

Solid-Phase Spectrophotometric Iodometric Determination of Nitrite and Selenium(IV) Using a Polymethacrylate Matrix

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Abstract—Procedures for the iodometric solid-phase spectrophotometric determination of nitrite and selenium(IV) using a polymethacrylate matrix are proposed. The procedures are based on the reaction of nitrite and selenium(IV) with iodine in an acidic medium with the release of free iodine in amounts equivalent to those of the substances to be determined, extraction of the iodine formed with a polymethacrylate matrix, and measurement of absorbance of the matrix at 370 nm. The developed procedures ensure the determination of 0.01–0.12 mg/L of nitrite and 0.05–0.40 mg/L of selenium(IV) with limits of detection of 0.005 and 0.03 mg/L, respectively. It was shown that the proposed procedures can be applied to the determination of selenium(IV) in mineral water and nitrites in vegetables and soil.

Keywords: selenium(IV), nitrite, polymethacrylate matrix, iodometry, solid-phase spectrophotometry

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Iodometry is widely used in chemical analysis [1, 2]. The concentration of an analyte is calculated from the amount of iodine released as a result of reaction between iodide ions and an analyte in an acidic medium. The simplest and less sensitive method for the determination of iodine is based on measurements of color intensity of an aqueous triiodide solution and an iodine solution in an organic solvent after extraction [3]. One of methods for improving sensitivity is the preconcentration of an analyte by solid-phase extraction followed by determination by solid-phase spectrophotometry [4–7]. It is important that the use of solid-phase extraction is in agreement with the principles of green analytical chemistry [8]. The polyurethane foams have been successfully used for the iodometric solid-phase spectrophotometric determination of nitrite in natural waters [9]. In our opinion, of not least promise is the use of polymethacrylate as a solid-phase extractant. The optical and processable properties of polymethacrylate favor the preparation of optically transparent thin plates with high transmission, which, in turn, considerably facilitates measurements of the analytical signal by spectrophotometric methods.

This work is aimed at the development of simple procedures for the determination of selenium(IV) and nitrite based on the application of solid-phase spectrophotometry to the determination of polymethacrylate-extracted iodine resulting from redox reactions between the analytes and iodide.

EXPERIMENTAL

Solutions, reagents. Stock solutions of nitrite, selenium(IV), and metals of the concentration 1 mg/mL were prepared according to *GOST 4212-76* [10] and using their certified reference materials (SRM) with the concentration 1 mg/mL. A stock 24% solution of potassium iodide was prepared by dissolving a weighed portion of a KI sample. Working solutions with lower concentrations were prepared by diluting stock solutions with distilled water in the day of experiment.

A 25% solution of sodium acetate and solutions with F^- , Br^- , S^{2-} , PO_4^{3-} , NO_3^- , and NH_4^+ ion concentrations of 1 mg/mL prepared according to procedures [10, 11] were used. The required acidity of test solutions was adjusted using HCl. All reagents were of reagent or analytical grade and used without additional purification.

The polymethacrylate matrix as a transparent plate with a thickness of 0.60 ± 0.04 mm was prepared by radical block polymerization according to the procedure [12]. Plates with dimensions 6.0×8.0 mm and a weight of about 0.05 g were cut from the starting sample.

Apparatus. The absorption spectra and absorbance of the polymethacrylate matrix were measured on a Shimadzu UV mini-1240, Unico 2800 UV/VIS, and Spekol 21 spectrophotometers. For this purpose, polymethacrylate matrix samples were placed in a glass cell with an optical path length of 0.1 cm. In mea-

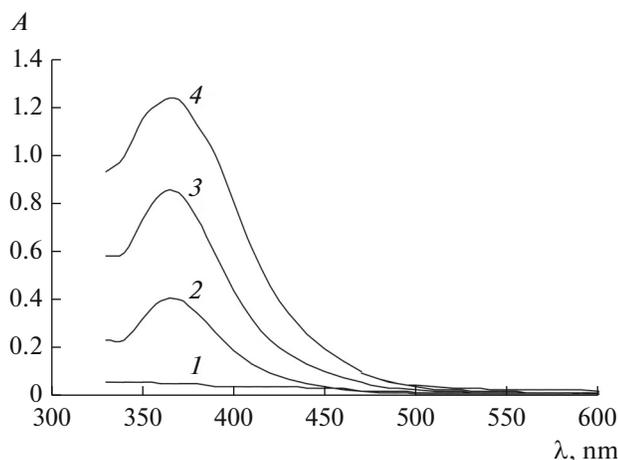


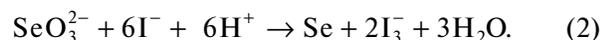
Fig. 1. Absorption spectra of iodine in the polymethacrylate matrix after its contact with a solution of selenium(IV) of different concentrations in the presence of iodide. Concentration of Se(IV) was (1) 0, (2) 0.05, (3) 0.10, and (4) 0.30 mg/L; $c_{KI} = 0.5\%$, and $c_{HCl} = 0.04$ M.

asuring optical characteristics of the polymethacrylate matrix after its contact with test solutions, the reference sample was the starting matrix sample.

Analytical procedure. The reaction between selenium(IV) and nitrite was studied under batch conditions. For this purpose, the matrix was placed in a solution (25 mL) of selenium(IV) or nitrite with different concentrations and acidities and a solution of potassium iodide was added. In the study of the reaction between selenium(IV) and iodide, sodium acetate was added to the analyzed solution 3 min after the initiation of the reaction. The resulting solutions were stirred for 5–30 min on a WU-4 multipurpose vibratory mechanical agitator at a rate of 150 ± 10 rpm, absorption spectra were recorded, and absorbance (A) at the absorption maximum of iodine in the polymethacrylate matrix was measured.

RESULTS AND DISCUSSION

The nitrite–iodide (1) and selenium–iodide (2) reactions in an acidic medium resulted in the formation of free iodine in amounts equivalent to those of nitrite and selenium(IV), followed by the formation of a triiodide complex, which was extracted from the solution with the polymethacrylate matrix:



The extraction of iodine was accompanied by a change in matrix color from pale-yellow to yellow-brown. The color of the plates remained unchanged for a long time. The absorption spectrum of iodine in the polymethacrylate matrix contained only one

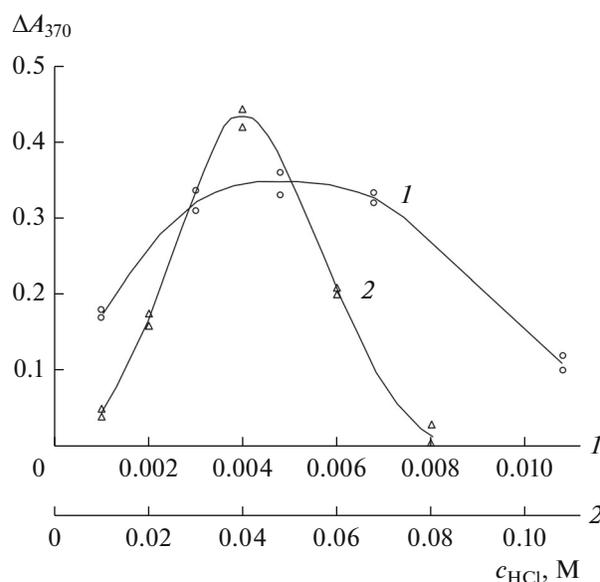


Fig. 2. Effect of hydrochloric acid concentration in solution on the analytical signal after a contact of the matrix with a solution of nitrite (1) and selenium (2) in the presence of iodide. c_{KI} , %: (1) 0.007 and (2) 0.5; $c_{\text{NO}_2^-} = 0.05$ mg/L; and $c_{\text{Se(IV)}} = 0.1$ mg/L.

absorption band at 370 nm, which corresponded to the absorption of the triiodide complex. Figure 1 shows the absorption spectra of iodine in the polymethacrylate matrix after its contact with a solution of selenium(IV) of different concentrations in the presence of iodide. A similar pattern was observed for the absorption spectra of iodine in the matrix after its contact with a solution of nitrite in the presence of iodide. The analytical signal was the absolute variation of absorbance $\Delta A_{370} = A - A_0$, where A and A_0 were absorbances of the polymethacrylate matrix at 370 nm after its contact with the analyzed solution in the presence and in the absence of a component to be determined, respectively.

To find optimum conditions for the determination of selenium and nitrite, analytical signal was studied as a function of the concentration of reacting species in the solution, acidity of the medium, and phase contact time.

Figure 2 shows analytical signal as a function of the concentration of HCl in the analyzed solutions. It can be seen that the acidity of the medium has a strong effect on the studied redox reaction with the release of free iodine and on the value of the analytical signal. The signal reached a maximum when the concentration of acid in the analyzed solution was 0.04 M in the determination of selenium(IV) and 0.005 M in the determination of nitrite.

The concentration of iodide in the solution has also a noticeable effect on the analytical signal (Fig. 3). The iodide ion is not only involved in redox reactions,

but also binds molecular iodine arising from reactions into the triiodide complex. It was found that, in the oxidation of iodide with nitrite, the optimum concentration of iodide in the solution was 0.0075%; its subsequent increase resulted in an increase in absorbance of the control experiment (A_0) and a decrease in the analytical signal. In the determination of selenium(IV), the analytical signal increased with an increase in the concentration of iodide and reached a maximum and virtually constant value when its concentration in a solution was $\geq 0.48\%$.

It should be noted that the oxidation of iodide with selenious acid, which is a basis of the procedure for determination of selenium(IV), proceeds at a noticeable rate only in a strongly acidic media; the absorbance of solutions changes with time. To stabilize it, sodium acetate was added 3 min after the initiation of the reaction between selenium and iodide; sodium acetate neutralized the acid in the solution because of which the reaction between selenium and iodide was retarded. In addition, the addition of sodium acetate to the system resulted in an increase in the sensitivity of selenium detection.

The interfering effect of a wide range of cations and anions on the determination of nitrite and selenium(IV) at a nitrite concentration of 0.1 mg/L and selenium(IV) concentration of 0.3 mg/L was studied. The relative deviation of the analytical signal in the presence of a foreign component was calculated by the formula $\delta (\%) = [(\Delta A_i - \Delta A) / \Delta A] \times 100$, where ΔA and ΔA_i were absolute changes in the absorbance of the polymethacrylate matrix at 370 nm after its contact with the analyzed solution in the absence and in the presence of a foreign ion. The determination of nitrite and selenium(IV) did not interfere with 100-fold amounts of Ca^{2+} , Co(II) , Mg^{2+} , Ni(II) , Zn(II) , Mn(II) , K^+ , Na^+ , PO_4^{3-} , CH_3COO^- , and Cl^- and 10-fold amounts of NO_3^- , F^- , Br^- , and NH_4^+ . In the presence of the above-mentioned ions, the relative deviation of the analytical signal in the determination of nitrite and selenium(IV) did not exceed $\pm 10\%$. Iron(III) in amounts comparable with those of the elements to be determined had a considerable effect on the determination of nitrite and selenium(IV): in the presence of iron(III), the relative deviation of the analytical signal reached 50%. The interfering effect of iron(III) can be eliminated by the addition of fluoride ions to a solution to the analyte–masking agent ratio 1 : 20. In the presence of fluoride ions, the relative deviation of the analytical signal was not higher than 3%. Copper(II) interfered only with the determination of selenium(IV), which was likely due to a high amount of iodide. The determination of selenium(IV) was found to be affected by Hg(II) and Ag(I) , forming poorly soluble compounds with iodides and sulfide; therefore, these elements should be preliminarily separated.

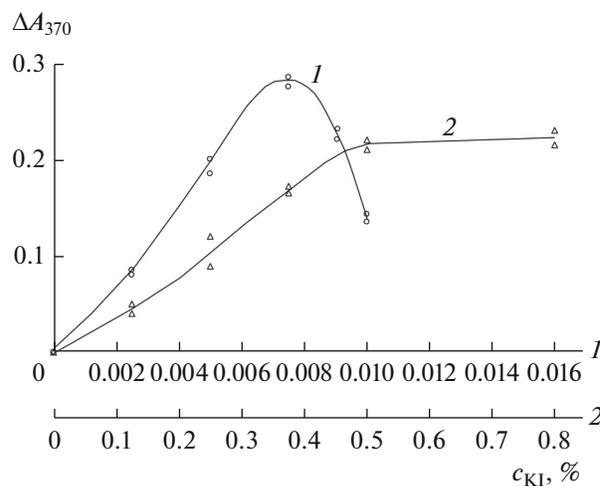


Fig. 3. Effect of iodide concentration in a solution on the analytical signal after a contact of polymethacrylate matrix with a solution of nitrite (1) and selenium (2) in the medium of 0.005 and 0.04 M HCl, respectively. $c_{\text{NO}_2^-} = 0.05$ mg/L; and $c_{\text{Se(IV)}} = 0.1$ mg/L.

The time of contact between the polymethacrylate matrix and the analyzed solution affected the absorbance and determined the linearity range for the dependence of the analytical signal on the concentrations of analytes in the solution, and also affected the sensitivity of detection and the limit of detection. The optimum time of contact between the polymethacrylate matrix and the analyzed solutions for the determination of nitrite and selenium was found. Table 1 gives the parameters of calibration curves and the limit of detection calculated by the 3s test under the selected conditions.

Based on the studies performed, iodometric solid-phase spectrophotometric procedures for the determination of nitrite and selenium(IV) using a polymethacrylate matrix were proposed and tested on real samples. The accuracy of the developed procedures was assessed by the standard addition method, where selenium(IV) was added to a mineral water sample and nitrite was added to soil and vegetable samples.

Selenium was determined in mineral water after 10-fold preconcentration by evaporation with the preliminary introduction of a selenium additive into the sample. An aliquot portion of 5–10 mL was sampled for analysis.

Procedure for determination of selenium(IV). An aliquot portion of a sample was placed in a 25-mL flask and 1 M HCl (1.0 mL), 24% KI (0.5 mL), and 25% CH_3COONa (2.5 mL) were added. A plate of a polymethacrylate matrix was placed in solutions and the solutions were stirred for 20 min. The plate was then removed and predried with a filter paper and absorbance at 370 nm was measured. The concentra-

Table 1. Parameters of calibration curves for the determination of nitrite and selenium(IV) using a polymethacrylate matrix ($\lambda = 370$ nm; $n = 3$, $P = 0.95$)

Analyte	Equation of calibration curve	r	AR, mg/L	LOD, mg/L	Contact time, min
Nitrite	$\Delta A = 3.64c$	0.997	0.01–0.12	0.005	10
Selenium(IV)	$\Delta A = 2.73c$	0.993	0.05–0.40	0.03	20

Notation: AR is analytical range and LOD is the limit of detection.

Table 2. Data from determination of nitrite and selenium(IV) in real samples ($n = 3$, $P = 0.95$)

Analyte	Sample	Sample dilution, n -fold	Added, mg/L	Found, mg/L	δ , %	RSD, %
Nitrite	Soil	25	4	4.4 ± 0.6	10	11
	Vegetables	50	10	9.8 ± 0.3	-2.0	2.4
		25	10	10.0 ± 0.3	0	9.0
Selenium(IV)	Kasmalinskaya mineral water	—	0.010	0.011 ± 0.006	10	22

tion of selenium(IV) in the sample was calculated from the calibration curve.

Nitrite in soil and vegetable samples was determined by the standard addition method to exclude multiplicative systematic errors associated with the effect of foreign substances present in the analyzed samples. The graphical version of the standard addition method with 2–3 additives of different values was used.

A soil sample was prepared for analysis according to the recommendations given in [13]. For this purpose, distilled water (200 mL) was added to the sample (50 g), stirred for 3 min, and filtered through a Red ribbon filter paper. 13% AlCl_3 (55 mL) and 7% KOH (32.5 mL) were added portionwise to the solution and the precipitate was filtered off. The resulting solution was transferred to a 500-mL flask and diluted with distilled water to the mark. An aliquot portion of 1.0–2.0 mL was sampled for analysis. Preparation of vegetables for analysis was performed following recommendations of [13, 14]: sliced vegetables (133 g) were submerged in water (350 mL), stirred for 20 min, and filtered. 30% AlCl_3 (50 mL) and 15% KOH (40 mL) were added to the solution. The precipitate formed was filtered off. The resulting solution was transferred to a 500-mL flask and diluted with distilled water to the mark. An aliquot portion of 0.5–1.0 mL was sampled for analysis. Nitrite was added to vegetable and soil samples at the first step of sample preparation.

Procedure for the determination of nitrite. An aliquot portion of a sample was placed into 25-mL flask, 0.1% KI (1.85 mL) and 0.5 M HCl (0.25 mL) were added, and the mixture was diluted with distilled water to the mark. Solutions in other flasks, where a working solution (0.25, 0.50, and 0.75 mL) of nitrite with a concentration of 10 mg/L was added additionally,

were prepared similarly. A plate of a polymethacrylate matrix was placed in a solution, the mixture was stirred for 10 min, plates were removed and predried with a filter paper, and absorbance at 370 nm was measured. The concentration of nitrite was determined graphically by extrapolating the linear dependence of the change in absorbance ΔA_{370} on the concentration of nitrite in the additive to the value of $A = 0$.

The data for the determination of selenium(IV) and nitrite in Table 2 suggest satisfactory accuracy and reproducibility. The developed procedures are simple in implementation, do not require toxic reagents and solvents, and are carried out on standard spectrophotometric equipment. In addition, the procedures are more sensitive and characterized by lower limits of detection for nitrite and selenium(IV) compared to the earlier proposed procedures using polymethacrylate matrix [15, 16].

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