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A new induction period based reaction rate method for determination trace amounts of phenylhydrazine in water samples

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ABSTRACT

A simple, selective, and sensitive kinetic spectrophotometric method is described for the determination of trace amounts of phenylhydrazine, which is based on its inhibition effect on the reaction between meta cresol purple (MCP) and periodate in the presence of bromide ions. The reaction was monitored spectrophotometrically by measuring the change in absorbance of MCP at 525 nm. The calibration graph was linear in the range of 1.0–10.0 μM. The detection limit (3σ) was 0.020 μM. The relative standard deviations for 10 replicate measurements of 3.0, 5.0 and 7.0 μM of phenylhydrazine were 2.0%, 1.4%, and 0.90%, respectively. The potential interfering substances were studied in the presence of phenylhydrazine. The proposed method was applied to the analysis of water samples.

1. Introduction

Phenylhydrazine, hydrazine, and their derivatives are used worldwide mainly as a chemical intermediate in the pharmaceutical, agrochemical, and chemical industries [1]. There is only limited information available on the toxicokinetics of phenylhydrazine. Phenylhydrazine is readily absorbed by the inhalation, oral, and dermal routes of exposure.

Adverse health effects on people living near hazardous waste sites caused by hydrazine and its derivatives have been described [2]. Contact with phenylhydrazine irritates skin and eyes [3]. In addition, some studies have suggested that exposure of laboratory animals to phenylhydrazine, hydrazine and their derivatives produces toxic effects [4]. Some data suggest that these substances are also carcinogenic [5]. Thus there has been an increasing trend for highly sensitive methods for determination of phenylhydrazine in various samples such as water and industrial or environmental samples. Different classical and instrumental methods have been reported for determination of phenylhydrazine in various samples. These include spectrophotometry [6–10], titrimetry [11], and gas chromatography [12]. These methods either lack sufficient sensitivity or are time consuming.

Due to their high sensitivity, kinetic spectrophotometric methods are of interest for trace determination of some species. A few kinetic procedures have been reported for determination of phenylhydrazine. Some of these procedures include determination of trace quantities of phenylhydrazine on the basis of its inhibition effect on the decolorization of methyl orange and Victoria Blue 4-R by bromate [13,14], the simultaneous determination of hydrazine and phenylhydrazine based on their reactions with *p*-(demithylamino) benzaldehyde (DAB) [15], and the simultaneous determination of hydrazine and phenylhydrazine using the H-point standard addition method (HPSAM) [16].

MCP has been used as an indicator for the catalytic determination of bromide [17], nitrite, nitrate [18], and thiocyanate [19]. However, there has been no report on MCP as an indicator for the kinetic determination of phenylhydrazine. In this paper we report the development of a kinetic spectrophotomtric method for determination of phenylhydrazine on the basis of its inhibition effect on the catalytic oxidation of MCP by periodate in hydrochloric acid media.

2. Experimental

2.1. Reagents and solutions

Analytical-reagent grade and doubly distilled water were used. A 5.0×10^{-3} M stock standard solution of phenylhydrazine was prepared by dissolving 0.0723 g of phenylhydrazinium chloride (Merck) in distilled water and diluting it to 100 mL. Working solutions were prepared by appropriately diluting the stock standard solution. A 100 mL–0.022 M potassium bromide solution was

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prepared by dissolving 0.2618 g of KBr (Merck) in distilled water and diluting it to mark in a 100 mL volumetric flask. A 2.6×10^{-4} M MCP solution was directly prepared by dissolving 0.0100 g of MCP (Merck) in 20 mL ethanol and diluting it with distilled water in a 100 mL volumetric flask. A 100 mL periodate ion solution (0.050 M) was prepared by dissolving 0.4278 g of $NaIO_4$ (Merck) in water. Hydrochloric acid solution (1.0 M) was prepared by diluting a known volume of its concentrated solution (Merck) and was standardized against sodium carbonate.

2.2. Apparatus

A Shimadzu UV–vis spectrophotometer model UV-160 with a 1.0 cm optical path quartz cell was used for the spectrophotometric measurements. A water bath thermostat (n-BIOTEK, INC, model NB-301) was employed to control the reaction temperature. A stopwatch was used for recording the reaction times.

2.3. Recommended procedure

The reagent solutions and water were kept at 20.0 °C in the thermostatic water bath for 30 min. A suitable aliquot of standard phenylhydrazine or sample solution with the concentration range of 1.0–10.0 μM was pipetted into a 10 mL volumetric flask, and then 1.0 mL of 1.0 M hydrochloric acid, 1.0 mL of 2.6×10^{-4} M MCP, and 1.0 mL of 0.022 M potassium bromide solutions were sequentially added. After dilution to the mark and mixing, exactly 2.0 mL of this reaction mixture was transferred into the spectrophotometer cell and then 100 μl of 0.050 M $NaIO_4$ was added to the cell using a calibrated micropipette. The chronometer was turned on immediately after addition of the last drop of the periodate solution to the cell. After mixing, the cell was placed inside the spectrophotometer and the absorbance changes were recorded at 525 nm against water for the first 10–200 s from the initiation of the reaction. Absorbance changes of the blank solution were recorded as described above, but in the absence of phenylhydrazine. A calibration graph was constructed by plotting the reaction induction period (t_{ip}) versus the phenylhydrazine concentration in a series of working standard solutions.

3. Results and discussion

Preliminary experiments show that the oxidation reaction of MCP with periodate in acidic media is very slow. On the other hand, the oxidation reaction is fast in the presence of bromide as a catalyst; the absorbance of the dye decreases rapidly at 525 nm (Fig. 1(a)). The catalytic cycle of this reaction can be shown as follows:

$$IO_4^- + 7Br^- + 8H^+ \rightleftarrows 4Br_2 + 4H_2O \quad (1)$$

$$4Br_2 + MCP_{(colored)} \rightleftarrows 8Br^- + MCP_{(colorless)} \quad (2)$$

It was found that phenylhydrazine has an inhibition effect on the catalytic reaction due to possible perturbation in the catalytic cycle via reaction by Br_2, periodate, and/or other reaction intermediates. Fig. 1 shows the absorption spectra for the reaction system, which were taken sequentially with scan time intervals of 15 s (a-h). As shown in Fig. 1(b), in the presence of phenylhydrazine, reaction rate decreases and an induction period appears. Fig. 2 shows that an increase in the phenylhydrazine concentration causes an increase in the induction period of the reaction due to the increasing inhibition ability of phenylhydrazine with concentration. A graph of the induction period versus phenylhydrazine concentration was linear over a certain range of phenylhydrazine concentration. Therefore, the induction period, evaluated from the absorption-time curves

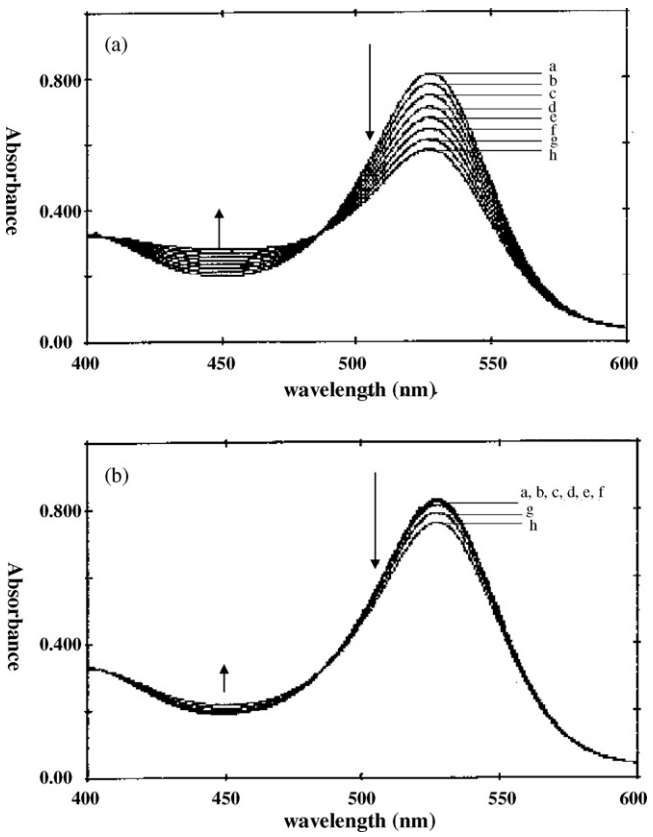

Fig. 1. Absorption spectra of reaction system. Conditions: HCl, 0.10 M; MCP, 2.6×10^{-5} M; $NaIO_4$, 2.5×10^{-3} M; KBr, 2.2×10^{-3} M and temperature of 20.0 °C with scan time intervals of 15 s: (a) in the absence of phenylhydrazine and (b) in the presence of 10.0 μM phenylhydrazine.

of the reaction mixture at λ_{max} = 525 nm was used as an analytical signal in the measurement of phenylhydrazine.

3.1. Optimization of variables

In order to maximize the sensitivity, the influences of various experimental parameters were studied in order to obtain an optimized system. In the one-at-a-time optimization procedure, the absorbance changes for the uninhibited reaction (without phenylhydrazine) and the inhibited reaction (with phenylhydrazine) at

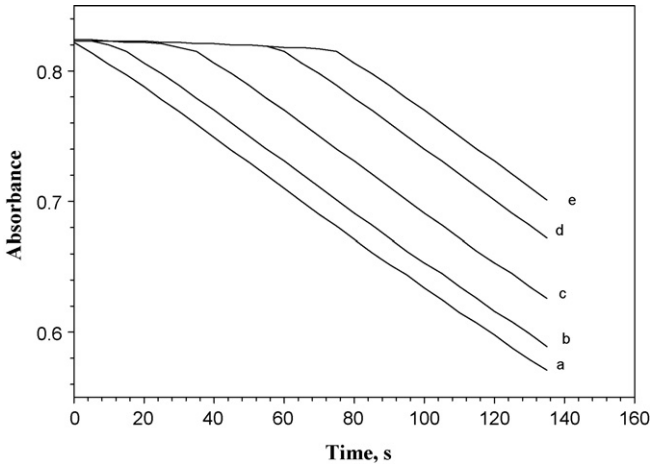

Fig. 2. Absorbance change profile. Conditions: same as Fig. 1 with phenylhydrazine concentrations of (a) 0.00, (b) 2.0, (c) 4.0, (d) 6.0, and (e) 8.0 μM.

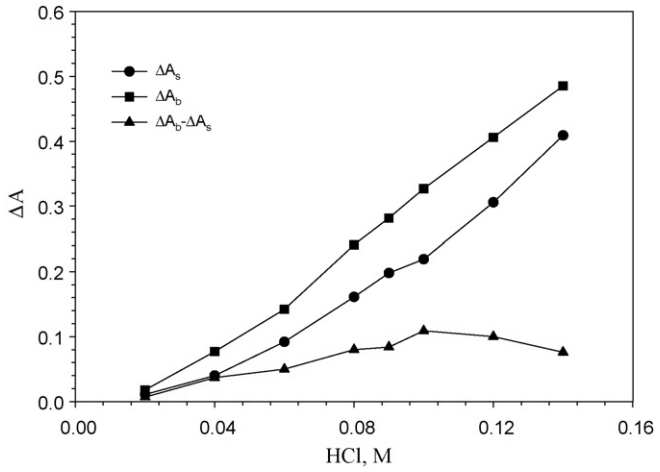

Fig. 3. Effect of HCl concentration. Conditions: MCP, 2.6×10^{-5} M; $NaIO_4$, 5.0×10^{-3} M; KBr, 2.00×10^{-3} M; phenylhydrazine, 10.0 μM and temperature of 20.0 °C.

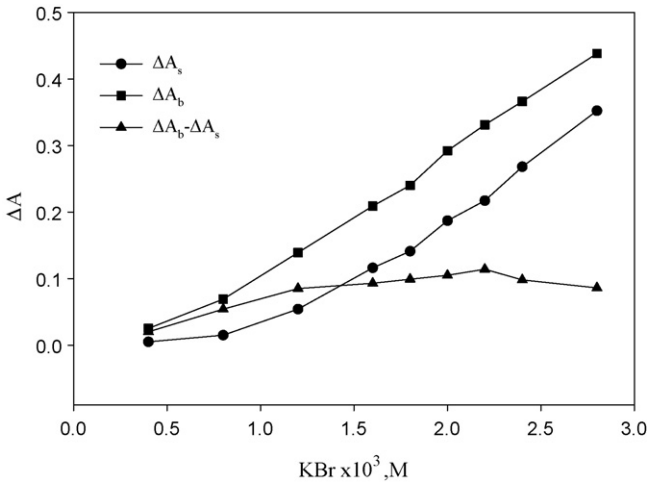

Fig. 4. Effect of potassium bromide concentration. Conditions: HCl, 0.10 M; MCP, 2.6×10^{-5} M; $NaIO_4$, 5.0×10^{-3} M; phenylhydrazine, 10.0 μM and temperature of 20.0 °C.

a fixed time of 10–100 s were measured and labeled as ΔA_b and ΔA_s, respectively. The difference between absorbance changes of the uninhibited and inhibited reactions ($\Delta A = \Delta A_b - \Delta A_s$) was used as an analytical signal.

Preliminary investigation showed that the inhibition effect could be observed in acidic media and thus some efforts were made for choosing the best type of acid as the reaction medium. Sulfuric, hydrochloric, and nitric acid with the same concentration of 0.15 M were tested. The obtained results show that hydrochloric acid has a better sensitivity. The low sensitivity in the presence of nitric acid is due to the oxidizing nature of nitric acid, which decolorizes the MCP as the indicator reagent. A sulfuric acid medium shows a lower sensitivity compared with the hydrochloric acid medium. This can be attributed to the fact that sulfuric acid produces a higher proton concentration than hydrochloric acid with the same concentration of 0.15 M. Thus hydrochloric acid was selected as the best reaction medium.

The effect of the hydrochloric acid concentration was studied in the range of 0.020–0.14 M. The results show that an increase in the hydrochloric acid concentration caused a decrease in the induction period and an increase in both absorbance changes for the uninhibited (ΔA_b) and inhibited (ΔA_s) reactions. As shown in Fig. 3, the difference between the absorbance changes for the uninhibited and inhibited reactions has a maximum value at 0.10 M. Therefore, the concentration of 0.10 M was selected as the optimum concentration for hydrochloric acid.

The dependence of sensitivity of the method on the potassium bromide concentration was studied in the range of 4.0×10^{-4} to 2.8×10^{-3} M bromide under the optimum concentration of hydrochloric acid and sodium periodate. Fig. 4 shows that both ΔA_b and ΔA_s increase with increasing KBr concentration, and their difference ($\Delta A_b - \Delta A_s$) reaches a maximum value at 2.2×10^{-3} M. The increases in ΔA_b and ΔA_s with increasing KBr concentration could be attributed to the catalytic nature of the reaction in the presence of bromide ion as the catalyst. According to the results, the KBr concentration of 2.2×10^{-3} M was chosen as the best concentration for further studies.

Effect of the sodium periodate concentration on the analytical signal (sensitivity) in the range of 1.0×10^{-3} to 5.0×10^{-3} M is shown in Fig. 5. This result shows that with increase in the periodate concentration, the absorbance changes for the uninhibited (ΔA_b) and inhibited (ΔA_s) reactions increase due to the increasing oxidation ability of periodate with concentration; also the analytical signal increases and reaches a maximum value at 2.5×10^{-3} M, and above this, decreases slightly. Thus the concentration of 2.5×10^{-3} M was selected as the optimum concentration for periodate.

The effect of MCP concentration on the sensitivity in the range of 5.2×10^{-6} to 3.7×10^{-5} M is shown in Fig. 6. The sensitivity increased as the concentration of MCP increased from 5.2×10^{-6} to 2.1×10^{-5} M, and then it remained constant. Therefore, the concentration of 2.6×10^{-5} M for MCP was chosen for the recommended procedure.

The effect of temperature on the rates of the catalyzed and inhibited reactions was studied in the range of 5.0–30.0 °C at the optimum reagent concentration. For each experiment, at a desired temperature, the reagent solutions and water were kept at the selected temperature in the thermostatic water bath for 30 min. The results in Fig. 7 show that 20.0 °C is the best temperature because at a higher temperature the inhibition effect of phenylhydrazine decreased. Therefore, 20.0 °C was used throughout the study.

The influence of ionic strength on the reaction induction period (the analytical signal used in the construction of the calibration curve) under the optimum condition was studied using sodium nitrate (1.0 M). The results showed that the induction period was independent from the ionic strength up to 0.2 M of sodium nitrate (maximum value tested).

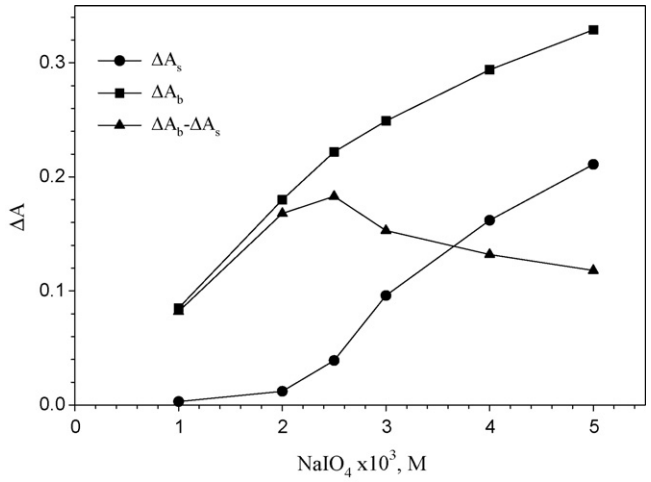

Fig. 5. Effect of sodium periodate concentration. Conditions: HCl, 0.10 M; MCP, 2.6×10^{-5} M; KBr, 2.2×10^{-3} M; phenylhydrazine, 10.0 μM and temperature of 20.0 °C.

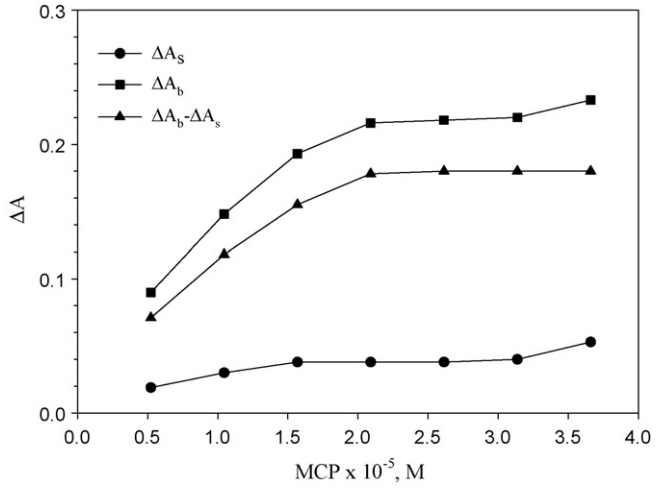

Fig. 6. Effect of MCP concentration. Conditions: HCl, 0.10 M; KBr, 2.2×10^{-3} M; $NaIO_4$, 2.5×10^{-3} M; phenylhydrazine, 10.0 μM and temperature of 20.0 °C.

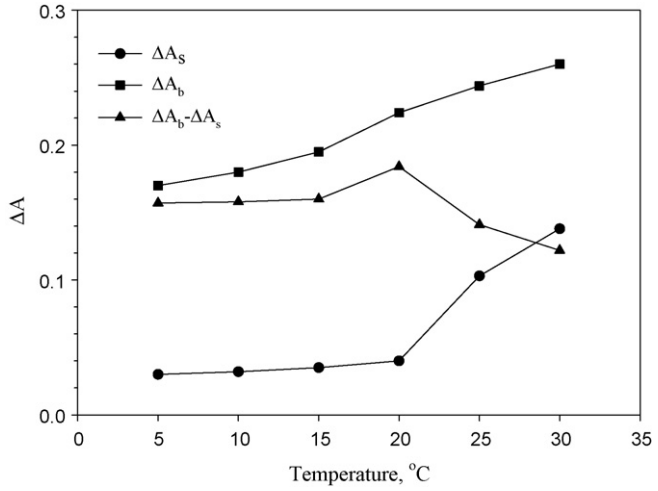

Fig. 7. Effect of temperature. Conditions: HCl, 0.10 M; MCP, 2.6×10^{-5} M; $NaIO_4$, 2.5×10^{-3} M and KBr, 2.2×10^{-3} M.

3.2. Calibration graph, detection limit, reproducibility, and accuracy

Once the optimum parameters for the analysis are chosen, a calibration could be made. As shown in Fig. 2, an increase in the phenylhydrazine concentration causes an increase in the induction period of the reaction, and a linear graph of the induction period versus phenylhydrazine concentration could be constructed over a certain range of phenylhydrazine concentration. A calibration graph for the determination of phenylhydrazine was prepared under the optimum conditions of 0.10 M hydrochloric acid, 2.5×10^{-3} M sodium periodate, 2.2×10^{-3} M potassium bromide, and 2.6×10^{-5} M MCP at 20.0 °C. The equation of the calibration graph for 1.0 to 10.0 μM of phenylhydrazine was $t_{ip} = 8.99\,C_{phenylhydrazine} + 0.227$, with $r = 0.9992$ ($n = 10$), where $C_{phenylhydrazine}$ is the phenylhydrazine concentration in μM and t_{ip} is the reaction induction period in seconds. The induction period was measured mathematically from the regression equations of the linear parts of the absorption-time graphs. The regression equation for the first linear part of the graph is $A = a_1 + m_1 t$, and for the second linear part is $A = a_2 + m_2 t$. By equating these equations, the induction period was calculated as:

$$t_{ip} = \frac{a_2 - a_1}{m_1 - m_2} \quad (3)$$

The experimental 3σ limit of detection was 20.0 nM. In order to examine the accuracy and precision of the method, standard solutions of 3.0, 5.0, and 7.0 μM of phenylhydrazine were analyzed using the recommended procedure. Ten replicate determinations of each concentration gave relative standard deviations (RSD) of 2.0%, 1.4%, and 0.90%, respectively. The results showed that at the 95% confidence level there was no systematic error in the proposed method.

Table 1
Interferences for the determination of phenylhydrazine (5.0 μM).

Foreign species	Tolerated ratio $W_{species}/W_{Phenylhydrazine}$
Na^+, K^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, SO_4^{2-}, Zn^{2+}, WO_4^{2-}, SO_3^{2-}, CN^-, NO_3^-, Acetate	1000[a]
Al^{3+}, F^-	800
Cr^{3+}, $C_2O_4^{2-}$, CO_3^{2-}, NO_2^-	500
Fe^{3+}, MoO_4^{2-}, PO_4^{3-}	100
Hg^{2+}	50
Cu^{2+}	10
Fe^{2+}, $S_2O_3^{2-}$	1

[a] Maximum ratio tested.

Table 2
Determination of phenylhydrazine in spiked water samples by the proposed method.

Sample	Added (μM)	Found (μM)	RDS% ($n = 6$)	Recovery (%)
Tap water	3.00	2.90	1.97	96.7
	5.00	5.02	1.83	100.4
Mineral water (Damavand)	2.00	1.91	1.80	95.5
	4.00	4.14	1.47	103.5
	6.00	5.94	1.20	99.0

3.3. Selectivity

In order to assess the possible analytical application of the described method, the effects of various substances present in the real samples on the determination of phenylhydrazine were investigated. A synthetic mixture of a solution containing 5.0 μM of phenylhydrazine and various excess amounts of diverse ions were analyzed. The tolerance limit was defined as the concentration of the added ions causing a change in the induction period more than ±5%. The results are given in Table 1. Many substances did not interfere in 1000-fold excess than phenylhydrazine. Thiosulfate caused positive error because it could also inhibit the indicator reaction. Iron(II) interference was negative because it accelerated the indicator reaction. The interference of iron(II) could be reduced (up to 150-fold) in the presence of 0.0010 M EDTA.

3.4. Analysis of samples

Because of the lack of suitable real samples, analyses of water-spiked samples were used to assess the accuracy of the proposed procedure. Replicate determinations were made on mineral and tap water samples spiked with various amounts of phenylhydrazine using the standard addition method. The results are listed in Table 2. These results show the validity of the proposed method in the determination of phenylhydrazine in water samples.

4. Conclusion

The results presented clearly demonstrate the inhibition effect of phenylhydrazine on the catalytic oxidation of MCP by periodate. The results were applied to develop a simple methodology for the

determination of phenylhydrazine at trace level. The validation of method was made by comparing the results obtained using the proposed method and the known spiked amounts in water samples. No statistically significant errors were found. The detection limit of the proposed method was in the nanomolar range. The method was found to be accurate, reproductive, sensitive, and selective. Also the method is simple and can be performed with available and cheap chemicals. Therefore, the method could be proposed for environmental and toxicological analyses.

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