

# **Solid Phase Extraction for Evaluation of Occupational Exposure to Pb (II) Using XAD-4 Sorbent Prior to Atomic Absorption Spectroscopy**

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*Lead is an important constituent widely used in different industrial processes. For evaluation of workers' exposure to trace toxic metal of Pb (II), solid-phase extraction (SPE) was optimized. SPE using mini columns filled with XAD-4 resin was developed with regard to sample pH, ligand concentration, loading flow rate, elution solvent, sample volume, elution volume, the amount of resins, and sample matrix interferences. Lead ions were retained on a solid sorbent and then eluted, followed by a simple determination of analytes with flame atomic absorption spectrometry. The obtained recoveries of metal ions were greater than 92%. This method was validated with 3 different pools of spiked urine samples; it showed a good reproducibility over 6 consecutive days as well as 6 within-day experiments. This optimized method can be considered successful in simplifying sample preparation for a trace residue analysis of lead in different matrices when evaluating occupational and environmental exposures is required.*

lead    sample preparation    atomic absorption spectroscopy

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## 1. INTRODUCTION

Heavy metals can be considered as a unique class of environmental toxicants. They occur and persist in nature; most of them are advantageous to humans because of their vast usage in different industries, agriculture, and medicine. However, they may pose health hazards to the public because of their presence in the air, water, and food chains. They are also dangerous for workers engaged in mining, smelting, alloys, painting, electroplating, the use of pesticides, and a variety of other industrial activities. Some heavy metals such as lead have a wide range of toxicity, leading to toxic effects on the renal, respiratory, and nervous systems. Some symptoms of lead poisoning are weakness, weight loss, insomnia, neuromuscular dysfunction, colic, and hypochromic anemia. Nephropathy has been associated with chronic lead poisoning. Mild neurophysiological changes including reductions in motor and sensory nerve conduction velocities have been documented in lead-exposed workers [1, 2, 3].

Because the use of this heavy metal is unavoidable, from occupational viewpoints studying this compound can be of great interest. One of the most important aspects of metal studies is determination of such compounds in different matrices. In biological and environmental samples, either exposed compounds or their metabolites, metals are mostly present at trace level, causing major problems at the stage of their determination [4, 5, 6]. Therefore, an essential need for precise, reliable, and sensitive techniques for the analysis of such trace chemicals has been clearly recognized [6, 7, 8, 9].

Although the use of a detection system has improved the selectivity of the analytical procedures, these sensitive, selective methods require expensive equipment; moreover, they may not be available in all laboratories. Consequently, sample preparation procedures which can be performed in any laboratory have been developed to simplify analytical approaches as these reduce expenses too [7, 9, 10, 11]. For this purpose, to extract heavy metals many sample preparation procedures are being used such as Soxhlet

extraction [12], liquid liquid extraction (LLE) [13, 14, 15], supercritical fluid extraction (SFE) [16], and solid phase extraction (SPE) [17, 18, 19, 20]. Of these, Soxhlet and LLE are time-consuming procedures and also the recoveries obtained from such methods are not reproducible and efficient. Therefore, more sensitive and precise methods are required to measure trace heavy metals in biological and environmental samples. In contrast, SPE methods using silica have proven useful in simplifying sample preparation prior to using an analytical technique. This method refers to the adsorption of a chemical constituent from a liquid sample (water, urine, etc.) on a solid sorbent and subsequent desorption of the retained constituent by elution from the sorbent. Through this procedure, isolation and purification of the compound of interest can be achieved in a short time and only low volumes of solvents are used during the application of the method. The use of commercially available low-cost vacuum allows many samples to be processed at the same time. Furthermore, complete automation of procedures based on SPE is now possible using commercially available instrumentation [21, 22, 23, 24, 25, 26]. A wide range of phases based on silicas are also available from many suppliers, including reversed phase, normal phase, ion exchange, and mixed mode phases. These phases can be screened and selected, depending on the chemical nature of the analyte [27]. Therefore, the variety of available phases can improve the selectivity of the sample preparation procedures.

This study aimed to achieve optimum factors necessary for the development of an optimized procedure for Pb (II) present in water and urine samples, leading to a simple protocol of the SPE method.

## 2. MATERIAL AND METHODS

### 2.1. Reagents and Chemicals

All solutions were prepared using distilled water. A lead stock solution was prepared from an appropriate amount of the nitrate salt of this analyte (Merck, Germany) as a 1 000 mg/L

solution in 0.01M HNO<sub>3</sub>. Working and standard solutions were prepared daily by diluting the stock solution. Acids and other chemicals used in this study were obtained from Merck. Standard buffered solutions (di-sodium hydrogen phosphate/potassium di-hydrogen phosphate) at various pH values, APDC, and amberlite XAD-4 resin (20–40 mesh) were also purchased from Merck.

## 2.2. Apparatus

Determination of lead was made with spectra AA/plus 20, a Varian flame atomic absorption spectrometer (FAAS; Varian, Australia), using an air-acetylene flame at a wavelength of 217 nm. Other operating parameters for the metal of interest were set as recommended by the manufacturer. The pH values of the solutions were measured with a Metrohm 744 digital pH meter (Metrohm, Switzerland). The amount of reagents was measured using a Satorius CP225D balance (Sartorius, Germany).

## 2.3. Preparation of Mini Columns

Glass mini columns (100 × 10 mm) were packed with 500 mg of resin. After packing, a small amount of glass wool was placed at both ends of the glass tube. Before using the column, XAD-4 resin was washed in turn in methanol, water, 1M HNO<sub>3</sub>, water, 1M NaOH, and water. Finally, resin was preconditioned with a buffer solution.

## 2.4. Preconcentration Procedure

In this study, SPE using amberlite XAD-4 resin was optimized with regard to sample pH, sample and eluent flow rates, elution solvent, eluent

volume, ligand concentration, the amount of resin, and sample volume. Fifty milliliters of the solution containing 20 µg of Pb (II), 10 ml of the buffer solution with desired pH, and 6 ml of an ammonium pirrolidine dithio carbamate (APDC) solution were prepared. Samples were then passed through the column packed in our laboratory at a flow rate of 5 ml/min. The column was then washed with 5–10 ml of the same buffer solution. Therefore, metal ions were eluted from the mini column with 10–15 ml of different solvents. Finally, the concentration of lead in the solution was determined with FAAS.

## 3. RESULTS

### 3.1. Sample pH

The influence of sample pH on the adsorption of Pb (II) ions on XAD-4 resin was investigated, using pH values of 2, 4, 7, and 9. The pH values were adjusted with a buffer solution. A 50-ml sample containing 20 µg of Pb (II) and 6 ml of an APDC solution was loaded on the column. The column was then washed and the retained analyte was eluted using 2M HNO<sub>3</sub>. Table 1 shows the influence of sample pH on the extraction recovery for Pb (II). Finally, sample pH of 9 was selected as an optimum value for further experiments.

### 3.2. APDC Concentration

The concentration of APDC is an important parameter that could affect the recovery obtained with the optimized method. Throughout this investigation, the amount of 0.01–0.07% (w/v) of APDC was used. The results obtained from

**TABLE 1. Effect of Sample pH, Ligand Concentration, Eluent Type, and Eluent Volume on Recovery of Pb (II) From XAD-4 Resin (Eluent: 2M HNO<sub>3</sub>)**

Sample pH	Ligand			Eluent Type	Eluent		
	<i>M</i> ± <i>SD</i> (%) ( <i>N</i> = 5)	Concentration (%) (w/v)	<i>M</i> ± <i>SD</i> (%) ( <i>N</i> = 5)		<i>M</i> ± <i>SD</i> (%) ( <i>N</i> = 5)	Volume (ml)	<i>M</i> ± <i>SD</i> (%) ( <i>N</i> = 5)
				1M HCl	18 ± 4.47		
2	72 ± 8.36	0.01	42 ± 4.47	acetone	12 ± 4.47	5	12.00 ± 1.76
4	78 ± 4.47	0.03	56 ± 5.47	(HNO <sub>3</sub> in acetone)	92 ± 4.47	10	62.00 ± 7.58
7	94 ± 5.47	0.05	98 ± 4.47	1M HNO <sub>3</sub>	96 ± 5.47	15	95.38 ± 4.21
9	98 ± 4.47	0.07	94 ± 5.47	2M HNO <sub>3</sub>	98 ± 4.47	20	98.00 ± 5.47

this investigation showed that by increasing APDC concentration up to 0.05% the recoveries also increased; afterward, constant values were recovered.

### 3.3. Eluent Type

Evaluation of eluent strength on recovery of Pb (II) was another experiment performed during this study. Five solvents were screened for their ability to produce optimum elution of the retained Pb (II) from XAD-4 resin. They were 1M HCl, acetone, 1M HNO<sub>3</sub> in acetone, 1M HNO<sub>3</sub>, and 2M HNO<sub>3</sub>. The same sequence of conditioning, washing, and elution was used as in the previous section. The results are presented in Table 1. A quantitative recovery (>95%) was obtained for Pb (II) ions, using 2M HNO<sub>3</sub> as an efficient eluent; therefore, it was used as a suitable solvent for further studies.

### 3.4. Eluent Volume

Eluent volume is an influencing parameter, affecting the preconcentration of the analytes using SPE. Enrichment of the analyte in SPE is achieved by applying a large volume of the sample and eluting the analyte in a minimal volume of the eluent. The volume of the eluent must be just sufficient to elute the compound of interest from the sorbent. Thus, the recovery of metal ions was studied in applying eluent volumes of 5, 10, 15, and 20 ml. The results are given in Table 1. The volumes of 15 and 20 ml provided efficient recovery for the analyte of interest. In order to obtain a confident concentration factor, the smallest satisfactory volume (15 ml) was chosen for the next experiments.

### 3.5. Eluent Flow Rate

In order to evaluate the influence of the eluent flow rate on the recovery of the analytes, the retained metal ions were eluted using the eluent at flow rates of 2, 5, 7, and 10 ml/min. The same sequence of conditioning, washing, and elution were used as described in the previous section. As Table 2 shows, the metal of interest was quantitatively recovered at an eluent flow rate of up to 7 ml/min. A flow rate of 5 ml/min was then selected as an optimum value for the next experiments.

### 3.6. Sample Volume

In order to evaluate sample volume, 20 µg of Pb (II) were diluted into volumes of 50, 150, 250, 500, and 750 ml. These samples were loaded on XAD-4 mini columns. The columns were then washed and the retained analyte was eluted according to the optimized method. The results are shown in Table 2. It can be seen that up to 500 ml of samples could be applied without a significant loss of recovery (94%). Therefore, the highest concentration factor was 33.3 when the final volume was 15 ml.

### 3.7. Sample Flow Rate

Following a demonstration of the feasibility of using large sample volumes, the effect of a sample flow rate on metal ion adsorption on XAD-4 was studied at sample flow rates of 2, 5, 7, and 9 ml/min. A 50-ml sample, using optimum pH, containing 20 µg of metal ions and an APDC solution was prepared. Thereafter, the same sequence of conditioning, washing, and elution was used as in the previous section. No significant reduction in recovery was found for a sample flow rate of up to 9 ml/min. A flow rate of

**TABLE 2. Effect of Eluent Flow Rate, Sample Volume, Sample Flow Rate, and Sorbent Mass on Recovery of Pb (II) From XAD-4 resin (Eluent: 2M HNO<sub>3</sub>)**

Eluent Flow Rate (ml/min)	$M \pm SD$ (%) (N = 5)	Sample Volume (ml)	$M \pm SD$ (%) (N = 5)	Sample Flow Rate (ml/min)	$M \pm SD$ (%) (N = 5)	Sorbent Mass (mg)	$M \pm SD$ (%) (N = 5)
		50	100 ± 0.00				
2	100 ± 0.00	150	98 ± 4.47	2	96 ± 5.47	100	66±5.47
5	98 ± 8.36	250	96 ± 5.47	5	98 ± 4.47		
7	96 ± 5.47	500	94 ± 5.47	7	96 ± 5.47	500	98±4.47
10	92 ± 4.47	750	48 ± 4.47	9	90 ± 0.00		

5 ml/min as an appropriate value was then used to continue further experiments. Table 2 shows the results obtained in this experiment.

### 3.8. XAD-4 Sorbent Mass

The effect of the amount of XAD-4 was investigated, using 100 and 500 mg of the sorbent packed in a mini column. The same preparation procedure was used as in the previous section. The obtained recovery of metal ions was most efficient when 500 mg were utilized (Table 2).

### 3.9. Matrix

The effect of various matrix ions mostly present in environmental and biological samples, including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$ , was another parameter, influencing the efficiencies of analyte recoveries. The procedure was performed using a 50-ml sample containing 20  $\mu\text{g}$  of the analyte and a different concentration of matrix ions. The results are in Table 3.

**TABLE 3. Effect of Matrix Ions on the Adsorption of Pb (II) on XAD-4 Resin (Eluent: 2M  $\text{HNO}_3$ )**

Ions (Added)	Concentration (g/L)	Recovery (%)
		$M \pm SD (N = 5)$
$\text{Na}^+(\text{NaCl})$	2.5	$98 \pm 4.47$
	10	$100 \pm 5.47$
	20	$94 \pm 4.47$
$\text{K}^+(\text{KCl})$	0.3	$100 \pm 0.00$
	0.5	$100 \pm 4.47$
	1	$94 \pm 4.47$
$\text{Mg}^{2+}(\text{MgCl}_2)$	0.3	$102 \pm 5.47$
	0.5	$100 \pm 5.47$
	1	$96 \pm 4.47$
$\text{Ca}^{2+}(\text{CaCl}_2)$	0.3	$98 \pm 4.47$
	0.5	$98 \pm 4.47$
	1	$94 \pm 4.47$
$\text{SO}_4^{2-} [(\text{NH}_4)_2\text{SO}_4]$	0.5	$98 \pm 4.57$
	1	$94 \pm 5.47$
	1.5	$94 \pm 4.47$

**TABLE 4. Day-to-Day (D-day) and Within Day (W-day) Reproducibility of Pb (II) Spiked in Urine, Sample Volume: 50 ml ( $N = 6$ )**

Statistical Data	Concentration Added ( $\mu\text{g/ml}$ )					
	1		1.5		2	
	D-Day	W-Day	D-Day	W-Day	D-Day	W-Day
$M$	0.980	0.986	1.450	1.440	1.940	1.940
$SD$	2.530	1.320	0.983	0.983	1.602	1.640
$CV\%$	2.580	1.340	1.010	0.990	1.640	1.690

Notes.  $CV\%$ —coefficient of variation.

### 3.10. Reproducibility

A preliminary validation of the possible use of the optimized method for measuring metal ions of Pb (II) in urine was carried out using spiked samples. As spiked urine may contain some interference compounds similar to the real sample, it can be considered as an appropriate sample, better than water, for validation of the optimized method. Therefore, further experiments were carried out on urine; however, the working samples were made in an aquatic solution. Samples of 50 ml were used for extraction with subsequent FAAS. Linear standard curves (extracted) over the concentration range of 1, 1.5, and 2  $\mu\text{g/ml}$  were obtained each day ( $n = 6$ ) for 6 consecutive days with a correlation coefficient of .993 or greater. The day-to-day (for 6 consecutive days) and within-day reproducibility of the method was investigated. Table 4 shows the results obtained in this experiment.

## 4. DISCUSSION

The results showed that an efficient recovery was obtained from XAD-4 resin using sample pH of 9. For Pb (II), the amount of the analyte recovered from the sorbent at a sample pH value of 7 was also efficient. However, the pH value of the sample should be adjusted according to the chemistry of the compound of interest. It seems that at sample pH of 9 the analyte of interest is mostly in an ionized form, making it easily retained on the ionized ligand already conjugated to the sorbents. From these pH values, sample pH of 9 was selected for further study as this pH seemed to be a rather confident value.

In this study, a nonpolar sorbent was used, in which there was no affinity between this type

of sorbent and the ionized analyte, so there was a need of conjugating the ionized ligand on the sorbents to follow up the ionized extraction mechanism. APDC showed to be an appropriate ligand for capturing Pb (II) from the sample; however, from the four concentrations of the ligand, the amounts of 0.05 and 0.07 (%) showed to be good enough for an efficient retaining of the analyte. However, to prevent saturation of the sorbent with the ligand and also to reduce the reagents through the extraction process, a lower percentage of the ligand (0.05%) was used as this amount provided the same recovery required for the method.

Understanding the chemistry of the compound under analysis, such as ionizability and hydrophobicity, can be useful in designing appropriate conditions for obtaining an efficient extraction recovery. Highly ionic compounds can result in a strongly retained analyte making elution difficult and leading to subsequent poor recovery from an ionic conjugated sorbent. From the eluents used in this study, the HNO<sub>3</sub>-based solutions were more efficient (Table 1). From these solvents 2M HNO<sub>3</sub> was selected, because it is an organic free eluent and it can prevent coelution of organic compounds possibly present in real samples. It can also reduce exposure to such evaporative and hazardous compounds. Moreover, maximum recovery was achieved using this eluent.

The results obtained from an evaluation of the elution volume (Table 1) showed that the smallest satisfactory volume for 2M HNO<sub>3</sub> from the XAD-4 sorbent was 15 ml. As a consequence, the volume required to elute the analyte from the sorbent, depends on two important parameters. Firstly, the strength of its retention; a solvent with greater elution strength can be used to elute an analyte in a lower volume, but it may incorporate undesirable contaminants into the eluted fractions. Secondly, the cartridge containing more sorbent mass requires a greater volume of the eluent for extracting the compound of interest. Table 1 shows that the lowest satisfactory eluent volume is 15 ml, giving a suitable concentration factor of 33.3. Using this volume, an efficient recovery of 95.38% can be achieved.

Although a low volume of the eluent helped to achieve an appropriate concentration factor, a faster elution of 15 ml of the eluent by itself can affect the whole analysis time when numerous samples are applied. Therefore, throughout this experiment, the reduced eluent flow rate of 5 ml/min was enough to reduce the elution time to one third.

The experiment on the sample volume made an accurate measurement as low as 0.04 µg/ml (0.04 ppm) of lead possible, when a large sample volume (500 ml) was applied on the column, resulting in a possible trace enrichment of the analyte with an appropriate concentration factor of 33.3, which was compatible with the current atomic absorption spectroscopy detection system.

As a high volume of the sample was applicable with an efficient recovery, it would be good if a high sample flow rate could be applied. In this study a sample flow rate of up to 9 ml/min was applied with an acceptable recovery of 90% or more (Table 2). Therefore, to be confident, a sample flow rate of 5 ml/min was selected, providing a reduced extraction time for as large as a 500-ml sample volume. However, as the results show, it would be possible to increase the sample flow rate by even more than 9 ml without significant loss in the analyte recovery.

Regarding the sorbent mass, 100 mg of the sorbent was not enough for retention of lead; therefore, unretained lead was passed through the sorbent when the sample solution was applied. Consequently, a nonefficient amount of retained lead (66%) was recovered, which was not acceptable in our optimized method. Using a sorbent mass as large as 500 mg, made it possible for a longer interaction to take place, causing retention of a significant amount of lead on the sorbent and a subsequent efficient recovery of 98%. However, using a large amount of the sorbent mass requires a large volume of a washing solvent and eluent to be applied for the efficient removal of possible interferences.

In order to show the effect of possible matrix components on the optimized method, similar ions, illustrated in Table 3, with three different concentrations were added to the sample. The ions added to the sample are mostly present in real

environmental samples and can be used as closely related interferences present in matrices. The results clearly showed the noneffectiveness of all of the added components for each concentration on the recoveries obtained from the optimized method. As it can be seen, the recoveries were 94% or greater which is promising: either there had been no cross-reactivity between the added interferences and the XAD-4, or no coelution had taken place.

Finally, in order to validate the method, reproducibility of the optimized method was performed for day-to-day and within-day experiments. A linear standard curve (for an extracted sample) over the range concentrations of 1, 1.5, and 2  $\mu\text{g/ml}$  was obtained every day for 6 consecutive days ( $n = 6$ ) with the correlation coefficient of .993 or greater. In within-day experiments, six experiments were performed per day for 3 consecutive days. The extraction procedure was reliable and reproducible from day-to-day and within-day. Coefficients of variation (CV%) of 2.58, 1.01, and 1.64 were obtained for 1, 1.5, and 2  $\mu\text{g/ml}$  respectively for day-to-day, and 1.34, 0.99, and 1.69 at the same concentrations respectively for within-day, showing suitable accuracy and precision (Table 4).

On the other hand, the method recently reported [15] used LLE for some heavy metals. Although the technique may be useful in some conditions, there are still no basic rules for selecting a solvent system for extraction of a given analyte; therefore, selection of a solvent is still an empirical and of course time-consuming as well as tedious step. Sometimes, emulsion formation of the sample makes analyte extraction too hard as such solutions are extremely difficult to break and often cannot be isolated by either centrifugation or ultrasonication. Other problems associated with LLE include the use of large volumes of toxic and sometimes inflammable solvents, contamination of extracts from solvents and glassware, low recovery due to degradation by heat, and volatilization or adsorption to glassware. Therefore, nowadays, there is a strong tendency towards replacing LLE with SPE. Based on reported methods [20, 22, 23, 24, 26] for optimizing SPE, authors have generally used

five to six factors to optimize the method, while, in this study, nine parameters were screened, including significant factors of sorbent mass, eluent flow rate, sample matrix interferences, and ligand concentrations. This makes it possible to introduce a robust and a more reliable method. Moreover, to use the advantage this study has over other studies [18, 19, 20, 21, 22, 23, 24], further experiments of the reproducibility of the method were carried out on spiked urine samples. This was to validate the possible use of optimized SPE for measuring Pb (II) when an environmental study and biological monitoring of a worker exposed to such a pollutant were required. Although the concentration factor obtained from this study is high, the relatively low sensitivity of atomic absorption spectroscopy did not allow the authors to get an even greater concentration factor.

## 5. CONCLUSION

Through this study factors influencing SPE were optimized, showing an efficient sample preparation procedure for Pb (II) as a solid phase extraction method with more advantages than LLE. Depending on the chemical and physical properties of the analyte, manipulating factors including sample pH, ligand concentration (APDC), loading flow rate, elution solvent, sample volume (up to 500 ml), elution volume, amount of resin (XAD-4), and sample matrix interferences can play essential roles in optimizing the method, providing a reliable, easy-to-use, and cost-effective procedure to overcome difficulties associated with other sample preparation techniques. The concentration factor was 33.3 and resin could be used several times. The optimized method can be used for preconcentration of other metal ions when analysis of trace heavy metals in biological and environmental samples is of interest. The authors are sure that SPE is a highly fertile area for sample preparation and based on the needs and facilities, these method protocols can be further developed in the near future.

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