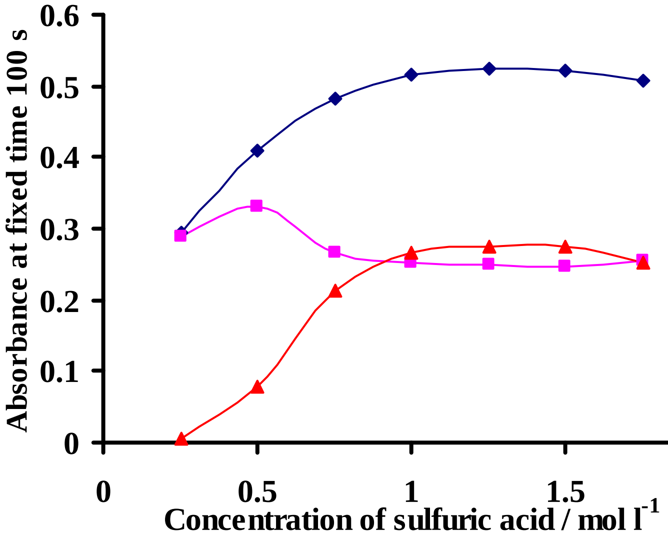
Absorbance at fixed time 100 s
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
Concentration of sulfuric acid / mol l^{-1}

Fig. 4.

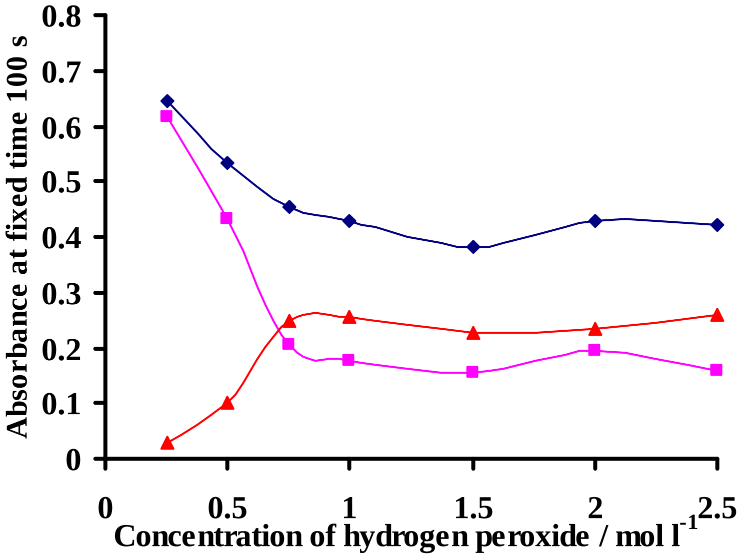
Absorbance at fixed time 100 s
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
Concentration of hydrogen peroxide / mol l^{-1}

Fig. 5.

Table 1

[MB] **(mol l^{-1})**	**Linear range** **(µg l^{-1})**	**Signal range** **($\Delta A_{15-115s}$, a.u.)**	**Standard equation**	**R^2**
$2x10^{-5}$	40 - 700	0.018 – 0.398	$\Delta A = 5.60x10^{-4}\ C_{Br-} + 4.5x10^{-3}$	0.998
$2.6x10^{-5}$	80 - 960	0.014 – 0.537	$\Delta A = 5.83x10^{-4}\ C_{Br-} - 19.0x10^{-3}$	0.998
$3.2x10^{-5}$	240 - 1400	0.097 – 0.784	$\Delta A = 5.73x10^{-4}\ C_{Br-} - 44.7x10^{-3}$	0.998

C_{Br-}: concentration of bromide, µg l^{-1}.

Table 2

Ions	**Tolerance molar ratio of ion to Br^-** [a]
Mn(II), Ni(II), Co(II), Cd(II), As(V), Al(III), Na^+, K^+, F^-, SO_4^{2-}, NO_3^-, ClO_3^-, ClO_4^-	500 [b]
Fe(III), Zn(II), Cr(III), Li^+, Mg^{2+}, Ca^{2+}, Cl^-	250
Cu(II)	100
Pb(II)	50
Mo(VI), V(V), EDTA	10
I^-	2
NO_2^-, ClO^-	0.75
Fe(II)	0.25

[a] A ±5% relative error of the $\Delta A_{15\text{-}115s}$ for 480 μg l^{-1} bromide was considered to be tolerable.

[b] Maximum concentrations of foreign ions tested.

Table 3

Sample No.	Added (mg l^{-1})	Found [a] (mg l^{-1})	Recovery (%)	Br^- content in sample (mg l^{-1})	
				Proposed method [b]	Titration [b]
1	0	2.39	97.3	59.8 ± 1.6	56.3 ± 0.8
	2.40	4.73			
2	0	2.44	99.2	61.0 ± 4.0	61.5 ± 1.7
	2.40	4.82			
3	0	2.93	100	73.3 ± 1.4	71.3 ± 0.4
	2.40	5.34			
4	0	2.33	106	58.3 ± 3.8	62.8 ± 0.5
	2.40	4.90			
5	0	2.21	95.4	55.3 ± 3.2	56.7 ± 0.9
	2.40	4.50			
6	0	2.53	96.4	63.2 ± 4.5	61.8 ± 0.3
	2.40	4.84			
7	0	2.68	98.5	67.1 ± 2.2	64.3 ± 0.8
	2.40	5.05			
8	0	2.46	95.2	61.4 ± 2.1	61.3 ± 0.7
	2.40	4.76			

[a] Dilution factor: 25 times

[b] Triplicate determination.