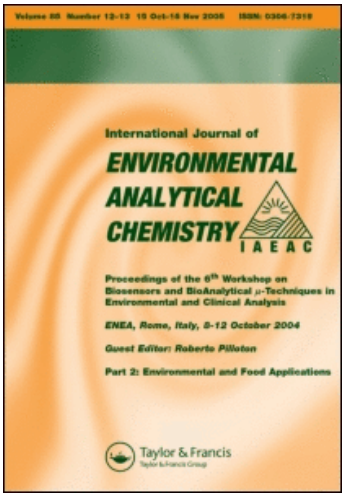

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Kinetic fluorimetric determination of trace hydrazine in environmental waters

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Two simple and sensitive methods for rapid determination of hydrazine in water are described, based on the inhibition effect of hydrazine on the reaction of oxyhalogen ion (XO_3^-) + halogen ion (X^-) with rhodamine B in an acid medium. It is found that the linear range and the detection limit for the determination of hydrazine are 7.88–78.8 ng mL^{-1} and 1.7 ng mL^{-1}, respectively, in the system of potassium chlorate in hydrochloric acid. They are 3.49–78.8 ng mL^{-1} and 0.81 ng mL^{-1}, respectively, in the system of potassium bromate + potassium bromide in sulphuric acid solutions. Recoveries are in the range of 94–104%. A comparison was made for the analytical characteristics of different methods, and a possible reaction mechanism was proposed.

Keywords: Kinetic fluorimetric method; Environmental water; Hydrazine

1. Introduction

Hydrazine (N_2H_4) has been widely used in industry and agriculture. It is an essential building block to synthesize chemical products, such as polymers, pesticides, pharmaceuticals, and others [1, 2]. Hydrazine reagents have also been used as derivative agents in environmental, food, and industry analysis. The toxicity of hydrazine is well known. Sulphuric hydrazine is regarded as the primary form to induce high incidence of excessively occurring lung gland cancer and gland cancer [3]. Moreover, hydrazine can damage internal organs, and teratogenic and mutagenic effects have been documented [4, 5]. Its threshold limit values in the water and air are seriously limited in many countries [6]. For example, in 1991, the American Conference of Governmental Industrial Hygienists (ACGIH) recommended the threshold limit values (TLVs) for hydrazine to be lowered from 100 to 10 μg L^{-1} in the air [7].

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In 2002, the Chinese National Environmental Quality Criterion recommended that the concentration of hydrazine hydrate should be set at $0.01\,mg\,L^{-1}$ in ground water [8]. Hence, it is important to develop simple and sensitive methods for the determination of hydrazine in these matrices.

Several methods for the determination of hydrazine have been reported. These mainly include spectrophotometric and flow injection-chemiluminescence methods. Spectro-photometric methods are mainly based on derivative reactions [9, 10], which have a higher selectivity but low sensitivity. Some kinetic spectrophotometric methods for the determination of hydrazine have also been reported [11–13]. One of these methods [13] is based on the inhibition effect of hydrazine, where a better sensitivity was obtained. Flow injection-chemiluminescence methods [14, 15] are simple and fast, but are less selective. Fluorescence methods based on the derivative reaction between hydrazine and aromatic aldehyde [16, 17] have been reported to have a high sensitivity, but they are time-consuming. To the best of our knowledge, there is no report in the literature on the determination of hydrazine by kinetic fluorimetry.

Recently, we found that under certain conditions, the oxyhalogen ion (XO_3^-) cannot quench the fluoresence intensity of rhodamine B (RhB) in an acid medium. Nevertheless, the fluoresence intensity of rhodamine B decreases greatly with the addition of proper halogen ion (X^-), and trace amounts of hydrazine can inhibit the decrease in fluorescence intensity of the system. Also, there is a linear relationship between the increment of fluorescence value of the system and the amounts of hydrazine added in a certain concentration range. Based on these observations, we wish to report, in this work, a new kinetic fluorimetric method for the determination of hydrazine. This method has been used to the determination of hydrazine in tap water, ground water, surface water, and spring water with satisfactory recoveries. At the same time, the possible reaction mechanism has been suggested.

2. Experimental

2.1 *Apparatus*

The following equipment was used: an FP-6200 spectrofluorometer (JASCO, Japan), 930A fluorophotometer (Shanghai, China), and 501 thermostat bath (Chongqing, China).

2.2 *Reagents*

All chemicals used in the experiments were analytical reagents, and double-distilled water was used throughout. A stock solution ($2.0\,mg\,mL^{-1}$) of hydrazine sulphate and $1.0 \times 10^{-3}\,mol\,L^{-1}$ stock solution of rhodamine B were prepared by dissolving given amounts of hydrazine and rhodamine B in a given volume of water. Their working solutions ($8\,\mu g\,mL^{-1}$ for hydrazine and $1.0 \times 10^{-4}\,mol\,L^{-1}$ for rhodamine B) were freshly prepared by appropriate dilution of the stock solution. Potassium chlorate solution: $0.2\,mol\,L^{-1}$; potassium bromate solution: $1.0 \times 10^{-3}\,mol\,L^{-1}$; potassium bromide solution: $3 \times 10^{-2}\,mol\,L^{-1}$; sulphuric acid solution: $2.0\,mol\,L^{-1}$; hydrochloric acid solution: $2.0\,mol\,L^{-1}$; sodium acetate solution: $3.0\,mol\,L^{-1}$.

2.3 *Procedure*

2.3.1 System potassium chlorate + rhodamine B in hydrochloric acid. One millilitre of 1.0×10^{-4} mol L^{-1} rhodamine B, 2.4 mL of 2.0 mol L^{-1} hydrochloric acid solution, an appropriate amount of hydrazine, and 3.0 mL of 0.1 mol L^{-1} potassium chlorate were successively added into a 25 mL volumetric flask one by one, diluted to the mark, and mixed well. After heating at 72°C for 7 min in a thermostat bath, the sample was cooled with running water to stop the reaction.

2.3.2 System potassium bromate + potassium bromide + rhodamine B in sulphuric acid. One millilitre of 1.0×10^{-4} mol L^{-1} of rhodamine B and 1.1 mL of 2.0 mol L^{-1} sulphuric acid were transferred to a 25 mL measuring flask, then 0.5 mL of 1.0×10^{-3} mol L^{-1} potassium bromate solution was added, followed by the addition of the correct amount of hydrazine. The solution was diluted to about 20 mL with water; then, 1.1 mL of 3×10^{-2} mol L^{-1} potassium bromide solution was added and diluted to the mark with double-distilled water and mixed well by shaking. The solution was heated at 40°C in the water bath for 6 min, then 1.0 mL of 3.0 mol L^{-1} sodium acetate solution was added to terminate the reaction.

Both the fluorescence value (F) and blank value (F_0) were determined at an excitation wavelength of 556.0 nm and an emission wavelength of 578.0 nm. The values of $\Delta F = F - F_0$ were then calculated.

3. Results and discussion

3.1 *Spectral characteristics*

Rhodamine B can emit strong fluorescence. Its excitation and emission spectra at different experimental conditions were scanned using FP-6200 spectrofluorometer.

3.1.1 System potassium chlorate + rhodamine B in hydrochloric acid. As shown in figure 1, hydrazine has little effect on the fluorescence intensity of the system RhB + $KClO_3$ (1–1′, 2–2′) and RhB + HCl (3–3′, 4–4′). However, the fluorescence intensity decreased greatly in the presence of both $KClO_3$ and HCl (6–6′). In the presence of trace hydrazine, the reaction speed was reduced significantly (5–5′). This confirms the inhibition effect of hydrazine, which is most obvious at an excitation wavelength of 556 nm and an emission wavelength of 578 nm. It is noted that there is a linear relationship between ΔF and the concentration of hydrazine in the system. Based on this observation, a new kinetic fluorimetric method has been established for the determination of trace hydrazine.

3.1.2 System potassium bromate + potassium bromide + rhodamine B in sulphuric acid. It can be seen from figure 2 that in a neutral medium, $KBrO_3 + KBr$ has almost no influence on the fluorescence intensity of rhodamine B (1–1′, 2–2′). However, in an acid medium, an influence of $KBrO_3$ on the fluorescence intensity of rhodamine B (3–3′, 4–4′) is observed. In the presence of $KBrO_3 + KBr$, the fluorescence intensity

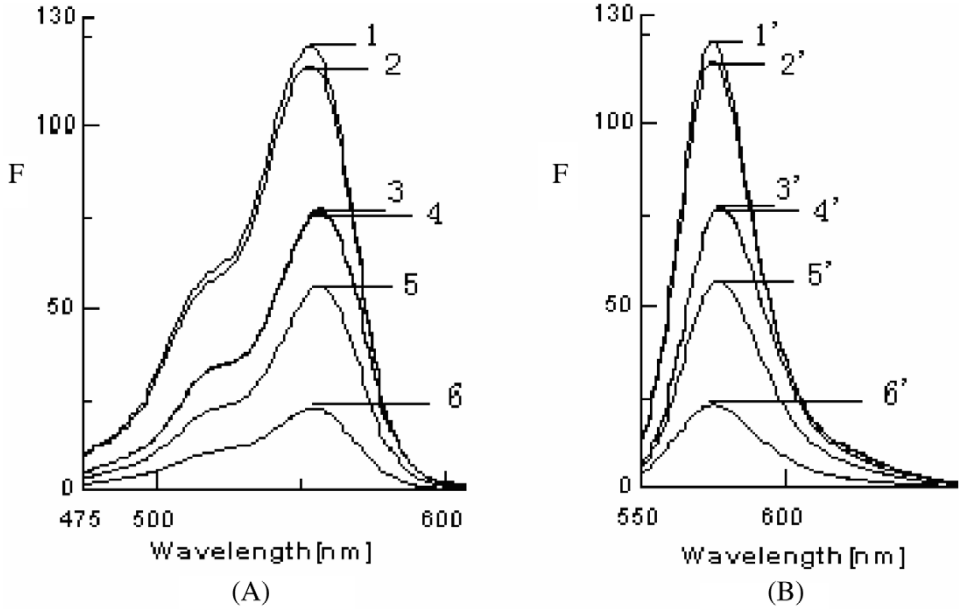

Figure 1. Excitation (A) and emission (B) spectra of RhB in the presence of different reagents: (1–1′), $RhB + KClO_3$; (2–2′), $RhB + N_2H_4 + KClO_3$; (3–3′), $RhB + HCl$; (4–4′), $RhB + N_2H_4 + HCl$; (5–5′), $RhB + HCl + N_2H_4 + KClO_3$; (6–6′) $RhB + HCl + KClO_3$. RhB, 4.0×10^{-6} mol L^{-1}; HCl, 0.192 mol L^{-1}; $KClO_3$, 1.2×10^{-2} mol L^{-1}; N_2H_4, 47.3 ng mL^{-1}; temperature: 72°C; time: 7 min.

of rhodamine B was greatly reduced (6–6′) in acid solutions. On the other hand, trace hydrazine significantly enhances the fluorescence intensity of $KBrO_3 + KBr$ + rhodamine B in sulphuric acid (5–5′), which shows the inhibition effect of hydrazine on the reaction. In addition, there is a linear relationship between ΔF and the concentration of hydrazine. This fact forms the basis for a new kinetic fluorimetric determination of trace hydrazine.

3.2 *Optimized conditions for the determination*

To obtain an optimized analytical system, various experimental parameters including reagent concentration, reaction temperature, and time were investigated (with the hydrazine concentration being 47.3 ng mL^{-1} for the system of $KClO_3 + Cl^- + RhB$ and 39.36 ng mL^{-1} for the system of $KBrO_3 + Br^- + RhB$ under all conditions). The operating conditions were optimized by a univariate approach, and the results are shown in table 1 for the system of $KClO_3 + Cl^- + RhB$ and in table 2 for the system of $KBrO_3 + Br^- + RhB$.

Under optimized conditions, the kinetic analysis for the system $KClO_3 + Cl^- + RhB$ indicates that there is a linear relationship between ΔF and the reaction time in the range of 3–7 min (see figure 3). The regression equation is $\Delta F = -10.8 + 5.60t$ (min), with a correlation coefficient of 0.998. Therefore, the apparent reaction rate constant for RhB should be $\partial \Delta F / \partial t = 5.60\,\text{min}^{-1} = 9.33 \times 10^{-2}\,\text{s}^{-1}$. Thermodynamic analysis indicates that $\ln(\Delta F)$ increases linearly with the reciprocal of the thermodynamic

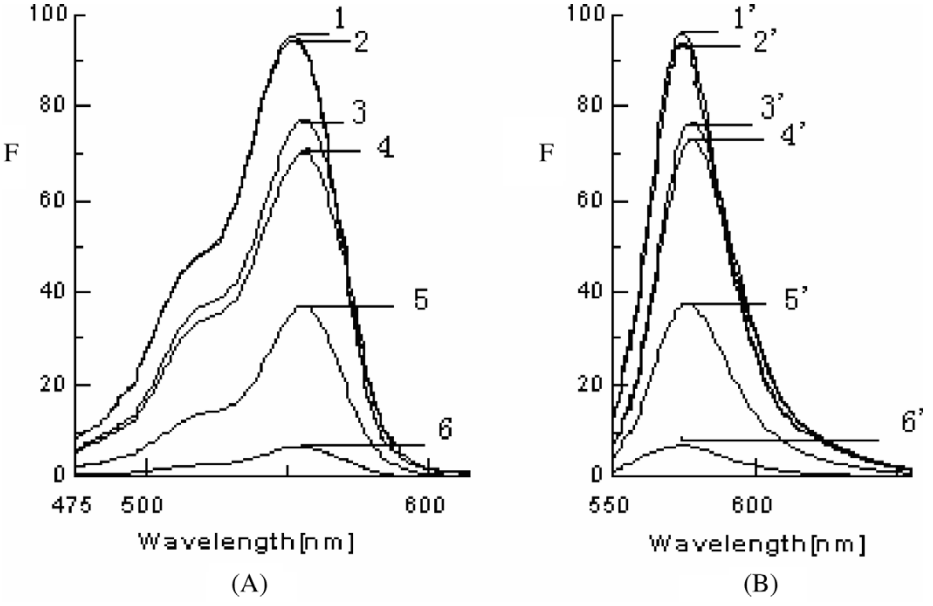

Figure 2. Excitation (A) and emission (B) spectra of RhB in the presence of different reagents: (1–1′), $RhB + KBr + KBrO_3$; (2–2′), $RhB + KBrO_3$; (3–3′), $RhB + H_2SO_4 + KBrO_3$; (4–4′), $RhB + H_2SO_4$; (5–5′), $RhB + H_2SO_4 + KBrO_3 + N_2H_4 + KBr$; (6–6′), $RhB + H_2SO_4 + KBrO_3 + KBr$. RhB: 4.0×10^{-6} mol L^{-1}; H_2SO_4: 0.088 mol L^{-1}; KBr: 1.32×10^{-4} mol L^{-1}; N_2H_4: 39.36 ng mL^{-1}; $KBrO_3$: 2.0×10^{-5} mol L^{-1}; time: 6 min; temperature: 40°C.

Table 1. Optimized experimental conditions for the determination of trace hydrazine in the $KClO_3 + Cl^- + RhB$ system.

Parameters of study	Range of study	Optimum conditions
Hydrochloric acid	0.12–0.24 mol L^{-1}	0.192 mol L^{-1}
Potassium chlorate	0.60×10^{-2}–1.6×10^{-2} mol L^{-1}	1.2×10^{-2} mol L^{-1}
Rhodamine B	2.0×10^{-6}–6.0×10^{-6} mol L^{-1}	4.0×10^{-6} mol L^{-1}
Temperature	50–80°C	72°C
Time	3–9 min	7 min

Table 2. Optimized experimental conditions for the determination of trace hydrazine in the $KBrO_3 + Br^- + RhB$ system.

Parameters of study	Range of study	Optimum conditions
Sulphuric acid	0.040–0.12 mol L^{-1}	0.088 mol L^{-1}
Potassium bromate	0.40×10^{-5}–4.0×10^{-5} mol L^{-1}	2.0×10^{-5} mol L^{-1}
Potassium bromide	0.36×10^{-4}–1.8×10^{-4} mol L^{-1}	1.32×10^{-4} mol L^{-1}
Rhodamine B	2.0×10^{-6}–6.0×10^{-6} mol L^{-1}	4.0×10^{-6} mol L^{-1}
Temperature	12–50°C	40°C
Time	3–8 min	6 min

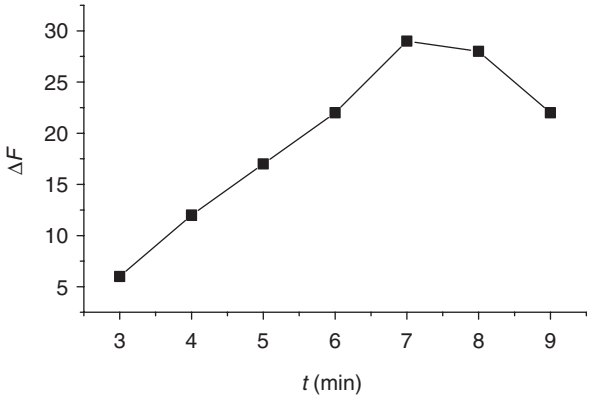

Figure 3. Fluorescence changes with the reaction time for the system $KClO_3 + Cl^- + RhB$. Conditions: RhB, 4.0×10^{-6} mol L^{-1}; HCl, 0.192 mol L^{-1}; $KClO_3$, 1.2×10^{-2} mol L^{-1}; N_2H_4, 47.3 ng mL^{-1}; temperature: 72°C.

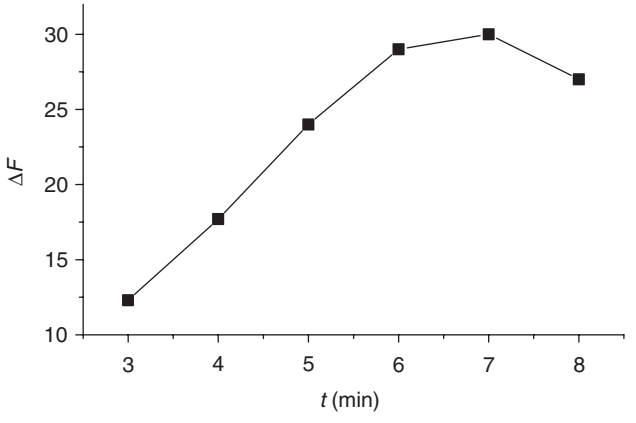

Figure 4. Fluorescence changes with the reaction time for the system of $KBrO_3 + Br^- + RhB$. Conditions: RhB, 4.0×10^{-6} mol L^{-1}; H_2SO_4, 0.088 mol L^{-1}; KBr, 1.32×10^{-4} mol L^{-1}; N_2H_4, 39.36 ng mL^{-1}; $KBrO_3$, 2.0×10^{-5} mol L^{-1}; temperature: 40°C.

temperature of the reaction ($1/T$) in the range of 50–80°C. The regression equation is $\ln(\Delta F) = 44.95 - 1.432 \times 10^4/T$, with a correlation coefficient of 0.994. The apparent reaction activation energy $E = 119.1$ kJ mol^{-1}.

Similarly, kinetic and thermodynamic analyses have been carried out for the system of $KBrO_3 + Br^- + RhB$. As shown in figure 4, the linear relationship between ΔF and the reaction time is in the range of 3–6 min. The linear regression equation is $\Delta F = -5.02 + 5.76t$ (min), with a correlation coefficient of 0.9987. From this equation, the apparent reaction rate constant for RhB was calculated to be 9.60×10^{-2} s^{-1}. In the range of 12–40°C, a linear regression equation between $\ln(\Delta F)$ and $1/T$ is found to be $\ln(\Delta F) = 14.15 - 3.349 \times 10^3/T$. The correlation coefficient is 0.998, and the reaction activation energy $E = 27.8$ kJ mol^{-1}.

3.3 *Analytical characteristics*

3.3.1 System potassium chlorate + rhodamine B in hydrochloric acid. A linear calibration graph of fluorescence intensity of the system *versus* hydrazine concentration was obtained under the optimized experimental conditions as shown in table 1, covering the concentration range of 7.88–78.8 ng mL^{-1} for hydrazine. The regression equation is $\Delta F = 0.083 + 0.472C$ (ng mL^{-1}) with a correlation coefficient of 0.9996. The detection limit (C_L) can be calculated by $C_L = 3S_b/S$, where S_b and S are the standard derivation of the reagent blank ($n = 11$) and the slope of the calibration graph, respectively. Thus, the calculated detection limit is 1.7 ng mL^{-1}, and the relative standard derivations are 1.1% and 0.9%, respectively, for 11 determinations of 23.64 ng mL^{-1} and 47.28 ng mL^{-1} of hydrazine.

3.3.2 System potassium bromate + potassium bromide + rhodamine B in sulphuric acid. Based on the optimized conditions shown in table 2, a linear relationship was found between ΔF and the concentration of hydrazine in the range of 3.94–78.8 ng mL^{-1}. The regression equation is $\Delta F = 5.85 + 0.542C$ (ng mL^{-1}) with a correlation coefficient of 0.9993. The detection limit is 0.81 ng mL^{-1}, and the relative standard derivation is 4.1% and 0.84% for 11 determinations of 15.76 ng mL^{-1} and 63.06 ng mL^{-1} of hydrazine, respectively.

Furthermore, it is noted that fluorescence intensity of the system $KClO_3 + Cl^- + RhB$ can remain constant within 40 min at room temperature. The system of $KBrO_3 + Br^- + RhB$ is not stable; its fluorescence intensity remains constant only for 20 min with the addition of sodium acetate solution.

3.4 *Interference of matrix compounds*

In order to apply these methods to determine hydrazine in environmental water samples, the influence of common ions and organic compounds for the determination of 6.1×10^{-5} mol L^{-1} hydrazine was investigated when the permitted relative deviation from the F value is ±5%. The results are summarized in tables 3 and 4, respectively.

It is shown that most of the investigated cations did not interfere with determination, whereas some investigated anions interfered in the determination of hydrazine. However, their interfering effect can be completely removed by using an anion-exchange resin [13].

3.5 *Sample analysis*

The system of $KClO_3 + Cl^- + RhB$ was used to determine hydrazine in tap water, ground water, and surface water. The system of $KBrO_3 + Br^- + RhB$ was used to determine the hydrazine in spring water, ground water, and surface water. No hydrazine was detected. The possibility of using these methods for the analysis of these samples was tested by determining the recovery of known amounts of hydrazine added to the samples. The results are shown in tables 5 and 6. It can be seen that the recoveries are close to 100%, indicating that there is no serious interference in such water samples.

Table 3. Influence of matrix compounds on the system of $KClO_3 + HCl + RhB$ for the determination of hydrazine.

Matrix compounds	Ratio[a]	Matrix compounds	Ratio[a]
NH_4^+, F^-	1.0×10^4	Cr^{3+}	416
Na^+, K^+, Ca^{2+}	9.0×10^3	Fe^{3+}, CO_3^{2-}	333
Al^{3+}, Cu^{2+}	6.7×10^3	PO_4^{3-}, phenol	180
NO_3^-	6.0×10^3	Phenylhydrazine	80
Pb^{2+}, Hg^{2+}, Cd^{2+}, Mn^{2+}	3.0×10^3	As(III)	4
Zn^{2+}, Mg^{2+}	1.5×10^3	Cr(VI)	0.7
Ni^{2+}	1.1×10^3	NO_2^-	0.1

[a]'Ratio' denotes the ratio of the concentration between the interfering substance and hydrazine, i.e. [ion]/[N_2H_4].

Table 4. Influence of matrix compounds on the system $KBrO_3 + Br^- + RhB + H_2SO_4$ for the determination of hydrazine.

Matrix compounds	Ratio[a]	Matrix compounds	Ratio[a]
NH_4^+, F^-	1.0×10^4	Pb^{2+}, Fe^{3+}	330
Cu^{2+}, Ca^{2+}	6.7×10^3	Ni^{2+}	300
Hg^{2+}	3.0×10^3	Phenol	110
Mn^{2+}	2.3×10^3	Phenylhydrazine	80
Na^+, K^+, Cl^-, Co^{2+}, CO_3^{2-}	1.7×10^3	PO_4^{3-}	61
Mg^{2+}, Cd^{2+}, Cr^{3+}	1.3×10^3	As(III)	2
Zn^{2+}	1.1×10^3	NO_2^-	0.7
NO_3^-	660	Cr(VI)	0.4
Cu(I)	500		

[a]'Ratio' denotes the ratio of the concentration between the interfering substance and hydrazine, i.e. [ion]/[N_2H_4].

Table 5. Determination of hydrazine in water samples ($n = 4$) by the system of $KClO_3 + HCl + RhB$.

Samples	Hydrazine added ($ng\,mL^{-1}$)	Hydrazine found[a] ($ng\,mL^{-1}$)	Recovery (%)	RSD (%)
Surface water	15.8	15.7	99	1.80
	31.6	31.1	98	0.95
Ground water	23.7	24.2	102	1.09
	47.4	46.4	98	0.84
Tap water	39.5	41.1	104	1.77
	63.2	63.2	100	1.40

[a]Average of four determinations.

Table 6. Determination of hydrazine in water samples ($n = 4$) by the system of $KBrO_3 + Br^- + RhB + H_2SO_4$.

Samples	Hydrazine added ($ng\,mL^{-1}$)	Hydrazine found[a] ($ng\,mL^{-1}$)	Recovery (%)	RSD (%)
Surface water	7.88	7.85	99	1.83
	23.64	24.50	104	1.67
Ground water	31.52	31.48	99	1.48
	63.04	61.85	98	1.08
Tap water	15.76	15.16	96	1.87
	47.28	44.39	94	2.04

[a]Average of four determinations.

3.6 *Possible reaction mechanism*

In neutral medium, no reaction between oxyhalogen ion and halogen ion can be appreciated, at least during a certain period of time. The reaction is suggested according to the following stoichiometry in acid medium:

$$XO_3^- + 5X^- + 6H^+ = 3X_2 + 3H_2O. \quad (1)$$

This reaction is slow and the rate law below is obeyed:

$$\frac{d[X_2]}{dt} = K_x[XO_3^-]^a[X^-]^b[H^+]^c,$$

where the superscripts a, b, and c denote the reaction progression of XO_3^-, X^-, and H^+, respectively.

In acid medium, the fluorescence intensity of rhodamine B cannot be quenched only by the oxyhalogen ion under certain conditions. However, with the addition of the correct amount of halogen ion to the solution, the fluorescence intensity was quenched considerably. According to data reported in the literature [13, 18–20], the possible reaction mechanism was suggested as follows:

1. The products (X_2) react with rhodamine B. A low-fluorescence substance could be produced because of the effect of weight atom [18–20]. Another possibility is that the structure of rhodamine B was broken by the products [13]. Both of these reactions caused the decrease in fluoresence intensity in the systems.
2. The presence of hydrazine in the medium slows down the reaction, and possibly follows the stoichiometry below [21–24]:

$$2X_2 + (N_2H_6)^{2+} = N_2 + 6H^+ + 4X^-, \quad (2)$$

which is fairly fast in the absence of hydrazine or when the medium is very acidic [22].

3.7 *Comparison of analytical characteristics*

According to the experimental results, the following comparison for the analytical characteristics was made between the two methods:

1. From the tables 1 and 2, it can be seen that in the system potassium bromate + potassium bromide + rhodamine B in sulphuric acid, less amounts of reagents, except for RhB, a lower reaction temperature and shorter reaction time are used before the kinetic equilibrium is reached. From the thermodynamic analysis, it is known that the reaction activation energy of the system potassium chlorate + rhodamine B in hydrochloric acid is 119.1 kJ mol^{-1}, but that of the system potassium bromate + potassium bromide + rhodamine B in sulphuric acid is smaller (27.8 kJ mol^{-1}). According to the formula [25] $k = A\exp(-E_a/RT)$, the reaction activation energy (E_a) has a considerable influence on the reaction rate.
2. From the calibration graph, it can be seen that the system potassium bromate + potassium bromide + rhodamine B in sulphuric acid has a

greater slope and higher ΔF values than the system of potassium chlorate + rhodamine B in hydrochloric acid.

3. Compared with the system of potassium bromate + potassium bromide + rhodamine B in sulphuric acid, the stability of the system potassium chlorate + rhodamine B in hydrochloric acid is better. At room temperature, the system of potassium chlorate + rhodamine B in hydrochloric acid can be stable for 40 min, but the system of potassium bromate + potassium bromide + rhodamine B in sulphuric acid only remains stable for 20 min after the addition of sodium acetate.
4. The reaction of the system of potassium chlorate + rhodamine B in hydrochloric acid can be controlled by the reaction temperature (react at high temperature, and stop at low temperature). For the system potassium bromate + potassium bromide + rhodamine B in sulphuric acid, the reaction takes place at room temperature because of the smaller reaction activation energy. The reaction is not easy to control, but we can control it by changing the acidity of the system (adding sodium acetate into the system to end the reaction).
5. Comparison of interferences: from the experimental results shown in tables 3 and 4, it can be seen that a different system has a different main interference substance. Pb^{2+}, Ni^{2+}, PO_4^{3-}, and As(III) have less influence on the determination of hydrazine when the system potassium chlorate + rhodamine B in hydrochloric acid is applied. However, CO_3^{2-}, Cr^{3+}, acetaldehyde, and NO_2^- have less influence on the determination of hydrazine when the system potassium bromate + potassium bromide + rhodamine B in sulphuric acid is used.

4. Conclusion

In summary, the system $KBrO_3 + Br^- + RhB + H_2SO_4$ takes a short time to achieve kinetic equilibrium, saves analysis time, and has a better sensitivity, but the reaction in this system is not easy to control, and the stability and repetition are not good. The system $KClO_3 + HCl + RhB$ has a good stability and repetition, and the reaction in the system can be controlled easily by changing the temperature, but it takes a longer time to reach kinetic equilibrium, and the sensitivity is lower. On the other hand, the interference of the two systems has several differences. Thus, according to the different analysis purposes and different components of samples, the appropriate method can be chosen appropriately for the determination of hydrazine.

Acknowledgements

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