Articles

Determination of Lead in Different Samples by Atomic Absorption Spectrometry after Preconcentration with Dithizone Immobilized on Surfactant-Coated Alumina

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A simple and rapid technique for the separation and preconcentration of lead in water and biological samples has been devised. Preconcentration is based on the deposition of analyte onto a column packed with dithizone immobilized on sodium dodecyl sulfate coated alumina at pH ≥ 3. The trapped lead is eluted with 5 mL of 4-M nitric acid and determined by flame atomic absorption spectroscopy. A sample of 1 L, results in a preconcentration factor of 200, and the precision at 20 μg L^{-1} is 1.3% (n = 8). The procedure is applied to tap water, well water, river water, vegetable extract and milk samples, and accuracy is assessed through recovery experiments and by independent analysis by furnace atomic absorption.

Introduction

The measurement of very low levels of environmental pollutants is becoming increasingly important. The toxic effects of lead on the human body are well known,[1-2] and its monitoring in environmental samples is of major interest. Lead is emitted into the biosphere in considerable amounts, owing to its increased industrial use and its application as a fuel additive.[3-4] In recent years concern has increased over the concentration of lead in drinking and natural waters; the EC recommends a limit of 50 μg L^{-1} of lead in potable waters[5], which requires a much greater sensitivity in measurement than is obtainable by flame spectrometry. Therefore, a preliminary preconcentration of lead is usually a necessity for most procedures.

The most frequent methods used for preconcentration are liquid-liquid extraction, evaporation, sorption and chelating ion exchange.[6-9] Much interest has been shown recently in replacing conventional liquid-liquid extraction with solid-phase extraction techniques,[10-14] owing to its high enrichment capability and operational simplicity. The effectiveness and versatility of immobilized water-insoluble chelating agents on surfactant coated alumina have been demonstrated. Surfactant molecules form self-aggregates called "hemi-micelles" or "ad-micelles" on solid surface. The hydrocarbon cores of these micelles have the unique ability to solubilize hydrophobic compounds, which are otherwise sparsely soluble in water.[15-18] The traditional water-insoluble chelating agents, such as dithiozone, can be trapped in the hemi-micelles on alumina. This sorbent is useful for the preconcentration of trace amounts of copper and mercury in aqueous sample.[16-18] To date no such studies have been directed at lead.

The purpose of this work is to investigate the feasibility of the dithizone immobilized on surfactant-coated alumina for the preconcentration of lead from different samples. The possibility of immobilization of dithizone on surfactant-coated alumina fiber and its capability for preconcentrarion of lead is briefly considered.

Experimental Section

Instrumentation. A Buck Scientific atomic absorption spectrometer Model 210 VGP was used for all measurements. The hallow cathode lamp for lead was used as the light source. The analytical wavelength and spectral bandwidth were 283.3 nm and 0.7 nm, respectively. The flow of the sample through the column was adjusted with a J/B vacuum pump model DV-42.

Reagents. All the reagents were of analytical-reagent grade. A stock 1000 μg mL^{-1} of lead (II) was prepared by dissolving 0.1599 g of Pb(NO$_3$)$_2$ (Merck) in triply distilled water and was diluted to 100ml. The solution was then standardized by EDTA solution. Standard solutions of lead (II) were prepared daily by appropriate dilution of stock solution. High-purity water was used throughout the sample preparation, and all the solutions were stored in precleaned poly(propylene) (Nalgene) containers. Alumina (10-50 μm, g type, chromatographic grade, Katayama chemicals) was purified by shaking with 5 M nitric acid and washing three times with water. Sodium dodecyl sulfate (SDS, Katayama chemicals) and dithizone (Merk) were used without further purification. The dithizone-coated alumina was prepared as follows:

Preparation of dithizone-SDS solution. A dithizone-SDS solution was prepared by dissolving 1 g of SDS and 15.0 mg of dithizone in 50 mL of 0.1 M aqueous ammonia

and diluting to 100 mL with water.

Preparation of dithizone-coated alumina. 10 mL of dithizone-SDS solution was added to an Erlenmeyer flask containing 1.5 g of alumina and 40 mL of water. The suspension was acidified to pH 2 with hydrochloric acid (4 M) and shaken 15 min; the solution was then transferred to a Millipore filter holder for the preparation of the column (15 mm diameter *7 mm height).

Procedure. The pH of the solution (500-1000 mL) was adjusted to ~3 with hydrochloric acid and passed through the dithizone coated alumina column at a flow rate of 5 mL min^{-1} with the aid of a suction pump. The analyte was then eluted with a solution of nitric acid (4 M) and the eluent was collected in a 5 mL volumetric flux. The lead content of the eluent was measured by flame-AAS.

Analysis of vegetable samples: 3 g of dried powdered vegetable were digested in 20 mL of concentrated nitric acid for 30 min and diluted to 100 mL. The solution was filtered through a membrane filter and was washed with 20 mL of 3 M nitric acid. However, as a high concentration of anions interferes with lead absorption, the filtrate was passed through a strong anion exchanger. The pH of the resultant solution was then adjusted to 3, and it was analyzed according to the above procedure.

Analysis of milk: A few drops of concentrated nitric acid were added to 1.0 L of milk sample, and the solution was boiled for a few minutes and filtered through a filter paper. The filtrate was passed through a strong anion exchanger to remove the interfering anions, and the lead content was determined according to the procedure.

Results and Discussion

The initial experiments established that dithizone immobilized on surfactant coated alumina had the capability to retain lead according to the following equation:

$$2[H_2DZ] + [Pb^{2+}] \Rightarrow Pb(HDZ)_2 + 2H^+,$$
where "DZ" represents dithizone
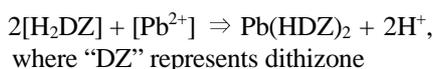
Therefore, systematic study aimed at optimizing the deposition/ elution stages and identifying analytically useful operating conditions were performed. The capability of different alumina
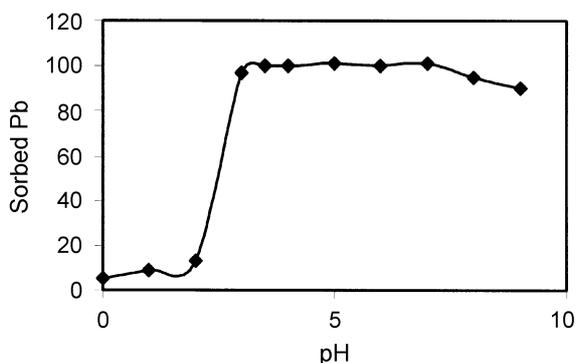
Figure 1. Effect of pH on lead deposition; lead concentration: 4 μg L^{-1}; sample volume: 50 mL; eluent: 5 mL of HNO$_3$ (4 M).
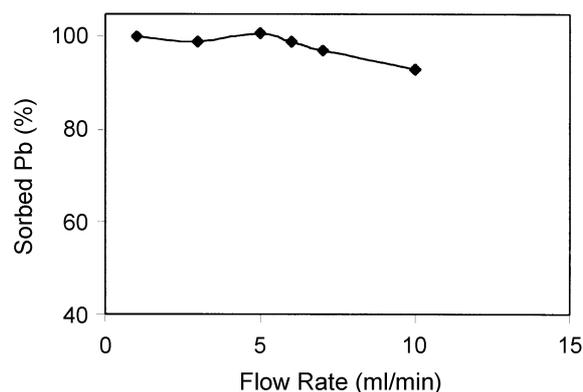
Figure 2. Effect of flow rate on lead deposition: lead concentration: 2 μg L^{-1}; sample volume: 100 mL; eluent: 5 mL of HNO$_3$ (4 M).

on absorption of SDS was examined and similar results to the work of Manzoori *et al.*[17] were obtained, *i.e.* up to 160 mg of SDS were adsorbed on one gram of γ alumina over the wide range of pH (1-6), but the sorption of SDS on α alumina was minimal. The concentration of SDS was fixed below the critical micellization concentration (CMC) (8 × 10^{-3} M) of SDS.[19]

Analyte deposition depended on the sample pH, and as shown in Figure 1, high deposition efficiency was achieved at a pH range of 3-7. The progressive decrease in the retention of lead at a low pH is due to the competition of the hydrogen ion with the lead for absorption on dithizone. The decrease in absorption at pH > 7 is probably due to the precipitation of lead as lead hydroxide and formation of a negative charge on the alumina surface, which results in the reduction of SDS adsoption. To achieve high efficiency and good selectivity, a pH of ~3 was selected for subsequent work.

The efficiency of the analyte deposition depended on the flow rate of sample through the column, as shown in Figure 2. For flow rates less than 5 mL min^{-1}, the signal response was independent of the flow rate. Use of a higher flow rate, however, resulted in a decrease in the signal, suggesting impaired deposition efficiency as a consequence of the short contact time. Subsequent sample loading was performed at a flow rate of 5 mL min^{-1}. However, the kinetic of desorption of lead was slower: with 5 mL of eluent, the complete elution of analyte was possible at a flow rate of 3 mL min^{-1}.

The nature and concentration of eluents were found to have a significant effect on the desorption process of lead from the column. Different eluents, such as HCl, HNO$_3$, NH$_3$, and EDTA at various concentrations, were examined. It was found that 5 mL of nitric acid with a concentration of 4 M were sufficient for quantitative recovery of absorbed lead.

The amount of immobilized dithizone on surfactant coated alumina on absorption of lead was examined and found to be 404.0 μg g^{-1}. This indicates that the column is capable of absorbing large amounts of lead. Furthermore, there was concern whether fibrous alumina can display properties similar to the powdered form and serve as a base for

trapping chelating agents. Therefore, the fibrous alumina was activated according to the given procedure by Dadfania *et al.*[20] at 300-700 °C for 3 hr, and the dithizone was immobilized on it according to the given procedure for powdered form.[17] The amount of this sorbent was found to be 41.4 μg g^{-1}, which is approximately 11% of the powdered form, indicating the differences in retention powers of the two forms of alumina.

Basic analytical performance. One concern was whether the high enrichment factor could be realized for natural water. However, the effect of sample processing volume on analyte absorbance was considered, and the results show that the responses increased linearly with volume. For a sample with a concentration of 20 μg L^{-1}, the calibration graph exhibits linearity over the range of 100-1000 mL, with a correlation of 0.999.

Performance characteristics of this technique were obtained by processing standard solutions of lead. For a sample of 1000 mL, the calibration graph exhibits linearity over the range of 10-120 μg L^{-1} with a correlation of 0.9998 (Y = 1.6×10^{-3}C + 1.8×10^{-4}). The relative standard deviation (n = 8) at 20 μg L^{-1} (sample volume 500 mL) was 1.3% and the Sandell sensitivity[21] was found to be 0.5 μg L^{-1}.

Effect of diverse ions. The possibility of water matrix constituents, such as calcium, magnesium, sodium, potassium, chloride and sulfate, interfering with lead for absorption was considered. A series of lead(II) solutions containing each of the above-mentioned ions at the weight ratio of 2000, was subjected to the procedure. With the exception of sulfate, no reduction in response was detected for the five solutions containing matrix elements relative to that for the simple aqueous lead standard. The sulfate ion showed no interfering up to the weight ratio of 180. The selectivity and utility of the method were further examined in the presence of various ions (Table 1). An error of ± 3% in recovery was considered tolerable. As the results indicate, with the exception of some anions, most of the cations and anions are tolerable at the

Table 1. Effect of divers ion on recovery of lead; Lead concentration: 20 μg L^{-1}, (pH~3); sample volume: 500 mL; eluent: 5 mL of HNO$_3$ (4 M)

Ion	Molar ratio	% Recovery of lead	Ion	Molar ratio	% Recovery of lead
NH$_4^+$	24	97.5	Pd^{2+}	15	97.8
Sr^{2+}	24	98.5	Ni^{2+}	15	96.9
Ba^{2+}	24	99.0	Sn^{2+}	15	96.5
Mn^{2+}	24	99.0	NO$_3^-$	24	99.5
Cr^{3+}	24	98.0	HCO$_3^-$	24	98.5
Fe^{2+}	24	96.0	ClO$_4^-$	24	97.5
Fe^{3+}	24	97.0	SO$_3^{2-}$	24	97
Bi^{3+}	24	97.5	CH$_3$COO$^-$	24	95
Co^{2+}	20	96.7	F$^-$	24	98.6
Zn^{2+}	20	96.5	Br$^-$	15	96.7
Cu^{2+}	20	97.5	I$^-$	10	95
Ag$^+$	15	96.6	C$_2$O$_4^{2-}$	10	98
Hg^{2+}	15	98	PO$_4^{3-}$	10	96
Cd^{2+}	15	99.5			

Table 2. Determination of lead in natural waters; sample volume: 1000 ml (pH = 3); eluent: 5 mL of HNO$_3$ (4 M)

Samples	Concentration μg/L		Recovery %	Furnace-AAS
	Added	Found*		
Tap water	0	2.4 ± 0.1	98 ± 3.6	2.43
	5.0	7.3 ± 0.3		
River water	0	2.8 ± 0.1	97 ± 2.6	2.90
	5.0	7.6 ± 0.2		
Well water	0	2.0 ± 0.1	103 ± 4.0	1.95
	5.0	7.2 ± 0.3		
Spring water	0	3.2 ± 0.1	102 ± 2.4	3.18
	5.0	8.3 ± 0.2		

*Results are means of three independent measurements.

level examined. These results suggest a preferential uptake of lead (relative to the matrix cations) and that in the analysis of samples, the deposition efficiency would not be affected by the presence of high concentrations of matrix cations. Passing the solution through a strong anion exchanger before analysis eliminated interference from a high concentration of the matrix anions. Furthermore, although Hiraide *et al.* used dithizone immobilized on surfactant coated alumina to determine traces of copper in lead samples,[16] the results of this study indicate that by varying the effective factor on the deposition/elution stage the sorbent can be used effectively for separating traces of lead from different matrices.

Application. We have explored the feasibility of the methodology using preconcentration with dithizone immobilized on surfactant for the determination of lead in different matrices. The procedure was applied to the determination of lead in different samples, including tap water, well water, spring water and river water. Reliability was checked by spiking experiments and independent analysis by furnace atomic absorption. The results are presented in Table 2: The recovery of spiked samples is satisfactory, and agreement between the two set of data is good, which indicate the capability of the system in the determination of lead for most

Table 3. Determination of lead in different samples; solution pH 3; eluent 5 mL of HNO$_3$ (4 M)

Samples	Concentration μg/g		Recovery %	Furnace-AAS
	Added	Found*		
Beat leaves	0	9.7 ± 0.4	95 ± 3.6	9.67
	10	19.2 ± 0.7		
Parsley	0	5.1 ± 0.3	98 ± 3.4	5.05
	10	14.9 ± 0.5		
Leek leaves	0	8.9 ± 0.4	98 ± 3.2	9.01
	10	18.7 ± 0.6		
Whole nonhomogenized pasteurized milk	0	6.4 ± 0.2	98 ± 2.7	6.46
	5.0	11.3 ± 0.3		
Whole homogenized pasteurized milk	0	5.9 ± 0.1	96 ± 1.9	5.95
	5.0	10.7 ± 0.2		
Whole unpasteurized milk	0	5.2 ± 0.2	96 ± 3.0	5.45
	5.0	10.0 ± 0.3		

*Results are means of three independent measurements.

water samples.

The results for the determination of lead in vegetable and milk samples are shown in Table 3, and comparative data obtained by furnace atomic absorption are also presented. As the results show, the recovery of spiked samples was very good, and agreement between the two sets of data is good; which indicates that the system is reliable for the analysis of lead in different matrices.

Conclusion

It has been demonstrated that dithizone immobilized on surfactant coated alumina can absorb lead, and the method can be used for the separation and determination of lead in different matrices. Furthermore as present results for the determination of lead in water, detection limit, and precision of the method satisfy the regulatory limits of the EC, the technique employed would be useful for the determination below the EC, set level for lead in water intended for human consumption. Future work will be directed at environmental samples and assessment of the multielement enrichment capability of dithizone immobilized on surfactant coated alumina.

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