ARTICLES

Sorption–Photometric and Test Determination of Lead in Environmental Materials

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Abstract—The main analytical characteristics of the reaction of hexaoxacycloazochrom with lead were determined. A method for the sorption preconcentration of lead on the Thiopan 14 sorbent was proposed. Procedures were developed for the photometric determination of lead in natural waters, air, and soil at the level of the maximum permissible concentration. A new melange gel technique for preparing silicic acid xerogels modified with hexaoxacycloazochrom was developed for the test determination of lead in environmental samples at the level of the maximum permissible concentration.

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Lead compounds have carcinogenic, mutagenic, and gonadotoxic effects and cause the affection of central and peripheral nervous systems, paralysis, and blood and vessel diseases [1]. Inorganic lead compounds disturb metabolism and are enzyme inhibitors. Lead can replace calcium in bones and is accumulated there, yielding a permanent source of intoxication [2]. Lead has a detrimental effect on soil and water biota [3, 4].

The major suppliers of lead compounds to the environment are mineral resources, metallurgy, glass, and ceramic industries; television and radio equipment manufacturing; paint and varnish industry; motor transport, plants manufacturing lead accumulators, etc. Therefore, lead monitoring in environmental materials is necessary, especially near possible pollution sources.

Low values of the maximum permissible concentration (MPC) of lead in environmental materials (MPC $_{\rm Pb}$ is 0.03 mg/L in water (sanitary regulations) [34], 0.001 mg/m³ in air [35], and 130 mg/kg in soil (tentative permissible concentration, TPC) [36]) require the development of procedures for analysis with very low detection limits.

Currently, lead is determined in environmental materials using atomic absorption and atomic emission spectrometry (including inductively coupled plasma), voltammetry, X-ray fluorescence analysis, luminescence analysis, and neutron activation analysis [4–16]. Atomic absorption spectrometry is included in GOST (State Standard) as the main method [17].

An available and simple photometric method for the determination of lead in environmental materials with the use of organic reagents is also popular [4, 18–25]; the characteristics of the reagents are presented in Table 1. The majority of these reagents exhibit low selectivity, which substantially decreases their value. Therefore, the development of selective photometric methods for the determination of lead at a level of a fraction of the MPC is an important problem.

In this work, we examined the photometric determination of lead in environmental materials with the use of hexaoxacycloazochrom, which, according to [26, 27], exhibits high selectivity for lead(II) ions.

EXPERIMENTAL

A stock 1.0×10^{-1} M solution of lead nitrate was prepared by dissolving a weighed portion of lead metal (high-purity grade) in conc. HNO₃. Working 1.0×10^{-3} and 1.0×10^{-4} M solutions of lead were prepared by dilution with 0.05 M HNO₃ or HCl directly before use. Stock solutions of acids (HCl, H_2SO_4 , and HNO₃) were prepared from commercial volumetric solutions. Solutions of NaOH (chemically pure grade), NaCl (analytical grade), and CH_3COONH_4 (chemically pure grade) were prepared from weighed portions of the corresponding compounds.

To prepare a 0.01% solution of hexaoxacycloazochrom, 0.01 g of the compound was dissolved in 100 mL of doubly distilled water and passed through a KU-2 cation exchanger pretreated with 2 M HCl and washed with doubly distilled water to pH 4 (by Methyl Orange) for converting into the H form.

Acidity was controlled on a pH-673M pH meter with a glass electrode. Absorbance was measured on an SF-46 spectrophotometer. Atomic-absorption determinations were performed on an AS-1 spectrometer (a non-flame atomizer was used in the analysis of waters). Solutions were stirred on a mechanical shaker (Laboratory Shaker type 358S).

For the construction of the calibration plot in the determination of lead in natural waters, portions of 0.04–0.1 mg of a reference solution of lead were places

Reagent	LDL* $(AR**), \mu g/mL$	Conditions of determination	Material	References
Dithizone	0.05 $(3-70 \mu g \, Pb/50 \, mL)$	λ_{max} = 520 nm, $\epsilon = 6.86 \times 10^4$, $pH 8-10$ (CHCl ₃)	Water, soil, air	[4, 22, 23, 24]
Sulfarsazene	0.1 (up to $11 \mu g/5$ mL)	$\lambda_{\text{max}} = 500 \text{ nm},$ $t = 30$ min. pH 9.2 (CHCl ₃)	Soil, natural water	[18, 24]
Arsazene	$0.5 \mu g / 50 \text{ mL}$	$\lambda = 480$ nm, pH 9-8 (butanol)	Natural water	$[24]$
4-(2-Pyridylazo)re- sorcinol	0.01	λ = 520 nm, 3.5 M HCl, $DRS***$ pH 10 (sorption preconcentration)	Air, fresh water	[19, 22, 25]
Formazan VIII	0.16	λ = 690 nm, $\epsilon = 2.47 \times 10^4$, $t = 5$ min	Model solutions	$[18]$
Hexaoxacycloazo- chrom	0.002 $(0.5-10 \mu g/250 \text{ mL})$	λ = 720 nm, extraction with a dithizone solution, 0.05 M HCl	Natural water	[26, 27]
Xylenol Orange [Fe(III)]	$(10-100 \mu g/L)$	pH 5.0, NH_4F ; t 5 min, test method	Deep-well water	$[20]$
Arsenazo III, Sulfona- zo III, Pyrocatechol Violet	0.04 $(0.04-4.4)$	Solid-phase spectrophotometry	Model mixtures (food samples)	$[21]$

Table 1. Reagents for the photometric determination of lead(II) in environmental materials

* LDL is lower determination limit.

** AR is analytical range.

*** DRS is diffuse reflectance spectrometry.

in fused-silica test tubes, $K_2S_2O_8$ was added, and the mixtures were irradiated for 30 min with ultraviolet light from a DRT 375 mercury lamp. Next the solutions were transferred to conical flasks, pH 4 was adjusted, and Seignette salt and Thiopan 14 were added. Sorption was performed for 30 min with continuous stirring on an oscillating agitator. The sorbent with the adsorbate was separated from the mother solution, washed with distilled water, and poured over with 0.05 M HCl. Within 20 min, the eluate was transferred to a 25-mL volumetric flask, and the operation was repeated once again. Wash solutions were combined. A solution of hexaoxacycloazochrom (1 mL) was added to the flask, the mixture was diluted with 0.05 M HCl to the mark, and the absorbance $(720 \text{ nm}; l = 5 \text{ cm})$ was measured with respect to the reference solution.

To construct a calibration plot for the determination of lead in air, 0.04- to 0.1-mg portions of a reference solution of lead were placed on Petryanov filters. The filters were treated with a H_2SO_4 : HNO_3 : $HClO_4$ = 2 : 1 : 1 mixture and heated on a sand bath until the filters were completely incinerated. The resulting solutions were evaporated. The dry residue was dissolved with heating in 0.6 M HCl and quantitatively transferred into 25-mL volumetric flasks, 1 mL of a solution of hexaoxacycloazochrom was added to each flask, the

mixtures were diluted to the mark, and photometry was performed within 10–15 min at 720 nm and $l = 5$ cm. The absorbance was measured with respect to a solution passed through all operations but containing no lead salt.

For the construction of the calibration plot in the determination of the total concentration of lead in soil, portions of 0.04–0.1 mg of a reference solution of lead, 5 mL of a mixture concentrated $HCl : HNO₃ = 3 : 1$, and 10 mL of HF were placed in porcelain dishes and slowly evaporated to dryness on a closed-coil plate. Next, 0.05 M HCl was added to the dry residue, and the mixture was heated to complete dissolution. The solution was quantitatively transferred to 25-mL volumetric flasks, Seignette salt and 1 mL of a solution of hexaoxacycloazochrom were added to each flask, the mixtures were diluted to the mark with 0.05 M HCl, and the absorbance was measured within 15 min.

A sample of Thiopan 14 was pretreated with 0.1 M NaOH for 10 min and next washed with distilled water to pH 8.0.

Modified silicic acid xerogel was obtained as follows: 5 mL of a 20% solution of OP-10, 2 mL of a solution of hexaoxacycloazochrom, and 3 mL of 0.1 M HCl were placed in a 5-mL conical test tube and heated on a glycerol bath to the complete segregation of the micel-

Fig. 1. Absorption spectra of (*1*) hexaoxacycloazochrom and (*2*) its complex with lead(II).

lar phase of the nonionic surfactant containing the organic reagent. The micellar phase was separated by decantation and thoroughly stirred with a weighed portion of xerogel obtained from silicate glue. Melange gel was dried at 100° C to the granular state.

For the construction of the sorption isotherm, a series of reference solutions of the lead salt (0.1– 2.0 mg/mL) were prepared, pH 4.0 and ionic strength 0.1 were adjusted, and the solutions were diluted to 20 mL. Thiopan 14 (0.1 g) was added, and the solutions were placed in a shaker. Within 30 min, the concentration of lead in the solution was determined by spectrophotometry. Specific adsorption (Γ, mg/g) was calculated by the formula [37]

$$
\Gamma(mg/g) = \frac{(c_0 - c)V}{m},
$$

where c_0 and c are the concentrations of lead in the solution before and after sorption, respectively, mg/mL; *V* is the volume of the solution, mL; *m* is the mass of the sorbent, g.

RESULTS AND DISCUSSION

Because of the scarce data on the behavior and properties of hexaoxacycloazochrom in complex systems [26], we refined the optimum conditions of its interaction with lead ions in the studied system: 0.05–0.1 M HCl; *t* = 10 min; 25–30°C. The absorption spectra of the reagent and its complex are presented in Fig. 1. By the variable concentration method, it was confirmed that the ratio of the components in the complex is $Pb(II)$: hexaoxacycloazochrom = $1:2$ (Fig. 2). The arbitrary molar absorptivity is 5.5×10^4 .

Curves of the saturation of the complex with one of the reagents (Fig. 2) were used for the calculation of the stability constant (K_{stab}) [28] by the formula

$$
\frac{1}{K_{\text{stab}}} = \frac{(c_{\text{Pb}} - c_x)(c_{\text{R}} - nc_x)^n}{c_x},
$$

Fig. 2. Curves of saturation with (a) lead(II) and (b) the reagent in the system Pb(II)–hexaoxacycloazochrom: (a) $c_{\text{HOCAC}} = 9 \times 10^{-6}$ M, 720 nm, $l = 2$ cm; (b) $c_{\text{Pb(II)}} =$ 5×10^{-6} M, 720 nm, $l = 2$ cm.

where c_x is the equilibrium concentration of the component, M; c_{Ph} , and c_{R} are the initial concentrations of lead(II) and the reagent, respectively, M; and *n* is the number of molecules of the reagent per one metal ion $(n=2)$.

The equilibrium concentration of the complex (c_x) was calculated by the formula

$$
c_x = \frac{\Delta A}{(\epsilon_{\rm C} - \epsilon_{\rm R})l},
$$

where ε_c and ε_R are the molar absorptivities of the complex and the reagent, respectively, at the given wavelength.

As a result of calculations, it was found that $K_{stab} =$ 5×10^7 . The stability of the resulting complex and the high selectivity of this reaction are typical for the products of the interaction of crown ethers with metal ions.

The Beer law is fulfilled in the concentration range 0.04–0.1 mg/L lead. Taking into account that the concentration of lead in natural waters can be lower than this interval, the preconcentration of lead is sometimes necessary. The technique described in [26] on the basis of extraction with a chloroform solution of dithizone is complicated and has some disadvantages in chemism. Therefore, we developed a sufficiently simple technique for the preconcentration of lead with the use of chelating sorbents.

Fibrous chelating sorbents with high sorption capacity with respect to metal ions (Thiopan 2, Thiopan 13, Thiopan 14, Polyorgs VII, and Polyorgs VII M) were approved for the sorption preconcentration of lead [29,

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Table 2. Main characteristics of chelating sorbents with respect to 0.04–0.1 mg/mL lead

30]; the characteristics of these sorbents are presented in Table 2.

From the data in Table 2, it follows that Polyorgs VII M and Thiopan 14 exhibit the best sorption properties with respect to lead(II). For the subsequent studies, we selected Thiopan 14 because of the milder conditions of its preliminary preparation. In the determination of the conditions of the sorption of lead, we studied the effect of the acidity of the solution, the technique for the preliminary preparation of the sorbent, the equilibration time, and the ionic strength of the solution.

It was found that the sorption of lead in the concentration range 0.01–10.0 mg/L on Thiopan 14 is maximum within 30 min. The acidity of the initial solution is a substantial factor. Figure 3 presents the dependence of the sorption capacity of Thiopan 14 with respect to lead ions (SC_{Ph}) on the pH of the studied solution. From the figure, it follows that the sorption is maximum at pH 4.0. The optimum ionic strength of the solution is $\mu \geq 0.1$. Heating to 70–80°C does not change the sorption properties of Thiopan 14.

The sorption isotherm of lead on Thiopan 14 was constructed under the optimum conditions (Fig. 4). According to Gils's classification [31], the isotherm has the H form, which is indicative of chemisorption. The sorption isotherm of lead on Thiopan 14 is described by the Langmuir equation and has the linear form in the Γ^{-1} -c⁻¹ coordinates.

For the convenience of the subsequent photometric determination with hexaoxacycloazochrom, lead was desorbed with 0.05–0.1 M HCl. Under the determined optimum conditions at concentrations of 0.01–10.0 mg/L lead, the recovery is 89–95%.

The sorption of other metal ions at the surface of Thiopan 14 was studied under the determined optimum conditions. The data are presented in Table 3. From the figure, its follows that the sorption of $Hg(II)$, Fe(III), Al(III), Cu(II), Cd(II), and some other metal ions is also possible at pH 4.0. Only mercury ions interfere, because their sorption is comparable with the sorption of lead. The presence of 500-fold amounts of iron(III) and 1000-fold amounts of aluminum(III) does not affect the sorption of lead.

We additionally studied the effect of these ions on the photometric determination of lead with hexaoxacycloazochrom. The experimentally determined high selectivity factors $(Hg(II) > 1000; Cu(II) > 100;$ $Zn(II) > 200$; Cd(II) > 200; Mo(VI) > 200; Fe(III) > 200; Al(III) > 150 ; Fe(II) > 400) clearly demonstrate the absence of the interfering effect of these ions in the analysis of environmental materials.

As a result of our studies, we developed procedures for the sorption–photometric determination of lead(II) in natural materials.

Photometric determination of lead(II) in natural waters. An aliquot portion of natural water is placed in a fused-silica test tube, $K_2S_2O_8$ is added, and the mixture is irradiated for 30 min with ultraviolet light from a DRT 375 mercury lamp for the destruction of natural organic compounds. After cooling, the sample is transferred into a conical flask, pH 4.0 is adjusted with an ammonium solution, Seignette salt is added, and Thiopan 14 previously converted into the OH form is introduced into the sample. Sorption is performed for 30 min with continuous stirring. Next the sample of water with the sorbent is passed through a white ribbon filter; the sorbent is quantitatively transferred into a

Table 3. Results of the determination of lead (μ g/L) in natural waters (MPC = 30 μ g/L)

Source	n	Spectrophotometry (SP) method	RSD, $%$	AAS	RSD, $%$
Volga River (Saratov)	10	12.4 ± 0.8		12.2 ± 0.8	
Volga River (Vol'sk)		17.3 ± 1.6		17.1 ± 2.4	12
Akhmat River		5.8 ± 0.3		5.7 ± 0.3	
Chapaevka River		5.0 ± 0.3		4.8 ± 0.4	

Fig. 3. Dependence of the sorption capacity of Thiopan 14 on pH for different metal ions; (*1*) Pb(II), (*2*) Hg(II), (*3*) Cd(II), (*4*) Fe(III), (*5*) Al(III), (*6*) Cu(II), (*7*) In(III), (*8*) Zn(II), (*9*) Ni(II), (*10*) Ca(II), (*11*) Cd(II), (*12*) Co(II), (*13*) Cr(III), and (*14*) Mg(II).

beaker, washed with distilled water, and flooded with 0.05 M HCl. Within 20 min, the eluate is separated from the sorbent and transferred into a 25-mL volumetric flask; the sorbent is washed with a new portion of HCl. The wash solution is combined with the first portion of acid. A solution of hexaoxacycloazochrom is added to the obtained solution, and the mixture is diluted with water to the mark with 0.05 M HCl. Within 10–15 min, the absorbance (720 nm, $l = 5$ cm) is measured with respect to a reference solution. The concentration of lead is determined by the calibration plot.

The proposed procedure was approved with natural waters (Table 3). The accuracy of the results was verified by atomic absorption spectrometry (AAS). The

Table 4. Results of the determination of lead in samples of atmospheric air (μ g/m³) (MPC_{Pb} = 1.0 μ g/m³)

SP method	RSD, %	AAS	RSD, %
0.28 ± 0.03	11	0.31 ± 0.02	10
0.65 ± 0.03	5	0.66 ± 0.05	
0.68 ± 0.02	3	0.69 ± 0.06	
0.38 ± 0.03	5	0.35 ± 0.04	
0.27 ± 0.01	11	0.29 ± 0.03	
0.41 ± 0.02		0.40 ± 0.05	

Fig. 4. Sorption isotherm of lead(II) on Thiopan 14 (pH 4.0, $\mu = 0.1, t = 30$ min).

data in Table 3 indicate that systematic errors are absent. The determined range of concentrations of lead in natural waters is in good agreement with the data reported in the literature for other aqueous samples [4, 26].

Photometric determination of lead in air. Samples are taken using a Post-2 complex stationary laboratory passing air through Petryanov filters at a height of 1.5–2 m over the ground surface taking into account the wind direction. The flow rate of air is 100 L/min; the time of sampling is 20 min. Next the filter is treated with a H_2SO_4 : HNO_3 : $HClO_4 = 2 : 1 : 1$ mixture and heated on a sand bath to complete incineration. The resulting solution is repeatedly treated with several portions of the acid mixture to complete clarification. Next the solution is evaporated. The dry residue is dissolved with heating in 0.6 M HCl and quantitatively transferred into a 25-mL volumetric flask, a solution of hexaoxacycloazochrom is added, water is added to the mark, and photometry is performed (after 10–15 min at 720 nm and $l = 5$ cm). The results of the analysis of air samples are presented in Table 4. The accuracy of the results was verified by atomic absorption spectrometry, which confirms the absence of systematic errors in the proposed procedure (Table 4).

Photometric determination of lead in soil. Samples of soil are taken according to GOST (State Standard) 17.4.3.01-83. Samples are taken by the "envelope" rule in the turf horizon (down to 0.2 m) and in the humus horizon ($h \approx 0.5{\text -}0.7$ m) with a total mass of 1– 1.5 kg. After drying the samples to the air-dry state at 18–25 $\rm{°C}$, grinding, sieving with *d* ≤ 1 mm, and successive quartering, laboratory samples with a mass of 1.00–5.00 g are taken. In the determination of the total concentration of lead, samples are decomposed with a mixture of HCl, $HNO₃$, and HF [23]. For this purpose, 3–5 mL of a mixture of concentrated HCl and $HNO₃$ $(3:1)$ and 10 mL of HF are added to 1.00 g of soil wetted with distilled water, and the sample is slowly heated on a closed-coil plate to wet salts. The treatment with 5-mL portions of HF is repeated two or three times. To remove excess fluorine, the dry residue is treated with concentrated $HNO₃$ and next evaporated to dryness; the operation is repeated two times. Next, 0.5 M HCl is added to the residue; the mixture is heated to boiling, filtered trough a white ribbon filter into a volumetric flask, and diluted to the mark with HCl. An aliquot portion of the resulting solution is placed in a 25-mL volumetric flask, a 5% solution of Seignette salt and a solution of hexaoxacycloazochrom are added, and the mixture is diluted to the mark with 0.05 M HCl. Within 15 min, the absorbance is measured at 720 nm, and the concentration of lead is calculated by the calibration plot.

The determined values of the total concentration of lead in samples of soil about pollution sources are presented in Table 5. The accuracy of the obtained results was verified by atomic absorption spectrometry.

In recent years, test systems on the basis of sorbents modified with organic reagents have been widely used for analysis at sampling locations [19, 20, 22, 29, 32]. However, the immobilization of hexaoxacycloazochrom on solid matrices has not been performed previously.

Test determination of lead in soil extracts. We obtained silicic acid xerogel modified with hexaoxacycloazochrom from silicate glue. The immobilization of hexaoxacycloazochrom was performed by the new melange gel technique [33], which is based on applying the reagent concentrated in the micellar phase of a nonionic surfactant to the surface of xerogel. The obtained indicator powder is used for the test determination of lead with the visual detection of the analytical signal.

The optimum conditions of the interaction of immobilized hexaoxacycloazochrom with lead were determined: $0.05-0.1$ M HCl or HNO₃; mass of the sorbent 0.1 g; minimum volume of the solution 2 mL; and time of color development 10–15 min. The concentration of lead is determined from the color intensity of the indicator powder placed in the analyzed solution by comparing with the previously constructed calibration color scale.

The lower determination limit of lead by the test method is 10^{-6} M or 0.2 μ g/mL. This value of the lower determination limit allows the determination of lead in soil at a level of the maximum permissible concentration and its fractions. Silicic acid xerogel modified with hexaoxacycloazochrom as an indicator powder was used for the determination of lead in acidic extracts from soils [23]. For this purpose, a weighed portion of soil, which was previously dried and ground to the powder state, is flooded with $HNO₃$ in the ratio 1 : 10. The mixture is continuously stirred on a shaker for 1 h, and next filtered through a blue ribbon filter. A weighed portion of the indicator powder is added to an aliquot

Table 5. Total concentration of lead in soil samples (mg/kg) $(TPC_{[Pb(II)]} = 130 \text{ mg/kg})$

Industrial source of pollution			Highway		
sample number	SP meth- od	AAS	sample number	SP meth- od	AAS
1	98 ± 2	103 ± 5	1	75 ± 3	75 ± 4
$1d*$	118 ± 3	120 ± 7	$1d*$	42 ± 1	40 ± 3
3	141 ± 6	138 ± 9	2	98 ± 1	
$3d*$	171 ± 7	176 ± 11	$2d*$	55 ± 4	51 ± 4
5	80 ± 2		3	70 ± 3	75 ± 4
$5d*$	56 ± 4		$3d*$	36 ± 1	
8	93 ± 3	92 ± 3	4	57 ± 1	
$8d*$	74 ± 4	77 ± 5	$4d*$	52 ± 1	51 ± 4
9	57 ± 3	60 ± 4	5	53 ± 2	55 ± 5
10	42 ± 4	40 ± 1	$5d*$	50 ± 3	52 ± 4
12	17 ± 2	16 ± 3	6	52 ± 1	53 ± 5
			$6d*$	61 ± 2	62 ± 7
			7	112 ± 3	
2011	\sim 1	\sim 1.1	$7d*$ $c \wedge r \wedge r$	96 ± 5	

* Soil layer taken at a depth of 0.5–0.7 m.

Table 6. Results of the analysis of soil samples by the test method (concentration of Pb(II), mg/kg)

Test method	Spectrophotometry
40	43.2 ± 3.1
50	49.4 ± 2.2
60	58.1 ± 6.0
100	108.4 ± 4.2
95	98.2 ± 7.3
20	$18.4 + 2.2$

portion of the acidic extract, and within 15 min its color is compared with the color scale. The obtained results are presented in Table 6.

The accuracy of the results of the test determination of lead was verified by spectrophotometry (Table 6).

Thus, the high selectivity of the interaction of hexaoxacycloazochrom with lead(II) in combination with sorption preconcentration allowed the development of simple and available photometric and test procedures for the determination of lead in different environmental materials at a level of fractions of the maximum permissible concentration.

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