Spectrophotometric determination of trace concentrations of lead using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of nonionic surfactants

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On the basis of thorough spectrophotometric study of the chelate-forming reactions of the Pb(II) ions with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP) in aqueous—ethanolic medium containing nonionic surfactants, the optimum conditions for elaboration of a highly sensitive and selective method of determination of trace concentrations of lead have been found. In the medium containing 50 vol. % ethanol, TRITON X-100 ($\varrho = 3\ \mathrm{g\,dm^{-3}}$), and $0.1\ \mathrm{mol\,dm^{-3}}$ ammonia or hexamethylenetetramine buffer of pH = 8, the $\mathrm{PbL^+}$ chelate exhibits the value of molar absorption coefficient $\varepsilon = 6.5\ \mathrm{mmol^{-1}\,m^2}$ at $\lambda = 575\ \mathrm{nm}$, the logarithm of the conditional stability constant being $\log \{\beta\} = 10.6$. By using KCN ($c = 2 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$), thiourea ($c = 1 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$), and KF ($c = 5 \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$) the interfering influence of the majority of multivalent elements can be eliminated and the method enables us to determine $\varrho(\mathrm{Pb})$ present in tens of $\mathrm{ng\,cm^{-3}}$ ($c = 2 \times 10^{-8}$—$2 \times 10^{-5}\ \mathrm{mol\,dm^{-3}}$) within accuracy exceeding 1 % rel.

На основе подробного спектрофотометрического изучения хелатообразующих реакций ионов Pb(II) с 2-(5-бром-2-пиридилазо)-5-диэтиламинофенолом (BrPADAP) в водно-этанольной среде в присутствии неионных тензидов были определены оптимальные условия для разработки высокочувствительного и селективного метода определения следовых концентраций свинца. В среде с 50 об. % этанола и ТРИТОНА X-100 ($\varrho = 3\ \text{г дм}^{-3}$), 0,1 моль дм$^{-3}$ аммониевого или гексаметилентетраминового буферного раствора с pH = 8 хелат $\mathrm{PbL^+}$ характеризуется величиной мольного коэффициента поглощения $\varepsilon = 6{,}5\ \text{ммоль}^{-1}\ \text{м}^2$ при $\lambda = 575\ \text{нм}$ и логарифмом условной константы устойчивости $\log\{\beta\} = 10{,}6$. В присутствии KCN ($c = 2 \,.\, 10^{-2}$ моль дм$^{-3}$), тиомочевины ($c = 1 \,.\, 10^{-2}$ моль дм$^{-3}$) и KF ($c = 5 \,.\, 10^{-4}$ моль дм$^{-3}$) было устранено мешающее влияние большинства многовалентных элементов и, таким образом, данный метод позволил определить $\varrho(\mathrm{Pb})$ в количестве десятков нг см$^{-3}$ ($c = 2 \,.\, 10^{-8}$—$2 \,.\, 10^{-5}$ моль дм$^{-3}$) с точностью лучшей, чем 1 % рел.

Lead gives colour reactions with *N*-heterocyclic azo dyestuffs. These reactions may be used as a basis for highly sensitive but poorly selective determination of lead [1]. The elaboration of the spectrophotometric methods of determination of the Pb(II) ions is frequently based on the formation of the chelates of lead with 4-(2-pyridylazo)-resorcinol (PAR), 4-(2-thiazolylazo)-resorcinol (TAR) or 1-(2-pyridylazo)-2-naphthol (PAN). Recently, the greatest attention has been especially concentrated on the class of azo dyestuffs on the base of the derivatives of 2-(2-pyridylazo)-5-diethylaminophenol (PADAP) which belongs among the most sensitive reagents in the series of *N*-heterocyclic azo dyestuffs. The monohalo derivatives BrPADAP and ClPADAP are most frequently used in practice.

BrPADAP as well as analogous ClPADAP reacts with a great number of cations [2—4]. A high sensitivity of these reactions with the majority of elements is pointed out in literature. In most cases, the reactions of BrPADAP are approximately twice more sensitive than the corresponding reactions of the most frequently used PAR. The molar absorption coefficients ε of its chelates with ions of the transition metals assume the values of about $10\,\mathrm{mmol^{-1}\,m^2}$. The absorption maxima of these metal chelates occur in the range of wavelengths 520—600 nm, which makes possible to determine several ions present with each other as demonstrated by the example of the mixture of Co(III) and Zn(II) or other mixtures [2]. The colour contrast arising in chelate-forming reactions of BrPADAP is much stronger than that one arising in the corresponding reactions of PAR and is $\Delta\lambda_{\max} = \lambda_{\max}(\mathrm{ML}) - \lambda_{\max}(\mathrm{L}) > 100\,\mathrm{nm}$.

Some metal chelates, especially $\mathrm{ML_2}$ chelates are easily extractable into organic solvents of the type of chloroform, benzene, cyclohexanone, tributyl phosphate, nitrobenzene, *etc.* [5, 6]. The sensitivity of the spectrophotometric methods of determination may, in many cases, be improved by the presence of surface-active substances — surfactants of the ionic as well as nonionic character [6, 7].

Gusev and *Nikolaeva* [8] were the first authors who used the reaction of Pb(II) with BrPADAP for extractive photometric and titrimetric determination of the Pb(II) ions in the analysis of lead alloys containing antimony, tin, and copper. They found the absorption maximum at $\lambda = 575\,\mathrm{nm}$ ($\varepsilon = 4.9\,\mathrm{mmol^{-1}\,m^2}$) for the metal chelate with the amount of substance ratio 1 : 1. They quantitatively extracted the chelate into chloroform, tributyl phosphate or benzene at pH > 6. They performed the proper extractive photometric determination of the Pb(II) ions in the medium of the borate buffer solution of pH 8—9 by using the absorption maximum of the chloroform extract at $\lambda = 560\,\mathrm{nm}$.

The aim of this study has been to find out the optimum conditions for elaborating a highly sensitive method of determination of the Pb(II) ions on the basis of a thorough study of the chelate-forming equilibria of the Pb(II) ions with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.

Experimental

Chemicals and instruments

2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP) ($M_r = 349.233$) was a preparation of Merck (Darmstadt, GFR) (Art. No.: 10731). The stock solutions were prepared by dissolving the weighed amounts of the preparation in 1 cm^3 of dimethylformamide (DMF) and filling up to the required volume with ethanol.

The standard solution of $\mathrm{Pb(NO_3)_2}$ of $8.204 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ concentration was prepared by dissolving the weighed amount of anal. grade $\mathrm{Pb(NO_3)_2}$ (Lachema, Brno) in $1.0\,\mathrm{mol\,dm^{-3}}$ $\mathrm{HNO_3}$. The final concentration of $\mathrm{HNO_3}$ was adjusted to $0.1\,\mathrm{mol\,dm^{-3}}$. The content of lead was determined chelatometrically using xylenol orange as indicator.

TRITON X-100 (poly(ethylene glycol) octylphenyl ether), preparation of scintillation grade (Koch-Light, Ltd., Great Britain) was used. The stock solution ($\varrho = 20\,\mathrm{g\,dm^{-3}}$) was prepared by dissolving 1 g of the preparation in 50 cm^3 of ethanol. BRIJ-35 (poly(oxyethylene) monolauryl ether, $n \approx 20$, $M_r \approx 900$) (Merck, Darmstadt, GFR) and sodium dodecyl sulfate (SDS, $M_r = 288.38$) (Koch-Light, Ltd., Great Britain) were used in the form of solutions ($\varrho = 20\,\mathrm{g\,dm^{-3}}$ resp. $c = 10^{-2}\,\mathrm{mol\,dm^{-3}}$) which were obtained by dissolving the weighed amounts of the preparations in ethanol.

Ethanol was distilled with EDTA ($1\,\mathrm{g\,dm^{-3}}$) which served for removing the trace amounts of the present heavy metals. It contained 4.1 vol. % of $\mathrm{CH_3OH}$ and 4.3 vol. % of $\mathrm{H_2O}$. The water used was redistilled in quartz apparatus Bi-18 Destamat (Heraeus Quartzschmelze, Hanau, GFR).

Other chemicals were anal. grade reagents (Lachema, Brno) and were tested for the content of heavy metals. The organic solvents were distilled before use.

The measurements were carried out in quartz cells of 10 mm optical length by using a recording double-beam spectrophotometer Superscan 3 (Varian A. G., Switzerland) controlled by a desk-top computer HP 9815 A (Hewlett—Packard, USA).

The acidity of solutions was measured with a digital pH-meter PHM 84 equipped with a glass electrode (G 202 B) and saturated calomel electrode (K 401) from Radiometer (Copenhagen, Denmark). The apparatus was calibrated by a set of standard buffers of pH 1.68, 7.00, and 9.28 of the same production. The pH values measured in mixed media or in solutions containing surfactants were not corrected.

The chelate-forming equilibria of the Pb(II) ions with BrPADAP were studied in aqueous medium or in the ethanol—water mixture in the presence of the nonionic and ionic surfactants of varying concentration, the ionic strength being $I = 0{:}1\,\mathrm{mol\,dm^{-3}}$. The working solutions were prepared by mixing the corresponding volumes of the components in the order solvent, ethanol, surfactant, $\mathrm{HNO_3}$, solution of metal ions, buffer solution (or $\mathrm{NH_3}$), and redistilled water at $(20 \pm 1)\,^\circ\mathrm{C}$. The measurement was carried out for 5 min after mixing all the components.

The high sensitivity of the reaction demands high purity of chemicals and vessels. The purity of chemicals was tested before use by comparing the absorbance of their solutions with reagent at pH 7—8 for $\lambda = 575$ nm with the absorbance of the reagent itself.

The glass, electrodes, and cells were always cleaned before use. The adsorbed impurities and trace sediments of the chelate of Pb(II) with BrPADAP were removed by means of hydrochloric acid (volume ratio = 1 : 1), ethanol and repeated washing with redistilled water.

Chelate-forming equilibria of Pb(II) *with* BrPADAP

The absorption spectra of the solutions containing the Pb(II) ions and BrPADAP recorded at the ionic strength $I = 0.1\,\text{mol}\,\text{dm}^{-3}$ for different concentration ratios c_L/c_M as function of acidity of the medium (for other experimental conditions see Table 1) in the region $\lambda = 350$—650 nm always exhibit the characteristic doubled absorption band with absorption maxima at $\lambda = 545$ nm and 575 nm. The high colour contrast produced by the reaction is given by a significant shift in absorption maxima by 105 nm or 135 nm towards longer wavelengths with respect to the position of the absorption maximum of BrPADAP itself ($\lambda_\text{max} = 440$ nm, $\varepsilon_\text{max} = 4.2\,\text{mmol}^{-1}\,\text{m}^2$). The formation of a metal chelate is indicated by sharp isosbestic point at $\lambda_\text{IP} = 496$ nm.

In solutions with concentration excess of the Pb(II) ions ($c_\text{M} = 8.10 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}$, $c_\text{L} = 1.50 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$) the chelate starts to arise already at pH ≈ 2.5 and is quantitatively formed at pH ≈ 7. It is characterized by the value of molar absorption coefficient $\varepsilon = 5.79\,\text{mmol}^{-1}\,\text{m}^2$. In solutions with concentration excess of BrPADAP ($c_\text{L} = 1.99 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$, $c_\text{M} = 8.21 \times 10^{-6}\,\text{mol}\,\text{dm}^{-3}$, $c_\text{L}/c_\text{M} = 2.45$, pH = 3.6—9.5) the metal chelate starts to arise at pH > 4 and is quantitatively formed at pH $\geqslant 7$. The absorbance does not change up to pH = 8.5 approximately. The chelate is characterized by the value $\varepsilon = 5.75\,\text{mmol}^{-1}\,\text{m}^2$.

The absorption spectra of the solutions of the Pb(II) ions with BrPADAP containing 50 vol. % of ethanol and TRITON X-100 ($\varrho = 3\,\text{g}\,\text{dm}^{-3}$) at constant values of pH (pH = 8.0 and pH = 6.5) measured for varying ratio of concentrations $c_\text{M} : c_\text{L}$ under analogous experimental conditions ($c_\text{L} = 2.00 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$, $c_\text{M} = 0.00$—$9.03 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$) corroborate in the whole concentration range the origination of single reaction product characterized by equal optical parameters (Fig. 1). A summary of optical characteristics is given in Table 1.

A colloidal turbidity appeared in aqueous—ethanolic solutions with reagent excess and concentration excess of the Pb(II) ions at higher values of pH. This turbidity increased by standing and its intensity depended on the concentrations

Table 1

Optical characteristics of the chelate of Pb(II) with BrPADAP

Medium	pH[a]	c_L/c_M	$\frac{\lambda_{max}}{nm}$[b]	$\frac{\lambda_{IP}}{nm}$[c]	$\frac{\lambda_{max}}{nm}$[d]	$\frac{\varepsilon_{max}}{10^3\,mol^{-1}\,m^2}$[e]	$\frac{\varepsilon_{max}}{10^3\,mol^{-1}\,m^2}$[f]
50 vol. % EtOH	8.0	> 1	442	496	545, 575	6.40	
TRITON X-100	6.5	< 1	442	496	545, 575	5.50	
($\varrho = 3\,g\,dm^{-3}$)		4.52			575	6.427 ± 0.033	6.42
		10.63			575	6.392 ± 0.052	6.46
		21.26			575	6.402 ± 0.047	6.40
		0.183			575	5.762 ± 0.025	5.87
		0.101			575	5.786 ± 0.011	5.93
		0.037			575	5.902 ± 0.031	6.02
30 vol. % EtOH	7.0	> 1	440	496	545, 575	5.75	
	5.9	< 1	440	496	545, 575	5.66	

a) Value of pH of the plateau or extrapolated pH value; *b*) absorption maximum of the LH form of reagent; *c*) position of isosbestic point; *d*) absorption maxima of the chelate; *e*) molar absorption coefficient of the chelate at $\lambda = 575\,nm$ determined from absorption spectra or obtained by calculating by means of program PRCEK from the absorbance—pH curves; *f*) molar absorption coefficient of the chelate at $\lambda = 575\,nm$ determined by graphical analysis of the absorbance—pH curves.

of ethanol and surfactant. Among the investigated variants (30 % of EtOH with $\varrho = 1$, 2, and 3 g dm^{-3} of TRITON X-100; 50 % of EtOH with $\varrho = 1$, 2, and 3 g dm^{-3} of TRITON X-100) the medium containing 50 vol. % of ethanol and TRITON X-100 ($\varrho = 3$ g dm^{-3}) appeared to be the best. In this medium, the investigated solutions were stable in the whole acidity and concentration interval at least for 1 h and no turbidity appeared in the solutions.

The absorbance—pH curves were measured in detail at ten wavelengths ($\lambda = 540$, 550, 560, 565, 570, 575, 580, 585, 590, and 600 nm) and at the ionic strength $I = 0.10$ mol dm^{-3} ($HNO_3 + NH_3$) for three different excess concentrations of BrPADAP ($c_M = 1.13 \times 10^{-5}$ mol dm^{-3}, $c_L = 5.1 \times 10^{-5}$ mol dm^{-3}, $c_L/c_M = 4.5$, $c_L = 1.2 \times 10^{-4}$ mol dm^{-3}, $c_L/c_M = 10.6$, $c_L = 2.4 \times 10^{-4}$ mol dm^{-3}, $c_L/c_M = 21.3$). The relationship $\Delta A = A - A_{OL} = f(\text{pH})$ for the wavelength of 575 nm is represented in Fig. 2. The curves are characterized by one ascending branch and plateau which indicate the formation of one metal chelate. The curves shift to acid region with increasing concentration of BrPADAP.

The absorbance—pH curves were measured for concentration excess of the Pb(II) ions ($c_L = 1.5 \times 10^{-5}$ mol dm^{-3}, $c_M = 8.21 \times 10^{-5}$ mol dm^{-3}, $c_M/c_L =$ $= 5.5$, $c_M = 1.48 \times 10^{-4}$ mol dm^{-3}, $c_M/c_L = 9.9$, $c_M = 4.10 \times 10^{-4}$ mol dm^{-3}, $c_M/c_L = 27.4$) under equal experimental conditions. Their course at the wavelength $\lambda = 575$ nm is represented in Fig. 3. The shape of these curves is

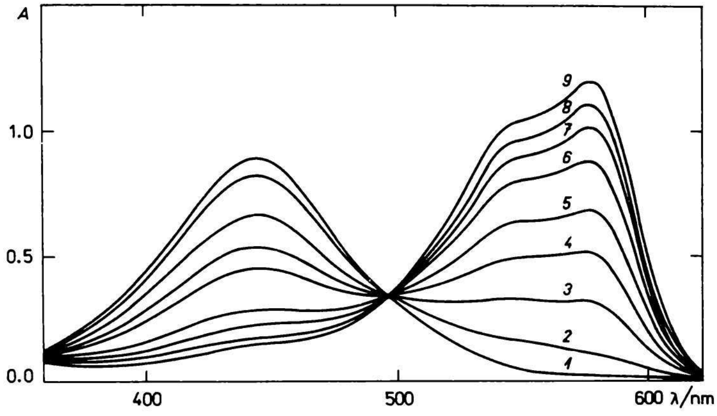

Fig. 1. Absorption spectra of the chelate of the Pb(II) ions with BrPADAP measured at increasing concentration of the metal ions: $c_L = 2.0 \times 10^{-5}$ mol dm^{-3}, 50 vol. % of ethanol, TRITON X-100 ($\varrho = 3$ g dm^{-3}), $I = 0.1$ mol dm^{-3} ($HNO_3 + NH_3$), pH = 6.5. c_M/(mol dm^{-3}) (c_L/c_M): *1.* 0 (∞); *2.* 2.05×10^{-6} (9.75); *3.* 4.62×10^{-6} (4.33); *4.* 8.21×10^{-6} (2.44); *5.* 1.03×10^{-5} (1.95); *6.* 1.33×10^{-5} (1.50); *7.* 2.67×10^{-5} (0.75); *8.* 5.34×10^{-5} (0.37); *9.* 9.03×10^{-5} (0.22).

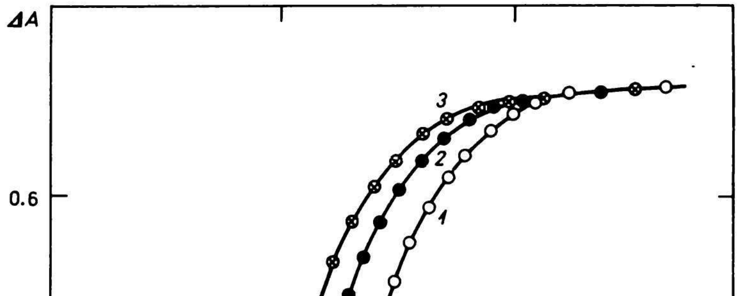

Fig. 2. The absorbance—pH curves of solutions containing the Pb(II) ions, BrPADAP, and concentration excess of ligand.

$c_M = 1.128 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, 50 vol. % of ethanol, TRITON X-100 ($\varrho = 3\,\mathrm{g\,dm^{-3}}$), $I = 0.1\,\mathrm{mol\,dm^{-3}}$ ($HNO_3 + NH_3$), $\lambda = 575\,\mathrm{nm}$.

$c_L/(\mathrm{mol\,dm^{-3}})$ (c_L/c_M): *1.* 5.1×10^{-5} (4.52); *2.* 1.2×10^{-4} (10.63); *3.* 2.4×10^{-4} (21.26).

equal to the shape of the absorbance—pH curves for solutions with concentration excess of BrPADAP. They shift to more acid region with increasing concentration of the Pb(II) ions. Owing to hydrolysis of the Pb(II) ions in the region of the plateau, only the ascending part of the curves was measured (up to pH = 6.5 approximately).

The graphical analysis of the absorbance—pH curves [9] was performed for all investigated concentration ratios and the wavelength $\lambda = 575\,\mathrm{nm}$. Since the formation of the chelate of Pb(II) with BrPADAP took place in the pH interval 4—9 where BrPADAP was present predominantly in the LH form in the solution, we took into consideration the following model

$$LH + Pb^{2+} \leftrightharpoons PbL^{+} + H^{+} \qquad (A)$$

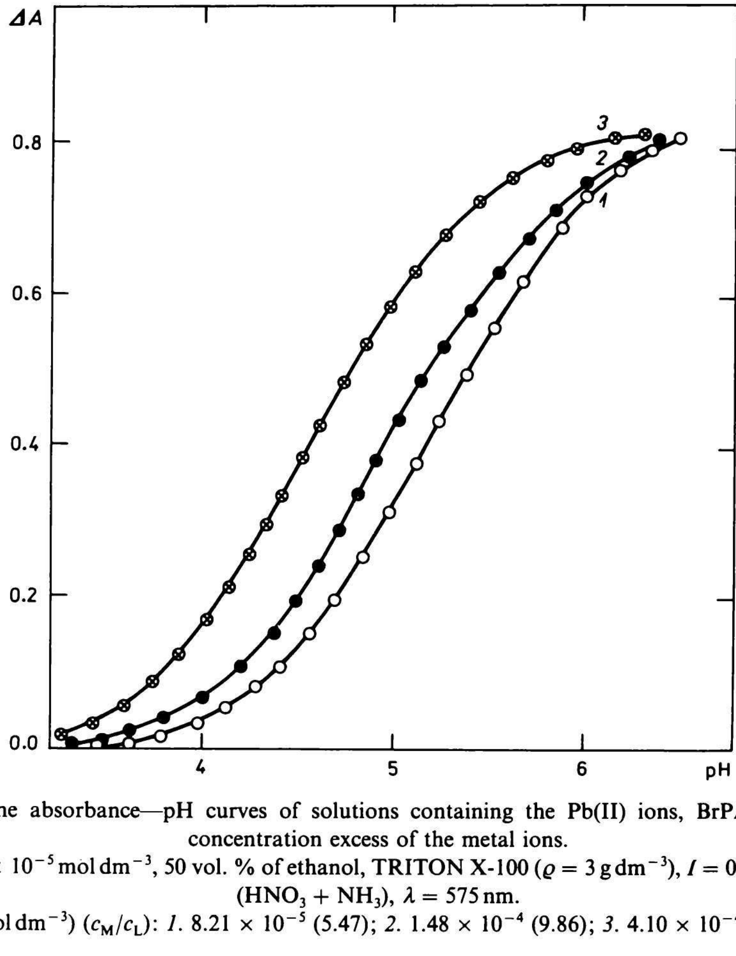

Fig. 3. The absorbance—pH curves of solutions containing the Pb(II) ions, BrPADAP, and concentration excess of the metal ions.
$c_L = 1.5 \times 10^{-5}$ mol dm^{-3}, 50 vol. % of ethanol, TRITON X-100 ($\varrho = 3$ g dm^{-3}), $I = 0.1$ mol dm^{-3} ($HNO_3 + NH_3$), $\lambda = 575$ nm.
c_M/(mol dm^{-3}) (c_M/c_L): *1.* 8.21×10^{-5} (5.47); *2.* 1.48×10^{-4} (9.86); *3.* 4.10×10^{-4} (27.36).

Assuming 10 mm optical path length, the relationships $c_M/\Delta A = f([H]/c_L)$ and $c_L/\Delta A = f([H]/c_M)$ as well as the relationships $\log(\Delta A/(\varepsilon c_M - A)) = f(\mathrm{pH})$ and $\log(\Delta A/(\varepsilon c_L - A)) = f(\mathrm{pH})$ are linear according to graphical logarithmic analysis [9]. The sections on the axis $c_M/\Delta A$ and $c_L/\Delta A$ were used for determining the molar absorption coefficients the values of which are given in Table 2 together with the data obtained from the plateau of the absorbance—pH curves and absorption spectra. The sections on the pH axis obtained by graphical logarithmic analysis served for determining the conditional equilibrium constant of reaction (*A*) and the conditional stability constant of reaction (*B*).

$$L^- + Pb^{2+} \leftrightharpoons PbL^+ \qquad (B)$$

Table 2

Values of conditional equilibrium constants of the reaction of Pb(II) with BrPADAP (reaction (*A*)) 50 vol. % ethanol, TRITON X-100 ($\varrho = 3\,\mathrm{g\,dm^{-3}}$), $I = 0.10\,\mathrm{mol\,dm^{-3}}$ ($HNO_3 + NH_3$)

c_L/c_M	pK^{*a}	pK^{*b}	c_M/c_L	pK^{*a}	pK^{*b}
4.52	1.30	1.278 ± 0.024	5.47	1.22	1.247 ± 0.048
10.63	1.38	1.295 ± 0.030	9.86	1.17	1.279 ± 0.053
21.26	1.38	1.301 ± 0.017	27.56	1.17	1.295 ± 0.066

a) Values determined by graphical methods; *b*) mean values for 10 wavelengths determined by program PRCEK, $K^* = [PbL^+]\,[H^+]/[Pb^{2+}]\,[LH]$, conditional stability constant of chelate $\beta = [PbL^+]/[Pb^{2+}]\,[L^-] = K^*/K_{a3}$ where $K_{a3} = [L^-]\,[H^+]/[LH]$ was calculated for $pK_{a3} = 11.85$ as $\log\{\beta\} = 10.58$.

These data as well as the results of mathematical processing of the absorbance—pH curves by using the program PRCEK and a desk-top computer HP 9815A are presented in Table 2 for the whole set of wavelengths. The results of both methods of processing are in conformity and confirm the correctness of the proposed model.

Mole ratio method and the method of continual variations

The composition of the metal chelate was verified by the method of mole ratios which involved measuring the relationship $A = f(c_L)$ at $\lambda = 575\,\mathrm{nm}$ for pH = 5.6, 6.6, 8.0, and 9.0. The concentration of BrPADAP varied in the range $c_L = 1 \times 10^{-6}$—$1.43 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ at constant concentration of the Pb(II) ions $c_M = 1.44 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$. The relationship $A = f(c_M)$ was measured under equal experimental conditions at pH = 5, 5.5, and 6.5 for constant concentration of BrPADAP $c_L = 2.4 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ and varying concentration of the Pb(II) ions $c_M = 0$—$1.23 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$. The method of concentration relations (mole ratios) confirms the ratio $n(\mathrm{M}):n(\mathrm{L}) = 1:1$ at higher values of pH.

The Pb(II) chelate with BrPADAP is quantitatively formed at excess BrPADAP concentrations exceeding $c_L/c_M = 2$—3. At least a 5-fold concentration excess of BrPADAP was chosen for further measurements.

The curves of continual variations at pH = 5.6, 6.6, 8.0, and 9.0 ($c_0 = c_L + c_M = 3.29 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, $\lambda = 575\,\mathrm{nm}$, $I = 0.1\,\mathrm{mol\,dm^{-3}}$) are symmetrical with respect to the straight line occurring at $x_M = 0.5$ and exhibit only one maximum of absorbance at $x_M = c_M/c_0 = 0.50$. This fact corroborates the stoichiometric ratio $n(\mathrm{M}):n(\mathrm{L}) = 1:1$.

The curves of continual variations exhibit equal form at pH = 8.0 and pH = 9.0 in the region $x_M < 0.5$. The curves are deformed in the descending part ($x_M > 0.5$) because of the colloidal cloudiness due to formation of the hydrolytic products of the Pb(II) ions.

Extraction of the metal chelate

Gusev and *Nikolaeva* [8] have described quantitative extraction of the PbL^+ complex into chloroform, tributyl phosphate, and benzene at $pH \geqslant 6$, the maximum absorption being at $\lambda = 560$ nm.

Though we used a wide concentration range of the Pb(II) ions and BrPADAP, the pH interval 7—9, varying ratio of the aqueous and organic phase (10 : 1—1 : 10), and sufficiently long time of extraction, we did not succeed in extracting more than 20 % of the total quantity of the metal chelate into chloroform, benzene, *o*-dichlorobenzene, xylene, n-butyl alcohol, and other solvents. In the main, only the molecular form of the agent LH^0 was extracted under given experimental conditions. The attempt to eliminate the positive charge of the PbL^+ chelate by adding different voluminous anions in a wide concentration range (F^-, ClO_4^-, dodecyl sulfate, I^-, *etc.*) was not successful and the extraction did not improve significantly.

The method of determination of the Pb(II) *ions by using* BrPADAP

The horizontal plateaus of the absorbance—pH curves of the solutions of the Pb(II) ions with excess concentrations of BrPADAP encompass the optimum acidity region for elaborating a highly sensitive method of determination of lead in the pH interval 7.5—9.0 where the chelate is quantitatively formed. Because of a poor solubility of the chelate in water, all further measurements were carried out in the mixture containing 50 vol. % of ethanol and TRITON X-100 ($\varrho = 3\,g\,dm^{-3}$), the ionic strength being $I = 0.1\,mol\,dm^{-3}$ ($HNO_3 + NH_3$ or hexamethylenetetramine buffer solution).

A decrease in absorbance due to hydrolytic equilibria of the Pb(II) ions appeared at higher pH values. Simultaneously, the acid—base equilibrium of free BrPADAP manifested itself at pH > 9.5 by increasing absorbance of the reagent itself owing to origination of the violet-red acid-base form L^- exhibiting an absorption maximum at $\lambda = 520$ nm.

As for the tested buffer solutions serving for adjusting the acidity of solutions in the concentration range 0.05—1.0 mol dm^{-3}, hexamethylenetetramine (HMT) proved to be the best because it exhibited a deviation of absorbance under 0.2 % in the whole concentration interval. Other buffer solutions (triethanolamine, tris-(hydroxymethyl)aminomethane, pyridine, borate) showed changes in absorbance up to 5 % when compared with the values of absorbance of equal solutions without buffer (pH adjusted with NaOH) or in the 0.1 M medium of ($HNO_3 + NH_3$).

The calibration curves ($c_L = 1.2 \times 10^{-4}$ mol dm^{-3}, 0.1 mol dm^{-3} HMT or ammonia buffer) were linear for the whole concentration interval of Pb $c_M = 2 \times 10^{-8}$—2×10^{-5} mol dm^{-3} at the pH values 7.5, 8.0, 8.5, 9.0 and the wavelengths $\lambda = 565$, 570, 575, 580, and 585 nm. A survey of statistical parameters obtained by processing the experimental data by the use of the program STAT and a desk-top computer HP 9815A is given in Table 3.

Table 3

Statistical parameters of calibration curves for the Pb(II)—BrPADAP system
50 vol. % ethanol, TRITON X-100 ($\varrho = 3$ g dm^{-3}), $c_M = 2.05 \times 10^{-8}$—$2.05 \times 10^{-5}$ mol dm^{-3}, $c_L = 1.2 \times 10^{-4}$ mol dm^{-3}, pH = 8.0, c(HMT) = 0.1 mol dm^{-3}

pH[a]	ε / mmol^{-1} cm^2 [b]	A_{bl} [c]	s / ng cm^{-3} [d]	m / ng cm^{-3} [e]	DL[f] / ppb	SI[g]
7.5	65440 ± 142	0.077 ± 0.0015	4.4	18.7	40.2	31.6
8.0	65410 ± 137	0.076 ± 0.0010	3.7	15.7	40.8	31.7
8.5	65360 ± 112	0.076 ± 0.0018	3.5	14.9	41.3	31.7
9.0	65310 ± 128	0.077 ± 0.0013	3.8	16.0	41.5	31.7
λ/nm						
565	61250 ± 240	0.148 ± 0.0027	6.6	28.1	95.0	33.8
570	63780 ± 215	0.107 ± 0.0017	4.2	17.7	57.6	32.5
575	65440 ± 158	0.760 ± 0.0012	3.1	13.0	41.2	31.7
580	64150 ± 159	0.054 ± 0.0013	3.1	13.1	42.4	32.3
590	58250 ± 169	0.038 ± 0.0013	3.3	14.0	49.7	35.6

a) Value of pH or wavelength; *b*) molar absorption coefficient; *c*) absorbance of blank solution; *d*) estimate of standard deviation (ng cm^{-3}) $s = (U/(n-2))^{1/2}$. $A_r \cdot 10^3/\varepsilon$ where $U = \Sigma(A_{exp} - A_{calc})^2$ is the sum of squares of deviations of experimentally found and calculated values of A, $n = 9$; *e*) limit of determination (ng cm^{-3}); *f*) limit of determination; *g*) index of sensitivity according to Sandel for $A = 0.010$.

The highest values of molar absorption coefficients were found at $\lambda = 575$ nm. The acidity of medium has no significant influence on sensitivity of the method of determination. The precision of determination ($c_L = 1.2 \times 10^{-5}$ mol dm^{-3}, pH = 8.0, $\lambda = 575$ nm, 10 consecutive determinations) was better than 0.5 % ($c_M = 5 \times 10^{-6}$ mol dm^{-3}) or 0.25 % ($c_M = 1.0 \times 10^{-5}$ mol dm^{-3}).

Table 4

Interference of ions and reagents for the Pb(II)—BrPADAP system

50 vol. % ethanol, TRITON X-100 ($\varrho = 3\,\mathrm{g\,dm^{-3}}$), $c_M = 1.03 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, $c_L = 1.2 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, pH = 8.0, $c(\mathrm{HMT}) = 0.1\,\mathrm{mol\,dm^{-3}}$, $\lambda = 575\,\mathrm{nm}$, threshold interference corresponds to the absorbance change of ± 2 %

Ion/compound	$\frac{c_x}{\mathrm{mol\,dm^{-3}}}$ [a]	c_x/c_M [b]	Ion/compound[c]	$\frac{c_x}{\mathrm{mol\,dm^{-3}}}$ [a]	c_x/c_M [b]
K^+ (KNO_3)	1.0	1×10^5	Ni^{2+}	3.07×10^{-7}	0.035
Na^+ (NaCl)	1.0	1×10^5	Ni^{2+}	1.03×10^{-5}	1
NH_4^+ (NH_4NO_3)	1.0	2×10^4	Cd^{2+}	4.17×10^{-7}	0.041
Li^+ (LiCl)	1.0	1×10^5	Cd^{2+}	2×10^{-4}	20
NO_3^- (KNO_3, $NaNO_3$)	1.0	1×10^5	Cu^{2+}	4×10^{-7}	0.04
Cl^- (NaCl, KCl)	1.0	1×10^5	Cu^{2+}	2.5×10^{-5}	2.5
Mg^{2+} ($MgCl_2$)	9.5×10^{-2}	9×10^3	Co^{2+}	1.23×10^{-7}	0.012
Ca^{2+} ($Ca(NO_3)_2$)	5.6×10^{-3}	5.5×10^2	Co^{2+}	2.46×10^{-5}	2.4
SO_4^{2-} (K_2SO_4)	2.0×10^{-3}	200	Hg^{2+}	1.06×10^{-6}	0.098
$H_2PO_4^-$ (KH_2PO_4)	1.5×10^{-7}	0.015	Hg^{2+}	1.06×10^{-3}	100
EDTA	3.0×10^{-7}	0.03	Fe^{2+}	1.56×10^{-5}	1.52
Tartrate	3.0×10^{-5}	2.9	Fe^{2+}	3.12×10^{-4}	30[d]
Citrate	5.1×10^{-7}	0.05	Fe^{3+}	6.25×10^{-8}	0.006
Oxalate	5.0×10^{-6}	0.49	Fe^{3+}	7.2×10^{-5}	7[d]
Thiourea	1.12×10^{-2}	1090	Al^{3+}	3.71×10^{-6}	0.36
F^-	8.4×10^{-4}	81	Al^{3+}	4.5×10^{-5}	4.4[e]
CN^-	2.3×10^{-2}	2250	TCA[f]	2.06×10^{-2}	2050
Ascorbic acid	1.1×10^{-4}	11			

a) Concentration of interfering ion or compound; *b*) concentration ratio of interfering substance and Pb^{2+}; *c*) the second value found in the presence of masking mixture ($c(\mathrm{KCN}) = 2 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, $c(\mathrm{thiourea}) = 1 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$); *d*) addition of ascorbic acid ($c(\text{ascorbic acid}) = 1 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$); *e*) addition of F^- ($c(F^-) = 5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$); *f*) trichloroacetic acid.

High concentrations of inert electrolytes (KNO_3, KCl, KBr, LiCl) up to $1.0\ \mathrm{mol\ dm^{-3}}$ do not interfere with the determination. Table 4 gives a survey of limiting concentrations of some other interfering ions, masking agents, and some substances in reference to the relative change of absorbance ± 2 % with respect to the corresponding absorbance of the chelate of Pb(II) with BrPADAP itself ($c_L = 1.2 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$, $c_M = 1.0 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$, pH = 8.0, $c(\mathrm{HMT}) = 0.1\ \mathrm{mol\ dm^{-3}}$). By using $c(\mathrm{KCN}) = 2 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$, c(thiourea $= 1 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$, and $c(\mathrm{F^-}) = 5 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$, we succeeded in eliminating the influence practically of all cations. Only phosphates, citrate, EDTA, and some transition elements (Fe, Co, Ni) significantly interfere with the determinations, which makes possible a fairly selective and highly sensitive determination of the Pb(II) ions in many materials.

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