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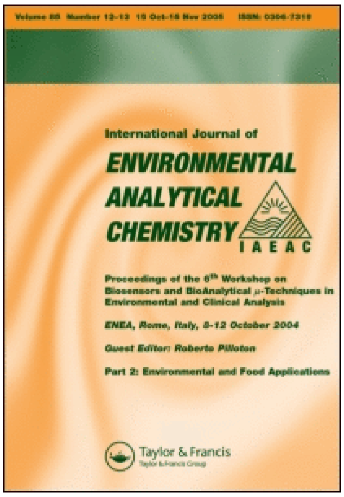

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DETERMINATION OF LEAD WITH A CARBON PASTE ELECTRODE MODIFIED WITH A CHELATING RESIN IN RAINWATER AND HUMAN URINE

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A method is described for determination of lead using a carbon paste electrode modified wtih Dowex A-1 chelating ion-exchanger resin and cyclic voltammetry for the electrochemical measurement. The best conditions for preconcentration were found to be open circuit for 10 min in ammonium acetate, pH 5. Optima parameters for the stripping measurements were a HCl 0.1 M solution as supporting electrolyte, a delay time of 48 s at -1.0 vs. S.C.E. and a scan rate of 150 mv/s. The anodic peak at -0.52 V vs. S.C.E. permits adequate quantification of lead in concentration between 4 and 200 ng/ml with a LD (3σ) of 1.2 ng/ml. The method was used for determination of lead in rainwater and human urine.

KEY WORDS: Lead determination, chemical modified electrode, Dowex A-1 resin.

INTRODUCTION

Lead is a very toxic metal that is cumulative, slow acting and produces a variety of symptoms. It may be absorbed into the body by ingestion, inhalation and through the skin. The major routes of lead absorption are the respiratory and gastrointestinal tracts. Ingestion of 600 μg of lead daily can result in lead intoxication.[1]

Various methods can be used for monitoring of lead concentration in the environment and biological materials: spectrophotometry with different reagents;[2] atomic absorption with flame[3–5] or flameless atomization techniques;[6–9] and electrochemical techniques such as stripping voltammetry[9–14] and galvanic stripping.[15]

The determination at very low levels of concentration in complex matrix requires the use of fast, sensitive and selective methods. For this purpose, chemical modified electrodes (CME) can offer these advantages. CME has been the topic of a lot of research in recent years in analytical chemistry.[16–18] Various applications of CME in trace analysis incorporating ion-exchange resins have been reported.[19,20]

In this paper, a method for determination of very low quantities of lead, using a carbon paste electrode modified with Dowex A-1 resin is described.

EXPERIMENTAL

Reagents

Milli Q–Milli RO water was used throughout the preparation of the solutions. All reagents were of analytical-reagent grade.

Lead (II) stock solution, 1000 μg/ml, was prepared by dissolving lead nitrate in 1% (V/V) HNO_3. Working standard solutions were prepared by dilution as required.

Dowex A-1 chelating resin (50–100 mesh), in the H^+ form and purified by successive washing with 6 M HNO_3 and water. The beads were swollen in water before preparing the electrodes.

All solutions were stored in polyethylene containers.

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Preparation of the Electrode

Modified carbon pastes were prepared by mixing in an agate mortar, 1.0 g of spectrographic graphite powder, 1.0 g of Dowex A-1 resin and 0.6 g of paraffin oil.

The electrode consisted of a teflon tube with a pool (4.0 mm i.d., 1.7 mm depth) in the end, with an inner contact of Cu wire. Portions of the different assayed pastes were packed into the pool at the end of the electrode.

Urine samples were collected during working hours from volunteers from our laboratory. Rainwater samples were collected in several areas of urban Madrid, and they represent the precipitation that occurred during one month.

Apparatus

We lused an AMEL Modèl 448 cathode-ray polarograph equipped with a saturated calomel electrode (SCE) as reference electrode along with platinum counter electrode.

The modified carbon paste electrode described was used as the working electrode for the electrochemical measurement after preconcentration.

The flameless atomic-absorption spectrometric analysis was performed with a Perkin-Elmer Model 372 atomic-absorption spectrometer equipped with a graphite furnace (HGA-2200), a deuterium-arc background corrector and a Linseis Model L-6512 recorder.

A Metrohm Model 654 pH meter was also used.

PROCEDURES

Lead Determination by CME Method: Procedure

The carbon paste electrode modified with Dowex A-1 resin was immersed in a cell containing 20 ml of lead sample adjusted to a pH value of 5.0 with ammonium acetate buffer (0.1 M in this solution) while this solution was being stirred over a 10 min period.

In the case of lead determination in urine, 45 ml of sample were taken and 5 ml of 1.0 M ammonium acetate buffer were added in order to adjust to adequate pH value and electrolyte concentration.

The preconcentration step was carried out at open circuit.

After preconcentration, the electrode was removed from this solution, rinsed with water and placed in another cell containing 0.1 M HCl as supporting electrolyte, for the electrochemical measurement. No deaeration of the electrolyte solutions was required. Then a delay time of 48 s at −1.0 V was applied at electrode and an anodic potential scan was run.

Once the scan was completed, the electrode was cleaned, keeping it in the supporting electrolyte, at 0.0 V vs. S.C.E., for 1 min.

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Sample Preparation and Analysis by Flameless Atomic Absorption Spectrometry

Ten ml of urine sample were pipetted into a pyrex digestion tube and 5 ml of high-purity nitric acid were added. The digestion tube was placed in a heating block and heated to just below boiling to reduce volume to approximately 0.5 ml. Then 0.5 ml of 30% v/v H_2O_2 were added to the sample and the heating was continued at the same temperature to dryness. The residue was dissolved in 10 ml 1% v/v nitric acid.

For the analysis, 20 μl aliquots of the standards and samples were injected into the furnace and the determination was made using the following instrumental conditions: drying, 50 s at 110 °C (ramp, 10 s); charring, 50 s at 525 °C (ramp, 20 s); and atomizing, 5 s at 2300 °C (ramp, 2 s). Uncoated graphite tubes were used in the furnace and were purged with argon at a flow rate of 8 ml/min when used in the "interrupt" ("gas-stop") mode. The absorbance peaks were recorded at 283.3 nm with the hollow cathode lamp operating at 10 mA.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms of lead solution obtained with a conventional carbon paste electrode and our modified carbon paste electrode containing Dowex A-1 resin, after immersion in a stirred lead solution. We obtained an important increase in sensitivity of electrochemical measurement with the modified electrode as a consequence of the previous preconcentration step. The well defined anodic peak (−0.52 V vs. SCE), higher and sharper than the cathodic wave, is adequate for the quantification of lead at low concentration levels.

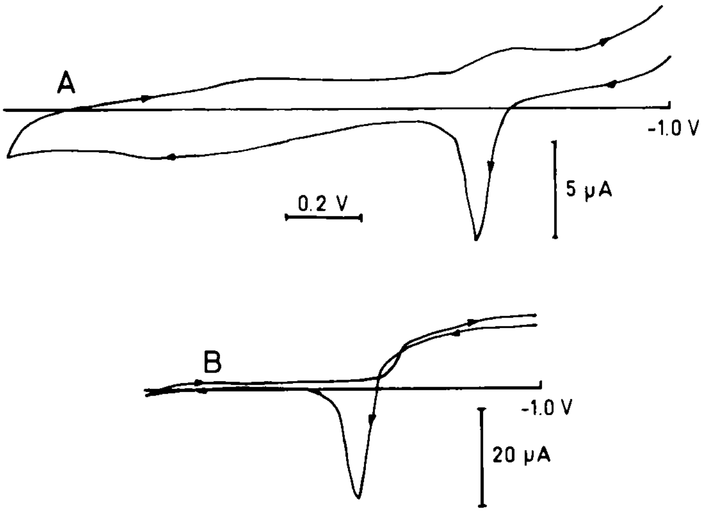

Figure 1 Comparison of sensitivity in the voltammetric determination of lead: (A) carbon paste electrode; lead concentration, 20.7 μg/ml. (B) Modified carbon paste electrode; lead concentration, 10.4 ng/ml; preconcentration time, 10 min.

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To choose the best conditions for preconcentration of lead on the electrode, we consulted available bibliographical data about the retention and elution of heavy meatals on Dowex A-1 resin.[21–24] Our experiences confirmed that in weakly acidic to neutral media (pH values between 3 and 8) the preconcentration is maximum. In more acidic or alkaline media no preconcentration was observed. A disolution of 0.1 M ammonium acetate was chosen for the preconcentration step.

The three stages that make up the process can be described as follows. When protonated form modified carbon paste electrode is immersed in a stirred solution of lead in ammonium acetate buffer, the exchange of H^+ ions for ammonium and lead ones was achieved. The replacement of hydrogen ions by ammonium ions in the surface of the electrode yields up lower residual currents and hence lower detection limits.

The results obtained using different preconcentration times showed a linear increase of the peak current with the time up to 10 min (Figure 2). For longer times at concentrations over 1 μg/ml saturation of the electrode surface was observed. At very low concentration levels, longer preconcentration times can be used for improvement of the analytical signal.

When the preconcentration step was completed, the electrode was transferred to a voltammetric cell containing 0.1 M HCl as supporting electrolyte for the electrochemical measurement, and a potential of −1.00 V was applied to the electrode for 48 s. In this stripping step a chemical–electrochemical mechanism occurs. The use of an acidic solution as supporting electrolite in the electrochemical measurement produces chemical elution of the preconcentrated lead on the electrode, which is reduced by applying a cathodic potential for a time. An

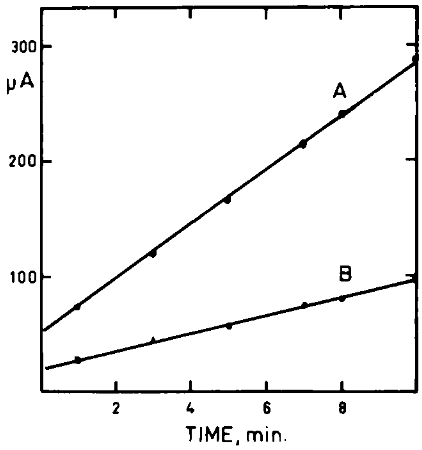

Figure 2 Influence of the preconcentration time on peak current. Lead concentration: (A) 1 µg/ml and (B) 0.2 µg/ml.

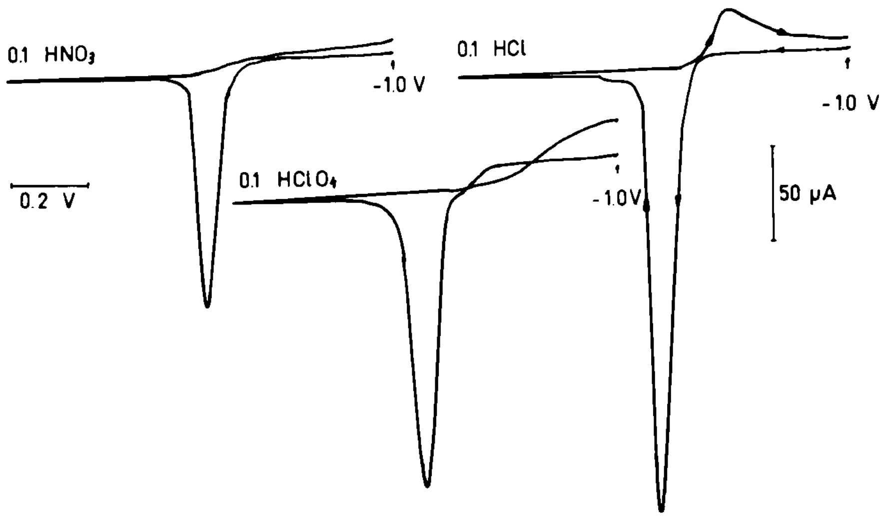

Figure 3 Voltammograms obtained using different acids as supporting electrolyte. Lead concentration, 1 µg/ml; preconcentration time, 5 min.

anodic scan releases the lead from the electrode. By means of this double mechanism a higher peak current is obtained.

In the last stage of analysis, the electrode is maintained in the 0.1 M HCl for 1 min at 0.00 V in order to obtain complete regeneration of the electrode surface. The use of an acidic solution as supporting electrolyte favours a faster cleaning of the electrode surface and reduces the time of analysis.

Solutions of nitric, perchloric and hydrochloric acid at different concentrations were assayed as possible supporting electrolytes. In hydrochloric acid solutions a higher peak current than in other acid media was observed (Figure 3). On the

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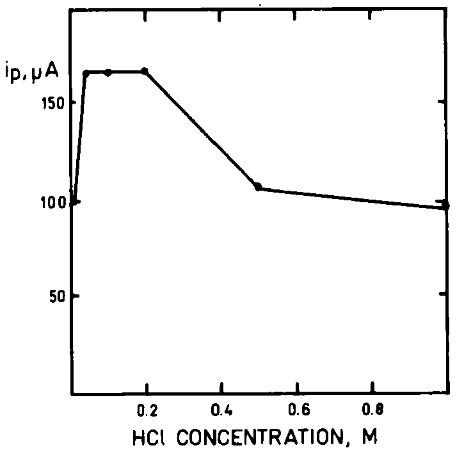

Figure 4 Effect of concentration of chloridic acid on peak current. Conditions as in Figure 3.

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other hand, a higher analytical signal was obtained for acidic concentrations ranging from 0.1 to 0.3 M in HCl (Figure 4). A 0.1 M HCl solution was chosen for subsequent studies.

The conditions of time and potential of delay previous to the anodic scan were also studied. Application of potentials 200 mV more negative than the anodic peak and delay times higher than 48 s do not significantly affect the analytical signal. However, a delay time longer than 48 s produces an increase in background owing to electrode surface protonation. A potential of −1.0 V vs. for 48 s was used throughout in order to obtain a better signal.

Another electrochemical parameter studied was the effect of scan rate on peak current. It was observed that peak current increases when increases scan rate. This result is expected for an electrochemical process where adsorption of electroactive specie is observed. A scan rate of 150 mv/s was used for the analytical measurement. Faster rates have a negative effect on the reproducibility of the signal.

Another important parameter considered in performing the analytical method was the ratio of carbon:resin incorporated into the electrode. When the amount of resin was small, a lower peak current was observed as a consequence of a lower adsorbent ability of the electrode. For ratios greater than 1:1, although an increase of the peak current was produced, the signal was less reproducible and background was higher due to the severe interference of the protons rapidly adsorbed on the electrode during the measurement step. The best results were obtained with 1:1 carbon:resin ratios.

In the optimum analytical conditions deduced from the different studies, the linearity of peak current versus lead concentration in solution was checked. When a preconcentration time of 10 min was used a linear response for concentrations between 4–200 ng/ml was obtained, with a LD (3σ) of 1.2 ng/ml. The precision, expressed as relative standard deviation, was 3.2% for a 100 ng/ml concentration level and 7.3% for a 10 ng/ml one.

Good preparation and packing the paste into the electrode exert an important

Table 1 Determination of lead in rainwater by this method (CME), anodic stripping voltammetry with hanging mercury drop electrode (ASV) and flameless atomic-absorption spectrometry (FAAS)

Sample	*Lead concentration, ng/ml*[a]		
	CME	*ASV*	*FAAS*
Madrid 1	46	50	46
Madrid 2	35	33	36
Madrid 3	76	72	88
Madrid 4	43	39	46
Madrid 5	27	33	35
Madrid 6	30	27	26
University zone	13	15	9

[a] Mean values of 5 assays.

influence on the variability of the analytical signal. Thus, preparation of new calibration plots is recommended each time a new modified carbon paste is prepared.

The interference from different substances which can be present in the samples in high concentrations was checked: alkali and alkaline earth metals, chloride, nitrate, carbonate and bicarbonate ions as well as other heavy metals that can be present in investigated samples in similar concentrations, such as cadmim, copper, zinc and iron. Solutions containing 1 μg/ml of lead and up to 100 μg/ml of the substance assayed were used. The anions that precipitate with lead (i.e. carbonate, bicarbonate) produced interference. Alkaline earth metals caused a significant diminishment of the peak current. This interference, due to the preferential adsorption of these metals on the resin, is avoided when ammonium acetate of $pH = 5$ is used as preconcentration solution. No interference was observed with other investigated ions. No interference was observed from the heavy metals studied, although in the described conditions, they are adsorbed because of their lower sensitivities and because their oxidation takes place at different potentials than lead, in the supporting electrolyte used in this work.

The method was applied to determine lead in rainwater and human urine. The samples of rainwater were collected in an urban area of Madrid (zone with medium atmospheric contamination) and in our University (outside urban area).

The results obtained for water samples with this method were in very close agreement with those of the anodic stripping voltammetric method and flameless atomic absorption spectroscopy (Table 1).

For lead determination in urine the method was compared with flameless atomic absorption spectrometry. The results obtained (Table 2) are in close agreement for both methods and with other bibliographical data dealing with these samples.[8,14] For the CME method, the digestion of samples was not necessary: this is its main advantage. For the anodic stripping volammetric and flameless atomic absorption spectrometric measurements the samples must be decomposed by acidic digestion. Figure 5 shows voltammograms obtained for real samples.

Similar results were obtained in lead determination by CME method in analysis

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Table 2 Lead determination in filtered urine samples by the CME method and flameless atomic-absorption spectometry (FAAS)

Urine sample	*Lead concentration, ng/ml*[a]	
	CME	*FAAS*
1	17	19
2	25	27
3	18	21
4	39	31
5	16	20
6	18	18
7	29	36
8	28	32
9	49	31
10	25	27

[a] Mean values of 5 assays.

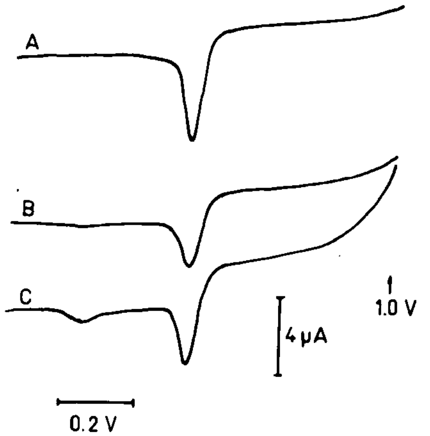

Figure 5 Voltammograms of standard and real samples of lead. (A) Standard of lead, 40 ng/ml; (B) rainwater sample, 27 ng/ml; and (C) urine sample, 39 ng/ml.

of samples with and without nitric acid digestion. For instance, for urine sample no. 8 a value of 31 ng/ml was obtained when the sample was treated with nitric acid and a value of 28 ng/ml were obtained when it was not treated with nitric acid, respectively.

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