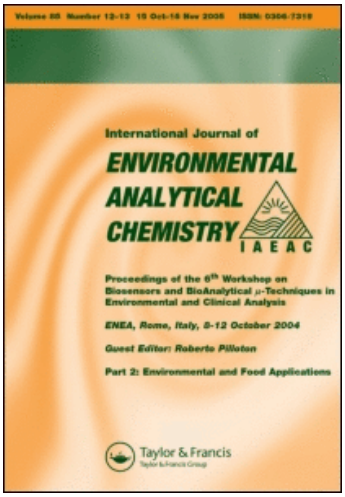


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# Speciation, Preconcentration and Determination of Lead in Natural Water Using Chelating Resin and Direct GFAAS

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# SPECIATION, PRECONCENTRATION AND DETERMINATION OF LEAD IN NATURAL WATER USING CHELATING RESIN AND DIRECT GFAAS

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A method has been developed for determination of trace metals in natural waters at the sub ppb level using sorption under static conditions on fine chelating resin beads. The metal can be quickly eluted from loaded beads with acid for GFAAS analysis, or the beads can be slurried in acid solution for direct GFAAS measurement. The method was applied to natural fresh water samples and lead was detected at levels down to 0.1 μg/L. The method distinguishes between lead in stable complexes and free lead ion. It permits preconcentration of trace metals from water in the field, thus avoiding the need to transport bulky water samples to the laboratory, and prevents the possibility of species interconverting during storage and transportation. The sample-loaded beads can be stored before analysis with no apparent change in results.

*Keywords:* Speciation, preconcentration, graphite furnace AAS, lead, chelating resin

## INTRODUCTION

Determination of the physical and chemical species in which trace metals exist in water is equally as important as the measurement of the total concentration. It is well established that speciation measurements are necessary for studies of the toxicity of metals toward aquatic organisms as well as for understanding the transport and fate of trace metals in the environment[1,2]. Most studies of the susceptibility of fish to heavy metal poisoning have shown that the free hydrated metal ions are the most toxic[3]. Ions which are strongly complexed or associated with colloidal particles are usually considered to be non-toxic.

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The routine procedures for "dissolved" lead and other toxic heavy metals in natural waters require filtering of the sample through a 0.45 μm membrane and acidification of the filtrate to release complexed and colloidally bound metals. Free hydrated ions of lead, organic and inorganic complexes and many colloidal particles with adsorbed lead ions are able to pass through the membrane. Contribution of these species to the toxicity and bioavailability to aquatic organisms is quite different[1-3]. Lead usually exists in unpolluted natural waters at levels below 1μg/L. Therefore, even with modern sensitive instrumentation such as GFAAS or ICP MS, preconcentration and/or separation steps are often necessary[4,5].

Of the available methods for concentrating specific metal species from water, ion exchange is attractive. Sorption of the ions of interest on ion exchange resins can concentrate them so that analysis can be carried out with little manipulation of the sample, and thus with less chance of contamination. Conventional cation and anion exchange resins have been used for preconcentration and speciation of heavy metals, but an iminoacetate chelating resin, such as Chelex–100 has been found to be even more suitable for this purpose[3,5–7]. There are many published examples of the use of this resin for preconcentration and separation of ionic copper, lead, zinc, nickel, cadmium, and chromium (III) from natural waters. Chelex–100 binds ionic metals strongly, but, since its pore size is only 1.5nm, large complexes and colloids are not retained on the resin beads. It was shown that that solutions of colloidal hydrated ferric oxide and bulky organic dye molecules are quantitatively rejected by the resin[8]. This resin, therefore, provides a simple and efficient method for preconcentration and separation of ionic metals from metal species associated with colloids or present in strong complexes.

In most cases, the preconcentration of lead from natural waters on ion-exchange beads is done under dynamic conditions, by passing the sample through a column filled with the resin. The analyte is then eluted from the beads with a small amount of a high purity acid[5–7,9,10]. This can be a time consuming process. To reduce the time required for complete sorption, some researchers use fine mesh Chelex resin in a batch process for lead preconcentration[11,12]. The resin is stirred with the water sample, at a pH adjusted by addition of buffer solution, until sorption is complete. The beads are filtered from the sample, and the sorbed analyte is removed with an acid wash. This batch technique is more readily carried out under field conditions than is column sorption and elution[3,12].

GFAAS is one of the most cost-effective and sensitive techniques for determining trace elements in natural waters, but preconcentration steps are still needed for very low concentration samples. Recently, direct analysis of solid samples by GFAAS has become more popular[13]. Instrumental improvements, such as stabilized temperature platform furnaces and Zeeman or Smith-Hieftje background corrections, have allowed a significant increase in the achievable accuracy for

solid samples, especially if the sample is delivered to the furnace as a slurry. Powered solid samples are often slurried in dilute nitric acid with a surfactant added to prevent agglomeration. A small ultrasonic probe, inserted directly into the autosampler cup, is used to agitate the slurry immediately before injection into the graphite furnace, insuring homogeneity[14]. This method, developed for biological materials and soil, has not previously been applied to metals preconcentrated on fine ion-exchange resins. Recently it has been shown that quantitative extraction of lead, copper, cadmium and manganese from biological powdered samples can be achieved using ultrasonic mixing with 1 M nitric acid at 40°C for 5 min.[15]. Lead from 1–50 mg of a powdered biological sample can be completely extracted with 5 ml of more dilute 0.3M nitric acid solution under the same conditions. This technique can overcome some of the problems associated with slurry sampling. However, acid extraction must be checked for completeness for each particular type of sample.

The goal of this investigation was to develop a method for determination of trace metals in natural waters at the sub μg/L level using sorption under static conditions on fine chelating resin. The metal can be quickly eluted from loaded beads with acid or run as a slurry in acid solution in the GFAAS for the final measurement. We anticipated that sorption on Chelex–100 resin would allow the metals which are bound to particles or form stable complexes to be distinguished from free metal ions. We also wished to examine the use of the chelating resin in simple and reliable methods for speciation and preconcentration of trace metals from water in the field, thus avoiding the need to transport bulky water samples to the laboratory, and preventing the possibility of species interconverting during storage and transportation.



## EXPERIMENTAL

The experiments were carried out with ultrapure deionized water(MilliQ, 18MΩ), tap water from Newark, NJ, water from the lake in Branch Brook Park and the Passaic River, both in Newark, and from the Delaware-Raritan canal in Princeton, NJ. Samples were stored at 4°C for up to 5 days.

All reagents were reagent grade and nitric acid was ultra high purity (Fisher Sci.). Chelex–100 in $Na^+$ form (analytical grade, 100–200 and 200–400 mesh samples) was supplied by Bio-Rad Lab. All plastic laboratory ware used throughout the experiment was precleaned with nitric acid solution and thoroughly rinsed with deionized water.

A Thermo Jarrel Ash atomic absorption spectrometer (Model 188) with furnace atomizer and Smith-Hieftje background correction was used for lead deter-

mination. All analyses were done using solid pyrolytic graphite forked platforms inserted in pyrolytically coated graphite tubes. Standards for calibration were prepared by dilution of 1000 mg/L stock lead solution (Aldrich) in 5% nitric acid. Manual injections of 20 µl of the sample or standard were made into the furnace with an Eppendorf pipette. Both 217.0 and 283.3 nm wavelengths were tested for lead determination. Because the reproducibility of standards and spiked samples were similar for both wavelengths, the more sensitive line at 217.0 nm was chosen. Peak areas were measured for quantitation.

For lead speciation and preconcentration, 250 ml of the sample was stirred in a covered plastic beaker with 0.25g of Chelex–100 resin. A pH value of 5 was maintained during the sorption process by addition of 5ml of acetate buffer solution. After sorption was completed, a vacuum filtering apparatus with a polypropylene holder and 0.2 µm Whatman membrane filter was used in order to separate the Chelex resin. The resin was washed off the filter into a plastic test tube with 5 ml of 5% (v/v) nitric acid. A 50 fold preconcentration was achieved by this procedure. Slurry samples were prepared by shaking the resin with the nitric acid solution for 2 min. by hand or by use of an ultrasonic probe (Sonic & Materials, Vibracell 50). A 20 µl aliquot of the prepared slurry was immediately injected into the furnace. In other experiments, an aliquot of the supernatant solution produced after 2 min. shaking and 2 minute settling of the Chelex beads was injected into the furnace for analysis, instead of the slurry. Sorption on the Chelex resin allowed the determination of lead present in the water sample in ionic form and in relatively unstable complexes. We have termed these sorbable species "ionic lead". Blanks consisting of Chelex beads in deionized water and standard aqueous solutions containing 0.4, 0.6, 0.8 and 1 µg/L of lead were each carried through the preconcentration procedure, and run by GFAAS. Solutions containing 20, 30, 40 and 50 µg/L of lead in 5% nitric acid, without preconcentration were also used as standards.

To examine the effect of complexing agents on lead sorption, experiments were carried out with aqueous solutions of lead containing EDTA or the sodium salt of humic acid (both Aldrich). Humic acid salt was added to deionized water and the insoluble particles were filtered out using a 0.45 µm membrane. Then the solution was spiked with a known concentration of lead. The solution was stored for several days to allow equilibration, and then the ionic lead was preconcentrated and determined.

In natural water samples, the total lead, including the dissolved ions, lead complexes, and lead adsorbed on various particles was measured. Also, the so called dissolved lead, consisting of species which pass through a 0.45 µm Whatman membrane filter, was determined. For the total lead measurement, the sample was acidified to a pH of about 1.5 with nitric acid at the time of collection. The

sample was not filtered. An aliquot was taken and the lead was preconcentrated by evaporation to 1/5 or 1/10 of the original volume, depending on expected concentration. Then $HNO_3$was added to adjust the acid concentration to about 5% and GFAAS analysis was performed. For determination of 'dissolved lead', the sample was filtered through a 0.45 μm membrane in a plastic filtering apparatus, within a few hours of collection. The filtrate was acidified with $HNO_3$ to pH 1.5, and the lead was preconcentrated by a factor of 10 to 40, by evaporation. Nitric acid was added to bring the acid concentration to about 5%, and 20 μl of the sample was injected into the furnace for analysis. Thus, the so called 'ionic', 'dissolved' and total lead species were determined in natural water samples. In tap water only the concentrations of ionic and dissolved lead were evaluated.

For trace element analysis, the use of a special clean room is recommended. Although such room was not available for our research, every effort was made to reduce contamination (daily wet cleaning, ventilation with filtered air, prewashed new plastic ware, appropriate storage of reagents, etc.). Content of lead in all reagents was checked by GFAAS. Evaluation of blanks was performed before each series of analyses.



## RESULTS AND DISCUSSION

First, different temperature programs for GFAAS determination of lead in a slurry and in nitric acid solutions were investigated. Experiments were performed using a slurry containing 0.25g of 100–200 mesh Chelex resin and 5 ml of 5% $HNO_3$. It was found that the pyrolysis temperature was critical for accurate analysis. At temperatures above 490°C loss of lead by early volatilization became significant, while at lower temperatures, background absorption due to incompletely ashed matrix was high (Figure 1). The optimized program for the GFAAS analysis is shown in Table I.

TABLE I Program for lead determination by GFAAS

| | *Drying* | *Pyrolysis 1* | *Pyrolysis 2* | *Atomization* | *Cleaning* |
|---|---|---|---|---|---|
| Temp (°C) | 110 | 300 | 490 | 1800 | 2550 |
| Ramp (°C/min) | 10 | 20 | 40 | | |
| Hold (sec) | 5 | 5 | 25 | 4 | 4 |

This program was used in all experiments with solutions and in the initial experiments with slurries. In comparison with a standard program recommended for lead in waste, the second pyrolysis temperature is lower, and the pyrolysis time is increased.

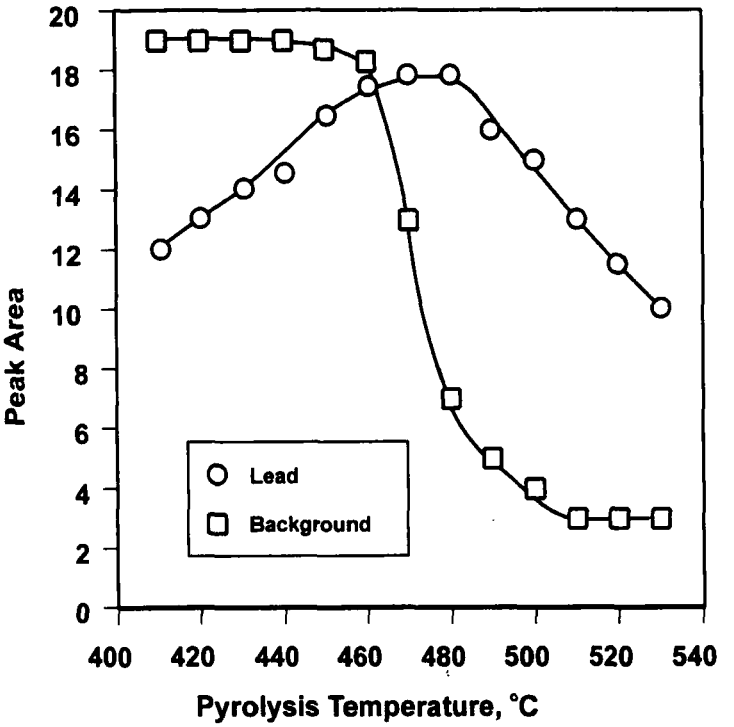


FIGURE 1 Effect of Pyrolysis Temperature of Chelex–100 Slurry on Lead and Background Absorption Peak Areas

At first, a 2 min mixing with a titanium ultrasonic probe was used to prepare the slurry. Later it was found, by comparison of GFAAS measurements, that for this matrix vigorous manual shaking of Chelex beads with $NHO_3$ solution for 2 min. gave practically the same results as ultrasonic mixing. The density of Chelex–100 beads (about 1.1 g/ml) is similar to that of the water, and the beads are much more readily slurried than plant materials, soils and other types of samples, where sonification is needed for adequate slurrying. Ion exchange beads are also not prone to form aggregates in suspension and the addition of surfactant to stabilize the slurry is not necessary. Therefore, the slurrying procedure for the resin beads is simpler than that for many other sample matrices, although the ultrasonic method is more universal and has been proved to be beneficial in many applications.[14]

The sensitivity and reproducibility of analysis for both solutions and slurries (0.25g of Chelex in 5ml of 5% $HNO_3$) were determined and compared. In both cases, the sensitivity of the determination was similar and concentrations of lead at 1 ppb were easily detected. However, the reproducibility of the GFAAS deter-

mination in solutions was better than that in slurries. For 7 replicate injections of a 20μg/L sample, the standard deviations were 1.68 and 2.45 μg/L respectively.

The absorbance of lead in solutions of 5% nitric acid, and in 5.0 ml of the same solution with 0.25 g. of Chelex added was determined. It was found that the absorbance in the slurry samples was 10 to 15% lower than that in the solutions. To achieve acceptable results using slurried samples, standards also had to be run as slurries. To avoid this extra step, two methods were tried. First, 8 μl of 1% palladium nitrate modifier was added to the 20 μl sample and the atomization temperature was increased to 600 °C. This greatly diminished the difference between the solution and slurry samples, but still left a difference of 2–4%. Salts of Pd are often used as modifiers in lead determination in solid samples to allow the pyrolysis temperature to be increased significantly without loss of lead by volatilization[13,16].

Later, it was found that the lead was rapidly and completely eluted from the Chelex beads, simply by shaking them in 5% nitric acid for two minutes. It was determined that the supernatant solution obtained when the beads were allowed to settle for two minutes gave results which could be compared with standard aqueous solutions. Nitric acid at a concentration of as little as 2% is needed for complete desorption of lead from the sorbent. Desorption efficiency decreased sharply if $HNO_3$ concentrations less than 1% were used. The completeness of desorption of the lead from the beads was determined from spike recovery data and by analysis of the rinsed beads after elution. The signal from the analysis of the eluted beads was comparable to the blank. Therefore, normal aqueous standards were useable and slurried standards were not necessary. No palladium modifier was used, and the temperature program shown in Table I was followed.

For all further work, the supernatant solution was used. This rapid elution in acid was tested only for lead, and must be checked for other metals before being applied to those determinations. The slurry injection method is more universal, as it is applicable both to metals which are not readily removed form the beads, as well as to those which are.

The kinetics of lead sorption from deionized water at different pH levels was investigated. It was found that pH 5 was optimal. This pH was recommended for sorption of many trace metals including lead from natural waters under static conditions[12]. The kinetics of sorption from 250 ml of 0.4 μg/L aqueous lead solution using 0.25g of 100–200 and 200–400 μm Chelex beads at pH 5 is shown in Figure 2. Lead concentrations were determined by GFAAS in the aqueous phase after a 10-20 fold volume reduction by evaporation. Although the sorption process is somewhat faster on finer beads, their separation from solution is more difficult and takes more time. Therefore, 100-200 mesh resin and 1.5 hours sorption time were chosen for the preconcentration procedure. The same preconcen-

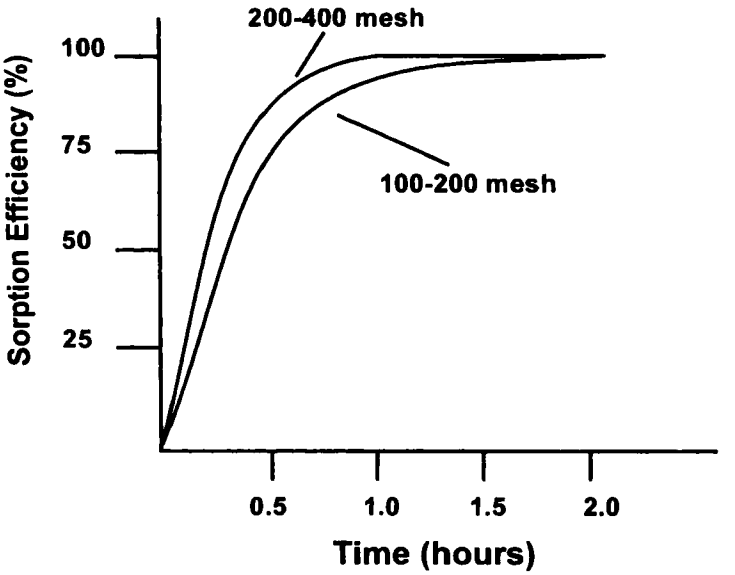


FIGURE 2 Kinetics of Lead Sorption on Chelex–100 Resin from 0.6 μg/L Lead Solution at pH 5



tration method was carried out with a blank (untreated Chelex resin mixed with the buffered distilled water). In 5 replicates, the concentrations found in blanks varied from non detectable to 0.03 μg/L, with a mean concentration of 0.018 μg/L. Washing of the Chelex beads with $HNO_3$ solution followed by rinsing with water before use did not reduce blank contamination significantly. So, the untreated commercial resin was used in further experiments. The use of a clean room for sample preparation would undoubtedly reduce the level of the blanks, but such a facility was not available to us. However, even under these conditions, and using untreated resin, it was possible to speciate, preconcentrate, and reliably quantify lead at concentrations in water above 0.1-0.2 μg/L

The method developed was tested on duplicate aqueous solutions containing 0.2, 0.8 and 1.0 μg/L of lead. After a 50 fold preconcentration by sorption on Chelex–100 under static conditions, separation of beads from the sample, and desorption with 5% nitric acid, as described above, the supernatant solution was injected into the furnace. Solutions containing 10, 30, and 50 μg/L of lead in 5% nitric acid were used as standards. Recoveries of lead from aqueous samples were above 98% in all cases. (Table II)

Storage of Chelex–100 resin after sorption of lead from water samples was studied to determine if it was practical to hold the beads for a period of time before GFAAS determination. The usual preconcentration procedure was carried out on duplicate samples, containing 0.2; 0.8 and 1.0 μg/L of lead in deionized

water. The Chelex resin was filtered out, using a disposable plastic filter apparatus. The filter cup was covered with paraffin film, and stored for 18 days at room temperature. After storage, the loaded beads were treated in the same manner and the supernatant solution was injected into the furnace. The recovery of lead for these samples is presented in Table II

TABLE II Recovery of lead from samples preconcentrated using Chelex-100 and the effect of storage on the sample-loaded beads

| *Original Concentration (μg/L)* | *Storage (days)* | *Amount determined (μg/L)* | *% Recovery* |
|---|---|---|---|
| 0.200 | 0 | 0.197 | 98.8 |
| 0.800 | 0 | 0.790 | 98.7 |
| 1.00 | 0 | 0.989 | 98.9 |
| 0.200 | 18 | 0.196 | 98.3 |
| 0.800 | 18 | 0.789 | 98.7 |
| 1.00 | 18 | 0.990 | 99.0 |



Within experimental error, no difference was seen between the stored and the immediately run samples. This indicates that speciation and preconcentration can be performed in the field and GFAAS determination carried out at least 18 days later in the laboratory.

The effect of the presence of a strong complexing agent, EDTA, on lead sorption and determination in aqueous solution was tested. From a solution containing 0.001M EDTA and 0.4 μg/L of lead, only traces of lead were found after the usual preconcentration and determination procedure. Chelex sorbed only 3 % of the lead in 1.5 hours in the presence of EDTA. Experiments on a solution containing 0.4 μg/L of lead and 0.01% of the milder complexing agent, humic acid, demonstrated that about 85% of the lead was sorbed by the Chelex beads. However, in real water samples, humic complexes of trace elements can be adsorbed on inorganic colloid particles[3] and distribution coefficients can change.

Finally, the speciation and determination of lead in real samples was performed. Each measurement, including the preconcentration procedure, was repeated three times, and the mean concentrations and standard deviations were calculated. Analysis of Newark tap water was carried out for dissolved and ionic lead as described in the experimental section. The analysis showed comparable results for the dissolved and ionic species, 1.35 μg/L for dissolved and 1.26 μg/L for ionic. Total, dissolved, and ionic lead were measured in local lake, river and canal water. The largest total concentration of lead, 10.3 μg/L, was found in the

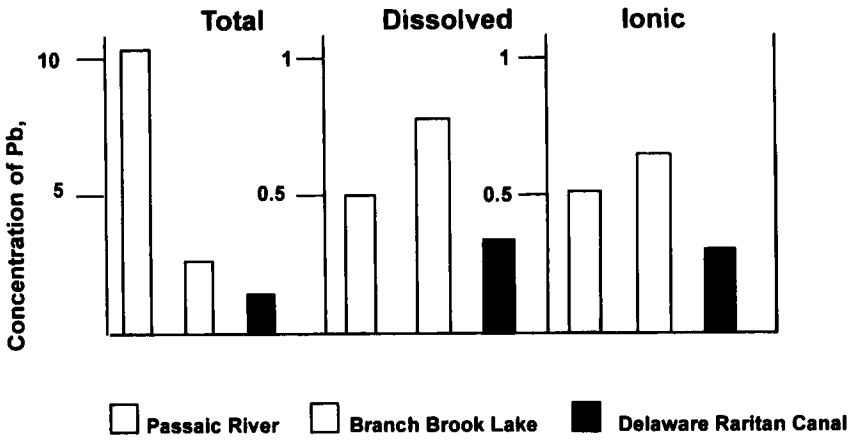


FIGURE 3 Concentrations μg/L of Total, Dissolved, and Ionic Lead Determined in Natural Water Samples



Passaic River sample (Figure 3). However, in the studied samples, the major portion of the lead was concentrated on particles and could neither pass through the 0.45 μm filter nor be adsorbed by the Chelex resin. Concentrations of dissolved and ionic lead for all samples were similar, in the range of 0.3-0.7 μg/L (Figure 3). For the Branch Brook Lake water samples, the dissolved lead was slightly higher than the ionic. For other samples the dissolved and ionic concentrations were practically equal. Results for ionic lead were more reproducible than for dissolved lead, apparently because the evaporation procedure performed at elevated temperature in the open air for the dissolved lead is more prone to contamination. The relative standard deviation for ionic lead samples was 7 % and for dissolved lead was 15 %.

For these particular water samples, a significant difference between lead determined after filtration and acidification and lead sorbed by Chelex–100 resin was not found. This indicates that only small part of lead occurred in water as strong complexes or was sorbed on fine colloid particles which could pass through the 0.45 filter. However, a greater difference in these forms of lead might be found in other samples.

The procedure developed has advantages over more traditional dynamic sorption in a column, followed by elution and GFAAS determination. Sorption under static conditions for large volumes of water samples is faster and can be easily carried out on site. It can be done under field conditions by using, for example, a filter-capped squeezable plastic bottle in which to carry out both the sorption and separation of the beads from the water as has been done for chromium determinations in the field.[17] Elution from a column, which takes time and requires

high purity concentrated acid, is eliminated. Only 5 ml of relatively dilute acid is necessary for determination in a slurry or for fast desorption in a test tube.

Although the speciation, preconcentration and determination procedure developed here has been demonstrated for lead in solutions and natural waters, we do not see major limitations for application of this method for speciation and determination of other trace metals, which can be sorbed on Chelex–100 resin. So, the determination of cadmium, zinc, copper, nickel, and other trace metals in natural waters at sub ppb level may be performed by the same method.

## CONCLUSIONS

A method for speciation, preconcentration and determination of lead in natural waters at the sub ppb level has been developed. The procedure included sorption of lead on fine Chelex–100 resin under static conditions, separation of the resin from the solution, rapid elution with 5% nitric acid, and GFAAS determination. Lead can also be measured, with somewhat lower precision, in a slurry of the beads in the nitric acid solution, using a higher temperature and a palladium modifier.

Lead occurring in water as strong complexes, such as that with EDTA, is not sorbed by Chelex resin, while about 85% of the lead in milder complexes, such as with soluble humic acids, is sorbed by the resin.

Storage of Chelex–100 resin loaded with lead for up to 3 weeks does not affect the results of analysis. Therefore, speciation and preconcentration procedure can be performed in the field and the loaded beads delivered to the laboratory for GFAAS determination.

Lead concentrations in tap water and three natural water samples were determined. Little difference between "dissolved" lead, determined after filtration and acidification and "ionic" lead, determined by the developed procedure was found.

Sorption under static conditions and direct GFAAS saves time and high purity reagents in comparison with more traditional sorption in the column followed by elution.

We feel that the method developed here can be used for lead as well as for other trace metals such as Cd, Cu, Ni, and Zn which can be sorbed on Chelex–100 resin, in samples of natural waters.

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