Cent. Eur. J. Chem. • 8(3) • 2010 • 559-565
DOI: 10.2478/s11532-010-0021-3

VERSITA

Central European Journal of **Chemistry**

Kinetic spectrophotometric determination of hydrazine

Research Article

Violeta D. Mitic[1]*, Snezana D. Nikolic[2] and Vesna P. Stankov-Jovanovic[1]

[1] *Faculty of Natural Science and Mathematics, Department of Chemistry, University of Nis, 18 000 Nis, Serbia*

[2] *Faculty of Chemistry, University of Belgrade, 11 000 Belgrade, Serbia*

Received 04 June 2009; Accepted 21 December 2009

Abstract: A kinetic spectrophotometric method for hydrazine determination in the range of 9.36×10^{-7} to 4.37×10^{-5} mol dm^{-3}, based on the inhibitory effect of hydrazine on the oxidation of Victoria Blue 4- R by $KBrO_3$, was developed and validated. Kinetic parameters are reported for both the indicating and the inhibiting reaction. The detection limit was established as 9.98×10^{-8} mol dm^{-3}. The selectivity of the proposed method was tested considering the influence of different ions that may be present in real samples. The method was successfully applied for hydrazine determination in various samples (very pure water from the water-steam system of a power plant and Isoniazid tablets, a pharmaceutical product).

The novel kinetic spectrophotometric method proposed was found to have satisfactory analytical characteristics as well as being widely applicable due to its simplicity and speed.

Keywords: *Hydrazine • Spectrophotometric kinetic method • Isoniazid*

1. Introduction

Hydrazine is a highly reactive base and reducing agent. The major use of hydrazine is as a rocket fuel because it burns rapidly and produces a large amount of heat. Hydrazine is used as a scavenger for dissolved oxygen in boiler systems and is used extensively for chemical pretreatment in high-pressure boilers. It is also able to form a protective magnetite coating as a result of its reaction with surface iron or rust. Hydrazine and its derivatives are also used as reactants in military fuel cells, in nickel plating, in photographic development, in the manufacture of algaecides, fungicides, insecticides, and agricultural chemicals. Hydrazine is also used in many processes including the production of spandex fibers (as a polymerization catalyst) or in urethane polymerizations (as a chain extender). Besides being reactive and explosive, hydrazine is also volatile and highly toxic if absorbed by oral, dermal or inhalation routes of exposure. Adverse health effects on people living near hazardous waste sites caused by hydrazine and its derivatives have been described [1]. It may cause skin sensitization, eye irritation, amyloidosis and hemosiderosis of the liver, thyroid amyloidosis, respiratory tract problems as well as systemic poisoning.

The drug Isoniazid, used in the treatment of tuberculosis, is isonicotinic hydrazine. Recently, drug regulatory authorities have established the necessity of monitoring hydrazine levels in all hydrazine-like drugs, due to its carcinogenic and hepatotoxic effects, concerning both quality control of the pharmaceuticals and environmental impact.

Various spectrophotometric methods [2-7] have been proposed for the determination of hydrazine. Electro-analytical [8-12], liquid and gas chromatography methods [13-15] have also been described. The need for pre-concentration and/or separation, as well as high instrumental costs, are common disadvantages of these methods.

Kinetic methods for hydrazine determination (Table 1) are very simple and low-cost alternatives to previously discussed methods.

The purpose of the present study is to establish a suitable procedure for hydrazine determination

* *E-mail: violetamitic@yahoo.com*

Table 1. Comparison of the method with other reported kinetic methods

Reaction system	Linearity range (mol dm^{-3})	Detection limit (mol dm^{-3})	Reference
Brilliant Cresyl Blue with nitrite in acidic media	1.56×10^{-6}-1.56×10^{-4}	1.25×10^{-6}	16
Neutral red with nitrite in hydrochloric acid	4.7×10^{-6}-3.1×10^{-5}	3.1×10^{-6}	17
Hydrazine with Mo(VI) in hydrochloric acid	1.0×10^{-4}-1.4×10^{-2}	3.12×10^{-5}	18
Methyl orange with bromate in hydrochloric acid	3.0×10^{-7}-3.2×10^{-5}	8.50×10^{-8}	19
Alizarine navy blue with $NaNO_2$	3.12×10^{-6}-4.37×10^{-5}	2.81×10^{-6}	20
Rhodamine B with potassium chlorate in hydrochloric acid	2.46×10^{-7}-2.46×10^{-6}	5.3×10^{-8}	21
Rhodamine B with potassium bromate + potassium bromide in sulfuric acid solutions	1.10×10^{-7}-2.46×10^{-6}	2.53×10^{-8}	21
Iron(III) with hydrazine, in the presence of 2,2′-bipyridine in sodium dodecyl sulfate	3.12×10^{-5}-2.18×10^{-3}	1.25×10^{-5}	22
Copper (II) with hydrazine in the presence of neocuproine in sodium dodecyl sulfate	3.12×10^{-6}-3.12×10^{-5}	-	23
Victoria Blue 4- R with $KBrO_3$ in hydrochloric acid	9.36×10^{-7}-4.37×10^{-5}	9.98×10^{-8}	Present work

in certain samples, which has desirable analytical properties (sensitivity, accuracy, precision, selectivity, wide linear range) as well as being widely available for application (low-cost instrumentation, simple laboratory procedures and speed).

2. Experimental procedure

2.1. Equipment

Spectrophotometric measurements were performed on a Perkin-Elmer Lambda 15 UV-Vis spectrophotometer at a wavelength of 596.3 nm. Cylindrical cells thermostated at 20.0±0.1ºC using a Julabo MP-5A model thermostatic bath were used. pH measurements were carried out using a Hanna Instruments pH meter.

2.2. Reagents

All chemicals used were analytical reagent grade and were provided by Merck unless otherwise indicated. Deionized water (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) was utilized for all solution preparations.

The stock solution of each reactant was prepared by weighing the exact mass of solid compound and dissolving it in an appropriate water volume. The Victoria Blue 4-R (VB) stock solution (Fluka AG Buchs SG c.i number 42563, c.i. name Basic Blue 8, structure published [24]) was prepared by dissolving in absolute ethanol. The concentration and stability of the solution was verified spectrophotometrically.

A KCl solution (2 mol dm^{-3}) was used to maintain a constant ionic strength (0.1 mol dm^{-3}).

All vessels used (glass, polyethylene) were initially washed with an ethanolic solution of KOH, then with HCl (1:1, v/v) and finally rinsed with tap, distilled and deionized water.

2.3. Spectrophotometry

Suitable volumes of VB, $KBrO_3$, and hydrazine solutions were placed in separate compartments of a Budarin's vessel, while solutions of KCl, HCl and deionized water (total volume 10 cm^3) were placed in the same compartment. The vessel was thermostated for ten minutes at the working temperature, then mixed; the stop-watch was turned on simultaneously. The reaction mixture was transferred immediately into the spectrophotometric cell and the absorbance was measured every 30 seconds (starting from the 30th second) during the first five minutes from the onset of the reaction.

2.4. Determination of hydrazine in real samples

2.4.1. Water samples

Three different water samples (feed water and condensate) were taken from the water-steam system of the thermal power plant "Nikola Tesla B", Obrenovac, Serbia before the condensates passed through an ion exchange column. The samples were directly analyzed without any treatment.

2.4.2. Isoniazid tablets

Five Isoniazid tablets produced by "Panfarm", Serbia were weighed, ground to a homogenized powder and a mass of powder corresponding to 250 mg of Isoniazid (58.35 mg hydrazine) was accurately weighed. The powder was then dissolved in water, filtered and the residue was washed thoroughly. The drug stock solution, prepared in the manner described above, was diluted to three different concentrations in the concentration range of the calibration curve. The Isoniazid tablets and the prepared solutions were protected from light.

3. Results and Discussion

3.1. Reaction kinetics study

As the Victoria Blue 4-R oxidation proceeds, the initial blue color of the reaction mixture disappears because the colorless reaction product is forming (Fig. 1). The presence of hydrazine inhibits the discoloring of the solution (Fig. 2). According to data reported earlier [19], the possible reaction

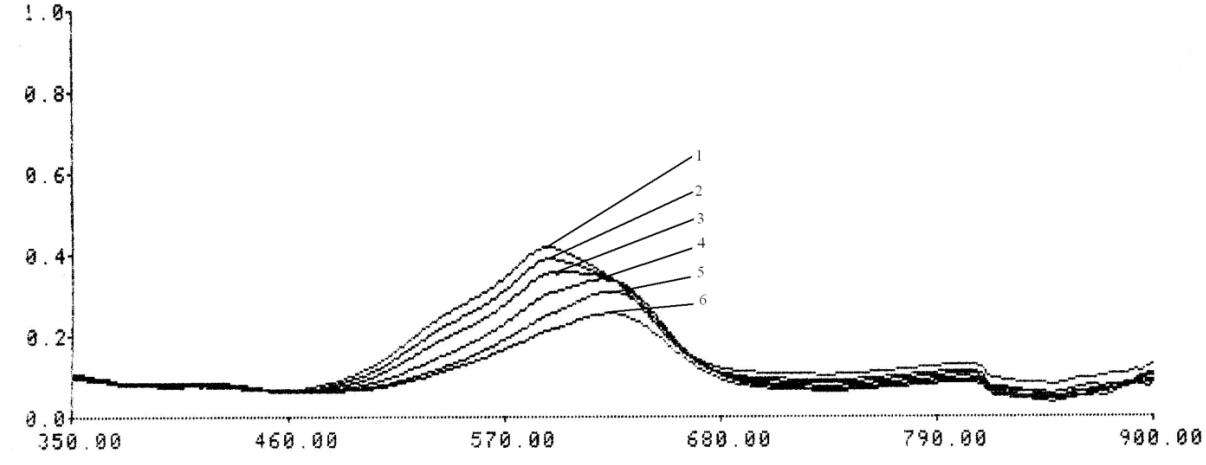

Figure 1. Absorption spectra of indicating reaction
$c(HCl)=2.0\times10^{-2}$ mol dm^{-3}; $c(VB)=1.5\times10^{-6}$ mol dm^{-3}; $c(KCl)=0.1$ mol dm^{-3}; $c(KBrO_3)=3\times10^{-4}$ mol dm^{-3}; $(C_2H_5OH)=13\%$;
t=0.5 min (1), t=1.0 min (2), t=2.0 min (3), t=3.0 min (4), t=4.0 min (5), t=5.0 min (6)

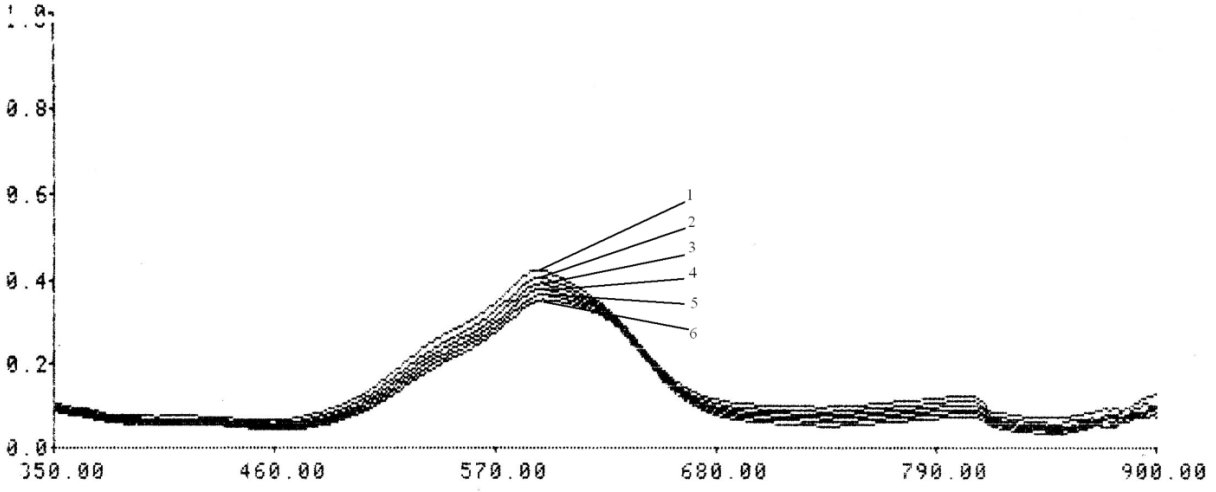

Figure 2. Absorption spectra of inhibiting reaction
Initial conditions: $c(HCl)=2.0\times10^{-2}$ mol dm^{-3}; $c(VB)=1.5\times10^{-6}$ mol dm^{-3}; $c(KCl)=0.1$ mol dm^{-3}; $c(KBrO_3)=3\times10^{-4}$ mol dm^{-3}; $(C_2H_5OH)=13\%$; $c(hydrazine)=3.12\times10^{-5}$ mol dm^{-3}; t=0.5 min (1), t=1.0 min (2), t=2.0 min (3), t=3.0 min (4), t=4.0 min (5), t=5.0 min (6)

mechanism was suggested as follows:

Bromate is reduced by chloride in acidic media

$2BrO^{3-} + 10Cl^- + 12H^+ \leftrightarrow Br_2 + 5Cl_2 + 6H_2O$ (1)

The presence of hydrazine in the reaction mixture significantly reduces the reaction progress. Possible consideration of this effect can be Reaction 2:

$X_2 + (N_2H_6)_2^+ \rightarrow N_2 + 6H^+ + 4X^-$ (2)

The molar absorptivity (ε) of Victoria Blue 4-R under the specified conditions was found to be 4.9×10^3 dm^3 mol^{-1} cm^{-1}. The differential variant of the tangent method was used and the reaction rate (dA dt^{-1}) was calculated from the slope of the initial linear part of the absorbance-time graph. The rate of the inhibiting reaction was expressed against the rate of the indicating reaction.

3.2. Optimization of chemical variables

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized. Each parameter was optimized separately, while keeping all of the other parameters constant. Keeping all other experimental parameters constant, the impact of hydrochloric acid was studied in a range of 1.0-2.4×10^{-2} mol dm^{-3} (Fig. 3) and a concentration of 2.0×10^{-2} mol dm^{-3} was selected as the optimal one.

The correlation between tg α and Victoria blue 4R concentration is shown in Fig. 4. and a VB concentration of 1.50×10^{-6} mol dm^{-3} was selected for further application.

The reaction rates for both the indicating and the inhibiting reaction were greatly increased by increasing the $KBrO_3$ concentration (Fig. 5), but more so over the range of 0.5×10^{-4} mol dm^{-3} to 2×10^{-4} mol dm^{-3} in comparison with the range of 2.0×10^{-4} mol dm^{-3} to 4.0×10^{-4} mol dm^{-3} $KBrO_3$. A concentration of 3.0×10^{-4} mol dm^{-3} $KBrO_3$ was selected as the most suitable.

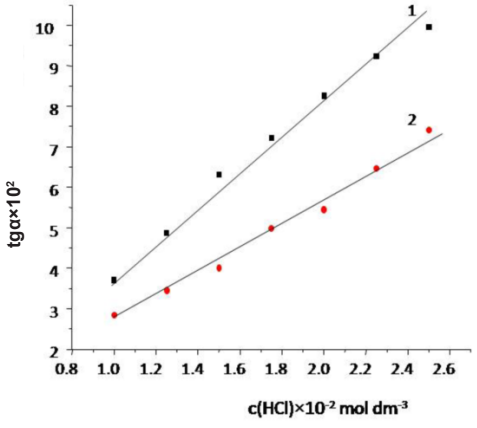

Figure 3. Dependence of the reaction rate on HCl concentration c(VP)=2.0×10^{-6} mol dm^{-3}; c($KBrO_3$)=2×10^{-4} mol dm^{-3}; c(KCl)=0.1 mol dm^{-3}; c(hydrazine)= 3.12×10^{-5} mol dm^{-3} t=20±0.1°C; 1 – indicating solution, 2 - inhibiting solution.

3.3. Validation of the method

The calibration graphs were constructed under the established optimal conditions for kinetic determination of hydrazine:

c(HCl)=2.0×10^{-2} mol dm^{-3};
c(VP)=1.5×10^{-6} mol dm^{-3};
c($KBrO_3$)=3.0×10^{-4} mol dm^{-3};
c(KCl)=0.1 mol dm^{-3}

Hydrazine concentrations and the slopes of the absorbance-time curves were found to be linearly dependent. The analytical and statistical data of the calibration graphs for the determination of hydrazine

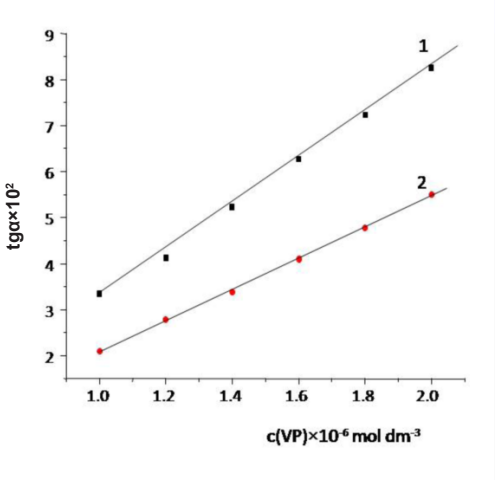

Figure 4. Dependence of the reaction rate on VB concentration c(HCl)=2.0×10^{-2} mol dm^{-3}; c($KBrO_3$)=2×10^{-4} mol dm^{-3}; c(KCl)=0.1 mol dm^{-3}; c(hydrazine)= 3.12×10^{-5} mol dm^{-3} t=20±0.1°C; 1 – indicating solution, 2 - inhibiting solution

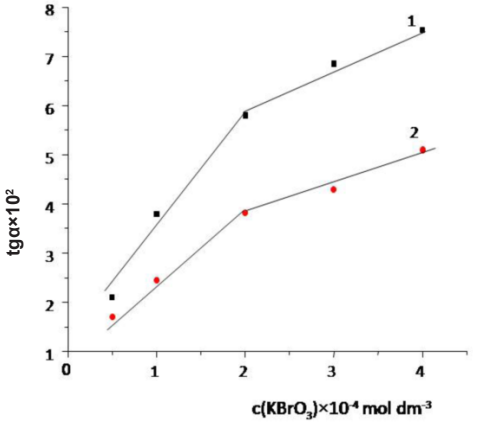

Figure 5. Dependence of the reaction rate on $KBrO_3$ concentration c(HCl)=2.0×10^{-2} mol dm^{-3}; c(VB)=1.5×10^{-6} mol dm^{-3}; c(KCl)=0.1 mol dm^{-3}; c(hydrazine)=3.12×10^{-5} mol dm^{-3} t=20±0.1°C; 1 – indicating solution, 2 - inhibiting solution

Table 2. Analytical and statistical analysis of the calibration graph for the determination of hydrazine

Analytical Data	Dynamic range μmol dm^{-3}	
	0.93 to 6.86	8.48 to 43.68
Number of points	10	7
Limit of detection μmol dm^{-3}	0.099	
Slope± standard deviation of the slope ×10^2	-0.178±0.002	-0.149±0.002
Intercept± standard deviation of the intercept ×10^2	6.935±0.009	5.69±0.02
Correlation Coefficient	0.9993	0.9995

estimated by the linear-regression method, along with the standard deviation of the fit and the correlation coefficient r are given in Table 2.

The following kinetic equations for the process investigated were deduced on the basis of the graphical correlations obtained.

For the indicating reaction:

$$-dc(VB)\,dt^{-1} = k_1 \times c(HCl) \times c(VB) \times c(KBrO_3) \quad (3)$$

For the inhibiting reaction:

$$-dc(VB)\,dt^{-1} = k_2 \times c(HCl) \times c(VB) \times \times c(KBrO_3) \times (c(hydrazine))^{-1} \quad (4)$$

where k_1 and k_2 are the rate constants for the indicating and inhibiting reactions.

In order to assess the accuracy and precision of the method, reaction rates were followed in five replicate experiments at each of five different hydrazine concentrations in the range of the calibration curves (1.56, 3.12, 6.24, 18.7 and 37.44×10^{-6} mol dm^{-3}). The relative error ranges from 0.5% to 2.4%, while the relative standard deviation is 1.81 to 8.00% for hydrazine in the concentration range from 3.74×10^{-5} mol dm^{-3} to 1.56×10^{-6} mol dm^{-3}.

In order to determine the selectivity of the method, the influence of numerous foreign ions on the reaction rate was studied. Solutions containing various amounts of foreign ions and a fixed amount of hydrazine (3.12×10^{-6} mol dm^{-3}) were subjected to the procedure described. The results are summarized in Table 3. The tolerance ratio was defined as the concentration of added ion causing less than 3% relative error. Most cations and anions did not interfere with the determination, even if they were present in concentrations thousands of times higher than hydrazine. Negative interference for Ni^{2+}, Co^{2+}, and positive interference for $Cr_2O_7^{2-}$ were observed (in 1:1 ratio). Inhibitory effects for As^{3+}, Sb^{3+}, I^- and phenyl hydrazine were observed, though it was expected that they could also inhibit the indicating reaction.

3.4. Application of the method

To evaluate the analytical applicability of the method, the proposed procedure was applied for determination of hydrazine in water samples and Isoniazid tablets. Since the concentrations of interfering cations in water (feed waters and condensate) are generally far below their tolerance limits shown in Table 3, the method was directly applied to the determination of hydrazine in these samples of water without any separation or pre-concentration. Hydrazine content was determined directly using prepared solutions of Isoniazid tablets. The results obtained are summarized in Tables 4, 5 and 6. The results were compared with those obtained by a standard method and with the label on Isoniazid

Table 3. Interference studies: Effect of foreign ions on the determination of hydrazine (c(hydrazine)= 3.12×10^{-6} mol dm^{-3})

Ion added*	Tolerated ratio of foreign species to hydrazine
Li^+, K^+, Na^+, NH_4^+, Ca^{2+}, Ba^{2+}, Sr^{2+}, $C_2O_4^{2-}$ CH_3COO^-, HCO_3^-, CO_3^{2-}, $C_4H_4O_6^{2-}$	1000
Pb^{2+}, SO_4^{2-}, NO_3^-, As^{5+}, Sb^{5+}	100
WO_4^{2-}, Mo^{6+}, Cd^{2+}	10
Sn^{2+}, Al^{3+},Cu^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, HPO_4^{2-}	1
Ni^{2+}, Co^{2+}, $Cr_2O_7^{2-}$	0.5
As^{3+}, Sb^{3+}, I^-, phenylhydrazine	Inhibited

*Cations added as chlorides or nitrates, anions as sodium or potassium salts

Table 4. Results of the analysis of hydrazine in feed waters

Samples			Amount hydrazine (μmol dm^{-3}) Found ±RSD (%)	
Feed waters	Taken Hydrazine (μmol dm^{-3})	Added Hydrazine (μmol dm^{-3})	Proposed method*	Standard method*
Sample 1	1.74	1.56	3.29± 0.02	3.31± 0.02
Sample 2	1.28	1.56	2.85± 0.03	2.84± 0.04
Sample 3	1.11	1.56	2.67± 0.02	2.68± 0.04

Table 5. Results of the analysis of hydrazine in condensates

Sample	Amount hydrazine (μmol dm^{-3})	Found±RSD(%)
Condensates	Proposed method*	Standard method*
Sample 1	3.41± 0.02	3.37± 0.03
Sample 2	3.56± 0.02	3.59± 0.04
Sample 3	3.94± 0.02	3.93± 0.04

*Average of five measurements

Table 6. Results of the analysis of hydrazine in Isoniazid tablets

Sample	Isoniazide Label (mg)	Hydrazine Label (mg)	Amount hydrazine (mg) Found (mg)±RSD (%)	
			Proposed method*	Standard method*
Tablet 1	50.0	11.7	11.5± 1.0	11.4± 1.3
Tablet 2	50.0	11.7	11.5± 1.1	11.6± 1.2
Tablet 3	50.0	11.7	11.6± 1.0	11.7± 1.3

*Average of ten measurements

tablets. The standard method is based on the reaction of hydrazine with 4-dimethylaminobenzaldehyde in acidic medium and spectrophotometric monitoring of yellow p-quinone product [25]. The results (Tables 4-6) show that the method is suitable for the determination of hydrazine in different realistic samples.

4. Conclusion

The system Victoria Blue 4-R + $KBrO_3$ + HCl + hydrazine takes a short time to achieve kinetic equilibrium and thus allows the development of a kinetic method which is time-economical. Besides good accuracy (relative error ranges from 0.5% to 2.4%), precision (relative standard deviation from 1.81 to 8.00%), wide linear range (9.36×10^{-7} to 4.37×10^{-5} mol dm^{-3}), low limit of detection (9.98×10^{-8} mol dm^{-3}), the proposed method is also more selective than most previously reported methods. Due to the method's good selectivity, it is possible to determine hydrazine in the presence of various interferences without any pre-concentration steps. The proposed method was validated and successfully applied for hydrazine analysis in water and pharmaceutical samples.

References

[1] H.W. Schiessl, In: K. Othmer (Ed.), Encyclopedia of Chemical Technology, 3rd edition (Wiley, NewYork, 1980)
[2] M. George, K.S. Nagaraja, N. Balasubramanian, Talanta 75, 27 (2008)
[3] E.I. Morosanova, E.A. Reznikova, A.A. Velikorodnyi, J. Anal. Chem. 56, 173 (2001)
[4] A.R. Zarei, Anal. Biochem. 369, 161 (2007)
[5] K.K.Tiwari, V.K. Gupta, J. Indian Counc. Chem. 23, 95 (2006)
[6] M. George, K.S. Nagaraja, N. Balasubramanian, Anal. Lett. 40, 2597 (2007)
[7] A. Afkhami, A.R. Zarei, Talanta 62, 559 (2004)
[8] V. Rosca, M.T. Koper, Electrochim. Acta 53, 5199 (2008)
[9] A. Salimi, L. Miranzadeh, R. Hallaj, Talanta 75, 147 (2008)
[10] D.R. Shankaran, S.S. Narayanan, Res. J .Chem. Environ. 5, 43 (2001)
[11] J.S.Pinter, K.L. Brown, P.A de Young, G. F Peaslee, Talanta 71, 1219 (2007)
[12] S.J.R Prabakar, S.S. Narayanan, J. Electroanal. Chem. 617, 111 (2008)
[13] H. Kirchherr, J. Chromatogr. Biomed. Appl. 617, 157 (1993)
[14] A.S. Riggs et al., Journal of AOAC International 91, 5 (2008)
[15] V. Vatsala et al., Chromatographia 38, 456 (1994)
[16] A.A. Ensafi, M.M. Sadeghie, F. Emamei, J. Anal. Chem. 54, 1024 (1999)
[17] S.H. Wang, L.Y. Du, A.M. Zhang, Mikrochim. Acta 134, 167 (2000)
[18] A. Safavi, A.A. Ensafii, Anal. Chim. Acta 300, 307 (1995)
[19] A. Afkhami, A.E. Akbar, Anal. Chim. Acta 419,101 (2000)
[20] M. Tabatabaee, A.A. Ensafi, M. Babaei, Asian J. Chem. 19, 1385 (2007)
[21] J. Fan, J. Kong, S. Feng, J. Wang, P. Peng, Int. J. Environ. Anal. Chem. 86, 995 (2006)
[22] M.A. Karimi, M.M. Ardakani, O. Moradlou, R. Behjatmanesh-Ardakani, F. Banifatemeh, J. Chin. Chem. Soc. (Taipei, Taiwan) 54, 15 (2007)
[23] M.A. Karimi, M.A. Taher, R.B. Ardakani, S. Abdollahzadeh, Asian J. Chem. 20, 2169 (2008)
[24] V.D. Mitic, S.D. Nikolic, V.P. Stankov-Jovanovic, Anal. Sci. 20, 931 (2004)
[25] G.W. Watt, J.D. Chrisp, Anal. Chem, 24, 2006 (1952)