

A STUDY OF LEAD SORPTION BY A CELLULOSE-BASED CHELATING ION EXCHANGER OSTSORB DTTA

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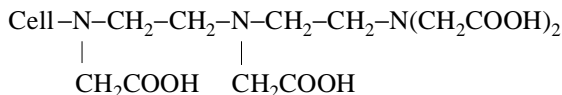
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Complexing properties of the chelating ion exchanger based on spherical cellulose modified by the functional groups of diethylenetriaminetetraacetic acid, Ostsorb DTTA, have been studied in the sorption of lead from aqueous medium at various experimental conditions, such as pH, the dynamic or static arrangement of experiment, the presence of other compounds, the concentration of the ion being sorbed, the form of ion exchanger etc. The results have been compared with the data found with the known selective ion exchanger Dowex A-1. Ostsorb DTTA exhibits good kinetics of the ion exchange at the exchange capacity of 210 mg Pb g⁻¹ for pH 6. For some applications, its lower mechanical stability and high water content in the swollen particles may be unfavourable.

The complexing properties of aminocarboxylic acids are generally known, and therefore it is logical that chelating ion exchangers containing the corresponding functional groups have also been prepared. Obviously the best known representative is the styrene-divinylbenzene copolymer modified with iminodiacetic active groups which has various commercial names, such as Dowex A-1¹, Chelex 100, Lewatit TP-207, Wofatit CM-50 or Diaion CR-10² which was used in a number of analytical applications in its usual granular form³⁻⁵ or in the form of filtration membranes^{6,7}. It was also applied technologically, viz. in purification of waste water^{8,9}.

The cellulose chelating materials based on aminocarboxylic acids are not too widespread at present. The iminodiacetate of cellulose was used successfully in analyses of soil extracts¹⁰ and in the on-line pre-concentrating of samples analyzed by the ICP method^{11,12}. With the use of the cellulose modified with diethylenetriaminetetraacetic acid it was possible to remove Cu(II), Zn(II), and Mg(II) ions from solutions of amino acids¹³. The sorption properties of this ion exchanger are dealt with in other reports too^{14,15}, and its specification can be found in the corresponding brochures of its producer.

The present communication deals with a study of sorption of lead on the cellulose sorbent Ostsorb DTTA, i.e. the pearl-formed spherical cellulose modified with the functional group of diethylenetriaminetetraacetic acid. Its formula reads as follows:



The present paper forms a continuation of our earlier studies of lead and/or cadmium sorption with the cellulose ion exchangers Ostsorb DETA¹⁶, Ostsorb P and Ostsorb SA-5¹⁷.

EXPERIMENTAL

Apparatus

The lead content in solutions was determined with the help of an atomic absorption spectrophotometer Atomspek H 1550 (Hilger and Watts, U.K.) operating at the wavelength of 217.5 nm and using the acetylene-air flame. The pH of solutions was determined with an OP 205/1 apparatus with combined glass electrode OP 0808P (Radelkis, Hungary). Mixing was performed with a shaking machine LT-1 (Kavalier, The Czech Republic), and the experiments in column arrangement were carried out in a glass column of 22 mm inner diameter with a sintered glass bed and ground glass joint connecting it with a separating funnel.

Chemicals

The buffers were prepared¹⁸ from potassium chloride and hydrochloric acid (pH 1), dipotassium phthalate and hydrochloric acid (pH 2), glycine, sodium chloride, and hydrochloric acid (pH 3), sodium acetate and acetic acid (pH 4.5 and 6). Ion-exchanger-treated (deionized) water. All the chemicals used were of p.a. purity grade (Lachema, The Czech Republic).

Some physical properties of the applied cellulosic ion exchanger Ostsorb DTTA (Spolek pro chemickou a hutni výrobu, The Czech Republic) (in the following text only "Ostsorb" if no confusion is possible) and Dowex A-1 (Dow Chemical Company, U.S.A.) (further only "Dowex") are given in Table I. The content of functional groups in the ion exchanger which were able of forming the chelate bonds with Cu²⁺ ions was 0.4 mmol g⁻¹ at least. The swollen Ostsorb contained 75 wt.% water, which agrees with the interval of 72 – 82% given by the producer¹⁵. If not otherwise stated, both ion exchangers were used in the swollen H⁺ form obtained by washing the swollen ion exchanger, placed in a glass column, with 0.2 M HCl (25 ml acid per 1 ml ion exchanger) and then with deionized water until neutral reaction. The NH₄⁺ form of the ion exchanger was obtained by washing it with 0.1 M NH₄OH (50 ml per 1 ml of ion exchanger) and with water until neutral reaction.

All the below-described experiments were repeated twice, and any of the values given is the arithmetic mean of the experimental results. Exceptions are mentioned in the text.

Measurement of Time Course of Sorption of Lead with Ostsorb DTTA and Dowex A-1 Ion Exchangers

Ostsorb (0.5 g) or Dowex (0.25 g) in H⁺ or NH₄⁺ form was placed in a 250 ml calibrated flask and 100 ml lead solution in acetate buffer (pH 4) was added thereto (the lead concentrations of 500 and 1 500 mg l⁻¹ for Ostsorb and Dowex, respectively). The flasks were shaken on a horizontal shaking

machine 2 h, and 1 ml samples were taken from the suspension during this time interval. After diluting, the samples were analyzed on the atomic absorption spectrophotometer.

pH Dependence of Analytical Exchange Capacity

Lead sorption. Ostsorb (0.5 g) or Dowex (0.1 g) was shaken with 100 ml lead solution in buffer (lead concentrations 500 and 1 500 mg l⁻¹ for Ostsorb and Dowex, respectively) 2 h. After finishing the sorption, 1 ml samples were taken from the suspensions and analyzed to find the decrease in lead concentration in solution and hence the lead amount captured by the ion exchanger.

Iron sorption. The cellulosic ion exchanger (0.5 g) was shaken with 100 ml buffer (1 M HCl solution was used for pH 0) containing 250 mg l⁻¹ Fe(III). The amount of sorbed iron was determined by the analysis of the sorption solution before and after the experiment.

Desorption of Lead

Time course of desorption with various inorganic acids. Shaking of 0.4 g Ostsorb or 0.2 g Dowex with 100 ml lead solution in buffer (pH 4, the lead concentration 400 and 1 000 mg l⁻¹ for Ostsorb and Dowex, respectively) for 3 h resulted in a sorption of certain amount of lead by the ion exchangers, which amount was determined from the lead concentration difference in the solution before and after the sorption. The ion exchanger was filtered off, washed with 10 ml buffer, and transferred into a 250 ml calibrated flask with the help of 100 ml 1 M HCl or 1 M HNO₃ or 1 M HClO₄. The flask content was shaken for 90 min (Ostsorb) or 200 min (Dowex). The desorption course was monitored by means of analyses of the samples taken from the solution.

Dependence of the efficiency of lead recovery upon concentration of desorbing acid. A known amount of lead was sorbed from 250 ml lead solution in buffer (pH 4, lead concentration 8 and 0.1 mg l⁻¹ for Ostsorb and Dowex, respectively) by the swollen ion exchanger (0.5 g Ostsorb or 0.1 g Dowex) after 3 h shaking. The ion exchanger was filtered off, transferred into a 50 ml flask (Ostsorb) or 25 ml flask (Dowex), and the lead was extracted with 25 ml (Ostsorb) or 10 ml (Dowex) hydrochloric acid of various concentrations.

TABLE I
Physical properties of Ostsorb DTTA and Dowex A-1

Property	Ostsorb	Dowex
Density, g cm ⁻³	1.10 ^a	—
Specific weight, g cm ⁻³	—	1.42 ^a
	0.61 ^b	0.83 ^b
Swelling capacity, g H ₂ O g ⁻¹	2.94	0.70
	1.83 ^c	—
Moisture content, %	9.2	5.7
Average size of particles, μm	595 ^a	450 ^a
	380 ^b	—

^a In swollen state; ^b dried at 20 °C; ^c after pre-drying at 70 °C.

Effects of Some Compounds on Lead Sorption by Ostsorb DTTA

Effect of K_3PO_4 . Calibrated 250 ml flasks were charged with 0.5 g ion exchanger and 100 ml solution containing 10 mg l⁻¹ lead and 0.10 – 1.65 mol l⁻¹ K_3PO_4 . After 3 h shaking, the sorbent was filtered off and extracted with 15 ml 1 M HCl in 50 ml calibrated flasks for 1 h.

Effect of iron. Calibrated 500 ml flasks were charged with 0.5 g ion exchanger and 250 ml buffer pH 4 containing 0.1 mg l⁻¹ lead and 1, 10, or 100 mg l⁻¹ iron. After 3 h shaking, the sorbent was filtered off, washed with 10 ml buffer, and extracted with 10 ml 1 M HCl in a 25 ml calibrated flask for 1 h.

Effect of EDTA. A 500 ml calibrated flask was charged with 0.5 g ion exchanger and 250 ml buffer pH 4 containing 0.1 mg l⁻¹ lead and $1 \cdot 10^{-5}$ mol l⁻¹ EDTA. After 2 h shaking, the sorbed lead was extracted with 10 ml 1 M HCl.

Effects of other cations. These cations (Ni, Cu(II), Mn(II), Ba, Mg, Bi, Al, Zn, Co(II), Ca, Cr(III), Sn(II), Fe(III)) were used either as chlorides (Ni, Cu, Mn, Ca, Fe, Sn) or as nitrates (Pb, Ba, Mg, Al, Bi, Zn, Co, Cr) and were added to a solution of 100 ml buffer pH 4 containing 0.8 mg l⁻¹ lead so as to make the final concentration of the respective added cation equal to 80 mg l⁻¹. The solutions were shaken with 0.2 g swollen ion exchanger in H⁺ form for 90 min. The sorbent was filtered off and extracted with 10 ml HCl (1 mol l⁻¹) 90 min.

Stability of Ion Exchangers in Inorganic Acids

Calibrated 100 ml flasks were charged with 0.1 g ion exchanger (pre-dried at room temperature) and 50 ml acid solution. Hydrochloric, perchloric, and nitric acids of 6 mol l⁻¹ concentration and perchloric acid of 1, 2, 3, and 4 mol l⁻¹ concentrations were adopted. The mixture was left to stand 17 h, whereafter the ion exchanger was filtered off, washed with water, and transferred into 250 ml calibrated flasks containing 100 ml acetate buffer pH 4 with 400 (Ostsorb) or 1 000 mg l⁻¹ lead (Dowex). The flasks were shaken 1 h (Ostsorb) or 3 h (Dowex), and the decrease of lead in solution was then determined by means of AAS. The blank test was carried out in the same way with the ion exchangers kept in deionized water. The exchange capacity of these sorbents was considered as the basic value for evaluating the effect of acids upon the capacity of ion exchangers.

Effect of Sorbent Amount, Sample Volume, and Lead Concentration

Various volumes of solutions (25 – 500 ml) buffered at pH 4 containing various lead concentrations (0.1 – 2 000 mg l⁻¹) were shaken with 0.5, 1, and 1.5 g swollen ion exchanger Ostsorb DTTA in calibrated flasks of double volume for 2 h. The ion exchanger was filtered off, washed with 15 ml deionized water, and the lead sorbed was extracted therefrom by shaking it with 15 ml 1 M HCl and determined by means of AAS. The blank test was carried simultaneously in the same way with 250 ml and 500 ml buffer pH 4 and 0.5 or 1 g sorbent.

Determination of Lead in Phosphoric Acid

Preparation of sample. Furnance phosphoric acid (10 and 20 ml) was diluted with water to ca 200 ml and, with stirring and cooling, neutralized with saturated KOH solution to pH 4. The volume of solutions thus prepared was adjusted at 250 and 500 ml, respectively, and the solutions were used for further experiments.

Sorption of lead by Ostsorb DTTA in batch-type arrangement. Each of ten 500 ml calibrated flasks was charged with 2 g swollen ion exchanger and 250 ml solution containing 10 ml phosphoric acid neutralized to pH 4. Into five of these flasks, 1 ml solution containing 28.7 µg lead was added, and

the flasks were shaken 2 h. Then the sorbent was filtered off, washed with 20 ml deionized water, transferred into 25 ml calibrated flasks, and extracted with 15 ml 1 M HCl 1 h.

Sorption of lead on ion exchanger column with Ostsorb DTTA. A solution obtained by neutralizing 20 ml phosphoric acid and diluting to 500 ml (pH 4) was left to pass at a rate of ca 2.5 ml min⁻¹ through a column containing 4 g swollen ion exchanger, whereafter the sorbent was washed with 2 × 25 ml water and extracted with 2 × 10 ml 1 M HCl by shaking the suspension in the same column fastened to a horizontal shaking machine for 2 × 45 min. The volume of the combined extracts was adjusted to 25 ml by addition of water, and the lead content was determined by means of AAS. The same procedure was applied to the experiments with 500 ml neutralized phosphoric acid with 55.3 µg lead added.

RESULTS AND DISCUSSION

pH Dependence of Analytical Exchange Capacity

From the values measured for analytical exchange capacity of Ostsorb DTTA and Dowex A-1 in the sorption of Pb(II) ions (Table II) it is obvious that the exchange capacity of both ion exchangers reaches its maximum value at pH ≥ 4. However, the absolute values of maximum capacity of the two exchangers differ, being equal to ca 1 100 and 210 mg Pb g⁻¹ for Dowex A-1 and Ostsorb DTTA, respectively. Also the course of the pH dependence is somewhat different for the two sorbents. The cellulosic ion exchanger captures a certain amount of lead as low as at pH 1, whereas the polymeric exchanger only at pH > 2, which is important for choosing the suitable conditions of desorption. The extraction agent in the case of Ostsorb DTTA must be an

TABLE II
pH Dependence of analytical exchange capacity Q_a^a

pH	Ostsorb DTTA		Dowex A-1
	Q_a , mg Pb g ⁻¹	Q_a , mg Fe g ⁻¹	Q_a , mg Pb g ⁻¹
0	–	4.7	–
1	52.2	22.1	–
2	87.2	50.2	8.4
2.5	–	–	92.1
3	178.8	59.9	214.2
4	207.3	57.6	811.4
5	189.1	58.2	984.8
6	210.2	–	1 075.9

^a Average value of two measurements, relative standard deviation $s_r \leq 8.3\%$.

acid with $[H^+] \geq 1 \text{ mol l}^{-1}$, whereas $[H^+] = 0.1 - 0.2 \text{ mol l}^{-1}$ is sufficient for Dowex A-1. The higher exchange capacity of Dowex is particularly favourable in the cases of sorption of lead and other metals from solutions with high concentrations of complex-forming ions. Such ions also include Fe(III) ions which often accompany Pb(II) ions in various samples. Therefore, we also measured the pH dependence of exchange capacity of Ostsorb DTTA in the sorption of Fe(III) ions (Table II). Like in the case of lead sorption, the capacity reaches the maximum value of 1 mmol g^{-1} , but this occurs at $\text{pH} \geq 3$ already. To a lesser extent, iron is captured also at $\text{pH} 0$.

Time Course of Sorption Process

The graph of dependence of relative lead concentration in solution upon the time of contact with ion exchanger (Fig. 1) shows that at the given set of experimental conditions the equilibrium is established relatively very quickly on the cellulosic exchanger (within 15 – 30 min), whereas this interval is perceptibly longer with Dowex A-1 (ca 70 – 90 min). In both cases the exchange reaction was faster with the exchangers in NH_4^+ form than that in H^+ form, however, the differences are not practically significant.

Lead Desorption

The simplest and most usual way of desorption of the ions captured by chelating sorbents is the desorption with solutions whose pH lies outside the region in which the complexing reaction takes place, most often at $\text{pH} \leq 1$. However, certain differences can be observed in the elution abilities of the individual acids and their aggressiveness to the bond between the complexing functional group and the ion exchanger matrix

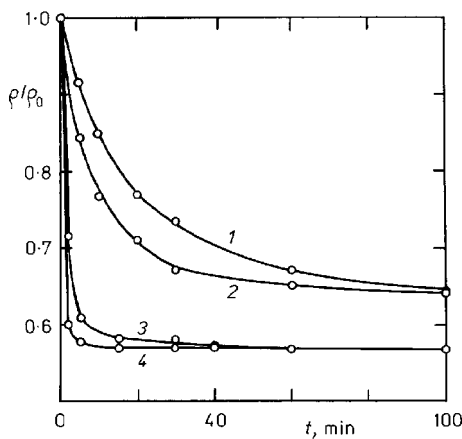


FIG. 1

Time course of ratio of actual (ρ) to initial weight concentration (ρ_0) of lead during its sorption by Ostsorb DTTA and Dowex A-1. The form of ion exchangers: Dowex A-1 1 H^+ , 2 NH_4^+ ; Ostsorb DTTA 3 H^+ , 4 NH_4^+

which can go as far as the destruction of exchanger. Therefore, we compared the elution abilities of the most common acids, viz. hydrochloric, perchloric, and nitric acids, and their effect upon the exchange capacity of ion exchanger.

From the kinetic viewpoint the desorption of lead from the exchangers by the given acids (concentration of 1 mol l^{-1}) is perceptibly faster with the cellulosic exchanger, as shown by repeated experiments. Without significant differences between the individual acids, the equilibrium state is established as soon as after 10 min extraction. In analogy to sorption, the desorption with Dowex is slower, too. The time necessary for establishing the equilibrium at the given set of experimental conditions is ca 20 – 30 min, but with 1 M HCl this interval is as long as 100 min, which perhaps is the reason of the fact that this acid is not used for extractions of ions sorbed by Dowex A-1, nitric acid being preferred almost exclusively.

Moreover, the results of desorption experiments with Ostsorb showed that even 1 M acids are insufficiently efficient eluents of lead from the exchanger, 90% of the metal being recovered at the most at the conditions used.

The results of monitoring of the desorption course of lead from Ostsorb using 0.2 and 1 M hydrochloric acid showed a faster desorption with 1 M HCl, the yield of recovered lead being also higher (87%) than that obtained with 0.2 M HCl (80%). However, in contrast to other experiments, these are results of a single measurement only, hence they can only be considered preliminary.

With Dowex we found a very distinct difference in the extraction efficiency of 0.01, 0.1, and 1 M HCl. After 5 h extraction the respective yields of recovered lead were 7%, 30%, and 92%. The extraction of 0.025 mg lead from this exchanger with 1 M HCl reached a 92% recovery, and for 20 mg the recovery it was almost quantitative. Also noteworthy is the fact that in the case of enriching lead from very dilute solutions, when the amount of sorbed metal is in the range of 10^{-3} – 10^{-2} mg, one must respect the value of blank test which was 0.001 mg Pb for 250 ml acetate buffer of pH 4.

If the exchanger had to be used repeatedly, it would be necessary to know how its properties are changed on contact with the desorption acid solutions. Table III gives the exchange capacities of both the exchangers tested in the case of sorption of lead from a solution of pH 4: before the tests the two exchangers were kept either in acidic media (6 M HCl, 6 M HNO₃, 1 – 6 M HClO₄) or in water for 17 h. When evaluating these results one must take into account that the reproducibility of determination of exchange capacity of Ostsorb DTTA expressed by relative standard deviation is $s_r = 3.7\%$ for 5 measurements at the given set of experimental conditions, whereas for Dowex it is $s_r = 3.2\%$, which means that the Q_a values in Table III for 1 – 6 M HClO₄ vary within experimental error. From among the three 6 M acids compared, HCl and HNO₃ affect negatively the capacity of both sorbents, the capacity decrease being more than 10% and up to 15% for HNO₃. 6 M HClO₄ had almost no effect on the properties of the cellulosic exchanger, and the capacity of Dowex A-1 was decreased by less than 5%

only. These facts must be respected when using repeatedly the exchangers after regeneration with concentrated HCl and HNO₃ solutions: in this way it is possible to avoid the discrepancies in results due to incorrect presumption of exchange capacity of exchanger. The unfavourable effect of long-term storage of exchanger in H⁺ form on its exchange capacity is pointed out in ref.¹. The application of HNO₃ to the extractions of cellulosic exchangers is to be avoided also with regard to possible nitration reaction of the exchanger matrix.

Effect of Some Ions on Sorption of Lead by Ostsorb DTTA

The metals accompanying lead in a number of samples, often even at higher concentrations than that of Pb, include iron, viz. Fe(III) ions. In order to evaluate their effect on the sorption of lead by Ostsorb DTTA, we monitored the amount of Pb(II) captured by the exchanger from solutions containing Fe(III) ions whose weight concentrations were three orders of magnitude higher than that of Pb(II). Whereas the sorption of lead from a solution without Fe(III) took place with the lead recovery $R_{\text{Pb}} = 95.3\%$, with the solutions in which the initial ratio of iron to lead was $\rho_{0,\text{Fe}}/\rho_{0,\text{Pb}} = 10, 100, \text{ and } 1\,000$ the respective R_{Pb} values were 93.7%, 70.7%, and 28.5%. Hence the lead recovery after sorption and extraction from exchanger was not negatively affected by Fe(III) ions until the total amount of both metals n_0 in the solution exceeded the exchanger capacity. At the given set of experimental conditions, the sorbent was able to capture 0.1 mmol metal ion, for the values $\rho_{0,\text{Fe}}/\rho_{0,\text{Pb}} = 10, 100, \text{ and } 1\,000$ the corresponding amount of

TABLE III

Exchange capacity of ion exchangers kept in acid solutions of various concentrations^a

Acid	Ostsorb DTTA		Dowex A-1	
	$Q'_a, \text{ mg g}^{-1}$	$Q'_a/Q_a, \%$	$Q'_a, \text{ mg g}^{-1}$	$Q'_a/Q_a, \%$
1 M HClO ₄	204	98.5	802	98.9
2 M HClO ₄	201	96.9	830	102.3
3 M HClO ₄	202	97.7	813	100.2
4 M HClO ₄	202	97.7	796	98.1
6 M HClO ₄	205	99.2	774	95.4
6 M HNO ₃	176	84.8	693	85.5
6 M HCl	185	89.2	719	88.6

^a Q'_a, Q_a the analytical exchange capacity of the ion exchanger kept in solution of acid and in deionized water. $Q_a(\text{Ostsorb DTTA}) = 207 \text{ mg Pb g}^{-1}$, $Q_a(\text{Dowex A-1}) = 811 \text{ mg Pb g}^{-1}$.

Pb(II) and Fe(III) ions in solution being $n_0 = 0.04, 0.45, \text{ and } 4.50$ mmol, respectively. At the values of ratio $\rho_{0,\text{Fe}}/\rho_{0,\text{Pb}} \geq 100$ the exchanger capacity was exceeded more than four times already, and the yield of recovered lead significantly decreased.

Table IV shows how the lead recovery is affected by other cations. Except for the alkaline earth metals all the cations studied, when present in the solution at concentrations higher than that of lead by a factor of 100, will significantly decrease the efficiency of lead sorption. The amount of exchanger was only sufficient for sorbing all lead but not for sorbing all the complex-forming ions present in the solution. The properties of the Ostsorb DTTA ion exchanger were verified, inter alia, with regard to potential applications to the determination of lead in phosphate compounds. Therefore we were also interested in the sorption of Pb(II) ions from the K_3PO_4 medium. The data about the yields of the processes of lead sorption and desorption in the presence of various phosphate concentrations indicate a significant negative effect of this medium upon the efficiency of Pb(II) sorption by ion exchanger. From Fig. 2 it can be seen that an acceptable recovery $R \geq 90\%$ can be reached with solutions of $c(\text{K}_3\text{PO}_4) \leq 0.1 \text{ mol l}^{-1}$. Similar conclusions were expressed earlier¹⁶ also for the Ostsorb DETA sorbent. The reason probably lies in the formation of stable complexes of lead and phosphate ions which, at higher phosphate concentrations in the sorption solution, competes with the formation of chelate between lead and functional group of ion exchanger. Also the considerable viscosity of concentrated K_3PO_4 solutions negatively affects the kinetics of sorption process, and the possibility of contacts between solid and liquid phases is worsened because the ion exchangers float on the surface of such solutions.

The experiments with lead solutions containing EDTA had to verify whether or not this common complexing agent can be used for masking the ions which interfere with the sorption of lead by Ostsorb DTTA. Under the conditions where the ratio of molar concentrations of functional groups of DTTA and EDTA and lead was 200 : 50 : 1, the recovery of lead sorbed from a solution with $\rho_{0,\text{Pb}} = 0.1 \text{ mg l}^{-1}$ was only 28%. Hence

TABLE IV
Effect of presence of some cations upon sorption of lead by Ostsorb DTTA^a

Cation	$R_{\text{pb}}, \%$	Cation	$R_{\text{pb}}, \%$
Ni(II) ^b	13.9	Co(II) ^c	26.3
Cu(II) ^b	15.5	Ca(II) ^b	97.6
Mn(II) ^b	49.4	Sn(II) ^b	28.9
Ba(II) ^c	98.8	Bi(III) ^c	15.2
Mg(II) ^c	94.1	Al(III) ^c	32.9
Zn(II) ^c	38.0	Cr(III) ^c	64.9

^a $\rho_{0,\text{Me}} = 80 \text{ mg l}^{-1}$, $\rho_{0,\text{Pb}} = 0.8 \text{ mg l}^{-1}$; ^b chloride; ^c nitrate.

EDTA forms a more stable complex with Pb(II) ions than that formed by the ion exchanger, and it is not suitable for masking the other ions.

Effects of Sorbent Amount, Sample Volume, and Lead Concentration upon Sorption of Lead by Ostsorb DTTA

Table V summarizes the results of the measurements whose aim was finding the optimum conditions of isolating and concentrating lead from solutions from the viewpoint of the concentration ratios in the system. With constant sorption time in all the experiments, the amounts of lead captured by 0.5 g swollen ion exchanger shows random differences only ($m = 17.2 - 19.8$ mg Pb), the factors investigated having no distinct effect on the sorption efficiency. The amount of metal captured was $m = 5$ mg in the sorption from a solution with the initial lead concentration $\rho_0 = 10$ mg l⁻¹, which corresponds to the total initial amount of lead in the solution. In the other experiments, the amount of Pb(II) ions introduced was always higher than that the ion exchanger could sorb, i.e. the exchanger capacity was saturated.

In these experiments we measured solutions with relatively high concentrations of lead ($\rho_0 \geq 10$ mg l⁻¹), whereas the concentrations practically encountered are substantially lower. Therefore, in another set of experiments we determined the yields of recovered lead from 250 and 500 ml solutions with $\rho_0 = 0.1$ mg l⁻¹ using various amounts of ion exchanger, and we treated the results statistically. The mean value of five blank tests using 250 ml buffer and 0.5 g sorbent each was 0.009 ± 0.003 mg lead, the corresponding value for 500 ml buffer and 1 g ion exchanger being 0.016 ± 0.002 mg lead. Taking into account these values, we found from five repeated measurements the average value of lead recovery $91.7 \pm 7.0\%$ after sorption from 250 ml solution by 0.5 g ion exchanger. With twofold values of volume and sorbent amount and the same initial lead

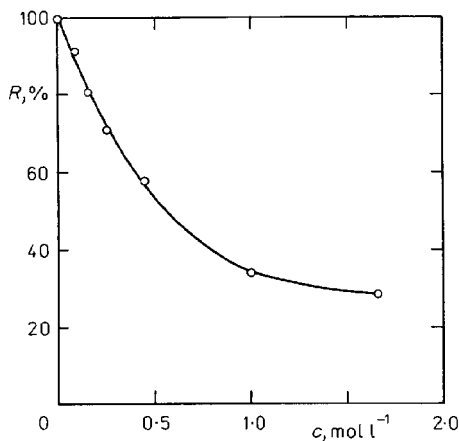


FIG. 2
Dependence of recovery of lead upon K₃PO₄ concentration in solution

concentration $\rho_0 = 0.1 \text{ mg l}^{-1}$ the lead recovery reached $92.2 \pm 5.4\%$. Furthermore, using 250 ml of the same solution, we tested the effect of sorbent amount on the yield of enrichment of lead. With 0.5, 1.0, and 1.5 g ion exchanger lead recovery values were 91.7%, 94.0%, and 97.0%, respectively. In the last two cases the figures are mean values of two experiments each.

On the basis of the conclusions given, the following conditions of batch-type arrangement can be recommended for concentrating lead from aqueous solutions: sample volume 100 – 500 ml, $\text{pH} \geq 4$, amount of swollen ion exchanger 0.5 – 1.5 g depending on the concentration of lead and other complex-forming ions, sorption time 2 h, desorption with 10 – 15 ml 1 M HCl for 1 h. The procedure suggested allows to concentrate the original lead solution up to 20 times with concomitant separation of ions which do not form complexes with Ostsorb DTTA.

Determination of Lead in Phosphoric Acid

The experimental results described show that the yields of recovered lead can vary considerably depending on the working conditions chosen and on the composition of the sample analyzed. Therefore it is reasonable to carry out simultaneous concentrating of original samples and those with added known amount of lead and to determine the yield of recovery and enrichment of the added metal, whereafter the result obtained for the original sample is corrected by dividing it by the recovery value found.

TABLE V

Sorption of lead by Ostsorb DTTA at various concentration ratios of lead and chelating functional groups^a

$\rho_0, \text{ mg l}^{-1}$	$c_0, \text{ mmol l}^{-1}$	$c_{\text{DTTA}}, \text{ mmol l}^{-1}$	c_0/c_{DTTA}	$V, \text{ ml}$	$m, \text{ mg}$
2 000	9.66	4.0	2.40	25	18.7
1 000	4.83	2.0	2.40	50	18.3
500	2.42	1.0	2.40	100	19.2
250	1.21	0.5	2.40	200	18.9
10	0.05	0.2	0.25	500	5.0
50	0.24	0.2	1.20	500	17.2
250	1.21	0.2	6.05	500	19.8
500	2.42	0.2	2.10	500	17.5

^a c_0 and ρ_0 are the initial molar and weight concentrations of lead, respectively, c_{DTTA} is the approximate concentration of functional groups of ion exchanger in the reaction solution, V volume of solution, m the amount of lead captured by 0.5 g of swollen ion exchanger.

The choice of furnace phosphoric acid as the sample for determination of lead content was motivated by the fact that this material is used in the production of fodder salts and can represent a potential source of contamination of these salts with traces of lead.

The statistically evaluated results of 10 parallel analyses of samples of the neutralized acid (28.7 μg lead was added to five of these samples) are presented in Table VI. For the calculation of the corrected values of lead content in the sample we adopted the mean recovery $R = 96.5\%$. The lead amount found in 10 ml phosphoric acid was 13.8 μg , which corresponds to the weight fraction $w = 8 \cdot 10^{-5}\%$.

On the basis of the experience from an earlier study¹⁶, the samples of neutralized phosphoric acid were also concentrated by the dynamic way on a column. With regard to larger amount of ion exchanger as compared with that in the batch-type arrangement (to prevent the penetration of lead through the column) the volume of acid necessary for desorption is also greater, which decreases the degree of enrichment by the factor of ca 1.5 – 2. The yield of lead recovery and the correction of the values of lead content found in the sample were calculated in the same way as in the static (batch-type) method, i.e. from pairs of parallel experiments. The average yield of recovery of the 55.3 μg lead added to the solution of neutralized phosphoric acid was 96.8%, the lead content recalculated to 10 ml sample of the acid was 14.3 μg , which agrees well with the result obtained from the static (batch-type) method.

TABLE VI
Statistical characteristics of determination of lead in phosphoric acid

Quantity ^a	\bar{x}	$s_{\bar{x}}$	s	s_r , %	$L_{1,2}$
m_1 , μg	41.1	0.54	1.21	2.94	39.6 – 42.6
m_2 , μg	13.4	0.95	2.12	15.87	10.8 – 16.0
m_3 , μg	13.8	0.81	1.81	13.11	11.6 – 16.1
R_{Pb} , %	96.4	1.88	4.20	4.36	91.2 – 101.6

^a \bar{x} Arithmetic mean; $s_{\bar{x}}$ standard deviation of the mean; s standard deviation; s_r relative standard deviation; $L_{1,2}$ 95% confidence interval; m_1 , m_2 , and m_3 are amounts of Pb in samples with added Pb, original samples without correction, and those with the correction for recovery, respectively; R_{Pb} recovery of Pb from the samples with added Pb.

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