

SORPTION OF LEAD BY THE SELECTIVE ION EXCHANGER OSTSORB DETA

Ladislav SVOBODA, Jan UHLÍŘ and Zdeněk UHLÍŘ

*Department of Inorganic Technology,
Institute of Chemical Technology, 532 10 Pardubice*

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The properties of Ostsorb DETA, a selective ion exchanger based on modified bead cellulose with chemically bonded diethylenetriamine functional groups, were studied, and its applicability to the preconcentration of trace amounts of lead from aqueous solutions was verified. The conditions of the preconcentration procedure in the column and batch modes were optimized for this purpose. The results obtained were applied to the determination of lead in phosphoric acid.

Sorbents containing complexing functional groups can be employed for the preconcentration, isolation and purification of small quantities of inorganic substances¹⁻³. Most frequently used are chelating ion exchangers, which are sorbents modified with groups capable of forming chelating bonds with some ions, giving thus stable cyclic complexes. There exist many organic compounds which exhibit this property and can be bonded to the surface of a support. The support is usually a polymeric material based on the styrene-divinylbenzene copolymer⁴, polyurethane⁵, dextran⁶, or cellulose^{7,8}; modified silica gel and glass beads have also been used⁹. The sorption process can be conducted in the conventional column (dynamic) arrangement or in the batch (static) arrangement; materials in the form of membranes (filters) made of cellulose¹⁰ or the styrene-divinylbenzene copolymer¹¹ modified with a suitable chelating group also find practical application.

The Czechoslovak selective cellulose sorbents Ostsorb are prepared by chemical modification of spherical bead cellulose. Owing to their high porosity, perfect hydrophilic nature and a high inner surface area, they exhibit very good ion exchange kinetics and the complexing equilibria establish rapidly¹².

The applicability of Ostsorb DETA, spherical bead cellulose with chemically bonded diethylenetriamine functional groups in the cellulose side chain, to the preconcentration of trace amounts of lead was studied in the present work.

THEORETICAL

The amount of active groups contained by the ion exchanger is expressed quantitatively by its exchange capacity, which can be defined in several ways¹³.

Theoretical mass exchange capacity Q_0 is the total amount of the active functional groups, in millimoles or milliequivalents, bonded to a gramme of the ion exchanger in the given form.

Analytical mass exchange capacity Q_a is the total amount of ions, in millimoles, exchangeable by a gramme of the dry exchanger under the given conditions.

Breakthrough capacity Q_b is the amount of ions, in millimoles or milligrams, retained by a gramme of the dry ion exchanger in the column through which the solutions of these ions are passed under the given experimental conditions, till the moment their first traces appear in the eluate leaving the column.

Breakthrough curves are plots of concentrations of the sorbed substances in the eluate leaving the column in dependence on the volume of solution passed through the column¹⁴.

Definitions of quantities characterizing physical properties of ion exchangers such as the particle size, density, water content, volume and mass swelling capacity, specific weight and specific volume, porosity, etc., can be found in the literature¹³.

EXPERIMENTAL

Chemicals

All chemicals were of reagent grade purity (Lachema, Brno). Buffers were prepared¹⁵ from sodium acetate and acetic acid (acetate buffer), potassium hydrogen phthalate, hydrochloric acid and sodium hydroxide (biphthalate buffer), boric acid, potassium chloride and sodium hydroxide (borate buffer according to Clark and Lubs).

Standard lead solution was prepared by dissolving 3.1971 g of lead nitrate in deionized water acidified with 1M-HNO₃ to pH 4 – 5 and diluting to a litre. The mass concentration of lead in this solution was 2 g l⁻¹. Stock solution of iron at a mass concentration of 1 g l⁻¹ was prepared by dissolving 1 g of iron powder in 15 ml of 5M-HCl containing 3 ml of 30% H₂O₂, diluting to approximately 100 ml with deionized water, boiling, and diluting to a litre.

The selective ion exchanger Ostsorb DETA (Spolek pro chemickou a hutní výrobu, Ústí nad Labem) possesses, according to the manufacturer's specification, a theoretical mass exchange capacity Q_0 of at least 1.5 mmol g⁻¹, porosity of the unmodified support 90% (v/v), carbonyl group content of the dry material lower than 0.02 mmol g⁻¹. The physical properties of the ion exchanger as established by the authors are given in Table I. The ion exchanger was used in the H⁺-form, which was obtained by washing the swelled exchanger in a glass column with 0.2M-HCl in amounts of 25 ml of the acid per ml of exchanger and by subsequent washing with deionized water to a neutral reaction.

Apparatus

Lead and iron in solutions were determined with an Atomspek H 1550 single-beam atomic absorption spectrophotometer (Hilger and Watts, U.K.). The solution pH was measured with an OP-8083 combined glass electrode interfaced to an OP-205/1 pH-meter (Radelkis, Hungary). For the sorption experiments in

the static mode, the solutions of lead were shaken with the ion exchanger on an LT 1 horizontal shaking machine (Kavalier, Czechoslovakia). In the column mode, a 315-type peristaltic pump (Zalimp, Poland) and a 100 × 25 mm glass column fitted with a ground-in outflow stopcock were used. The ion exchanger was dried in an M2 laboratory oven (Elektro Bad, Germany), its grain size was measured with an MP3 projection microscope (PZO, Poland).

Calibration Plots for the Determination of Lead and Iron

Calibration solutions of lead and iron were prepared by diluting the stock solutions of the salts to 1 – 5 mg l⁻¹ at pH < 6, and their relative absorbances were measured at 217.5 nm (Pb) and 386.4 nm (Fe) in an acetylene-air flame. The pH was adjusted with several drops of 5M-HCl. The correlation coefficients for the calibration straight lines were higher than 0.9990.

Sorption of Lead by the Ion Exchanger in the Column Mode

Dependence of the breakthrough capacity on pH. Two grams of the swelled ion exchanger were placed in a glass column and washed with approximately 25 ml of a buffer at the desired pH. A solution of lead at a mass concentration of 10 mg l⁻¹, prepared by diluting the stock solution with biphthalate buffer at pH 4.0 – 7.5, was pumped on the column by means of the peristaltic pump. The flow rate was adjusted to 1.5 ml min⁻¹. The eluate was collected in 5 – 25 ml fractions, made acidic with 5M-HCl, and submitted for AAS analysis. The results were used to plot the lead breakthrough curve at the given pH.

Effect of flow rate on the sorption process. The column was prepared as above, and a lead solution in biphthalate buffer at a lead mass concentration of 10 mg l⁻¹ and pH 7.0 was pumped through it at flow rates of 0.5 to 2.5 ml min⁻¹. Lead was determined in the fractions by AAS after acidification.

Effect of iron on the sorption of lead. Two glass columns containing 4 g of the swelled ion exchanger each were washed with 40 ml of borate buffer at pH 8. Solutions in this buffer containing lead in a mass concentration of 0.2 mg l⁻¹ and iron in mass concentrations of 0.2 and 2 mg l⁻¹, respectively, were pumped through the column at a flow rate of 2 ml min⁻¹; their volume passed through the column was 500 ml in either case. After washing the ion exchanger in the columns with approximately 10 ml of buffer, the sorbent was shaken in the closed columns for 2 h with 10 ml of 0.2M-HCl, the extract was drawn off, and the desorption was repeated with 10 ml of the acid for another 2 h. Lead and iron were determined by AAS in the combined extracts from each column.

TABLE I
Physical properties of Otsorb DETA

Property	Value
Density, g cm ⁻³	1.11 ^a
Specific weight, g cm ⁻³	0.71 ^a , 0.54 ^b
Specific volume, cm ³ g ⁻¹	1.41 ^a , 1.85 ^b
Mass swelling capacity, g H ₂ O / g	2.70
Volume swelling capacity, cm ³ g ⁻¹	5.22
Water content, %	9.1
Particle size ^a , μm	100 – 300

^a In the swelled state; ^b dried at approximately 20 °C.

Desorption of lead. After finishing the sorption the ion exchanger was washed with the buffer with which the pH of the analyzed solution had been adjusted, in amounts not exceeding 5 ml per gramme of wet ion exchanger. Two desorption procedures were then tested:

a) A solution of 0.2M-HCl was pumped through the column at a flow rate of 0.5 ml min⁻¹, the eluate was collected in 10 ml volumetric flasks and analyzed by AAS;

b) 10 ml of 0.2M-HCl were pipetted into the column containing the washed sorbent, the column was clamped to the shaking machine and shaken in the horizontal position for an hour. The extract was drained into a 10 ml volumetric flask, and the procedure was repeated. Lead was determined in the two desorbates.

Sorption of Lead by the Ion Exchanger in the Batch Mode

Dependence of the analytical exchange capacity on pH. 0.5 g portions of the swelled ion exchanger were placed in 250 ml volumetric flasks, and 100 ml volumes of lead solutions at a lead mass concentration of 2 mg l⁻¹ and at pH 4, 5, 6, 7 (acetate buffers), 7.5, 8, or 9 (borate buffers) were added. The systems were agitated for 2 h, and the sorbent was filtered out on a porous paper filter, washed with the corresponding buffer, and transferred into 20 ml of 0.2M-HCl in a 50 ml volumetric flask, where it was shaken for 2 h. After filtering, the extract was diluted with deionized water to 25 ml and analyzed by AAS.

Measurement of the sorption rate. An amount of 0.5 g of the swelled ion exchanger was added to a 250 ml volumetric flask, and 100 ml of a lead solution at a lead mass concentration of 2 mg l⁻¹ in a borate buffer (pH 8) were added. The suspension was agitated, and 5 ml fractions of the solution were drawn off in 2, 7, 20, 45 and 120 min, made acidic with a drop of 5M-HCl, and analyzed by AAS.

Desorption of lead. Porous paper filter was used to separate the sorbent from the solution. The ion exchanger, washed with the buffer in an amount of approximately 5 ml per gramme, was transferred into a 50 ml volumetric flask by perforating the filter and rinsing with 25 ml of 0.2M-HCl. The suspension was shaken for an hour. The desorbate was also separated from the ion exchanger by filtration on a paper filter, diluted to 25 ml, and analyzed. This desorption procedure was applied in the subsequent experiments.

Effect of iron on the sorption of lead. 2 g portions of the swelled ion exchanger were weighed into five 500 ml volumetric flasks, and 100 ml volumes of solutions of lead and iron in a buffer at pH 8 were added. The lead mass concentration was invariably 0.2 mg l⁻¹, the iron mass concentrations were 0, 0.2, 2, 10 and 20 mg l⁻¹, respectively. The mixtures were shaken for 2 h, after which the ions retained were desorbed and determined by AAS.

Effect of K₂HPO₄ on the sorption of lead. 0.5 g portions of the wet sorbent were added to 250 ml volumetric flasks, and 100 ml volumes of solutions containing lead in a mass concentration of 2 mg l⁻¹ and K₂HPO₄ in concentrations of 0.05 to 3.0 mol l⁻¹ were added. The systems were shaken for 2 h, after which the ion exchanger was washed with a buffer at pH 8, and the lead retained was desorbed and analyzed by AAS.

Effect of chloride on the sorption of lead. 0.5 g portions of the ion exchanger were shaken for 2 h in two 250 ml volumetric flasks with 100 ml volumes of lead solution at a lead mass concentration of 2 mg l⁻¹ in borate buffer, pH 9.5, at ionic strength *I* = 0.1. KCl and KNO₃, respectively, were used for adjusting the ionic strength in the two flasks. The same experiment was performed with a solution which contained K₂HPO₄ instead of the buffer; its ionic strength was also 0.1. The ion exchanger was filtered out, rinsed, and extracted with 0.2M-HCl; lead was determined by AAS.

Effect of EDTA on the sorption of lead. An amount of 1 g of the swelled ion exchanger was shaken for 2 h in a 500 ml volumetric flask with 250 ml of a solution of lead and EDTA in borate buffer at pH 8. The lead and EDTA concentrations were 0.2 mg l⁻¹ and 1 · 10⁻⁵ mol l⁻¹, respectively. The lead desorbed was determined by AAS.

Determination of the lead sorption isotherm. 2 g portions of the swelled ion exchanger were shaken for 2 h in 500 ml volumetric flasks with 250 ml volumes of lead solutions in borate buffer at pH 8. The

starting lead mass concentrations were 0.05, 0.2, 0.5, 1 and 1.5 mg l⁻¹. The equilibrium concentrations of lead in the solutions and retained by the ion exchanger were determined by AAS.

Effect of medium on the sorption of lead during its determination in phosphoric acid. Phosphoric acid (5 ml) in a beaker was diluted with approximately 300 ml of deionized water and neutralized with 21 ml of 60% KOH while cooled and stirred. The solution was transferred into a 500 ml volumetric flask and made to the mark with water. A solution containing, in addition, 0.063 mg of lead was prepared likewise. 6 g of the ion exchanger were then shaken for 2 h in 1 000 ml volumetric flasks with 500 ml of the solutions of neutralized phosphoric acid at pH 9.5. The ion exchanger was filtered out, rinsed with buffer at pH 8, and extracted with 2 × 12 ml of 0.2M-HCl.

In the column mode, 500 ml of solution of the neutralized acid was passed at a flow rate of 2 ml min⁻¹ through a column containing 6 g of the ion exchanger previously washed with approximately 60 ml of buffer at pH 8. Thereafter the column was washed with 30 ml of buffer, and the exchanger was extracted directly in the column with 2 × 12 ml of 0.2M-HCl.

RESULTS AND DISCUSSION

Dependence of the Breakthrough Capacity of Ion Exchanger on pH

The observed breakthrough capacities Q_b and analytical capacities Q_a of Ostsorb DETA for the sorption of lead ions from their solutions at mass concentrations of 10 or 2 mg l⁻¹ and at pH 4 to 9 are given in Table II. They indicate that stable complexes of lead with the diethylenetriamine functional groups of the ion exchanger are formed at pH > 6, the exchange capacity being highest at pH > 7. The lower Q_a values as compared to the Q_b values can be explained in terms of the higher equilibrium concentrations of the lead solutions, implying a higher number of ions trapped by the ion exchanger, in the column mode; this is also indicated by the sorption isotherm (Table III). The steric conditions for the complexation of the lead ions by the functional groups in the 1 : 2 ratio are also apparently more favourable in the column arrangement than in the stirred suspension.

TABLE II
Dependence of analytical exchange capacity and breakthrough capacity on pH

pH	Q_a , $\mu\text{mol g}^{-1}$	Q_b , $\mu\text{mol g}^{-1}$
4.0	0	0
5.0	0	0
6.0	0.2	0.8
6.5	—	7.9
7.0	0.6	10.0
7.5	2.9	10.3
8.0	3.1	—
9.0	3.1	—

The observed Q_b and Q_a values are several orders of magnitude lower than the Q_0 value reported by the manufacturer (1.5 mmol g^{-1}), viz. $Q_b = 1 \cdot 10^{-2} \text{ mmol g}^{-1}$ and $Q_a = 3 \cdot 10^{-3} \text{ mmol g}^{-1}$ at pH 7.5. The cause of this is probably steric effects arising due to the fixed localization of the functional groups on the cellulose, which hinders the formation of the complexes in the lead-to-ligand stoichiometric ratio of 1 : 2 which is predominant in the case of diethylenetriamine (1 : 1 complexes are only formed with triethylenetetramine¹⁶). The sorption of lead at high pH can be also affected unfavourably by the formation of stable hydroxo compounds.

The shape of the breakthrough curve at pH 7.5 (Fig. 1) demonstrates that for determining the Q_a value in these conditions, large volumes of the solution would have to be

TABLE III
Sorption isotherm of lead on 2 g of swelled Ostsorb DETA at pH 8^a

ρ_0 mg l^{-1}	$10^{-2} \rho_e$ mg l^{-1}	Q_a mg g^{-1}	R_{Pb} %
0.05	0.4	0.02	92.4
0.20	1.9	0.08	90.4
0.50	5.5	0.21	89.1
1.00	13.1	0.40	86.9
1.50	26.3	0.57	82.5
2.00	42.4	0.73	78.9

^a ρ_0 , ρ_e starting and equilibrium lead mass concentrations, respectively.

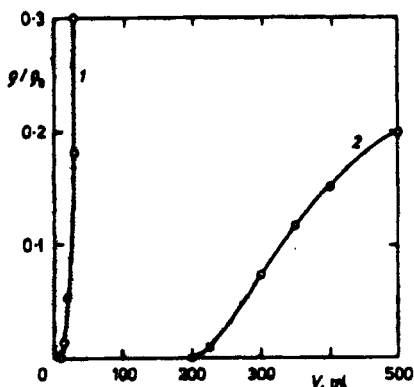


FIG. 1
Lead breakthrough curves for solutions at a lead mass concentration of 10 mg l^{-1} and pH 6 (1) and pH 7.5 (2). ρ , ρ_0 lead concentrations in eluate and in solution entering the column, respectively; V eluate volume

passed through the column until the inlet and outlet lead concentrations level out. The determination of the breakthrough capacity, however, is of much higher practical value because what the analyst is most interested in is the volume of sample that can be passed through the column without breakthrough of the ion sorbed.

Lead Desorption from the Ion Exchanger

In the case of chelating sorbents, desorption is usually accomplished using a solution at a pH at which no complexation takes place. For Ostsorb DETA, this pH is lower than 5. For the desorption to proceed as fast as possible and with the minimal volume of the desorption solution, hydrochloric, nitric or perchloric acids are largely employed at concentrations of 0.1 to 2 mol l⁻¹, which are low enough not to cause destruction of the ion exchanger. In the present work, a solution of HCl at a concentration of 0.2 mol l⁻¹ was used for the desorption of lead.

The simplest way of desorption in the column mode is continuous elution of the ions. However, for Ostsorb DETA at the working conditions applied, this approach did not appear optimal. To elute out 97% of the retained lead, 1.4 times more desorption solution than was the initial volume of the concentrated solution (200 ml, pH 7.5) had to be passed through the column. The high water content in the ion exchanger and the large grain size of the latter apparently play an adverse effect in this, and some nonuniformities in the sorbent column may also contribute. The adverse effect of the slow diffusion of the ions in the sorbent pores, which is probably the kinetically controlling step in the process, might be partly suppressed by reducing the elution solution flow rate, the time of the experiment, however, would thus extend considerably.

The most efficient and simplest desorption method consisted in the extraction of the retained ions by shaking the ion exchanger with 0.2M-HCl directly in the column. The first 10 ml desorbed 72.9% Pb in 1 h of shaking, the second 10 ml portion contained 23% Pb. In the conditions applied, 95.5% recovery was thus achieved, the degree of enrichment f_E was 8.

This approach was also successful in the batch sorption mode. The sorbent filtered out on a filter paper was extracted by shaking with 0.2M-HCl; in this way, 0.05 mg Pb was passed in 1 h from 0.5 g of the swelled sorbent into 25 ml of the acid with a recovery of 95.2% (mean value of three experiments).

The time dependence of the desorption is documented by Fig. 2, showing that 0.18 mg of lead was released from 1 g of the swelled sorbent with 100 ml of 0.2M-HCl in 30 min.

Time Behaviour of the Sorption Process

The plot of the time behaviour of the sorption of lead by Ostsorb DETA in the batch mode (Fig. 3) demonstrates that in the conditions applied, the exchange equilibrium establishes roughly in 45 min from the beginning of the sorption.

Effect of the Flow Rate Through the Column on the Sorption Process

The breakthrough capacities in the column mode at flow rates of 0.5, 1.0, 1.5, 2.0 and 2.5 ml min⁻¹ were (in 10⁻² mmol g⁻¹) 1.1, 1.0, 0.9, 0.7 and 0.2, respectively. As expected, the breakthrough capacity decreases on increasing the flow rate, the flow rate of 2.0 ml min⁻¹ being roughly the reasonable limit above which the resistance to the mass transport starts to play a role and the breakthrough capacity reduces significantly.

Sorption Isotherm of Lead on Ostsorb DETA

The sorption isotherm of lead in borate buffer is given in Table III, which also includes the starting lead concentrations and mean recoveries. To achieve a recovery of at least 90%, the starting lead mass concentration must not exceed 0.2 mg l⁻¹, which corresponds to an equilibrium mass concentration of 0.019 mg l⁻¹. No interfering ions (see later) are allowed to be present.

Effect of Some Ions on the Sorption of Lead by Ostsorb DETA

Among ions that can be present in actual samples analyzed for lead are Fe³⁺ ions. Their effect on the sorption of lead by the sorbent under study was examined in the column

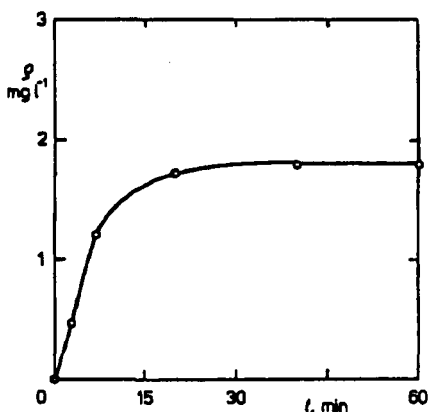


FIG. 2
Time course of lead desorption with 0.2M-HCl

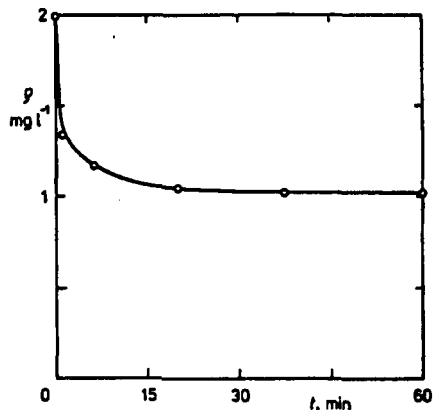


FIG. 3
Time course of lead sorption

as well as batch mode, and identical conclusions were arrived at, viz. that iron(III) ions do not affect the recovery of lead unless the sum of amounts of substance of the two metals in solution exceeds the ion exchanger capacity; otherwise the recovery of both metals is lower. This was found in the column mode using 500 ml of solution and 4 g of sorbent: when the solution contained lead and iron in mass concentrations of 0.2 mg l^{-1} each, their recovery was 94% and 96%, respectively, whereas if the mass concentrations were 0.2 and 2.0 mg l^{-1} , respectively, their recovery was mere 41% and 42%, respectively. The results obtained in the batch mode are given in Table IV. Using 250 ml of solution (pH 8) and 2 g of ion exchanger and applying a shaking time of 2 h, interfering effect of iron was experienced at lead and iron mass concentrations as low as 0.2 mg l^{-1} : the recovery of lead was lower than 90% and that of iron was still lower.

Experiments with lead solutions which contained EDTA in an amount tenfold higher than as necessary for the quantitative reaction of lead gave evidence that the complexes of lead with EDTA are considerably more stable than those with DETA. No lead was retained by Ostsorb DETA from such solutions. Thus, EDTA cannot be employed to mask iron(III) ions.

TABLE IV
Dependence of the recovery of lead and iron on their starting mass concentrations in solution ($\rho_{0,\text{Pb}} = 0.2 \text{ mg l}^{-1}$)

$\rho_{0,\text{Fe}}$ mg l^{-1}	R_{Pb} %	R_{Fe} %
0.2	86.2	61.5
2.0	86.1	44.2
6.0	45.1	18.2
10.0	11.8	9.1
20.0	8.7	4.8

TABLE V
Effect of chloride on the sorption of lead from solutions at pH 9.5^a

Property	A	B	C
$Q_s, \mu\text{mol g}^{-1}$	3.1	6.9	7.0
$R_{\text{Pb}}, \%$	43.3	96.4	97.8

^a A borate buffer containing KCl (0.1 mol l^{-1}), B borate buffer containing KNO_3 (0.1 mol l^{-1}), C solution containing K_2HPO_4 (0.033 mol l^{-1}).

To assess the recovery of lead sorbed from a solution of partly neutralized phosphoric acid, the effect was examined of HPO_4^{2-} ions, which predominate in such solution (pH 8). The analytical exchange capacity and recovery values for solutions where the starting lead mass concentration was 2 mg l^{-1} and which contained K_2HPO_4 in different concentrations are given in Table V. A satisfactory recovery, viz. 97.9%, was only achieved with solutions where the mass concentration of K_2HPO_4 was not higher than 10.6 g l^{-1} ; at higher concentrations, both Q_a and R decreased.

Interesting results were obtained in experiments aimed at seeking whether the formation of lead complexes with the diethylenetriamine groups is affected by the chloride ions present in the borate buffer. Experiments where KCl was replaced with KNO_3 at the same ionic strength, $I = 0.1$ (Table V), revealed that in the presence of KCl in the buffer the sorption of lead is appreciably lower than in the presence of KNO_3 (or in the medium of K_2HPO_4 at the same ionic strength). From this it can be deduced that the exchange capacities of the sorbent found in the borate buffer containing KCl are lower than as corresponds to the pH used. This fact must also be taken into account when evaluating the recovery of lead after its sorption from this buffer.

Effect of Medium on the Sorption of Lead by the Ion Exchanger during its Determination in Phosphoric Acid

Among sources of pollution of some phosphoric fertilizers and feeding salts with lead can be extraction phosphoric acid used for their production. Therefore, experiments were performed to establish whether the Otsorb DETA ion exchanger can be employed to preconcentrate the lead ions added to the phosphoric acid.

The fact was taken into account that if the concentration of HPO_4^{2-} ions in the solution (100 ml of solution containing lead in a mass concentration of 2 mg l^{-1} , per 0.5 g of sorbent) exceeds 0.2 mol l^{-1} (see Fig. 4), the recovery of lead is lower than 90%. For

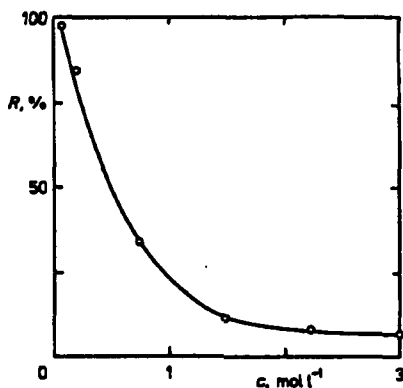


FIG. 4
Dependence of lead recovery on the concentration of K_2HPO_4 in solution

attaining higher recoveries, the amount of sorbent – for the same volume of solution – must be increased while the mass concentration of lead must not exceed 2 mg l^{-1} .

The results of preconcentration of lead added to phosphoric acid of reagent grade purity are virtually identical in the column and batch modes. In either case, a twenty-fold preconcentration was achieved, and the mean recovery from four parallel determinations was 81.5% in the column mode and 81.7% in the batch mode. The recoveries lower than the expected 90% were probably due to losses of lead during desorption, because the 6 g of swelled ion exchanger retain appreciable amounts of solution with the desorbed lead which cannot be eluted quantitatively with $2 \times 10 \text{ ml}$ of 0.2M-HCl . No lead was detected in the starting sample of the neutralized acid alone. With regard to the recoveries and enrichment factors found in this work as well as to the detection limit of atomic absorption spectrometry for lead (which is 0.02 to 0.5 mg l^{-1} according to the quality of the spectrometer), it can be concluded that the minimum amount of lead detectable in phosphoric acid is on the orders of 10^{-5} to $10^{-4} \%$ (m/m).

Conclusions

With respect to the recovery of lead, the column and batch preconcentration modes are equivalent; the former is more time consuming (time of analysis about 5 h as against 2 h in the batch mode) but less tedious. In either method, the low exchange capacity of the ion exchanger (of the batch used in the experiments) is a limitation; only highly dilute lead solutions free from interferences can be treated. The high pH at which the ion exchanger capacity (or the stability of the lead complex) is highest, is a drawback as well, because at $\text{pH} > 8$ the majority of heavy metal cations including lead form stable hydroxo complexes which, at high concentrations, separate from the solution as precipitates; this has an adverse effect on the quantitiveness of their sorption and recovery. Although applicable in some particular cases while respecting the above facts, Ostsorb DETA is not generally suitable for the preconcentration of trace amounts of lead.

REFERENCES

1. Mizuike A.: *Enrichment Techniques for Inorganic Trace Analysis*. Springer Verlag, Berlin 1983.
2. Zolotov J. A., Kuzmin N. M.: *Kontsentrirovanie mikroelementov*. Khimiya, Moscow 1982.
3. Zolotov J. A., Ryabukhin V. A.: *Opreделение mal'kh kontsentratsii elementov*. Nauka, Moscow 1986.
4. Myasoedova G. V., Bolshakova L. I., Shvoeva O. P.: *Zh. Anal. Khim.* 28, 1550 (1973).
5. Chow A., Buksak D.: *Can. J. Chem.* 53, 1373 (1975).
6. Myasoedova G. V., Eliseeva O. P., Savin S. B.: *Zh. Anal. Khim.* 27, 2004 (1972).
7. Imai S., Muroi M., Hamaguchi A.: *Anal. Chim. Acta* 113, 139 (1980).
8. Chaluf F.: *Využití derivátů celulózy při ionexové chromatografii kovových iontů*. Academia, Praha 1980.
9. Leyden D. E., Luttrell G. H., Sloan A. E.: *Anal. Chim. Acta* 84, 97 (1976).

10. Lieser K. H., Breitwieser E., Burba P., Röber M., Spatz R.: *Mikrochim. Acta* **1**, 363 (1978).
11. van Grieken R. E., Bresselurs C. M., Vanderborcht B. M.: *Anal. Chem.* **49**, 1326 (1977).
12. Tokar O.: *Sorbenty Ostsorb.* Spolek pro chemickou a hutní výrobu, Ústí nad Labem 1990.
13. Marhol M.: *Měničče iontů v chemii a radiochemii.* Academia, Praha 1976.
14. Svoboda L., Jandera P., Churáček J.: *Collect. Czech. Chem. Commun.* **56**, 317 (1991).
15. Sýkora V., Zátka V.: *Příruční tabulky pro chemiky.* SNTL, Praha 1967.
16. Komatsu M.: *Bull. Chem. Soc. Jpn.* **47**, 1636 (1974).

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