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ARTICLES

Kinetic Determination of Thiocyanate by the Reaction of Bromate with Crystal Violet Immobilized in a Polymethacrylate Matrix

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Abstract—A procedure is proposed for the kinetic solid-phase spectrophotometric determination of thiocyanate using a polymethacrylate matrix. The procedure is based on the Landolt reaction between Crystal Violet immobilized in a polymethacrylate matrix and a bromate oxidizer, accompanied by the discoloration of the indicator in the matrix. During some induction period after the introduction of thiocyanate into the test solution, the dye in the matrix is not discolored. The duration of the induction period is proportional to the concentration of thiocyanate in the solution. The change in the color of the polymethacrylate matrix was recorded by measuring its absorbance at 600 nm. The developed procedure ensures the determination of thiocyanate in the concentration range 0.025–12 mg/L, depending on the Crystal Violet concentration in the matrix. The limit of detection calculated according to the 3*s*-test is 0.02 mg/L with the indicator concentration in the matrix of 0.06 mg/g. A possibility of using the proposed procedure for the determination of thiocyanate in near-wellbore water is shown.

Keywords: thiocyanate, Crystal Violet, Landolt reaction, polymethacrylate matrix, solid-phase spectrophotometry

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Thiocyanate ions are rather widespread in the environment; they form naturally by reactions between cyanides and sulfur compounds [1]. The sources of their entry into the environment, as a rule, are manmade; these are wastewaters of various industrial productions. Thiocyanates have a toxic effect and are controlled along with other pollutants. The maximum permissible concentration of the thiocyanate ion in industrial waters, potable water, and waters culturaldomestic use is 0.1 mg/L [2]. Thiocyanate ions are also present in biological fluids, and such unfavorable factors as smoking and the state of the environmental situation as a whole affect their concentration [3]. Thiocyanate is also used as a chemical marker, that is, an indicator (tracer) in the oil industry in the study of the reservoir and near-wellbore waters [4].

Electrochemical methods are widely used to determine thiocyanate in biological fluids (saliva, urine, blood serum) and environmental samples (natural and waste waters). Electrodes modified with carbon nanotubes and containing silver or gold nanoparticles, used as voltammetric sensors for the determination of thiocyanates with limits of detection of the order of 1×10^{-9} M, were described in [5, 6]. Potentiometric sensors for the direct determination thiocyanate ions in saliva and environmental samples with limits of detection of the order of 3×10^{-7} M were proposed in [7, 8]. The use of gas chromatography with mass spectrometry for the determination of 5×10^{-7}–2×10^{-4} M of thiocyanate ions was described in [9–11]. The simplest spectrophotometric method ensures the determination of thiocyanate ions as a complex with iron(III) in reservoir water with a limit of detection of 0.1 mg/L [12].

Along with the methods listed above, kinetic methods for the determination of thiocyanate with spectrophotometric detection are in demand and successfully used. These methods are based on the ability of the thiocyanate ion to inhibit the oxidation of various indicators in solution [13–18]. Despite the fact that the kinetic method significantly increases the selectivity of the determination, measuring the rate of a chemical reaction requires recording kinetic curves of reactions, mathematical processing of the results, and sometimes a large consumption of reagents in using the fixed concentration method and the tangent method. A more simple but less precise method is the fixed time method, which requires stopping the indicator reaction by changing the conditions of its conduction (for example, changing the acidity of the medium or abrupt cooling) or by introducing additional "stop-reagents" into the test solution. The use of an indicator immobilized on a solid-phase carrier

enables the reaction time to be varied by stopping the contact of the solid-phase carrier with the analyte. In this paper, we propose the use of optically transparent polymethacrylate plates as solid-phase carriers of indicators, which allow measuring absorbance on conventional laboratory equipment [19, 20].

The present work is devoted to the development of a simple procedure for the solid-phase spectrophotometric determination of thiocyanate based on the Landolt reaction using a polymethacrylate matrix with immobilized Crystal Violet.

EXPERIMENTAL

Solutions and reagents. The initial 0.1% solution of Crystal Violet was prepared by dissolving a weighed sample of the preparation in distilled water. A stock solution of thiocyanate containing 1 mg/mL was prepared in accordance with *GOST* (State Standard) *4212-76* [21] from potassium thiocyanate KSCN. The stock 0.017 M $KBrO_3$ solution was prepared from a fixanal. Working solutions with lower concentrations were prepared by diluting stock solutions with distilled water in the day of the experiment. The necessary acidity of the test solutions was created by adding hydrochloric acid. The reagents were of cp or analytical grade and used without further purification.

Preparation of polymethacrylate matrix. Polymethacrylate matrix as a transparent plate 0.60 ± 0.04 mm in thickness was obtained by radical block polymerization [22]. The plates with a size of 6.0 × 8.0 mm and a weight of approximately 0.05 g were cut from the initial sample.

Apparatus. A Shimadzu UV 1800 spectrophotometer was used to record the absorption spectra and to measure the absorbance of the polymethacrylate matrix. For this purpose, samples of polymethacrylate matrices were placed in a glass cuvette 0.1 cm in thickness. When measuring the optical characteristics of the polymethacrylate matrix after contact with the test solutions, the original sample of the matrix was used as the reference sample.

Immobilization of the indicator in the matrix. Crystal Violet was immobilized in a polymethacrylate matrix by adsorbing it from an aqueous 0.01% solution in 6 M acetic acid in a batch mode. Ten milliliters of the reagent solution was mixed with the matrix. The concentration of the indicator in the polymethacrylate matrix (a_{CV}, mg/g) was calculated by the equation of $a = (c_0 - c)V/m$, where c_0 and c are reagent concentrations in the solution before and after its contact with the polymethacrylate matrix, mg/L; V is the volume of the solution, and m is the weight of the polymethacrylate matrix, g. The Crystal Violet concentration in the solution was determined from its absorbance at 600 nm before and after contact with the matrix. Below is the Crystal Violet concentration in the matrix as a function of the immobilization time.

Immobilization time, min	1	2	3	5
Concentration of the indicator in the matrix, mg/g	0.06	0.08	0.11	0.14

Procedure. The interaction of Crystal Violet immobilized in a polymethacrylate matrix with bromate in the absence and in the presence of thiocyanate was studied by placing the loaded matrix in 25 mL of a thiocyanate solution in the presence of bromate with different concentrations of reactants and acidity. The solutions were mixed for 30–300 s in a WU-4 universal vibrational mixer at a rate of 150 ± 10 rpm, and absorption spectra were recorded, or absorbance (A) was measured at the maximum of the Crystal Violet absorption band in the polymethacrylate matrix. All measurements were carried out at room temperature of 21–25°C.

Determination of thiocyanate. An aliquot portion of a sample was placed into a 25-mL flask; 2.1 mL of 3 M HCl and 0.45 mL of 0.017 M $KBrO_3$ solution were added, and the mixture was diluted up to the mark with distilled water. Other solutions were prepared similarly by adding from 0.75 to 3.00 mL of a working solution of thiocyanate with a concentration of 100 mg/L. A plate of polymethacrylate matrix with immobilized Crystal Violet was placed in the solutions, mixed for 3 min, then taken out, and dried with filter paper. Its absorbance was measured at 600 nm. The concentration of thiocyanate ions was determined graphically by extrapolating the linear dependence of the change in absorption ΔA_{600} at the concentration of thiocyanate ions for the addition to a value of $A = 0$, where $\Delta A_{600} = A_0 - A_1$ (A_0 and A_1 are the absorbances of the plates after contact with the sample without addition and with the addition of thiocyanate ions, respectively).

RESULTS AND DISCUSSION

The determination of the thiocyanate ion by the Landolt reaction is based on its specific property of inhibiting oxidation reactions of various dyes, including Crystal Violet, by the bromate ion [13]. In an acidic medium, bromate ions interacts with chloride ions to form Cl_2 and Br_2, that is,

$$2BrO_3^- + 10Cl^- + 12H^+ \rightarrow 5Cl_2 + Br_2 + 6H_2O.$$

The reaction products react with Crystal Violet and discolor it. Thiocyanate acts as a Landolt reagent and slows the decoloration of the dye by the products of reaction of $KBrO_3$ with HCl.

A polymethacrylate matrix with immobilized Crystal Violet is colored blue-violet and absorbs light at a maximum of 600 nm. When interacting with a solution of bromate in an acidic medium, the matrix becomes

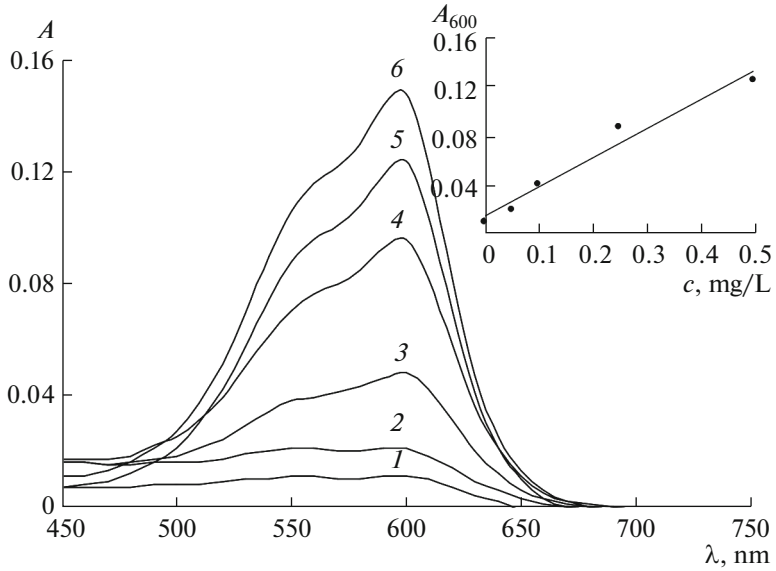

Fig. 1. Absorption spectra of Crystal Violet immobilized in a polymethacrylate matrix after contact with a solution of thiocyanate ions in the presence of bromate. Concentrations: SCN^- (*1*) 0, (*2*) 0.05, (*3*) 0.10, (*4*) 0.25, (*5*) 0.50, and (*6*) 1.00 mg/L; BrO_3^-, 3.0×10^{-4} M; HCl, 0.3 M ($a_{CV} = 0.08$ mg/g, $t_{contact} = 3$ min, $n = 3$, $P = 0.95$). Inset: concentration dependence for thiocyanate at $\lambda = 600$ nm.

discolored due to the oxidation of the indicator. At high concentrations of bromate in the solution, discoloration occurs instantaneously. The introduction of thiocyanate into the solution slows down the process of discoloration of the dye in the matrix, the induction time being proportional to the thiocyanate concentration in the solution. The absorption spectra of Crystal Violet in a polymethacrylate matrix after contact with a bromate solution in the presence of various concentrations of thiocyanate are presented in Fig. 1.

To find acceptable conditions for the determination of thiocyanate, we studied the dependence of the magnitude of the analytical signal on the acidity of the medium, the concentration of the reactants in the solution, and the contact time of phases.

The analytical signal was the absorbance of the polymethacrylate matrix with the immobilized indicator after contact with the test solution at 600 nm or the absolute change in the absorbance of $\Delta A_{600} = A - A_0$, where A and A_0 are the absorbances of the polymethacrylate matrix with the immobilized indicator at 600 nm after contact with the solution in the presence and in the absence of a detectable component, respectively.

The acidity of the medium is one of the most significant factors affecting the decoloration of indicators in the presence of the bromate ion. Figure 2 shows the results of study the effect of acid concentration in the test solution on the value of the analytical signal at constant concentrations of thiocyanate (5.0 mg/L) and bromate (3.0×10^{-4} M) ions. The value of ΔA_{600} is the highest when the acid concentration in the solutions under analysis is in the narrow range of 0.27–0.30 M. The smaller amount of acid in the solution is probably insufficient for the proceeding of the oxidation reaction, and a more substantial amount destroys the initial color of the plates.

The analytical signal is also significantly affected by the oxidant concentration in the test solution (Fig. 3). It

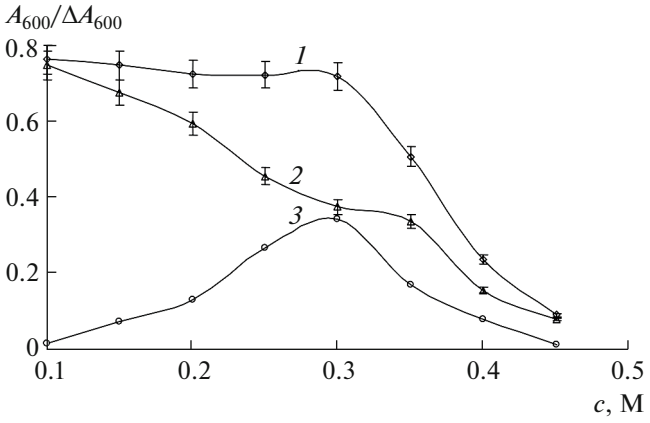

Fig. 2. Effect of the concentration of hydrochloric acid in the solution on the analytical signal A_{600} after contact of the matrix with the solution (*1*) in the presence and (*2*) in the absence of thiocyanate and (*3*) on ΔA_{600}. Concentrations: SCN^-, 5.0 mg/L; BrO_3^-, 3.0×10^{-4} M ($a_{CV} = 0.11$ mg/g, $t_{contact} = 3$ min, $n = 3$, $P = 0.95$).

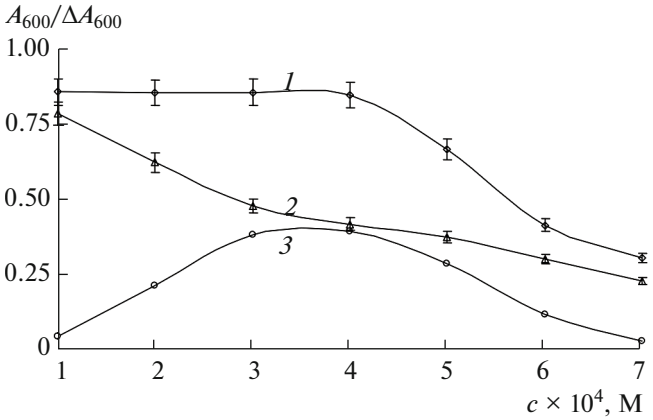

Fig. 3. Effect of the bromate ion concentration in the solution on the analytical signal A_{600} after contact of the matrix with the solution (*1*) in the presence and (*2*) in the absence of thiocyanate and (*3*) on ΔA_{600}. Concentrations: SCN^-, 5.0 mg/L; HCl, 0.3 M (a_{CV} = 0.11 mg/g, $t_{contact}$ = 3 min, n = 3, P = 0.95).

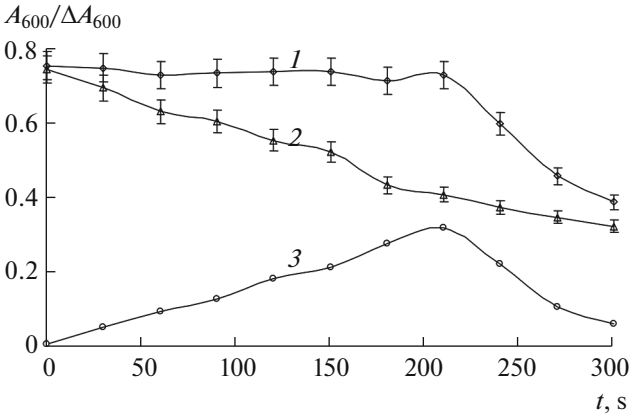

Fig. 4. Effect of the contact time of the polymethacrylate matrix with the solution (*1*) in the presence and (*2*) in the absence of thiocyanate on the analytical signal A_{600} and (*3*) on ΔA_{600}. Concentrations: SCN^-, 5.0 mg/L; HCl, 0.3 M; BrO_3^-, 3.0 × 10^{-4} M (a_{CV} = 0.11 mg/g, $t_{contact}$ = 3 min, n = 3, P = 0.95).

was found that in the oxidation of Crystal Violet immobilized in the polymethacrylate matrix, the most significant difference in absorption is achieved at a concentration of bromate ions in a solution of (3–4) × 10^{-4} M. Further increase in the bromate concentration in the test solution leads to discoloration of polymethacrylate plates with immobilized Crystal Violet both in the blank experiment and in the presence of thiocyanate in solution.

The effect of the contact time of Crystal Violet with bromate in the presence and absence of thiocyanate was studied at the most suitable concentration of the oxidant in the solution (Fig. 4). It can be seen that the absolute change in the analytical signal is maximal when the matrix interacts with the solution for 180–240 s. Based on the results, a contact time of 180 s was selected for further determination of thiocyanate.

The concentration of Crystal Violet in the matrix affects the absorbance of the plates after their contact with the test solution, determines the linearity range of the dependence of the analytical signal ΔA_{600} on the analyte concentration in solution, and affects the sensitivity of the determination and the limit of detection. The concentration of Crystal Violet in the polymethacrylate matrix was varied by changing the contact time of the matrix with the indicator during immobilization. The parameters of the calibration dependences for the determination of thiocyanate and the limit of detection calculated from the 3s-test, depending on the concentration of the indicator in the polymethacrylate matrix, are presented in Table 1.

When studying the interfering effect of foreign ions, we found that Ag(I), Cu(II), Fe(III), Hg(II), Cr(III), and Zn(II), which form complexes with the thiocyanate ion, and anions NO_2^-, I^-, and SO_3^{2-}, involved in redox reactions, have a significant effect on the determination of thiocyanate by the proposed procedure. The introduction of EDTA into the test solution decreased the interfering effect of metal cations. The standard addition method was used for plotting a calibration curve to eliminate the multiplicative system-

Table 1. Effect of Crystal Violet concentration in the polymethacrylate matrix on the parameters of calibration dependence for the determination of thiocyanate (λ = 600 nm, n = 3, P = 0.95)

Concentration of the indicator in the matrix, mg/g	Calibration equation	Analytical range, mg/L	LOD, mg/L	r
0.06	$\Delta A_{600} = 0.998c$	0.025–0.075	0.020	0.981
0.08	$\Delta A_{600} = 0.157c$	0.10–0.50	0.07	0.987
0.11	$\Delta A_{600} = 0.105c$	0.20–0.60	0.15	0.988
0.14	$\Delta A_{600} = 0.025c$	3.0–12.0	2.5	0.994

Table 2. Analytical characteristics of spectrophotometric and kinetic procedures for the determination of thiocyanate

Indicator reaction	λ_{max}, nm	Analytical range, mg/L	LOD, mg/L	Sample	Reference
Spectrophotometric procedures					
Fe(III)	490	0.4–8.0	0.104	Stratal water	[12]
König reaction	586	1.0–10* 0.13–1.33	–	Blood serum*, urine	[23]
Kinetic procedures					
Crystal Violet + $KBrO_3$	600	0.025–12.0	0.02	Reservoir water	This work
Methyl Orange + $KBrO_3$	525	0.01–2.32	0.004	Blood serum, saliva	[14]
Metacresol Purple + $KBrO_3$ + $NaIO_4$	525	0.02–0.80	0.005	Saliva, tap water, mineral water	[15]
Crystal Violet + $KBrO_3$	630	0.01–1.25	0.006	Saliva, tap water, mineral water	[16]
Methyl Red + $KBrO_3$ + $NaNO_2$	520	0.05–1.10	0.025	Urine, tap water, distilled water	[17]
Methylene Blue + $KBrO_3$	664	0.01–0.15	0.0038	Saliva, blood serum	[18]

atic errors associated with the effect of foreign components present in the test sample.

Based on the studies performed, a solid-phase spectrophotometric procedure involving a polymethacrylate matrix was proposed for the determination of thiocyanate; it was tested using a real sample. The accuracy of the developed procedure was evaluated by the results of the determination of a thiocyanate addition to the sample of near-wellbore water from the Festival'vnoye oil preparation unit in the Tomsk region. A graphical version of the standard addition method with three to four additions of the different amount was used. The calibration graph was described by the equation $\Delta A_{600} = 0.146 + 0.029c$, $r = 0.998$. To estimate the accuracy, we used the value σ, that is, the percentage ratio of the difference between the found (average) and the added concentration of the addition to the added amount. When 5.00 mg/L of thiocyanate was added, 5.0 ± 0.3 mg/L ($n = 3$, $P = 0.95$) was found; the relative standard deviation (RSD) and the measure of accuracy (σ) were 2.0 and 0.34%, respectively, indicating satisfactory accuracy and repeatability of the proposed procedure for the determination of thiocyanate.

Table 2 summarizes comparative characteristics of spectrophotometric and kinetic methods for the determination of thiocyanate ions. The proposed procedure is inferior to kinetic methods in the limit of detection, but it can be easily implemented on conventional spectrophotometric equipment and does not require the use of toxic reagents.

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