THE FIA DETERMINATION OF LEAD WITH 4-(2-PYRIDYLAZO)-RESORCINOL AFTER PRECONCENTRATION ON A MICROCOLUMN OF A CHELATING SORBENT

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Lead can be determined conveniently by the classical or reversed FIA technique using photometric detection with 4-(2-pyridylazo)resorcinol ($c_{PAR} = 0{\cdot}1$ mol l^{-1}) in 0·1M borate buffer (λ 518 nm). For injected volumes of 50 µl, the lead concentrations can lie in the regions of 1–20 and 0·4–18 µmol l^{-1}, respectively. The selectivity of determination can be increased one to two orders of magnitude by masking with a mixture of EDTA (5 µmol l^{-1}), tartaric acid (20 µmol . l^{-1}) and KCN (2 mmol l^{-1}). When combining the analysis with preconcentration on a 3 × 30 mm microcolumn of Spheron Oxin 1 000 chelating sorbent from 0·01M ammonium acetate solutions at pH 6·5 followed by elution with 0·1M-HCl, lead can be determined in concentrations of 0·1–1·2, 0·02–0·85 or 0·01–0·60 µmol l^{-1} for sample volumes of 5, 10 or 20 ml, respectively. The repeatability of determination for ten independent measurements on 5, 10 and 20 ml sample volumes at $c_{Pb} = 0{\cdot}2$, 0·05 and 0·05 µmol l^{-1}, respectively, was better than 4·7, 2·8 and 6·2%, respectively. The method of preconcentration on a chelating sorbent was applied to the analysis of clean industrial wastewaters. The relative deviation of the lead concentration did not exceed 6·5% in comparison with data obtained by AAS.

4-(2-Pyridylazo)resorcinol (PAR) forms with lead ions in aqueous solutions at pH > 4 the red-orange protonated chelate $PbLH^+$ ($\lambda_{max} = 515$ nm, $\varepsilon_{max} = 1{\cdot}4$ m^2 . . mmol^{-1}), which at pH 4·5 splits off the *p*-hydroxy group proton to form the red unprotonated chelate PbL ($\lambda_{max} = 518$ nm, $\varepsilon_{max} = 3{\cdot}9$ m^2 mmol^{-1}) (refs[1,2]). The optical properties and solubility of the chelate are unaffected by the presence of nonionic or cationic surfactants[3].

PAR is among the most widely used reagents for the determination of lead[1,2]. Actually, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP), for instance, is more sensitive ($\lambda_{max} = 6{\cdot}54$ m^2 mmol^{-1}) and gives a better colour contrast in the reaction ($\Delta\lambda = 135$ nm), its chelate, however, is lower soluble in water, so that water–ethanol mixed solvents have to be used and surfactants added[4].

Traces of lead can be determined with advantage by flow injection analysis (FIA) using optical or electrochemical detection; this technique is frequently combined with preconcentration by sorption on columns of chelating sorbents or by stripping voltammetry[5]. A method has been suggested for the simultaneous determination

of lead and vanadium making use of the different chelation of the two ions with PAR in acid and alkaline solutions due to the pH gradient in the reaction mixture zone[6]. A considerable improvement in the determination of lead can be achieved by its preconcentration by extraction of its chelate with dithizone into chloroform, followed by phase separation in the FIA analyzer[7].

In the present work, methods were worked out for the determination of trace concentrations of Pb(II) by classical and reversed FIA (ref.[8]) and by FIA after preconcentreation on a microcolumn packed with a chelating sorbent, using photometric detection with PAR in borate buffer solutions.

EXPERIMENTAL

Chemicals and Apparatus

Standard solution of Pb(II) (c_{Pb} = 99·9 mmol l^{-1}) was prepared by dissolving $Pb(NO_3)_2$ of reagent grade purity (Lachema, Brno) in 0·1M-HNO_3, and standardized by chelometric titration using xylenol orange as the indicator.

Stock solution of PAR (c_{PAR} = 1 mmol l^{-1}) was prepared by dissolving the recrystallized chemical in 1 ml of dimethylformamide (Reakhim, Moscow, U.S.S.R.) and diluting with water to 500 ml. The solution was steady for 10 to 14 days. Fresh working solutions at c_{PAR} = 0·1 mmol . l^{-1} in TRIS, ammoniacal or borate buffers at pH 9·2 for the FIA or r-FIA determination, or at c_{PAR} = 0·2 mmol l^{-1} in borate buffer at pH 11 for the PC FIA determination, were prepared daily. For some measurements, the solution also contained a masking mixture of EDTA (5 μmol . l^{-1}), tartaric acid (20 μmol l^{-1}) and KCN (2 mmol l^{-1}).

The other substances used were commercial chemicals of reagent grade purity. Tris-(hydroxymethyl)aminomethane (TRIS) was supplied by Serva Feinbiochemica, Heidelberg, the remaining chemicals were obtained from Lachema, Brno. Bidistilled water was prepared in a quartz still.

Preconcentration was achieved in glass microcolumns packed with Spheron Oxin 1000 (Lachema, Brno), a sorbent containing 8-quinolinol groups on a glycol methacrylate skeleton. A fraction 63—100 μm grain size was used; its sorption capacity for M^{2+} in stationary conditions was 0·25—0·30 mmol g^{-1}, its pore volume was 1·25—1·50 ml g^{-1}.

Measurements in the classical or reversed FIA mode were performed using a Spekol 10 single-beam photometer equipped with an EK 5 attachment and interfaced to a G1B1 recorder (all Carl Zeiss, Jena, G.D.R.); a homemade flow cell 18 μl volume and 10 mm optical pathlength was employed. The carrier liquid was delivered through Teflon capillaries 0·6 mm i.d. (Norton Chemplast, Wayne, U.S.A.) by means of a Zalimp 304 peristaltic pump (Zalimp, Warsaw, Poland) with an adapted rotary head. Sample or reagent solutions were injected by using a six-way valve with a 50 μl injection loop (Mikrotechna, Prague). This injection loop was filled by means of the peristaltic pump or a syringe.

An equipment as shown in Fig. 1 was used for the preconcentration of Pb(II) on 2 × 10 to 40 mm or 3 × 30 mm glass microcolumns packed with Spheron Oxin 1000. A Spekol 10 or Spekol 21 single-beam photometer (Carl Zeiss, Jena, G.D.R.) interfaced to a TR 4 200 recorder (Laboratorní přístroje, Prague) and equipped with an 18 μl flow cell 10 mm optical pathlength was employed for detection. Sample solution was repeatedly injected by means of a chromatographic six-way valve (80 μl) or by time-controlled dispensing (5, 10, 20 ml) by means of a four-way valve at a constant pumping rate of Q_S = 0·6 or 0·9 ml min^{-1}. Interchange of the carrier

liquid and the eluting agent and reversion of the liquid flow during the sorption and elution were accomplished by switching the four-way valves.

Lead ions sorbed were eluted with 0·1M-HCl or 0·1M-HNO_3 at a constant flow rate Q_E = = 0·3 ml min^{-1}. After passing through the column, the eluent was mixed with a continuous stream of the working solution of PAR (c_{PAR} = 0·2 mmol l^{-1}) and identical concentrations of the other components (Q_R = 0·3 ml min^{-1}) in a tee screen type mixing cell 0·6 µl active volume. The reaction mixture was fed to the photometric flow cell through a 0·6 × 400 mm reaction coil. The delivery of the working solution of PAR was provided by hydrostatic pressure from an infusion flask, or by pumping with an ABU 13 plunger burette (Radimeter, Copenhagen, Denmark).

Procedure

For classical FIA, 50 µl of solution of Pb(II) at c_{Pb} = 10 µmol l^{-1}, pH 4·0 (HNO_3), was injected into the continuous stream of PAR (c_{PAR} = 0·1 mmol l^{-1}). For reversed FIA, 50 µl of the working solution of PAR was injected into the continuous stream of the solution of Pb(II) ions, c_{ob} = 10 µmol l^{-1}, at pH 4·0.

The analytical signal was recorded in the peak form and recalculated to absorbance values at 518 nm in the peak maximum (the wavelength of 518 nm corresponds to the absorption maximum of the PbL chelate[3]). The $A = f(c_{Pb})$ calibration curves were processed by the least squares method. The limit of determination Q_L was identified with the concentration of lead corresponding to the absorbance $A = \langle A_{bl} \rangle + 10 s_{bl}$ where $\langle A_{bl} \rangle$ and s_{bl} are the mean absorbance value and its standard deviation, respectively, for 10 independent measurements on a blank solution.

RESULTS AND DISCUSSION

Optimization of the FIA *and* r-FIA *Determination*

The maximum analytical signal values were obtained for reaction coil lengths L_r = 36 to 40 cm at a carrier liquid flow rate Q_C = 0·7 ml min^{-1} for classical FIA, and for L_r = 36 to 42 cm at Q_C = 0·8 ml min^{-1} for reversed FIA (Fig. 2). Choosing the reaction capillary length L_r = 36 cm and Q_C = 0·7 and 0·8 ml min^{-1} for the two modes respectively, a throughput of 120 to 130 samples per hour was achieved.

The analytical signal attained its maximum and constant values ($\Delta A > 2\%$) using the working solution of PAR in 0·1M ammoniacal, TRIS or borate buffer at pH 8·0 to 9·5. At lower pH values the formation of the chelate with PAR was not quantitative, and at pH > 9·8, the own light absorption by the L^{2-} species of PAR had a negative effect.

When the Pb(II) solution was injected into the stream of PAR solution or the working solution of PAR was injected into the stream of solution of Pb(II) ions, the analytical signal increased with the concentration of PAR up to c_{PAR} = 35 and 50 µmol l^{-1}, respectively; additional increase up to c_{PAR} = 0·5 mmol l^{-1} had no effect upon the analytical signal of the Pb-PAR chelate. A concentration c_{PAR} = = 0·1 mmol l^{-1} was chosen, ensuring a sufficient excess of the reagent ($c_{PAR}/c_{Pb} > 5$) for quantitative chelation.

The suitability of the above-mentioned buffers was tested by measuring the $A = f(c_{Pb})$ curves over the region of $c_{Pb} = 1$ to 50 μmol l^{-1} in the optimum conditions (Table I). The highest selectivity was achieved in 0·1M borate buffer at pH 9·2. The calibration curves were linear over the widest region of $c_{Pb} = 1$ to 20 μmol l^{-1}. The working solution of PAR was sufficiently stable in this buffer (2 days at least), and the calibration curve parameters remained unaffected by the concentration of the buffer varied over the range of 0·02 to 0·2 mol l^{-1}. With TRIS the sensitivity of the determination was appreciably poorer and the absorbance of the blank was markedly higher. The repeatability of the determination was poorest with the ammoniacal buffer. The basic statistical characteristics for both the classical and reversed FIA modes for the determination of lead over the concentration regions of 1–20 and 0·4–18 μmol l^{-1}, respectively, in 0·1M borate buffer at pH 9·2 are given in Table I.

Optimization of the PC FIA *Determination*

For the optimization of parameters of the reaction capillary in the PC FIA mode, the function of the packed column was simulated by injection of 80 μl volumes of acid solution of Pb(II) ions at $c_{Pb} = 10$ μmol l^{-1} into the FIA equipment with the microcolumn empty (Fig. 1*a*). The analytical signal was highest at working solution-

TABLE I

Statistical parameters of the linear segments of calibration curves $A = f(c_{Pb})$ for the determination of Pb(II) with PAR ($y = ax + b$); $c_{buffer} = 0{\cdot}1$ mol l^{-1}, pH 9·2; $c_{PAR} = 0{\cdot}1$ mmol l^{-1} (FIA, r-FIA), 0·2 mmol l^{-1} (PC FIA); $L_r = 36$ cm (FIA, r-FIA), 40 cm (PC FIA); $Q_C = 0{\cdot}7$ (FIA), 0·8 (r-FIA), 0·3 ml min^{-1} (PC FIA); $V = 50$ μl (FIA, r-FIA), 5, 10 or 20 ml (PC FIA); λ 518 nm

Buffer	Method	$a \pm s_a$	$b \pm s_b$	c_{Pb} μmol l^{-1}	Q_L μmol l^{-1}	s_r %
Borate	FIA	11 650 ± 100	9·6 ± 1·1	1–20	0·99	4·7[a]
TRIS	FIA	6 160 ± 110	159·5 ± 2·3	4–30	2·0	—
NH_3[b]	FIA	10 970 ± 180	12·9 ± 2·5	4–20	1·7	—
NH_3[c]	FIA	4 950 ± 650	38·5 ± 3·7	1–10	3·2	—
Borate	r-FIA	21 730 ± 170	7·3 ± 1·7	0·4–18	0·4	2·8[a]
Borate	PC FIA	22 910 ± 95	3·9 ± 1·0	0·1–1·2	0·07	4·7[d]
Borate	PC FIA	21 690 ± 135	2·2 ± 1·3	0·02–0·85	0·009	2·8[e]
Borate	PC FIA	23 440 ± 173	2·8 ± 2·0	0·01–0·60	0·003	6·2[f]

[a] For $c_{Pb} = 2{\cdot}5$ (FIA) and 0·8 (r-FIA) μmol l^{-1}; $s_r = 0{\cdot}75\%$ for $c_{Pb} = 15$ μmol l^{-1} (FIA) and $s_r = 0{\cdot}79\%$ for $c_{Pb} = 6$ μmol l^{-1} (r-FIA); [b] fresh PAR solution; [c] PAR solution after a week's standing; [d] $c_{Pb} = 0{\cdot}2$ μmol l^{-1}, $V_S = 5$ ml; [e] $c_{Pb} = 0{\cdot}05$ μmol l^{-1}, $V_S = 10$ ml; [f] $c_{Pb} = 0{\cdot}05$ μmol l^{-1}, $V_S = 20$ ml.

-to-sample flow rate ratios Q_R/Q_S = 1 to 1·5 and a constant total flow rate $Q_R + Q_S$ = = 0·6 ml min^{-1} (Figs 2 and 3). The optimum length of the reaction capillary 0·6 mm i.d., inserted between the site of mixing the two streams in the mixing chamber and the detector, was L_r = 40 cm.

On a 2 × 10 mm microcolumn packed with Spheron Oxin 1 000, the sorption of 80 µl volumes of samples at c_{Pb} = 100 µmol l^{-1} was conducted from 0·01M ammonium acetate solution adjusted to pH 5–8·5 with HNO_3 or NaOH, and was found quantitative at pH 6·3 (Fig. 4). The sorption efficiency was independent of the flow rate of the Pb(II) solution stream over the region Q_S = 0·3 to 1·2 ml min^{-1}, and decreased only slightly with the concentration of Pb increasing from 1 to 100 µmol l^{-1} (Fig. 3, curve 3). A flow rate of Q_S = 0·6 or 0·9 ml min^{-1} and medium of 0·01M ammonium acetate at pH 6·5 were chosen for the preconcentration from large volumes.

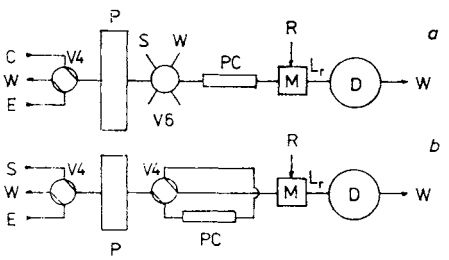

FIG. 1

Layout of the PC FIA equipment for preconcentration of lead on a microcolumn of Spheron Oxin 1000 with the concurrent or countercurrent eluting agent flow, for the injection of microlitre (*a*) or millilitre (*b*) sample volumes. C carrier stream, E eluent stream, S sample, P peristaltic pump, V4 four-way valve, V6 six-way valve, PC packed microcolumn, R working solution of PAR, M mixing chamber, L_r reaction capillary, D detector, W waste

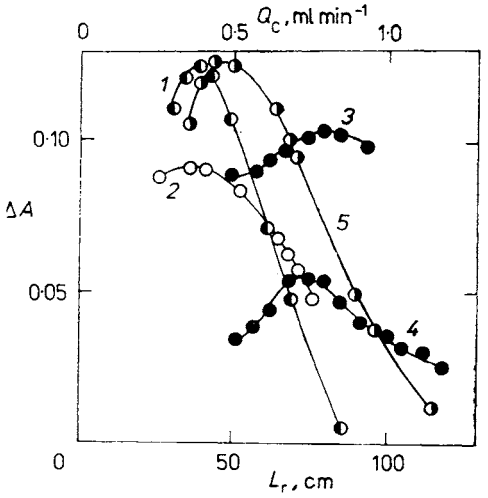

FIG. 2

Dependences of the analytical signal on the reaction capillary length L_r (curves *1*, *2*, *5*) and on the carrier liquid flow rate (curves *3*, *4*) for classical FIA (curves *1*, *3*), reversed FIA (curves *2*, *4*) and PC FIA (curve *5*). c_{PAR} = 0·1 and 0·2 mmol l^{-1}, respectively, borate buffer pH 9·2, c_{Pb} = 10 and 50 µmol . l^{-1}, respectively, elution with 0·1M-HCl, Q_E = 0·3 ml min^{-1}. Q_C (ml min^{-1}): *1* 0·7, *2* 0·8, *5* 0·5; L_r = 36 cm (*3*, *4*)

The dynamic breakthrough capacity was determined by repeated injection of 80 μl volumes of the Pb(II) solution (c_{Pb} = 10 μmol l^{-1}) until the appearance of the peak corresponding to the analytical signal $A = \langle A_{bl} \rangle + 3s_{bl}$. The value, 0·2 μmol Pb(II) per ml of swelled sorbent, was independent of the acidity of the lead solution over the region of pH 6·5–8·0 and of the sample flow rate over the region of Q_S Q_S = 0·6–0·9 ml min^{-1}.

For the injection of 80 μl of solution of Pb(II) ions, c_{Pb} = 50 μmol l^{-1}, from 0·01M ammonium acetate at pH 6·5, the maximum analytical signal was attained on continuous elution with HCl or HNO_3 at $c_{acid} \geq 0{\cdot}1$ mol l^{-1}, applying flow rates Q_E = 0·3 to 0·5 ml min^{-1}. For attaining the desired pH 9·2 of the resultant reaction mixture, the pH of the working solution of PAR in 0·1M borate buffer had to be adjusted to pH 10–12 with NaOH. For practical reasons, Pb(II) ions were continuously eluted from the Spheron Oxin 11000 microcolumn with 0·1M-HCl, with a simultaneous pH adjustment of the working solution of PAR to pH 11·0. Solution of 0·1M-HCl was also used as the carrier liquid.

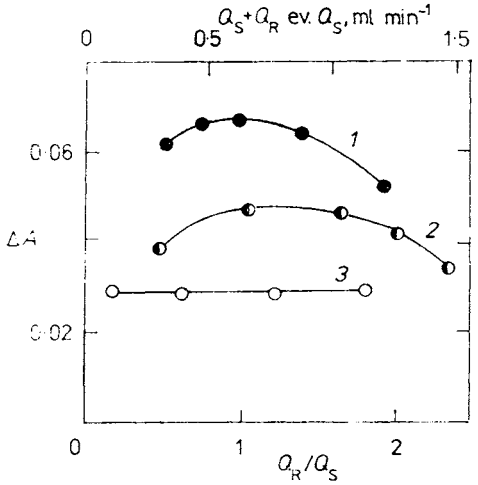

FIG. 3

Dependences of the analytical signal on the total flow rate of sample and PAR solution, $Q_S + Q_R$ (*1*), the Q_R/Q_S ratio (*2*) and the sample flow rate Q_S (*3*) in the PC FIA mode. c_{PAR} = 0·2 mmol l^{-1}, borate buffer (0·1M) pH 11, pH of the reaction mixture 9·2, c_{Pb} = 50 μmol l^{-1}, 80 μl, L_r = 40 cm

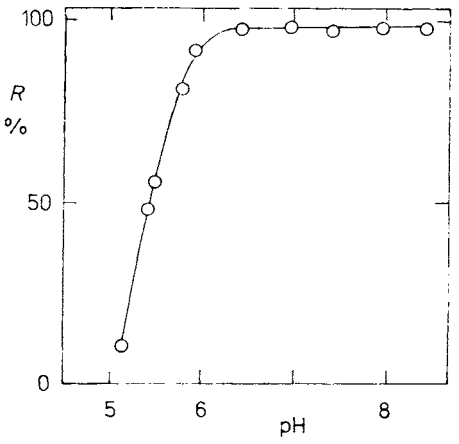

FIG. 4

Dependence of the sorption efficiency of the 2 × 10 mm column of Spheron Oxin 1000 for Pb(II) ions on pH. c_{PAR} = 0·2 mmol l^{-1}, 0·1M borate buffer pH 9·2, c_{Pb} = 100 μmol . l^{-1}, repeatedly 80 μl, Q_C = 0·9 ml min^{-1}, L_r = 40 cm, 0·01M ammonium acetate pH 5–8·5 adjusted with 0·1M-HNO_3 or 0·1M-NaOH

The calibration curves for the determination of lead after its preconcentration on the 3 × 30 mm microcolumn of Spheron Oxin 1000 from 5, 10 and 20 ml sample volumes were measured over the concentration regions of $c_{Pb} = 0{\cdot}05-1{\cdot}5$, $0{\cdot}01-1{\cdot}5$ and $0{\cdot}005-1\ \mu mol^{-1}$, respectively, with the eluting agent stream concurrent or countercurrent with respect to the sample solution flow direction during the sorption (Fig. 1*b*). Under the optimum conditions, the calibration curves were linear over the regions of $0{\cdot}1-1{\cdot}2$, $0{\cdot}02-0{\cdot}86$ and $0{\cdot}01-0{\cdot}60\ \mu mol^{-1}$, respectively, for the countercurrent flow of the eluting liquid; the repeatability was 4·7, 2·8 and 6·2%, respectively, for 10 independent measurements on solutions with $c_{Pb} = 0{\cdot}02$, $0{\cdot}05$ and $0{\cdot}05\ \mu mol\ l^{-1}$, respectively. The sensitivity of determination for the countercurrent mode was 5·6, 7·8 and 10·2%, respectively, higher than for the concurrent mode.

Effect of Interfering Ions

For the FIA, r-FIA and PC FIA modes, the effect of interfering ions was examined by injecting 80 µl or 10 ml volumes of solution with $c_{Pb} = 10$ or $0{\cdot}3\ \mu mol\ l^{-1}$, respectively, and various concentrations of interferents. The limiting concentrations

TABLE II

Effect of interfering ions on the FIA determination of Pb(II) with PAR. FIA, r-FIA: $c_{PAR} = 0{\cdot}1\ mmol\ l^{-1}$ (FIA), $0{\cdot}1\ mol\ l^{-1}$ (r-FIA), borate buffer pH 9·2, $c_{Pb} = 10\ \mu mol\ l^{-1}$, $L_r = 36$ cm, $Q_C = 0{\cdot}7$ (FIA) or 0·8 (r-FIA) ml min^{-1}; PC FIA: $c_{PAR} = 0{\cdot}2\ mmol\ l^{-1}$, borate buffer pH 11, $c_{Pb} = 0{\cdot}3\ \mu mol\ l^{-1}$, $L_r = 40$ cm, $Q_E = 0{\cdot}3$ ml min^{-1}, $V_S = 10$ ml, $Q_S = 0{\cdot}6$ ml . . min^{-1}, $Q_R = 0{\cdot}3$ ml min^{-1}. Masking mixture: EDTA (5 µmol l^{-1}), tartaric acid (20 µmol l^{-1}), KCN (2 mmol l^{-1})

Ion[a] X	c_X/c_{Pb}			Ion X	x_X/c_{Pb}		
	b	*c*	*d*		*b*	*c*	*d*
NH_4^+	5 200	>	>	Cu^{2+}	0·02	0·3	13
Ca^{2+}	720	>	>	Ni^{2+}	0·015	0·5	63
Mg^{2+}	630	>	>	Al^{3+}	0·2	0·3	17
SO_4^{2-}	0·013	—	1 000	Zn^{2+}	0·005	0·6	23
$H_2PO_4^-$	0·03	—	1 000	EDTA	0·63	—	—
Cd^{2+}	0·06	0·12	1	Tartrate	28	—	—
Co^{2+}	0·009	0·098	23	Citrate	0·07	—	—
Hg^{2+}	0·08	0·5	9	Oxalate	0·13	—	—
Fe^{2+}	0·15	0·7	14	F^-	92	—	—
Fe^{3+}	0·019	0·6	53				

[a] K^+, Na^+, Li^+, NO_3^-, Cl^- do not interfere up to $c_X/c_{Pb} \approx 10^5$; [b] no masking; [c] masking with masking mixture; [d] PC FIA, masking with masking mixture.

of interferents causing a 2% relative change in the analytical signal were determined graphically. Table II demonstrates that the reaction under study is little selective. A number of masking agents were tested for eliminating the effect of interferents. With the use of a mixture of EDTA (5 μmol l^{-1}), tartaric acid (20 μmol l^{-1}) and KCN (2 mmol l^{-1}), interferences decreased one to two orders of magnitude for the FIA, r-FIA as well as PC FIA modes (Table II).

Actual Samples

The PC FIA techniques was applied to the determination of Pb(II) in artificial samples (S1–S3) containing Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, HPO_4^{2-} and SO_4^{2-} ions in concentrations of 142, 5, 10, 4, 27, 103, 4 and 2 mmol l^{-1}, respectively; the concentrations of Pb(II) were 0·02, 0·1 and 0·4 μmol l^{-1} and volumes 10 or 20 ml. The results from five independent measurements were accurate and the maximum relative deviation did not exceed 6·5% (Table III).

Pb(II) was also determined in samples of clean technological wastewaters (W1 to W5). Volumes of 5, 10 or 20 ml were injected on column at pH 6·5 (0·01 ammonium acetate). The results were in a good agreement with those obtained by AAS and the relative deviation did not exceed 6·5%.

In conclusion, the suggested method for the determination of lead involving preconcentration on a microcolumn packed with Spheron Oxin 1 000 chelating sorbent

TABLE III

Determination of Pb(II) in artificial samples (S1–S3) and in wastewater samples (W1–W5) after preconcentration on a 3 × 30 mm microcolumn packed with Spheron Oxin 1000; c_{PAR} = = 0·2 mmol l^{-1}, 0·1M borate buffer pH 11·0, pH of the reaction mixture 9·2, Q_S = 0·9 ml min^{-1}, Q_E = 0·3 ml min^{-1}, Q_R = 0·3 ml min^{-1}, L_r = 40 mm, λ 518 nm, n = 5

Sample	V_S ml	c_{Pb}, μmol l^{-1}		s_r %	Δc %
		Added[a]	Found		
S1	20	0·020	0·0191 ± 0·0090	4·7	4·5
S2	10	0·100	0·103 ± 0·007	6·5	3·0
S3	10	0·400	0·374 ± 0·030	8·0	6·5
M1	20	0·0165	0·0164 ± 0·0014	7·6	1·5
M2	10	0·247	0·262 ± 0·017	6·4	6·1
W3	10	0·924	0·903 ± 0·049	5·4	2·2
W4	5	1·324	1·299 ± 0·069	5·3	1·8
W5	10	0·724	0·756 ± 0·015	1·9	4·4

[a] Found by AAS for samples W1–W5.

gives highly accurate and precise results. The limit of determination is better than or comparable with that of methods based on the use of highly sensitive organic analytical reagents[2] (Q_L on the order of hundredths of μmol l^{-1}) in stationary conditions or the FIA method after preconcentration by solvent extraction of Pb(II) chelates with dithizone into chloroform[7] (Q_L about 0·6 μmol l^{-1}), and is appreciably better than that of methods of determination of Pb(II) with PAR in the classical or reversed mode (Table I) or the method of simultaneous determination of Pb and V with PAR (Q_L abut 30 μmol l^{-1}).

In comparison to the FIA or r-FIA modes, the throughput is somewhat lower (about 50 samples per hour), the sensitivity of the method, however, is two to three orders of magnitude higher. When using the EDTA–tartaric acid–KCN masking mixture, the selectivity of determination is good; the majority of ions, except cadmium, only interfere if present in more than a tenfold excess.

The sorption of the lead ions on the chelating sorbent and their desorption is rapid and quantitative. The bands are narrow. The elution is mostly complete in 15 s, which corresponds to a total volume of the eluting agent (0·1M-HCl) of about 0·1 ml.

Owing to its simplicity and rapidity, the method can serve as alternative to other electrochemical and optical methods of determination of lead. A marked increase in the sensitivity and selectivity can be achieved by combining the preconcentration on chelating sorbents with flame AAS analysis[9].

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