The Use of Dithizone-Polyurethane Foam Sorbent in a Solid—Liquid Preconcentration Step of the Determination of Lead in Drinking and Surface Waters and in Soils

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The preconcentration of metal on a polyurethane foam modified by dithizone was used for the determination of the trace amounts of Pb in waters and soils. The optimum conditions for the sorption and the desorption were found. The detection limit was found out for the determination of Pb at 1.4 $\mu g \ dm^{-3}$.

Atomic absorption spectrometry (AAS) as a final step in the determination of Pb has been most often used next to the analytical methods. The flame AAS, as a method, is sufficiently rapid, easy to carry out sample treatment and relatively interference-free for the determination of trace amounts of various metals. Therefore, it is quite popular in common laboratory practice. Unfortunately, the detection limit used to be limited particularly because of low efficiency of nebulizer, dilution of analyte aerosols with the combustion products of fuel gases and short lifetime of free atoms in flame in optical path.

If sensitivity of measurement for present element is insufficient, it is necessary to use some preconcentration technique to enrich the sample with analyte [1, 2]. In this way, it is possible to improve the detection limits to the level of detection limits considered in graphite furnace AAS.

The liquid—liquid extraction is one of the most popular preconcentration techniques [3, 4]. During coprecipitation the trace amounts of element are concentrated on surface of the precipitate by adsorption [5, 6]. The modified ion exchangers with bounded chelating agent have achieved a major significance [7—9]. Recently the preconcentration techniques binding the advantages of liquid—liquid extraction and ion-exchange technique have begun to be used. These techniques can be classified as preconcentration techniques on modified sorbents or as a solid—liquid extraction [10].

Many authors have examined the content of lead in various samples for the toxicological and environmental purposes by spectral and/or electroanalytical methods [11, 12].

In this paper, the formation of chelate of lead with diphenylthiocarbazone (dithizone) bounded on a polyurethane foam was used [13, 14]. The preconcentrated chelate of lead was consequently eluated by diluted mineral acid. The proposed method seems to be simple and available due to chemicals and sorbent.

EXPERIMENTAL

A stock solution of Pb salt (ρ = 100 $\mu g \ cm^{-3}$) was prepared by diluting firm standard solution (Analytica, Prague) of Pb with a concentration of 1000 $\mu g \ cm^{-3}$.

Diphenylthiocarbazone, H_5C_6—N=N—CS—NH—NH—C_6H_5 (dithizone, M_r = 256.33) of anal. grade (Lachema, Brno) was used without further purification. The content of lead in substance was checked. The dithizone solution for the immobilization was prepared by dissolving 0.01 g of substance in 100 cm^3 of chloroform.

The polyurethane foam was commercially available; polyurethane mats were cut onto cubes sized 0.125 cm^3 and the sorbent was purified by washing with 1 M solutions of HCl and HNO_3 repeatedly in duration of half an hour, washing with redistilled water until the reactions for chlorides and nitrates were negative. Then the foam was washed with acetone and dried under the infrared lamp. The foam was stored in dark room under the vacuum.

The immobilization of chelating agent (dithizone) was carried out by the dipping of purified polyurethane foam into the solution of the complexing reagent and the intensive shaking for 15 min. The reagent consumption was approximately 10 cm^3 per 1 g of foam. The unspent reagent was poured off and the foam was cleaned out of the rests of chelating agent. Finally, the foam was dried under the infrared lamp in nitrogen atmosphere in the polyethylene flask [15]. Treated in this way, the foam kept its constant characteristics for 10 days at least.

The nitric and hydrochloric acids were of semiconductor purity grade and perchloric acid was of anal. grade. The other chemicals were also of anal. grade.

All laboratory vessels, including polyethylene materials were washed with 5 M-HNO$_3$, then repeatedly washed with quartz redistilled water and stored in polyethylene sacks.

The glass columns (i.d. = 8 mm and l = 90 mm) were used for the preconcentration purposes. After purification by the mineral acid they were filled up by modified sorbent under the pressure. The modified sorbent was always weighed exactly (1.0000 g). The columns filled were washed with redistilled water and they were kept filling with redistilled water until they were used.

The fundamental system properties (the effect of pH value, the sorption flow rate, the elution flow rate, the interferences) were examined in off-line column arrangement. The sorption and desorption solution flow rates were controlled by the peristaltic pump PP 15 (Zalimp, Poland) with variable flow speeds up to 30 cm^3 min^{-1}. The volume of Pb solution (100 cm^3) went through the column, then the column was washed with the little amount of redistilled water and immobilized metal was desorbed with 10 cm^3 of eluent (HNO$_3$, HCl, HClO$_4$, the preconcentration factor 10).

The absorbance was measured on a SPECTR AA-30 atomic absorption spectrometer, controlled by data station DS-15 (Varian Techtron, Mulgrave, Australia). The measurements were carried out for lead at analytical line 217.0 nm, with deuterium background correction. According to the experimental arrangement the absorbance values for certain integration time or analytical peak area were considered. The values of blank experiments were measured for each sample.

The checking measurement of Pb content in water and soil samples was carried out by the DPASV method with a polarographic analyzer PA-4 (Laboratorní přístroje, Prague) with static mercury drop electrode.

RESULTS AND DISCUSSION

The preconcentration was based on the chelate formation between metal(II) and complexing agent immobilized on a sorbent. The metal was eluated with the mineral acid.

The optimum conditions of sorption of lead on the modified sorbent were investigated. The effect of pH values of the solutions containing lead on the sorption was examined in the pH range 2—7. The effect of pH value on the Pb sorption is shown in Fig. 1. It is clear that the Pb — diphenylthiocarbazide complex begins to form above pH value 2. At pH values
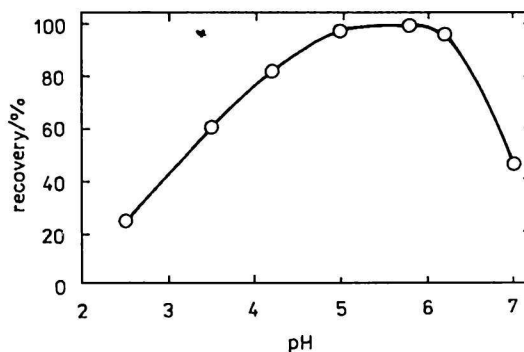

Fig. 1. The effect of pH on recovery of Pb. ρ_{Pb} = 0.1 µg cm^{-3} (100 cm^3), sorption solution flow rate 10 cm^3 min^{-1}, elution solution flow rate 0.5 cm^3 min^{-1}, eluent 1 M-HClO$_4$.
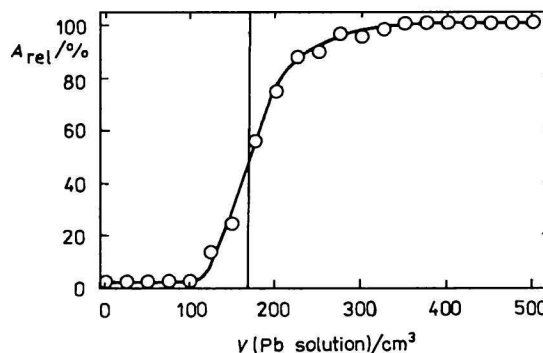

Fig. 2. The break-through curve. ρ_{Pb} = 1.0 µg cm^{-3} (1.0 dm^3), pH 5.5, sorption solution flow rate 10 cm^3 min^{-1}, sorbent capacity 170 µg of Pb per 1 g of modified sorbent.

4.5—6.0 the sorption reached approximately 100 %. At pH values higher than 7 the solubility of diphenylthiocarbazide in water began to be obvious.

The effect of the flow rate of sorption solution on the recovery of Pb content was observed. 100 cm^3 of Pb solution with ρ = 0.1 µg cm^{-3} was used at pH value of 5.5 and the flow rate of sorption varied in the range 1 to 15 cm^3 min^{-1}. No decrease of sorption efficiency below 100 % (from the point of view of the precision of the sorption efficiency, see the reproducibility of experimental results) was found up to the flow rate 10 cm^3 min^{-1} approximately. The recovery decline was not observed below 90 % within the whole flow rate range. The flow rate of 10 cm^3 min^{-1} was chosen for the next experiments.

The dynamic method of unlimited sorption solution volume was used for the determination of the solute retention. Due to the low flow rate of the lead solution (10 cm^3 min^{-1}, ρ = 1.0 µg cm^{-3}) the equilibrium state between the solution and modified sorbent was reached. The equilibrium was indicated when the concentration of sorbed ion was equal at the input and output of column. The typical shape of the break-through curve for the sorbent mass of 1 g is shown in Fig. 2. The sorbent capacity (170 µg

of Pb per 1 g of modified sorbent) was estimated by the solute retention obtained by the projection of the inflection point of the break-through curve onto the horizontal axis. The found sorption capacity of sorbent seemed to be relatively high for lead in the presence of other competitive metal ions.

The optimum conditions of desorption of lead from the column were investigated. It was obvious from the preliminary experiments that an acid can be simply used for the metal removal from the column. Therefore, the elution by various acids (HNO_3, HCl, $HClO_4$), with a concentration of 1 mol dm^{-3}, was examined. Perchloric acid seemed to be the most convenient for the next measurements. It provided the highest recovery in the minimum volume of acid required for the elution. Also the suitable concentration of acid was examined. The elution was carried out with the set of 0.5—5.0 M solutions of $HClO_4$. The sufficient concentration was 1 mol dm^{-3}.

The effect of flow rate of elution reagent on the desorption efficiency was examined in the range 0.1 to 3 cm^3 min^{-1}. From the found dependence, it is obvious that the flow rate of elution reagent has no significant influence on the metal recovery in the range 0.1—0.5 cm^3 min^{-1}. At the higher flow rates the desorption found was insufficient.

It is necessary to take into account the possible effect of other present ions in the preconcentration and determination of Pb in practical samples of drinking and waste water. These ions could be sorbed on the modified sorbent or affect the sorption of lead in another way.

The effect of the presence of mercury(II), cadmium(II), copper(II), zinc(II), iron(III), and manganese(VII) ions was studied. The interfering element contents were chosen in 100-fold excess in relation to the content of element determined. It was found that iron(III) and manganese(VII) did not interfere in the determination at this concentration ratio. The ions of the other metals provided the chelates with dithizone under the given conditions similarly as lead. Therefore, the capacity of column was decreased and lead was not sorbed quantitatively. If the sorption capacity was not overpassed the presence of mercury(II), cadmium(II), and zinc(II) ions did not interfere. The interference of copper(II) — the decrease of recovery to 90 % — can be removed by the masking with sodium diethyl dithiocarbamate in weak acidic solution (it means at the optimum pH value for the sorption of lead).

The effect of present anions, e.g. chlorides, sulfates, and phosphates was examined in excess of five orders of magnitude to the concentration of metal determined. It resulted from the experiments that these anions had no negative effect on the preconcentration of lead and its consequent determination by AAS.

Under the standard conditions (the preconcentration factor equals 100), the calibration dependence was measured and constructed in the calibration range of 0.005 to 0.2 µg cm^{-3} of lead.

The reproducibility of the determination of lead in water after the preconcentration step was examined with a set of ten samples (ρ = 0.05 µg cm^{-3}). These solutions were prepared by exact dilution of a standard stock solution of Pb with a concentration of 1.000 µg cm^{-3}. The determinations were carried out under the standard conditions — pH 5.5, sorption solution flow rate 10 cm^3 min^{-1}, elution solution flow rate 0.5 cm^3 min^{-1}, preconcentration factor 100. The average value of Pb recovery was found 98.70 % ± 0.30 % with relative standard deviation 0.9 %.

The detection limit (3σ) and limit of quantitation (10σ) were found out from ten parallel measurements of the blank experiment. The measurements were carried out under the same conditions as the reproducibility measurements. The found values of absorbance (recorded in five decimal points) were transferred via the slope of calibration line onto the Pb concentrations. The found values of the detection limit (3σ) and the limit of quantitation (10σ) for Pb with preconcentration were 1.4 µg dm^{-3} and 5.8 µg dm^{-3}, respectively, at the number of parallel measurements 10 and at the preconcentration factor 100.

To improve the detection limit, it would be possible to use the higher preconcentration factor but it would lead to the enormous prolongation of analysis. The other way is to use more sensitive AAS techniques with this preconcentration step, e.g. Flow Injection Analysis—Hydride Generation AAS.

Analysis of Practical Samples

The proposed method for Pb preconcentration with AAS determination was tested for samples of drinking and surface water. The samples of drinking water were the tap water samples and surface water samples were obtained from Botič river (Prague). The water samples were introduced into 1 dm^3 polyethylene flasks, immediately stabilized by 5 cm^3 of concentrated nitric acid and filtered. Then, 10 cm^3 of 1 × 10^{-4} M solution of sodium diethyl dithiocarbamate was added and pH was adjusted at the value of 5.5. Preconcentration factor was 100. Three samples of both drinking and surface water were analyzed. The results are summarized in Table 1.

Similarly, the content of lead was determined in the soil obtained from Prague area. The 1 M solution of ammonium acetate was used as an extraction agent (the preconcentration factor 10).

The parallel slope technique was tested for surface water samples to verify the validity of the calibration curve for the practical samples. A very good

Table 1. Analysis of Practical Samples

Sample	Flame AAS $\rho/(\mu g\ dm^{-3})$	DPASV $\rho/(\mu g\ dm^{-3})$	Preconcentration factor
Botič I	5.7	5.5*	100
Botič II	6.2	5.7*	100
Tap water I	$\leqq$ 1.4	0.3*	100
Tap water II	$\leqq$ 1.4	0.2*	100
Tap water III	$\leqq$ 1.4	0.3*	100
Soil extract I	420	430	10
Soil extract II	320	330	10
Soil extract III	280	310	10

*The measurements were carried out by standard addition technique.

agreement in the slopes of calibration line and standard addition line was found out. The difference of slopes was 1.1 %.

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