

APPLICATION OF CHELATING ION EXCHANGER OSTSORB DTTA TO DETERMINATION OF LEAD AND CADMIUM IN SOILS, PLANTS, AND FERTILIZERS

Ladislav SVOBODA, Miloslav TOMEK and Petr TOLAR

*Department of Inorganic Technology,
University of Chemical Technology, 532 10 Pardubice, The Czech Republic*

Received May 31, 1993

Accepted July 24, 1993

The paper investigates a possible application of chelating cellulose ion exchanger with the functional groups of diethylenetriaminetetraacetic acid to concentrating lead and cadmium in extracts from soils and industrial fertilizers or mineralizates of plant materials. A favourable recovery of the metals needs the knowledge of the approximate content of the complex forming cations in the solutions and the suppression of formation of iron and aluminium hydroxides during modification of acidity of extracts to the value of pH 4 which is the optimum for the formation of chelates. The degree of concentrating reached the values of $f_E = 10 - 50$, the recovery of lead and cadmium depended on the nature of sample and was in the range of $R = 60 - 100\%$.

The chelating ion exchangers have found broad applications in analytical practice for concentrating traces of metals able of formation of firm complexes at suitable conditions. They are adopted most frequently in analyses of various sorts of water^{1 - 12}, the applications to analyses of geological materials^{13 - 16}, metals and alloys^{17,18}, plants¹⁹, or soils²⁰ being less current. In the case of solutions, extracts, and mineralizates of solid samples, the matrix is substantially more complex, which brings problems connected with high ionic strength of solutions, considerable differences in concentrations of complex-forming ions, unsuitable acidity of medium, or the presence of interfering substances. The usually smaller volumes of solutions or extracts of solid materials, as compared with samples of water, lead to a smaller degree of concentration f_E by about one order of magnitude. The latter quantity, which is also referred to as the enrichment factor, is generally defined as the ratio of volumes of solutions of the monitored substance before and after the concentration procedure at a given recovery degree of the process. For instance, the determination of micro elements in carbonate rocks¹³ reached the value of $f_E = 40$, that of Cu, Pb, and Zn in water³ $f_E = 330$, a two-step concentration procedure² even reached the value of $f_E = 50\ 000$. For bigger volumes of samples it is more suitable to adopt the column procedure of sorption^{1 - 3,5}, whereas from smaller ones the micro elements can be trapped by the ion exchanger in the batch way^{16,18,21}. The dynamic arrangement also has the advantage in that the pre-concentration of

sample can be connected on-line with the apparatus for AAS or ICP-OES (ref.¹²). The sorbed metals can be eluted from the ion exchanger and then determined in solution^{3,5,9,14}, however, it is also possible to carry out the determination directly in the ion exchanger using the methods of emission spectroscopy²², X-ray fluorescence analysis^{6,7,23}, or neutron activation analysis²⁴.

When concentrating lead, cadmium, and other minor elements from soil extracts one encounters the main problem in the presence of iron and aluminium at concentrations several orders higher than those of the monitored elements. So far no chelating ion exchangers have been developed which would be selective for lead or cadmium and would not simultaneously trap the iron and aluminium ions (which themselves can saturate the capacity of ion exchanger and produce the respective hydroxide precipitates) at the same experimental conditions. If the lead content of extract is sufficiently high, it can be determined by a direct analysis using e.g. the AAS method²⁵; otherwise the lead must be extracted and concentrated with a solution of suitable complex-forming agent²⁶⁻²⁸ or iron ions must be removed from the extract in the same way²⁹. Chelating ion exchangers have been used only sporadically for such purposes²⁰.

The present communication describes the experiments in which a cellulose chelating ion exchanger based on diethylenetriaminetetraacetic acid, Ostsorb DTTA, has been used for the sorption of lead and cadmium from soil extracts, an industrial fertilizer, or a mineralizate of grass; the properties of Ostsorb DTTA in the sorption of lead were described in our previous communication³⁰ and turned out to be the most appropriate for these purposes out of the tested cellulose ion exchangers of the Ostsorb series.

EXPERIMENTAL

Apparatus and Chemicals

The metals in solutions were determined with the use of an atomic absorption spectrometer Atomspék H 1550 (Hilger and Watts, U.K.) with an acetylene-air flame (except for aluminium, where the acetylene-dinitrogen oxide system was adopted). The samples were shaken with the ion exchanger with the help of a longitudinal shaker LT 1 (Kavalier, The Czech Republic), their pH values were determined by means of an OP-205/1 apparatus with combined glass electrode OP-8083 (Radelkis, Hungary). Lead and cadmium were concentrated on a selective cellulosic chelating ion exchanger Ostsorb DTTA with chemically bound functional groups of diethylenetriaminetetraacetic acid (Spolchemie, The Czech Republic). Its properties are described in our previous communication³⁰. The ion exchanger was used in its swollen H⁺ form.

All the chemicals used were of p.a. purity grade (Lachema, The Czech Republic). The water used in experiments was deionized.

By its physico-chemical properties, the analyzed sample of soil can be classified as a light clay-sand soil. The grass species in the respective sample were not specified: it represented aerial parts of a mixed grass vegetation.

Three-component fertilizer GVH III (Istrochem, The Slovak Republic) was a granulated mixture of potassium, ammonium, and calcium salts of nitric, phosphoric, hydrochloric, and sulfuric acids with the minimum content (by wt.) of 8.5% N, 17.5% P₂O₅, and 17.5% K₂O.

Procedures: Determination of Lead in Soil

Preparation of soil extract. A soil sample dried at room temperature was ground and sieved through a 2 mm sieve. The undersizes (50 g) were shaken with 250 ml 1 M HCl in a calibrated flask 60 min, the suspension was filtered through a filter paper, the filtration cake was washed with 50 ml HCl solution, and the volume was adjusted by addition of water at 300 ml or another required value.

Analysis of soil extract by AAS. The soil extract was diluted with water to the volume of 500 ml and without any other modification directly analyzed on the atomic absorption spectrometer in the acetylene-air flame (Pb, Ni, Cu, Mn, Zn, Co, Fe) or acetylene-dinitrogen oxide flame (Al). The wavelengths of the individual metals were as follows: Pb 217.5 nm, Ni 232.5 nm, Cu 325.0 nm, Mn 403.5 nm, Al 309.6 nm, Zn 214.5 nm, Co 241.0 nm, Fe 386.4 nm. The concentrations of the above-mentioned metals in the extract were determined by the method of standard addition.

Concentrating of lead from extract by sorption on ion exchanger. The pH value of soil extract was adjusted at pH 4 by adding 2 M NaOH, the precipitate formed was removed by filtration, the filtration cake was washed with 20 ml water, and 0.2 g swollen Ostsorb DTTA was added to the filtrate. After 90 min shaking, the ion exchanger was filtered off, washed with water, and transferred into a 50 ml calibrated flask where it was extracted with 20 ml 2 M HClO₄ 90 min. The lead concentration in desorbate was determined by AAS. The experiment described was repeated with the following differences: in the first case an extract of dried soil sample with added lead (40 µg Pb in the form of Pb(NO₃)₂) of 10 mg l⁻¹ concentration was used, in the second case the same amount of lead was added to the extract after filtering off the soil, and in the third case after filtering off the precipitate formed upon the neutralization of extract. From the results we evaluated the losses of lead in the individual analytical operations.

Sorption of lead in the presence of Na₄P₂O₇. The dependence of recuperation efficiency of lead upon the amount of Na₄P₂O₇ added, the amount of sorbent, and pH of medium was studied in a series of experiments in which 100 ml extract of a known concentration of lead was mixed with 50 – 250 ml saturated Na₄P₂O₇ solution, 0.5 – 2 g ion exchanger, and its pH was adjusted at pH 3 – 9.5 by addition of 1 M NaOH. In these experiments (as well as those described below) the sorbent with extract was shaken 2 h, and the lead trapped was desorbed with 20 ml 2 M HClO₄ 1 h.

Desorption of lead from ion exchanger with HClO₄. The soil extract (300 ml) was adjusted at pH 4 by adding NaOH solution, and 250 ml Na₄P₂O₇ solution and 5 g Ostsorb DTTA were added thereto. After the sorption was finished, the lead trapped was desorbed with 2 × 20 ml HClO₄ of the concentrations of 1, 2, 3, 4, and 5 mol l⁻¹ for 2 × 1 h.

Sorption of lead after reduction of Fe(III) to Fe(II). The soil extract (100 ml) with a known lead concentration was treated with 2 – 15 g NH₂OH · HCl or 1 – 5 g ascorbic acid, the solution was heated on a 50 °C water bath, and its pH was adjusted at pH 4 by adding NaOH solution. The precipitate formed was filtered off and washed with water, and the filtrate was shaken with 2 g ion exchanger. Then followed the desorption of lead with 2 M HClO₄ and its determination by means of AAS.

Determination of lead in soil after reduction Fe(III) to Fe(II). The soil extract (300 ml) was treated with 250 ml Na₄P₂O₇ solution, 2 M NaOH solution to obtain pH 4, and 5 g swollen ion exchanger. After 3 h shaking the trapped lead was desorbed with 20 ml 2 M HClO₄. Five experiments were carried out with each: the original extract and the extract with added 1 mg lead. The same procedure of sorption and desorption of lead was used with the extracts treated with 6 g ascorbic acid instead of Na₄P₂O₇. The reduction of Fe(III) took place at 50 °C 30 min, and the precipitate formed was filtered off.

Determination of Lead in Grass

Mineralization of sample. A dried sample of grass (10 g) was carbonized in a porcelain crucible by gentle heating on a flame and further heated in an oven at 450 °C 15 h. After cooling, the crucible content was alternately sprinkled with 5 ml concentrated HNO₃ and, after evaporation of the acid on a water bath, annealed until a white mineralizate was obtained. The latter was digested with diluted (1 : 3, v/v) HNO₃ on a water bath, the mixture was filtered into a 100 ml calibrated flask, and the filter was thoroughly washed with hot water.

Concentrating of lead by sorption on ion exchanger. The extract of grass mineralizate was adjusted at pH 4 by adding 0.5 M sodium acetate, and the precipitate formed was filtered off, washed with water, and the solution was shaken with 0.25 – 2 g swollen Ostsorb DTTA. Then the ion exchanger was extracted with 10 ml 2 M HClO₄ and lead was determined by means of AAS in both the desorbate and the original extract. With the amount of 1 g ion exchanger, the procedure given was repeated five times without added lead and five times with added 0.5 mg Pb.

Determination of Lead and Cadmium in Industrial Fertilizer GVH III

Preparation of extract of fertilizer. The fertilizer (40 g) was ground, transferred into a 1 000 ml calibrated flask, and the volume was adjusted by adding water. The suspension was mixed, left to stand 24 h, and filtered. The clear stock extract of the fertilizer was used in the enrichment experiments.

Direct determination of lead and cadmium in fertilizer extract. The loosened granulated fertilizer (20 g) was placed in a 100 ml calibrated flask and extracted with water or 1 M HCl 24 h. After filtration, the clear solutions were analyzed by means of AAS at the wavelengths of 217.5 nm (Pb) and 229.0 nm (Cd) using an acetylene-air flame.

Determination of lead and cadmium after concentrating fertilizer extract. The aqueous extract of fertilizer (50 ml), a stock solution of 1 000 mg l⁻¹ lead (0.1 ml), and a solution of 500 mg l⁻¹ cadmium (0.1 ml) were pipetted into a 100 ml calibrated flask, and the volume was completed by adding water. In a 250 ml polyethylene flask, the extract was adjusted at pH 4 by adding 1 M NaOH, and the contents was shaken with 0.5 g swollen Ostsorb DTTA. The ion exchanger was filtered off and extracted with 10 ml 1 M HCl in a calibrated flask, and the extract was analyzed by means of AAS. The measurement was repeated five times like the experiment with the extract without added Pb and Cd.

RESULTS AND DISCUSSION

The data given in the following text and tables are average values of two parallel experiments, the exceptions are pointed out.

Determination of Lead in Soil

Content of Some Metals in Soil

As it is practically impossible to find such conditions at which a selective chelating ion exchanger would trap only lead ions during the sorption from a soil extract, it is necessary to know at least approximate proportions of chelate-forming elements in the soil extract so that such amount of sorbent may be used for the sorption to ensure a suffi-

cient capacity of trapping of all ions which form stable complexes with the functional groups of ion exchanger at the given conditions. The analysis of soil extract showed the following metals: 1 752 ppm Fe, 644 ppm Al, 122 ppm Mn, 28 ppm Pb, 16 ppm Zn, 11 ppm Cu, 2.5 ppm Ni, 1 ppm Co. Hence it is obvious that the sorption of Pb(II) ions will be competed especially by Fe(III), Al(III), and Mn(II) which are present in the extract at concentrations several times higher and form stable complexes with functional groups of the ion exchanger, the same being true of Zn(II) and Cu(II) ions whose concentrations are comparable with those of Pb(II). As the capacity of ion exchanger³⁰ is ca 1 mmol g⁻¹ at pH 4 – 5, trapping of all given ions present in the extract of 50 g soil would require ca 11.5 g swollen ion exchanger (the water content in swollen ion exchanger is 74.6 wt.%)³⁰.

Losses of Lead during Analysis

The high content of iron and aluminium in the extract brings, beside the necessity to use an inadequate amount of sorbent for efficient sorption of lead, another problem, viz. the formation of precipitate of hydroxides at pH 4, i.e. at the optimum conditions for the sorption of Pb(II) ions. The negative effect of the precipitate upon the overall recovery of lead in the analysis (starting from the extraction of soil sample and ending with the analysis of the solution obtained by the desorption of cations from ion exchanger) is indicated by the results of experiments in which the recovery of introduced amount of lead in the individual operations was determined in an orientational way. The adopted amount of ion exchanger was sufficient for trapping all the ions investigated except Fe(III) and Al(III). The average values of recovery of lead calculated from two repeated experiments were $95 \pm 2.1\%$ for the soil extraction and $93 \pm 1.8\%$ for the sorption-desorption process, but the removal by filtration and washing of the precipitate of iron and aluminium hydroxides decreased the original amount of lead to $18 \pm 4.3\%$. The interfering effects of iron and aluminium can be eliminated – at least to a certain extent – by suppressing the formation of hydroxides by suitable masking; those of iron, as the case may be, can be eliminated by the reduction of Fe(III) to Fe(II) which forms a less stable complex with the ion exchanger and whose hydroxide is separated at somewhat higher pH values than those in the case of Fe(III) ions. A different approach may consist in utilization of formation of hydroxides for co-precipitation and adsorption of lead ions along with the process of their sorption by the chelating ion exchanger. The resulting concentrate, however, will contain iron, aluminium, and manganese in considerably high concentrations which could unfavourably affect the subsequent quantitative determination of lead. Also the amount of acid necessary for desorption and dissolution of precipitated hydroxides will inadequately increase, which lowers the enriching effect of the method. Therefore, this alternative has not been experimentally tested yet.

Masking of Iron with $\text{Na}_4\text{P}_2\text{O}_7$

On the basis of orientational experiments with some complex-forming reagents we used sodium diphosphate for the masking of iron. The optimum conditions for sorption can be suggested on the basis of the procedures described in Experimental and the data of Table I giving the effects of volume of the saturated $\text{Na}_4\text{P}_2\text{O}_7$ solution used for masking iron and amount of sorbent upon the yield of lead during its concentration procedure from the soil extract. The masking of iron present in 100 ml extract, i.e. one third of extract from 50 g soil, needs the use of 80 – 100 ml saturated $\text{Na}_4\text{P}_2\text{O}_7$ solution, although the precipitate of hydroxides did not form with as little as 50 ml of this solution. Both a higher and a lower volumes lead to worsening of lead recovery due probably to sorption of Fe(III) (lower amount of $\text{Na}_4\text{P}_2\text{O}_7$) and to competing complex-forming reaction of Pb(II) with $\text{Na}_4\text{P}_2\text{O}_7$ (a higher amount of diphosphate), respectively. If iron is effectively masked with a sufficient amount of $\text{Na}_4\text{P}_2\text{O}_7$, then within the pH range of 3 – 9.5 no perceptible pH effect upon the lead recovery during sorption can be observed, the recovery values being randomly scattered about the mean value of $35.6 \pm 2.2\%$. Table I shows a significant dependence of lead recovery upon the ion exchanger amount. Satisfactory values are reached with the use of at least 1.5 g Ostsorb DTTA per 100 ml extract and 60 ml saturated $\text{Na}_4\text{P}_2\text{O}_7$ solution.

TABLE I

Dependence of lead recovery upon amount of $\text{Na}_4\text{P}_2\text{O}_7$ (A), ascorbic acid (B), ion exchanger (C), and concentration of HClO_4 used for desorption (D)^a

A	V, ml	0	50	60	80	100	150	250
	R_1 , %	21.2 ^b	45.8	54.0	57.2	58.1	47.3	37.8
B	m_a , g	1.0	1.5	2.0	2.5	3.0	4.0	5.0
	R_1 , %	64.1	72.6	78.2	65.7	59.1	58.8	59.6
C	m_s , g	0.5	1.0	1.5	2.0	2.5		
	R_1 , %	36.7	54.0	75.1	77.8	80.1		
D	c , mol l ⁻¹		1	2	3	4	5	
	R_1 , %		50.6	80.2	83.1	81.6	82.4	
	R_2 , %		68.2	81.6	82.4	82.1	82.2	

^a V volume of the saturated $\text{Na}_4\text{P}_2\text{O}_7$ solution per 100 ml soil extract, pH 4, 1 g swollen ion exchanger; R_1 and R_2 values of lead recovery after one-step and two-step desorptions, respectively; m_a and m_s amounts of ascorbic acid and ion exchanger, respectively, per 100 ml soil extract, pH 4; c concentration of HClO_4 . ^b On adjusting pH 4, a precipitate of hydroxides was formed which was removed by filtration before the sorption with ion exchanger.

Desorption of Lead from Ion Exchanger

The desorption of the lead trapped by the ion exchanger needs a solution of perchloric acid of 2 mol l^{-1} concentration at least. As it is shown by the data of Table I the increasing of concentration above this value does not lead to any further increase of lead recovery, its value being randomly scattered about 81.8% with the relative standard deviation $s_r = 1.5\%$. Also a repetition of extraction with the same volume of 2 – 5 M HClO_4 does not increase the lead recovery any further, its average value being 82.1%, $s_r = 0.4\%$. At the given experimental conditions a fifteen times greater concentration of soil extract was reached.

Sorption of Lead after Reduction of Fe(III)

The reduction of Fe(III) to Fe(II) was carried out using two common analytical reducing agents, viz. hydroxylamine hydrochloride and ascorbic acid. Neither of them, however, prevented the formation of hydroxide precipitate during adjusting the pH of extract, nevertheless the amount of precipitate was smaller than that without treatment of the extract. Anyway, the lead recovery and its reproducibility were negatively affected. Especially with hydroxylamine the differences of lead recovery between two parallel analyses were as high as 30%, the mean recovery values with various amounts of the reagent ranging from 32 to 71%. The results obtained with ascorbic acid are given in Table I too; the differences between results of parallel measurements did not exceed 4%.

Determination of Lead in Soil

The results of determination of lead in the extract from 50 g soil pre-treated with sodium diphosphate or ascorbic acid before adjusting pH 4 are presented in Table II. It must be noted that the recovery concerns the 1 mg of lead introduced into the original extract, not the overall recovery involving the extraction of soil. An acceptable recovery of 83% is attained by masking iron with sodium diphosphate, the reduction of Fe(III) with ascorbic acid leading to a less favourable recovery of 58%. In both the cases, however, the calculation of lead content in extract respecting the found recovery leads to practically identical values with those of direct determination of lead in extract by means of AAS, i.e. 28 ppm. The method with $\text{Na}_4\text{P}_2\text{O}_7$ gave the value of 26.9 ppm, the reduction method gave 28.1 ppm. If the detection limit of an average atomic absorption spectrometer is 0.5 mg Pb/l, then it is possible to determine approximately 0.01 – 0.02 mg lead in an extract of 50 g soil.

Determination of Lead in Grasses

The aim of the experiments with the mineralizate of sample of dried grass was to find the recovery of lead during the sorption from this medium adjusted at pH 4 by adding sodium acetate. The experiments showed that at these conditions the solutions separate a small amount of white precipitate whose removal by filtration decreases the lead amount, which was also confirmed by the analysis of the filtration cake by means of AAS. The minimum amount of ion exchanger necessary for reaching the maximum

TABLE II
Determination of lead and cadmium in soil, grass, and industrial fertilizer GVH III^a

Method	Amount	\bar{x}	s	s_r , %	$L_{1,2}$
A _I	m_1	1.899	0.081	4.27	1.799 – 1.999
	m_2	1.069	0.025	2.34	1.039 – 1.099
	m_3	1.288			
	R , %	83.0			
A _{II}	m_1	1.396	0.039	2.79	1.348 – 1.444
	m_2	0.816	0.033	4.04	0.774 – 0.858
	m_3	1.407			
	R , %	58.0			
B	m_1	0.412	0.013	3.16	0.396 – 0.428
	m_2	0.132	0.013	9.85	0.116 – 0.148
	m_3	0.236			
	R , %	56.0			
D_{Pb}	m_1	0.0800	0.0071	8.88	0.0712 – 0.0888
	m_2	0	–	–	–
	m_3	0			
	R , %	80.0			
D_{Cd}	m_1	0.0517	0.0025	4.84	0.0456 – 0.0578
	m_2	0.0021	0.0003	14.29	0.0018 – 0.0024
	m_3	0.0021			
	R , %	99.2			

^a \bar{x} arithmetic mean of results of 5 experiments; s standard deviation; s_r relative standard deviation; $L_{1,2}$ 95% confidence interval; A_I and A_{II} determination of lead in soil extract by the methods with Na₄P₂O₇ and ascorbic acid, respectively; B determination of lead in the mineralizate of grass; D_{Pb} and D_{Cd} determination of lead and cadmium, respectively, in the extract of fertilizer; m_1 , m_2 , and m_3 lead and/or cadmium amounts (in mg) determined in the extract with added lead and/or cadmium, in original extract without correction and with the correction for recovery, respectively; R lead and/or cadmium recovery from extracts with added Pb/Cd calculated from the arithmetic means m_1 and m_2 .

recovery of the lead added to the mineralizate before its neutralization was 1 g. The attained average recovery R in this case reached 56% and was not substantially improved by an increase of amount of ion exchanger to 1.5 and 2.0 g ($R = 59\%$ and 58% , respectively). On the contrary: with 0.5 g ion exchanger it significantly decreased ($R = 45\%$).

The results of five repeated experiments given in Table II, however, show a good reproducibility of determination of lead in the mineralizate after a tenfold concentrating by ion exchanger. The direct AAS analysis of mineralizate did not detect any lead, its concentration lying below the detection limit of the apparatus. Hence, in spite of the relatively low recovery the method can successfully be used for determination of low lead concentrations in plant materials, however, the calculations (like those for soil extracts) must take into account the determined recovery of added lead. The described method was adopted to analyze samples of grass gathered at distances of 5 and 100 m from a road: the found recovery of lead reached $57 \pm 3.8\%$ and $61 \pm 4.1\%$, respectively, the determined lead content being 38 ± 3.2 and 16 ± 2.6 mg per kg dry matter, respectively.

Determination of Lead and Cadmium in Industrial Fertilizer GVH III

Direct Determination of Lead and Cadmium in Extract of Fertilizer

The direct AAS analysis of the extract of fertilizer (extraction with distilled water or 1 M HCl) did not detect any lead, its concentration being below the detection limit of the apparatus (0.5 mg l^{-1}).

The average value of cadmium concentration in aqueous extract calculated from the results of three repeated experiments is $0.41 \pm 0.03 \text{ mg l}^{-1}$, that from the HCl extracts being $0.45 \pm 0.02 \text{ mg l}^{-1}$. These results correspond to the cadmium content in the fertilizer $2.1 \cdot 10^{-4} \text{ wt.}\%$ and $2.3 \cdot 10^{-4} \text{ wt.}\%$, respectively. The differences between both extracts are practically negligible, cadmium is present in the fertilizer in the form of salts that are practically completely water soluble. This means that for the enrichment experiments with ion exchanger we can recommend the aqueous extract, which eliminates the necessity of adjusting the acidity of acid extract to pH 4 (the optimum for the sorption of lead and cadmium). The aqueous extract has another advantage in the fact that the results of its analyses reveal the content of such substances in the fertilizer which can threaten the environment in the form of water soluble salts that can be either received by plants or contaminate the underground water etc.

Determination of Lead and Cadmium after Concentrating Extract of Fertilizer

The results of experiments with aqueous extracts of the GVH III fertilizer are presented in Table II. It also gives the experimental results obtained with extracts with added 0.1 mg Pb and 0.05 mg Cd. The lower recovery of lead, $R = 80\%$, is obviously due to the formation of stable complexes of lead with phosphate ions from the fertilizer competing with the ion exchange equilibrium at the exchanger. Lead was found neither by direct analysis of extract nor after tenfold concentrating it. The results of determination of cadmium in the extract are practically identical with those of direct analysis, the cadmium content found in the solid fertilizer being $2 \cdot 10^{-4}$ wt.%. The recovery of the cadmium added to the extract is very good, $R = 99.2\%$.

REFERENCES

1. Kingston H. M., Barnes I. L., Brady T. J., Rains T. C.: *Anal. Chem.* 50, 2064 (1978).
2. Burba P., Lieser K. H., Neitzert V., Rober H.-M.: *Z. Anal. Chem.* 291, 273 (1978).
3. Guedes da Mota M. M., Jonker M. A., Griepink B.: *Z. Anal. Chem.* 296, 345 (1979).
4. Sturgeon R. E., Berman S. S., Desaulniers J. A. H., Mykytink A. P., Mc Laren J. W., Russel D. S.: *Anal. Chem.* 52, 1585 (1980).
5. Vernon F., Eccles H.: *Anal. Chim. Acta* 72, 331 (1974).
6. Lieser K. H., Rober H.-M., Burba P.: *Z. Anal. Chem.* 284, 361 (1977).
7. Lieser K. H., Breitwieser E., Burba P., Rober M., Spatz R.: *Microchim. Acta* 1, 363 (1978).
8. Imai S., Muroi M., Hamaguchi A.: *Anal. Chim. Acta* 113, 139 (1980).
9. Riley J. P., Taylor D.: *Anal. Chim. Acta* 40, 479 (1968).
10. Riley J. P., Taylor D.: *Anal. Chim. Acta* 41, 175 (1968).
11. Akaiwa H., Kawamoto H., Ogura K.: *Talanta* 24, 394 (1971).
12. Prakash N., Csanady B., Michaelis M. R. A., Knapp G.: *Microchim. Acta* 3, 257 (1989).
13. Dorochova E. M., Shvoeva O. P., Cherevko A. S., Myasoedova G. V.: *Zh. Anal. Khim.* 34, 1140 (1979).
14. Kawabuchi K., Kante M., Muzaoka T.: *Jpn. Analyst* 25, 213 (1976).
15. Kurbakova I. V., Varshal G. M., Sedych E. M., Myasoedova G. V., Antokolskaya I. I., Shemarykina T. P.: *Zh. Anal. Khim.* 38, 2205 (1983).
16. Moroshkina T. M., Myasoedova G. V., Vanaeva L. V.: *Zh. Anal. Khim.* 24, 698 (1969).
17. Moroshkina T. M., Serbina A. M.: *Zavod. Lab.* 43, 1468 (1977).
18. Dumont J., Cote M., Hubert J.: *Appl. Spectrosc.* 43, 1132 (1989).
19. Vanaeva L. V., Kuznetsova N. I., Moroshkina T. M.: *Vestn. Leningr. Univ.* 16, 154 (1971).
20. Horvath Z., Falb K., Varju M.: *At. Absorpt. Newslett.* 16, 152 (1977).
21. Svoboda L., Uhlir J., Uhlir Z.: *Collect. Czech. Chem. Commun.* 57, 1393 (1992).
22. Vitkova J., Jambor J., Vrchlabsky M.: *Chem. Listy* 72, 417 (1978).
23. Clanet F., Deloncle R.: *Anal. Chim. Acta* 117, 343 (1980).
24. Lee Ch., Kim N. B., Lee I. Ch., Chung K. S.: *Talanta* 24, 241 (1977).
25. Faitondzije V., Brasnarova A.: *Landwirt. Forsch.* 32, 1 (1979).
26. In K. L., Pulford I. D., Duncan H. J.: *Anal. Chim. Acta* 106, 319 (1979).
27. Pedersen B., Willems M., Joergensen S. S.: *Analyst* 105, 119 (1980).
28. Patke S. K., Agrawal Y. K.: *Int. J. Environ. Anal. Chem.* 8, 67 (1980).

29. Klimov I. T.: *Gidrokhim. Mater.* 34, 131 (1961).
30. Svoboda L., Chutny J., Tomek M.: *Collect. Czech. Chem. Commun.* 59, 106 (1994).
31. Svoboda L., Canova L.: *Collect. Czech. Chem. Commun.* 57, 2089 (1992).

Translated by J. Panchartek.