

# Solid Phase Spectrophotometric Determination of Silver Using Dithizone Immobilized in a Polymethacrylate Matrix

N. A. Gavrilenko and N. V. Saranchina

Tomsk State University, Department of Chemistry, pr. Lenina 36, Tomsk, 634050 Russia

Received August 13, 2008

**Abstract**—Interaction of silver with Dithizone immobilized in a polymethacrylate matrix was studied. A simple procedure was proposed for the solid phase spectrophotometric determination of silver; the detection limit is 0.01 mg/L. The procedure was used for the analysis of mineral waters and the Protargol medication.

**DOI:** 10.1134/S1061934810020085

The utilization of silver-containing species in industry and engineering leads to the gradual accumulation of the metal in the objects of environment. Because of its bactericide activity silver is widely used for the disinfection of drinking water. However, earlier there was reported about the interaction of silver with selenium, copper, and vitamins E and B<sub>12</sub> followed by the formation of potentially hazardous materials [1]. Therefore, the development of a convenient and selective procedure for the determination of silver in low concentrations in various objects is a problem of current importance. A variety of spectrophotometric procedures was proposed for determining silver; one of the most sensitive organic reagents used in the extraction–photometric determination of small amounts of silver is Dithizone [2, 3]. The immobilization of Dithizone in a transparent polymer matrix would allow the preconcentration of silver with its subsequent spectrophotometric determination using common equipment. In contrast to the extraction–photometric procedure, solid phase extraction appears environmentally friendly since it does not require toxic solvents in use. Moreover, a polymer matrix with an immobilized reagent could serve as an analytical tool for determination through a visual test [4] or as a recognition element for optical sensors [5, 6].

Herein, we report a study on the interaction of silver with Dithizone immobilized in a polymethacrylate matrix and a procedure for the solid phase spectrophotometric determination of silver.

## EXPERIMENTAL

The polymethacrylate matrix as a transparent plate  $0.60 \pm 0.04$ -mm thick was prepared by radical block polymerization according to [7]. Then, the plate prepared was cut to make smaller articles of measuring  $6.0 \times 8.0$  mm and weighing approximately 0.05 g.

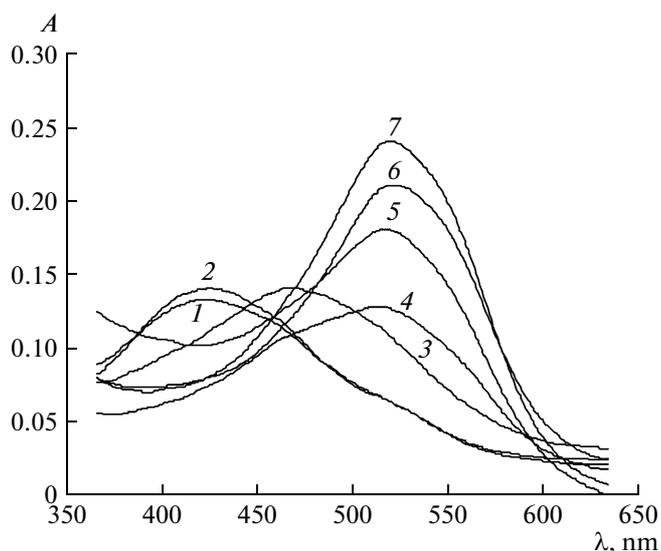
The working solution of Dithizone (0.002 M) was prepared by dissolving a precise portion in a 0.005 M

aqueous NaOH solution. The starting solution of silver with a metal concentration of 1 mg/mL was prepared by dissolving of a precise weight of silver nitrate in water according to the procedure published in [8]. The working solutions of silver with lower concentrations were prepared by the consecutive dilution of the stock solution in the day of experiments. All reagents were of chemically pure or analytical grades and used without additional purification. The required pH value was maintained with solutions of HNO<sub>3</sub> and NaOH and controlled by a I-160 potentiometer with ion-selective electrodes.

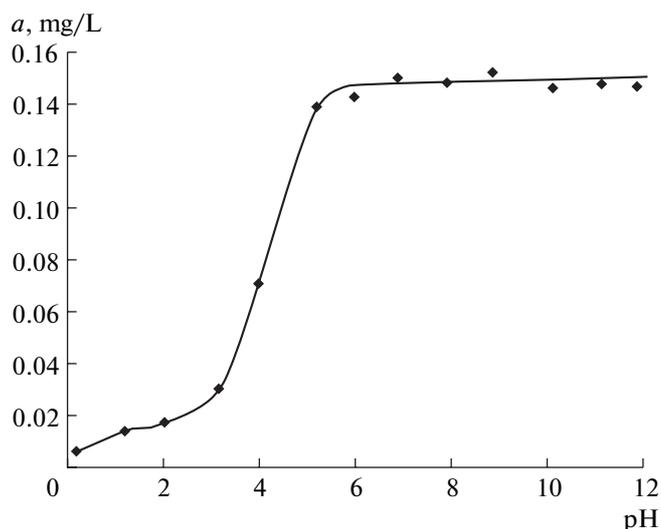
Dithizone was immobilized into a polymethacrylate matrix by adsorption from a solution in the batch mode. Therein, 25 mL of the reagent solution was stirred with polymethacrylate cuts for 1 min.; the matrix turned yellow-orange, because Dithizone in the matrix was in the enol [9].

The interaction of silver with Dithizone immobilized in a polymethacrylate matrix was investigated under batch conditions. A polymethacrylate cut with the immobilized reagent (0.05 g) was placed in the solution (50 mL) with various silver concentrations and pH values and stirred for 5–30 min. Then absorption spectra were registered or absorbance (*A*) was measured at the extinction maximum of the Ag(I)–Dithizone complex in the polymethacrylate matrix. The concentration of residual silver in the solution was determined by the spectrophotometric method [2, p. 111]. The degree of adsorption (*a*, mol/g) was calculated as follows:  $a = (c - [c]) V/m$ , where *c* and [*c*] are the initial and final concentrations of Ag(I) in the solution, M; *V* is the volume of the solution, L; *m* is the weight of the polymethacrylate cut.

The absorption spectra and absorbance of the solutions and polymethacrylate articles were determined on Evolution 600 and Spekol 21 spectrometers. The absorption properties of polymethacrylate cuts impregnated with Dithizone and those upon their



**Fig. 1.** Absorption spectra of a Dithizone-impregnated polymethacrylate matrix upon its contact with silver solutions at various pH ( $c_{\text{Ag}} = 1 \text{ mg/L}$ ,  $V = 50 \text{ ml}$ ). pH: 1—0; 2—2; 3—3; 4—4; 5—5; 6—6; 7—10.



**Fig. 2.** Amount of silver adsorbed on a Dithizone-impregnated polymethacrylate matrix as a function of pH ( $c_{\text{Ag}} = 1 \text{ mg/L}$ ,  $V = 50 \text{ mL}$ ,  $t = 30 \text{ min}$ ).

contact with silver solutions were measured with reference to the neat polymethacrylate matrix.

## RESULTS AND DISCUSSION

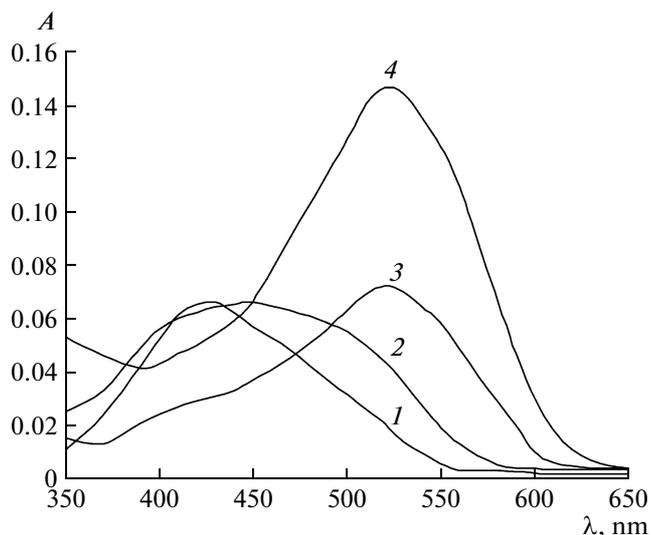
We studied the influence of the pH of solution on the adsorption of silver and the formation of its complex with the immobilized reagent in a polymethacrylate matrix. Figures 1 and 2 present absorption spectra and the quantity of silver adsorbed on the polymer matrix with immobilized Dithizone, respectively, as functions of the pH of solution. The adsorption of silver and the formation of complex occurred in the pH range from 3 to 12, achieving maximum values at pH 5–12. Upon the contact of the Dithizone-impregnated matrix with silver solutions at pH = 3, the absorption spectrum exhibited a maximum at the wavelength 465 nm, which indicated the formation of a keto-complex with a metal to reagent ratio of 1 : 1 ( $\text{AgDz}$ ). After treatment with silver solutions at pH 4–12, the cuts turned red-purple with a respective absorption maximum of 520 nm because of the formation of the enol-complex of silver dithizonate with a metal to reagent ratio of 2 : 1 ( $\text{Ag}_2\text{Dz}$ ).

The parameters of silver dithizonate in solution and in the polymethacrylate matrix are presented in Table 1. According to the published data [10], silver ions react with Dithizone in acid solutions to form monosubstituted silver keto-dithizonate. The compound is soluble in chloroform and  $\text{CCl}_4$ , has an intense yellow color, and is applicable for the extraction–photometric determination of silver. In contrast, in neutral and alkaline media, a doubly substituted silver enol-dithizonate forms, which is red-purple and soluble neither in water nor in common organic solvents. Thus, this compound is of no interest for spectrophotometric determination. However, the enol form of silver dithizonate formed upon the reaction of Dithizone in the polymethacrylate matrix with silver in neutral and alkaline solutions is compatible with the polymer matrix, does not affect its transparency and allows the direct measurement of optical parameters with high precision.

Figure 3 presents absorption spectra of the polymethacrylate matrix with immobilized Dithizone upon its contact with silver solutions of different concentrations at pH 10. Major changes in the spectra were observed at a wavelength of 520 nm.

**Table 1.** Properties of silver dithizonates in solution and in a polymethacrylate matrix

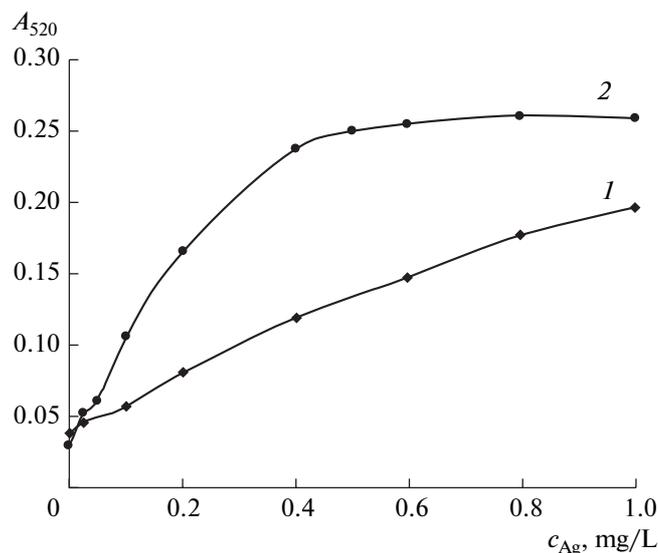
Medium	Complex stoichiometry	Complex color	$\lambda_{\text{max}}$ , nm	Acidity of Ag (I) solution
$\text{CCl}_4$ [5]	$\text{AgHDz}$	Yellow	462	Dilute mineral acid
	$\text{Ag}_2\text{Dz}$ (Insoluble in $\text{CCl}_4$ )	Red-purple	—	Neutral or alkaline media
Polymethacrylate matrix	$\text{AgHDz}$	Yellow	465	pH 3–4
	$\text{Ag}_2\text{Dz}$	Red-purple	520	pH 4–12



**Fig. 3.** Absorption spectra of a Dithizone-impregnated polymethacrylate matrix upon its contact to silver solutions of different concentrations ( $V = 50$  mL,  $t = 30$  min,  $\text{pH} = 10$ ).  $c_{\text{Ag}}$ , mg/L: 1—0; 2—0.025; 3—0.1; 4—0.2.

The time of the contact of the polymethacrylate matrix with the silver solution also affected the absorbance and determined the linearity range of the dependence analytical signal vs. the concentration of silver in the solution and the detection limit. The dependence of the analytical signal on the silver concentration in the solution at different contact times is shown in Fig. 4. Table 2 presents the parameters of calibration graphs and the detection limit calculated according to the  $3s$ -test.

The interference of equal, 10- and 100-fold amounts of the cations Ni(II), Zn(II), Co(II), Cu(II), Mn(II), Cd(II), Hg(II), Bi(III), and Pb(II) and anions  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  on the determination of silver was also investigated. The relative error of determining silver in the presence of a foreign ion was calculated by the equation  $\delta(\%) = [(A_i - A)/A] \times 100$ , where  $A$  and  $A_i$  are absorbances of polymethacrylate cuts impregnated by Dithizone upon their contact with silver solutions with and without interferences, respectively. As was shown in Table 3, a relative error of more than  $\pm 5\%$  was observed in the presence of Co(II), Zn(II), and chloride ions. To diminish the interference of Co(II), its preliminary separation was required; the effect of Zn(II) could be neutralized by



**Fig. 4.** Absorbance of a Dithizone-impregnated polymethacrylate matrix at 520 nm as a function of silver concentration in solution upon their contact for 10 (1) and 30 (2) min ( $V = 50$  mL,  $\text{pH} = 10$ ).

the addition of oxalic acid (0.05 mL of oxalic acid (0.01 M) per 50 mL of a tested test solution). The interference of up to 1000-fold excess of chloride ions was removed by the addition of Hg(II). The optimal concentration of Hg(II) depended on the concentration of chloride ions in the test sample; therefore, preliminary data on its concentration were necessary. The standard addition method can also be used. Iron(III) does not form a complex with Dithizone; moreover, it completely underwent hydrolysis under the conditions of determining silver at  $\text{pH} 10$  and did not interfere with the determination.

On the basis of the study performed, we developed a solid phase spectrophotometric procedure for the determination of silver. It was then verified in the analysis of mineral waters and the known Protargol medication. The determination was performed by the method of standard additions to avoid multiplicative systematic errors due to the interference of chloride and other sample components. Two or three replicate experiments using different additives values were performed; the results were presented in a graphical manner.

**Determination procedure.** A solution to be analyzed (0.10–10.00 mL) was placed in a 50-mL volumetric flask,  $\text{pH} 10$  was adjusted by adding NaOH

**Table 2.** Parameters of calibration graphs for the solid phase spectrophotometric determination of silver using Dithizone ( $V = 50$  mL;  $\lambda = 520$  nm;  $n = 5$ ;  $P = 0.95$ )

Time of contact, min	Equation	$R^2$	Analytical range, mg/L	$c_{\text{min}}$ , mg/L
10	$A = 0.04 + 0.17 c$	0.9939	0–0.80	0.04
30	$A = 0.03 + 0.68 c$	0.9916	0–0.20	0.01

**Table 3.** Determination of silver in the presence of foreign ions (added 0.2 mg/L Ag, pH = 10, time of contact 30 min)

Interfering ion	Ratio Ag : Me	$\delta$ , %
Co(II)	1 : 1	-20
	1 : 10	-39
Bi(III)	1 : 1	+3
	1 : 10	+4
Zn(II)	1 : 1	-20
	1 : 10	-20
	1 : 10*	-6
Pb(II)	1 : 10	+4
Cu(II)	1 : 10	+1
Cd(II)	1 : 10	0
Hg(II)	1 : 10	+1
Ni(II)	1 : 10	-1
NO <sub>3</sub> <sup>-</sup>	1 : 10	+3
PO <sub>4</sub> <sup>3-</sup>	1 : 10	-2
SO <sub>4</sub> <sup>2-</sup>	1 : 100	+5
Cl <sup>-</sup>	1 : 10	-28
	1 : 100	-36
	1 : 1000**	-4

Notes: \* In the presence of oxalic acid.

\*\* In the presence of Hg (II).

(checked by a pH-meter), the resulting mixture was diluted to the mark with water. Solutions to which 0.25, 0.50 and 0.75 mL of the working solution of Ag(I) (10 mg/L) was added were prepared similarly in other flasks. A cut of a Dithizone-impregnated poly-methacrylate matrix was put into the solutions followed by stirring for 10 or 30 min (depending on the concentration measured); then the cut was removed and dried with a piece of filter paper. Absorbance was measured at 520 nm. The concentration of silver was determined by the graphical method by extrapolating the linear dependence of absorbance (taking into account background absorbance) on the concentration of silver added to the value  $A = 0$ .

**Preparation of mineral water to analysis.** The determination of silver in mineral water was performed after its tenfold preconcentration by evaporation in the presence of a small amount of nitric acid. An aliquot portion of 10.00 mL was taken for the analysis.

**Preparation of Protargol samples to analysis.** A 1 mL portion of a 2 % solution of the medication was placed in a porcelain cap and concentrated nitric acid (3 mL) was added. The mixture was heated until silver dissolved and then cooled. Next the mixture was transferred into a 25.0-mL volumetric flask and diluted to the mark with water. An aliquot portion (0.10 mL) of the solution prepared was used for the analysis.

The results are presented in Table 4. The results were verified by the added found method and, in the case of Protargol, by comparison with the results of

**Table 4.** Determination of silver in real objects ( $n = 5$ ;  $P = 0.95$ )

Object	Official certificate data	Input, mg/L	Found, mg/L	$s_r$	$\delta$ , %
Mineral water					
"Crystalline Cedar" (Cl-content 0–19 mg/L)	0.005–0.05 mg/L	0	0.022 ± 0.005	0.18	–
		0.05	0.075 ± 0.004	0.04	106
"Aqua Minerale" (Cl-content 50 mg/L)	–	0	–	–	–
		0.06	0.061 ± 0.009	0.11	102
Medication "2 % aqueous protargol solution"	0.156–0.166%*	0	(0.153 ± 0.017)%	0.09	–
			0.152 ± 0.008)**	0.02	–

Notes: \* Calculated by the known concentration of silver in Protargol, 7.8–8.3 % to metal.

\*\* Found by potentiometric titration.

 $\delta$  is the ratio of added and found concentrations.

determining by potentiometric titration [11]. The data obtained indicated accuracy and reproducibility of the proposed procedure for determining Ag (I). The procedure developed is more convenient, sensitive, and environmentally safe in comparison to the extraction–photometric version [3].

#### ACKNOWLEDGMENTS

We are grateful to Dr. S.V. Shumar for determining silver in the Protargol medication by potentiometric titration. This work was supported by the Russian Foundation for Basic Research, project no. 08-03-90714.

#### REFERENCES

1. Shamsipur, M., Alizadeh, K., Hosseini, M., Caltagirone, C., and Lippolis, V., *Sen. Actuators, B*, 2006, vol. 113, no. 2, p. 892.
2. Pyatnitskii, I.V. and Sukhan, V.V., *Analiticheskaya khimiya serebra* (Analytical Chemistry of Silver), Moscow: Nauka, 1975.
3. *GOST (State Standard) 23268.13-78: Drinking Medicinal, Medicinal-Table and Natural-Table Mineral Waters*, Moscow: Izd-vo standartov, 2003.
4. Zolotov, Yu.A., Ivanov, V.M., and Amelin, V.G., *Khimicheskie test-metody analiza* (Chemical Test Methods of Analysis), Moscow: Editorial URSS, 2002.
5. *Optical sensors: Industrial, Environmental and Diagnostic Applications*, Narayanaswamy, R. and Wolfbeis, O.S., Eds., New York: Springer, 2004.
6. Narayanaswamy, R., *Acta Biologica Szegediensis*, 2006, vol. 50, nos. 3-4, p. 105.
7. Gavrilenko, N.A. and Mokrousov, G.M., RF Patent 2272284, 2004.
8. *GOST (State Standard) 4212-76: Reagents: Methods for Preparing Solutions for Colorimetric and Nephelometric Analysis*, Moscow.
9. Saranchina, N.V., *Cand. Sci. (Chem.) Dissertation*, Tomsk: Tomsk State Univ., 2008.
10. Sandell, E.B., *Colorimetric Determination of Traces of Metals*, New York: Interscience, 1959.
11. Mar'yanov, B.M., Zarubin, A.G., and Shumar, S.V., *Zhurn. anal. khim.*, 2003, vol. 58, no. 4, p. 342 [*J. Anal. Chem.* (Engl. Transl.), vol. 58, no. 4, p. 300].

SPELL: 1. Caltagirone