# SEPARATION OF LEAD, CADMIUM, AND IRON IN ANALYSES OF SOIL SAMPLES

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The conditions of sorption of chloride complexes of $Pb^{2+}$, $Cd^{2+}$, $Fe^{2+}$, and $Fe^{3+}$ ions from media of hydrochloric acid have been studied with a strongly basic anion exchanger – Ostion LG AT. The experiments used an exchanger microcolumn connected with atomic absorption spectrometer as a selective detector of metal ions. From the relation found between retention of the ions studied and hydrochloric acid concentration, conditions of separation have been suggested and used for separations of small amounts of lead and cadmium from many times higher amounts of iron and aluminium in soil extract before determination of both the foreign metals by means of AAS method. The yield of separation exceeded 95%.

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Chemical analyses of soils and other geological samples often face the problem of determination of low content of microelements beside metals present at several orders higher concentrations. Thus quite often the interfering effects of matrix complicate or prevent applications of not only the less specific analytical methods such as photometry or electrochemistry but cause troubles even to the more selective techniques involving inter alia flame atomic absorption spectrometry (FAAS).

## *Determination of Pb and Cd in Soils by Flame AAS Method*

Lead and cadmium belong among the microelements whose content in soils is one of ecological criteria of their agricultural utility. The amount of these metals in soil is primarily determined by chemical composition of geological subsoil and further affected by the fallout resulting from combustion of fossil fuels, emissions and wastes from chemical plants, metallurgical works and ore mines, automobile transport, and use of synthetic fertilizers and composts. The cadmium and lead content in soil vary in a wide interval of about 2–200 mg Pb $kg^{-1}$ and 0.1–2.5 mg Cd $kg^{-1}$ (ref.[1]). The average content given in ref.[2] is 10 mg Pb $kg^{-1}$ and 0.5 mg Cd $kg^{-1}$. The suggested maximum admissible concentrations of dangerous elements in agricultural soils[3] (1 M HCl extract) are 0.05–1.00 mg Cd $kg^{-1}$ and 10–20 mg Pb $kg^{-1}$ depending on the soil class. From the facts given it follows that the lower limit of content of both the metals in soils is – in the order of magnitude – $10^{-4}$% Pb and $10^{-6}$% Cd, which is approximately 10 times less than the accepted determination limit for these elements in soils when the FAAS technique is adopted. On the other hand, average content of iron in soils is 38 000 mg $kg^{-1}$, those of aluminium, silicon, calcium, magnesium, potassium, and sodium being 71 300, 330 000, 13 700, 6 300, 13 600, and 6 300 mg $kg^{-1}$, respectively[2]. The analytical signal of FAAS apparatus in analyses of solutions containing Pb, Cd, Cu, Zn and other metals decreases if the above-mentioned macroelements are present at concentrations exceeding 1–2 mg $ml^{-1}$ (ref.[4]). Hence, it can be expected that in the soil extracts obtained with the use of 1 M HCl (refs[3,5,6]) the mentioned limit concentrations of interfering elements will be exceeded and the sensitivity and reliability of measurements will be decreased. One of possible ways of solving this problem is to separate the components to be analyzed (or those which interfere) from the extract and – as the case may be – to concentrate the former ones[7,8].

### *Separation of Lead, Cadmium, and Iron on Ion Exchangers*

A number of papers[9–12] have already been published dealing with the theory of ion exchange and applications of ion exchangers to analytical and technological separations, the use of ion exchangers in analyses of geological samples inclusive of soils is dealt with e.g. by Reeves and Brooks[7]. Both selective[13] and (preferably) classical ion exchangers were used to separate and concentrate heavy metals present in soil extracts and to separate them from alkali and alkali earth metals. In most cases the separation procedures are based on the ability of transition metals to form more or less stable anion complexes in media of strong mineral acids whereby the elution of these metals from both cation and anion exchangers is significantly affected. The published procedures for separation on anion exchangers are based on formation of sulfate[14], nitrate[15], and particularly halogenide complexes out of which chloro complexes are dominant[16–19]. Using strongly basic anion exchangers it was possible to successfully separate even cadmium(II)[20–24], lead(II)[22,25–30], and iron(III)[16,31–35] from other heavy metals in hydrochloric acid solutions.

The present communication gives the results of investigation of sorption of $Pb^{2+}$, $Cd^{2+}$, $Fe^{2+}$, and $Fe^{3+}$ ions from hydrochloric acid medium using a strongly basic anion exchanger Ostion LG AT 0805 with the aim of application of the findings obtained to suggesting a method of separating lead and cadmium from soil extracts, their concentrating, and determining by FAAS.

## EXPERIMENTAL

### Chemicals and Apparatus

The measurements were carried out on an apparatus consisting of a peristaltic pump type 315 (Zalimp, Poland), a septum injection device, and a PVC holder for microcolumn which was constructed in

Workshops of University of Pardubice, atomic absorption spectrometer Atomspek-H 1550 (Hilger and Wats, U.K.) and recorder OH-814/1 (Radelkis, Hungary). The connecting elements were made from silicone polymers, Teflon, and glass capillaries. The capacity ratios of chloride complexes of the cations studied were determined with the help of a glass column of 20 mm length, i.d. 4 mm. For analyses of soil extracts, columns of 80 × 20 mm and 180 × 30 mm dimensions were used, packed with a strongly basic anion exchanger Ostion LG AT 0805 in chloride form: size of swollen particles 40–80 μm, volumes of columns 0.25, 25.1, and 127.2 $cm^3$, respectively. The styrene–divinylbenzene matrix of this ion exchanger is cross-linked with 8% divinylbenzene, the content of active benzyltrimethylammonium groups was 4 mmol $g^{-1}$. The lead and cadmium solutions were concentrated with the help of a selective cellulosic chelating ion exchanger Ostsorb DTTA with chemically bound groups of diethylenetriamine tetraacetic acid: for the experiments, it was adopted in swollen $H^+$ form. Both the ion exchangers are produced by Spolek pro chemickou a hutni vyrobu (Company for Chemical and Metallurgical Production, The Czech Republic). Hamilton syringes (Switzerland) were used to inject the solutions of 1–100 μl volume into the ion exchanger columns (the manufacturer guarantees the reproducibility of 1% of the volumes dosed). The soil samples were extracted on a transversal shaking machine LT-1 (Kavalier, The Czech Republic). Values of pH of solutions was determined with the use of an OP 205/1 apparatus with combined glass electrode (Radelkis, Hungary).

Deionized water and analytical grade chemicals (Lachema, The Czech Republic) were used throughout in the experiments.

### Procedures

*Determination of capacity ratios of* $Pb^{2+}$, $Cd^{2+}$, $Fe^{3+}$, *and* $Fe^{2+}$. Standard solutions of metals with weight concentrations of 20 g $l^{-1}$ ($Pb^{2+}$, $Fe^{2+}$, $Fe^{3+}$) or 0.2 g $l^{-1}$ ($Cd^+$) were prepared by dissolving the corresponding amounts of lead(II) nitrate, cadmium(II) sulfate, ferric ammonium sulfate, and ferrous sulfate in deionized water and in hydrochloric acid solutions of 0.001–7 mol $l^{-1}$ concentrations. The 20 × 4 mm column was washed with ca 10 ml HCl of the concentration chosen, and free volumes before the column were filled with the solution of metal in the acid of the same concentration. The outlet of the column was connected with the suction Teflon capillary of atomic absorption spectrometer. The connection was realized by means of a glass T piece whose third outlet was connected by means of a Teflon tube with water reservoir to ensure the flow rate of the liquid sucked at 8 ml $min^{-1}$ since the volume dosed by the pump is substantially smaller.

The working parameters were adjusted on the AAS apparatus for acetylene–air flame and detection of the metal chosen (372.3, 283.5, and 229.0 nm for Fe, Pb, and Cd, respectively), and solution of the metal was pumped through the column at a rate of 0.45 ml $min^{-1}$. The moment of start of delivery of eluent was marked on the recording. The experiment was finished after the metal concentrations in eluent before and after the column became equal, which was determined from the shape of the recorded break-through curve. The capacity ratio of ion in the elution solution given was calculated from the break-through volume and dead volume of the column.

*Determination of free volumes in system*. The total free volume of system, i.e. dead volume of column and extra-column volumes, was determined for the 20 × 4 mm column by injecting 1 μl standard solution of lead in water with the metal mass concentration of 20 g $l^{-1}$ into the column washed with deionized water at a flow rate of 0.45 ml $min^{-1}$ and by recording the elution maximum. The volume of connecting parts between the column and AAS detector was measured in the same way, the injection device being connected with the outlet capillary of column in this case. The dead volume of column was calculated as the difference between the results of the two measurements. Similar procedure was adopted for the 80 × 20 mm and 180 × 30 mm columns, 100 μl solution of lead being injected on the ion exchanger column at the water flow rates of 1.5 and 3 ml min$^{-1}$, respectively.

*Measurement of break-through volumes of lead on ion exchanger columns*. Using the procedure described in the paragraph on determination of capacity ratios, the 80 × 20 and 180 × 30 mm columns were washed with 20 and 100 ml 1 M HCl, respectively, and the solution of lead (20 g l$^{-1}$) in 1 M HCl was pumped to them at the flow rates of 1.5 and 3 ml min$^{-1}$, respectively. The eluate was continuously monitored by AAS and the signal was recorded. From the measured sorption curve, the break-through volume of lead was evaluated as the volume of solution passed through the column until the moment of detection of the presence of lead in eluate.

*Separation of $Pb^{2+}$, $Cd^{2+}$, $Fe^{3+}$, and $Fe^{2+}$*. The 20 × 4 mm column was washed with 1 M HCl (separation of $Fe^{3+}$ and $Cd^{2+}$, $Fe^{3+}$ and $Pb^{2+}$, $Fe^{3+}$ and $Pb^{2+}$ and $Cd^{2+}$) or 5 M HCl (separation of $Fe^{3+}$ and $Fe^{2+}$) at a flow rate of 0.45 ml min$^{-1}$, and 5 μl aqueous solution containing the individual metals at the mass concentrations of 10 g l$^{-1}$ (Pb, Fe) or 0.1 g l$^{-1}$ (Cd) was injected into it. In the separations of Fe from Pb and Cd, iron was eluted with 1 M HCl, lead with 0.1 M HCl, and cadmium with 0.001 M HCl, or lead was washed from the column first (using 8 M HCl) followed by iron (with 0.05 M HCl) and finally cadmium (with 0.001 M HCl). In the separation of $Fe^{2+}$ from $Fe^{3+}$ the divalent iron was eluted with 5 M HCl and the trivalent iron with 0.5 M HCl. At the beginning of the experiments, the AAS apparatus was adjusted for the detection of the first metal eluted, after its elution finished the pump was stopped, and conditions for detection of the next metal were adjusted, and the corresponding elution solution of acid was dosed in the column.

In order to find the conditions of separation of iron, lead, and cadmium from a soil extract we used the 80 × 20 mm glass ion exchanger column. After washing with 20 ml 1 M HCl, 25 ml soil extract containing 1 mg Pb and 0.5 mg Cd (added to it from the standard solutions) was introduced on the ion exchanger column which was connected between the pump and detector. The further procedure was identical with that of the separation on the 20 × 4 mm column, only the flow rate of elution acid being different (1.5 ml min$^{-1}$ in this case). The experiment was repeated with the difference that, after separation of iron, lead and cadmium were washed out together with deionized water, and the concentration of either Pb or Cd in the eluate was monitored by means of AAS.

*Determination of recovery of lead and cadmium*. The 80 × 20 mm (or 180 × 30 mm) column was washed with 20 ml (100 ml) 1 M HCl, and 25 ml (125 ml) extract containing 1 mg (5 mg) lead and 0.5 mg (2.5 mg) cadmium (added from the standard solutions) was introduced on the column by means of a pipette, whereafter the column was washed with 30 ml (150 ml) 1 M HCl followed by 50 ml (150 ml) water at the flow rate of 1.5 ml min$^{-1}$ (3 ml min$^{-1}$). The lead and cadmium content in the fractions taken from the eluate was determined by the AAS technique at the wavelength of 217.5 nm (Pb) or 229.0 nm (Cd) using calibration straight lines.

*Preparation of soil extract*. Dried soil sample (50 g) with the grain size up to 2 mm was placed in a 250 ml calibrated flask and extracted with 2 × 100 ml 1 M HCl by shaking for 2 × 60 min. The suspension was filtered through a paper filter and the filtration cake was washed with 1 M HCl to obtain the filtrate of 250 ml total volume.

*Determination of lead and cadmium in soil using pre-separation on anion exchanger and concentrating on chelating sorbent*. Using the 180 × 30 mm ion exchanger column, iron was separated from 125 ml soil extract by elution with 150 ml 1 M HCl and subsequent washing with deionized water to obtain 250 ml solution. After transferring to a 500 ml conical flask the solution was adjusted at pH 5 by addition of 2 M sodium acetate using a pH meter, and then it was shaken with 2 g swollen chelating ion exchanger Ostsorb DTTA for 3 h. The sorbent was filtered off and retained metals were desorbed in 50 ml volumetric flask by shaking with 20 ml 2 M HCl for 1 h. The Pb and Cd content in extract was determined by means of AAS. The experiment described was repeated 5 times for each the original extract and that with added 0.5 mg Pb and 0.05 mg Cd (in the form of lead(II) nitrate and cadmium(II) sulfate).

## RESULTS AND DISCUSSION

### *Dependence of Capacity Ratios of* $Pb^{2+}$*,* $Cd^{2+}$*,* $Fe^{3+}$*, and* $Fe^{2+}$ *on Concentration of Hydrochloric Acid*

The metal amount $m_s$ retained in a ion exchanger column from a solution of initial concentration $c_0$ is given by Eq. (*1*)

$$m_s = \int_{V_1}^{V_2} (c_0 - c)\, \mathrm{d}V \ , \tag{1}$$

where $c$ means the metal concentration in the eluate, $V_2$ is the volume of solution passed through the column until the moment of attaining equal concentrations before and after the column, and $V_1$ is the sum of the dead volume $V_M$ of the column and the inner volume $V_0$ of the capillaries between the column and the detector. The free volumes before the column can be considered zero in the given experimental arrangement. For symmetrical break-through curves the $m_s$ value can be calculated from Eq. (*2*)

$$m_s = c_0(V_{50} - V_1) \ , \tag{2}$$

where $V_{50}$ is the eluate volume passed through the column until the concentration of monitored substance in it reaches 50% of the initial value. If the amount of metal in the solution of volume $V_M$ is equal to $m_1 = c_0V_M$, then the capacity ratio defined as $k = m_s/m_1$ can be expressed by Eq. (*3*).

$$k = (V_{50} - V_1)/V_M \tag{3}$$

The retention of ions by a sorbent can also be characterized by a volume and a mass partition coefficients given by Eqs (*4*) and (*5*), respectively.

$$D_v = k\, V_M/V_s \tag{4}$$

$$D_g = k\, V_M/m_e \ , \tag{5}$$

where $V_s$ is volume of ion exchanger in column and $m_e$ is its weight in dry state.

Values of logarithms of capacity ratios of $Pb^{2+}$, $Cd^{2+}$, $Fe^{3+}$, and $Fe^{2+}$ on the Ostion LG AT anion exchanger in the medium of hydrochloric acid, which were calculated from Eq. (*3*), are given in Fig. 1. The value of dead volume of the 20 × 4 mm column calculated from results of five repeated measurements of $V_1$ and $V_0$ was $V_M = 0.145$ ml ($V_1 = 0.312$ ml, relative standard deviation $s_r = 5.7\%$, $V_0 = 0.165$ ml, $s_r = 7.1\%$); the $V_{50}$ values used in calculations of the capacity ratios were mean values from results of two measurements of break-through curves. The reproducibility of determination of capacity ratios was found by 5 times repeated measurement of retention of lead from 1 M HCl medium, and the mean value of capacity ratio was $k = 14.48$, $s_r = 4.2\%$ under these conditions.

From the results it follows that lead ions are retained by the anion exchanger studied from 1–2 M HCl solutions to the greatest extent, the capacity ratio value being $k \approx 14.5$. The elution of metal from column is best carried out with the acid solutions of $c(HCl) \leq 0.1$ mol $l^{-1}$ or $c(HCl) > 7$ mol $l^{-1}$. The volume partition coefficient in 1 M HCl has the value of $\log D_v = 0.9$ ($k = 14.5$, $V_s = 0.25$ ml); the value of $D_v \approx 1.2$ was published[18] for a similar anion exchanger Dowex 1-X10.

The retention of cadmium ions is increased with increasing concentration of acid in the whole range studied, i.e. $c(HCl) = 0.001–7$ mol $l^{-1}$, but in the interval of $c(HCl) = 5–7$ mol $l^{-1}$ it is not markedly changed and it can be presumed that the concentration region represents the maximum of the dependency. In contrast to lead, cadmium is strongly retained by the ion exchanger even from 0.1 M HCl solutions, which can be made use of for separating the two ions from each other. Cadmium cannot be washed from the column until with very dilute acid ($c(HCl) \leq 0.001$ mol $l^{-1}$). The values of $\log D_v = 1.7$ and $\log D_g = 1.8$ ($m_e = 0.195$ g) were determined for the partition coefficients in 5 M HCl ($k = 95$), while the data published are $\log D_v \approx 2.8$ (ref.[18]) and $\log D_g \approx 1.6$ (ref.[17]).

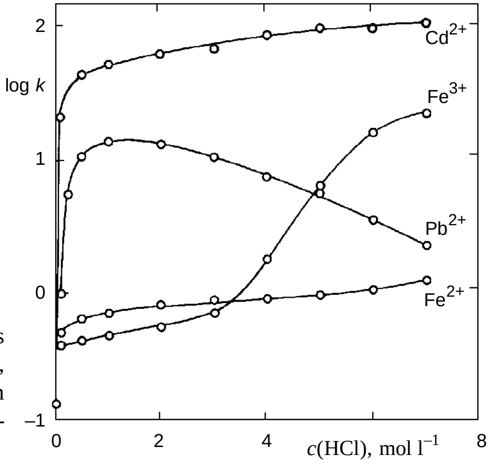

FIG. 1
Dependencies of logarithms of capacity ratios (*k*) of chloride complexes of $Pb^{2+}$, $Cd^{2+}$, $Fe^{3+}$, and $Fe^{2+}$ upon hydrochloric acid concentration (*c*) in the sorption on Ostion LG AT anion exchanger

Distinct retention of ferric ions by the ion exchanger did not occur until from the solutions of $c(\mathrm{HCl}) < 3$ mol l$^{-1}$; the maximum value of capacity ratio $k = 23$ was found in 7 M HCl. The partition coefficients found in this medium are log $D_v = 1.1$ and log $D_g = 1.2$ and are significantly lower than the data published: log $D_v \approx 4$ (ref.[18]) and log $D_g \approx 2.1$ (ref.[17]). The reasons of this difference have not been investigated.

Ferrous ions are retained from 0.001–7 M HCl solutions only slightly. Nevertheless, the results show that the retention increases with increasing acid concentration up to $k = 1.1$ for 7 M HCl, log $D_v = -0.2$ (ref.[18] gives log $D_v \approx 0$).

From the found dependencies of capacity ratios of investigated ions upon concentration of hydrochloric acid two procedures can be suggested for separation of these ions. The basis of the first one is obvious from the chromatogram in Fig. 2. Ferric and possibly also ferrous ions are washed from the ion exchanger column with 1 M HCl, whereafter there follows the elution of lead(II) ions with 0.1 M HCl and finally the elution of cadmium(II) ions with 0.001 M HCl. The separation of $Pb^{2+}$, $Cd^{2+}$, and $Fe^{3+}$ can be achieved with a different combination of HCl elution solutions too (Fig. 3). It is possible first to eluate lead from the column with 8 M HCl, followed by iron with 0.05 M HCl, and finally cadmium with 0.001 M HCl. However, when separating these metals from large sample volumes such as – inter alia – soil extracts in 1 M HCl, the second procedure is unsuitable and unnecessarily complicated. Figure 4 presents a chromatogram documenting the possibility of mutual separation of ferrous and ferric ions.

### *Separation of Lead and Cadmium from Soil Extract*

For separating lead and cadmium from soil extract and their separation from iron ions we chose the procedure in which the ion exchanger column is fed with soil extract in 1M HCl, i.e. a medium in which neither $Fe^{3+}$ nor $Fe^{2+}$ ions are retained by the anion

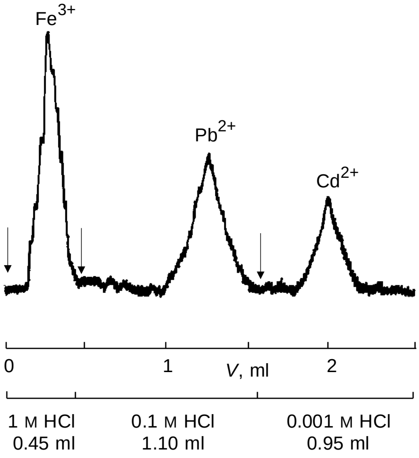

FIG. 2

Separation of $Pb^{2+}$, $Cd^{2+}$, and $Fe^{3+}$ on an Ostion LG AT column by elution with 1 M HCl, 0.1 M HCl, and 0.001 M HCl. Column: 20 × 4 mm; flow rate: 0.45 ml min$^{-1}$; feed (μg in 5 μl): Pb 50, Fe 50, Cd 0.5; AAS detection (nm): Pb 283.5, Fe 372.3, Cd 229.0

exchanger and pass immediately to the eluate. Thus the column capacity remains free for chloride complexes of $Pb^{2+}$, $Cd^{2+}$, and other metal ions which are retained in the column under the given conditions. Beside the iron ion, the following pass to the eluate: alkali metals, alkali earth metals, and also another major element – aluminium which is not retained by strongly basic ion exchangers from 0.1–12 M HCl (ref.[18]). The elution process of the metals investigated from the 80 × 20 mm column and the corresponding volumes of elution HCl solutions are given in Fig. 5. The elution of all iron from the column on which 25 ml extract had been introduced needed 30 ± 2 ml 1 M HCl, lead was eluated with 55 ± 3 ml 0.1 M HCl, and cadmium with 40 ± 3 ml 0.001 M HCl. If lead and cadmium are eluated together after the separation of iron, their quantitative washing out of the column needs 42 ± 3 ml water. The values given are mean values from three repeated experiments each.

The volume of extract introduced on the column and quantity of elution solutions cannot be chosen arbitrarily, it is necessary to respect the size of column and capacity ratios of ions to be separated. Therefore, for the procedure suggested we tried to find the maximum amount of extract and elution solution of 1 M HCl which can be passed through the column without any elution and loss of lead. At these conditions, cadmium is retained very strongly and its break-through through the column is unlikely. For this purpose, we determined the break-through volumes $V_b$ of lead(II) ions in 1 M HCl with both ion exchanger columns for which the analyses of extract were verified. The values of $V_b$ = 71 ± 3 ml and 340 ± 11 ml were found for the columns 80 × 20 and 180 × 30, respectively. The break-through curves were measured three times for each column. The smaller column can cope with 25 ml extract followed by 30 ml 1 M HCl to wash

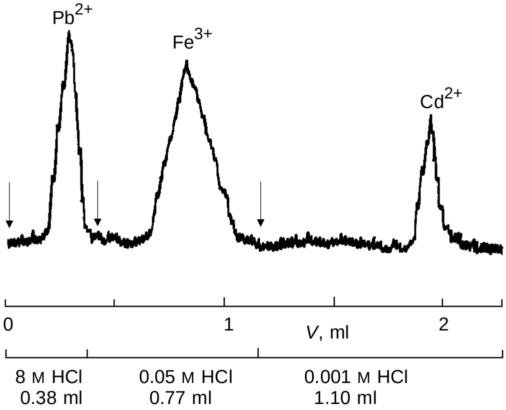

FIG. 3
Separation of $Pb^{2+}$, $Cd^{2+}$, and $Fe^{3+}$ on an Ostion LG AT column by elution with 8 M HCl, 0.05 M HCl, and 0.001 M HCl. For experimental conditions see Fig. 2

TABLE I
Determination of lead and cadmium in soil[a]

| Method | Quantity | $\overline{x}$ | $s$ | $s_r$, % | $L_{1,2}$ |
|---|---|---|---|---|---|
| $A_{Pb}$ | $m_1$, mg | 1.025 | 0.015 | 1.42 | 1.007–1.043 |
| | $m_2$, mg | 0.053 | 0.004 | 6.67 | 0.049–0.057 |
| | $m_3$, mg | 0.055 | | | |
| | $w$, mg kg$^{-1}$ | 11.0 | | | |
| | $R$, % | 97.2 | | | |
| $A_{Cd}$ | $m_1$, mg | 0.4817 | 0.0081 | 1.69 | 0.4716–0.4918 |
| | $m_2$, mg | 0.0012 | 0.0002 | 13.18 | 0.0010–0.0014 |
| | $m_3$, mg | 0.0013 | | | |
| | $w$, mg kg$^{-1}$ | 0.26 | | | |
| | $R$, % | 96.1 | | | |
| $B_{Pb}$ | $m_1$, mg | 5.075 | 0.219 | 4.32 | 4.803–5.347 |
| | $m_2$, mg | 0.260 | 0.023 | 8.92 | 0.231–0.289 |
| | $m_3$, mg | 0.270 | | | |
| | $w$, mg kg$^{-1}$ | 10.3 | | | |
| | $R$, % | 96.3 | | | |
| $B_{Cd}$ | $m_1$, mg | 2.3819 | 0.1065 | 4.47 | 2.2496–2.5142 |
| | $m_2$, mg | 0.0069 | 0.0009 | 12.59 | 0.0058–0.0080 |
| | $m_3$, mg | 0.0073 | | | |
| | $w$, mg kg$^{-1}$ | 0.29 | | | |
| | $R$, % | 95.0 | | | |
| $C_{Pb}$ | $m_1$, mg | 0.733 | 0.040 | 5.39 | 0.684–0.782 |
| | $m_2$, mg | 0.265 | 0.018 | 6.86 | 0.242–0.288 |
| | $m_3$, mg | 0.283 | | | |
| | $w$, mg kg$^{-1}$ | 11.3 | | | |
| | $R$, % | 93.6 | | | |
| $C_{Cd}$ | $m_1$, mg | 0.0534 | 0.0022 | 4.14 | 0.0507–0.0561 |
| | $m_2$, mg | 0.0070 | 0.0005 | 7.15 | 0.0064–0.0076 |
| | $m_3$, mg | 0.0075 | | | |
| | $w$, mg kg$^{-1}$ | 0.30 | | | |
| | $R$, % | 92.8 | | | |

[a] $\overline{x}$ is arithmetic mean of 5 experimental results; $s$ standard deviation; $s_r$ relative standard deviation; $L_{1,2}$ 95% confidence interval; $A_{Pb}$, $A_{Cd}$ determination of lead or cadmium after separation on a 80 × 20 mm column; $B_{Pb}$, $B_{Cd}$ determination of lead or cadmium after separation on a 180 × 30 mm column; $C_{Pb}$, $C_{Cd}$ determination of lead or cadmium after separation on a 180 × 30 mm column and concentrating on a chelation ion exchanger; $m_1$, $m_2$, $m_3$ amount of lead or cadmium (in mg) determined in soil extract with added lead or cadmium ($m_1$), in original extract without correction ($m_2$), and with correction ($m_3$) with regard to recovery; $w$ content of lead or cadmium in soil (in mg kg$^{-1}$); $R$ recovery of lead or cadmium from extracts with added metals calculated from arithmetic mean values of $m_1$ and $m_2$, %.

out iron without any risk of break-through of lead. For the 180 × 30 column, whose volume is 5 times larger than that of the previous one, 125 ml extract and 150 ml elution 1 M HCl solution can be adopted as “safe” volumes.

The recovery of lead and cadmium added to the extract which was subsequently processed on ion exchanger columns was determined as a mean value of five repeated experiments, and the same number of measurements were also carried out for the extract without added metals. The results obtained are summarized in Table I. It can be stated that the separation procedure being verified provides satisfactory recovery of lead and cadmium ($R \geq 95\%$); the values of standard deviations which characterize the reproducibility of the metal recovery reached ($s_r < 4.5\%$) are acceptable too, the 80 × 20 mm column giving more precise results ($s_r < 1.7\%$). The amounts of lead and cadmium in the original extracts were relatively low, hence the concentration of these metals in eluates from ion exchanger columns were only slightly higher than the detection limits of the atomic absorption spectrometer used (≈0.2 mg Pb $l^{-1}$, ≈0.02 mg Cd $l^{-1}$). This resulted in a worse reproducibility of experimental results obtained with these extracts, especially so in the determination of cadmium. The content of lead and cadmium in the given soil sample (its calculation takes into account the found recovery of these metals after separation on ion exchanger columns) is 10.9 mg Pb $kg^{-1}$ and 0.28 mg Cd $kg^{-1}$, respectively. A direct analysis of the soil extract on the AAS apparatus gave 12.2 mg Pb $kg^{-1}$ and 0.32 mg Cd $kg^{-1}$, i.e. values higher by ca 10%. However, as the soil sample

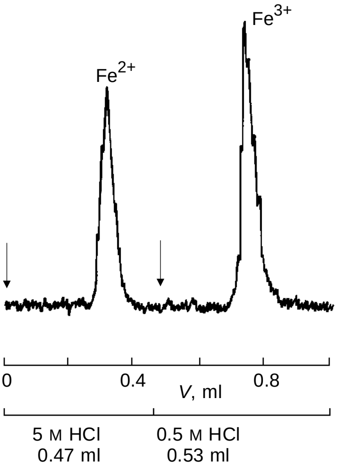

FIG. 4

Separation of Fe$^{3+}$ and Fe$^{2+}$ on an Ostion LG AT column by elution with 5 M HCl and 0.5 M HCl. For experimental conditions see Fig. 2

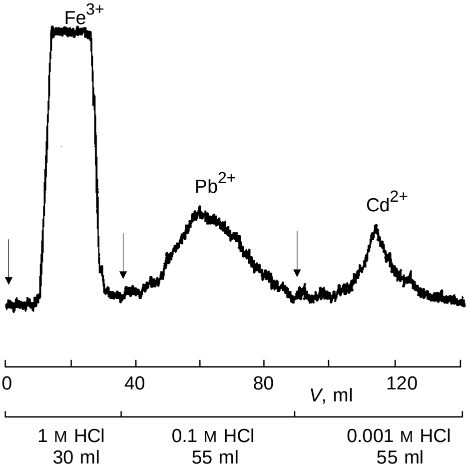

FIG. 5

Separation of lead and cadmium from soil extract on an Ostion LG AT column. Column: 80 × 20 mm; elution solutions: 1 M HCl, 0.1 M HCl, 0.001 M HCl; flow rate: 1.5 ml $min^{-1}$; sample: 25 ml soil extract with added 1 mg Pb and 0.5 mg Cd; for detection see Fig. 2

analyzed was not a reference material and no results of further independent analyses were available either, it is impossible to unambiguously tell which of the content values found are correct. With respect to the interferences encountered in analyses of minor metals in solutions of high ionic strength and high concentrations of interfering compounds (see above) it can be anticipated that the results obtained by direct analysis of extract with the help of AAS can be distorted by these effects.

### *Determination of Lead and Cadmium in Soil Using Pre-Separating on Anion Exchanger and Concentrating on Chelating Sorbent*

The results of analyses of extracts without added metals and the detection limits of atomic absorption spectrometer show that lead and cadmium can be determined by the given procedure in soils containing more than 2 mg Pb $kg^{-1}$ and/or 0.2 mg Cd $kg^{-1}$. A lowering of these detection limits and improvement of precision of determination can be achieved by concentrating the monitored metals in the eluates from ion exchanger column using the sorption by a chelating ion exchanger. The results of these experiments and their statistical treatment are given in Table I. Although the overall recovery of lead and cadmium somewhat decreased, the content of these metals in the original extract determined by this procedure are practically identical with the results obtained without the enrichment step. However, in the case of cadmium, which was present in the extract at a concentration near the detection limit of AAS, the reproducibility of determination significantly improved ($s_r$ = 7.14% instead of the original 12.59%). But what is still more important, the detection limit of both metals was decreased: with the experimental procedure described and the degree reached in concentrating the soil extract ($k_E$ = 6.25) it is possible to determine the content as low as 0.3 mg Pb $kg^{-1}$ and 0.03 mg Cd $kg^{-1}$, i.e. practically the lowest concentrations of these metals encountered in soils.

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