



## Study of matrix effects and spectral interferences in the determination of lead in sediments, sludges and soils by SR-ETAAS using slurry sampling

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### ABSTRACT

An interference-free, fast, and simple method is proposed for Pb determination in environmental solid samples combining slurry sampling and electrothermal atomic absorption spectrometry. Samples were ground to an adequate particle size and slurries were prepared by weighing from 0.05 g to 0.20 g of dry sediment, adding nitric acid, and a solution containing 0.1% Triton X-100. Ultrasonic agitation was employed for slurries homogenization. Analytical variables including acid pre-treatment conditions, particle size, slurry stability, temperature program of the graphite furnace, and type and concentration of the chemical modifier were studied. The undesirable effects of potential non-specific and spectral interferences on Pb signal were also taken into account. Continuum source and self-reversal methods for background correction were evaluated and compared. For calibration, synthetic acid solutions of Pb were employed. Calibration was linear within the range 1–30  $\mu\text{g L}^{-1}$  and 5–30  $\mu\text{g L}^{-1}$  when the 217.0 nm and 283.3 nm analytical lines were used. Correlation coefficients of 0.9992 and 0.9997 were obtained. Using optimized conditions, limits of detection ( $3\sigma$ ) of 0.025  $\mu\text{g g}^{-1}$  and 0.1  $\mu\text{g g}^{-1}$  were achieved for the 217.0 nm and 283.3 nm analytical lines, respectively. The method was successfully applied to the determination of lead in soil, contaminated soil, municipal sludge, and sediment samples. The accuracy was assessed by the analysis of two certified reference materials: municipal sludge (QC MUNICIPAL SLUDGE A) and lake sediment (TRAP-LRM from IJS).

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### 1. Introduction

Trace elements, especially heavy metals, are considered to be one of the main sources of pollution into the environment since they have a significant effect on its ecological quality. High levels of heavy metals in environmental samples like sediments, sludges, soils, and through transfer processes in groundwater and plants, possess a potential risk for animals and human health [1]. Lead is a non-essential element with a widespread distribution into the environment. As a consequence of a variety of industrial applications of this metal there is a health risk for plants, animals, and humans due to the element's potential toxicity [2]. This has led to a need for suitable analytical tools for the reliable determination of Pb in different matrices.

Electrothermal atomic absorption spectrometry (ETAAS) is one of the most reliable and powerful analytical techniques for the determination of trace elements in environmental and biological samples. It offers good sensitivity and requires low sample volume

(2–100  $\mu\text{L}$ ) [3–6]. When Pb is determined by ETAAS, the 217.0 nm line is noticeably more sensitive than the 283.3 nm line; however, more background absorption effects occur at the 217.0 nm line [7]. The extent of these interferences obviously depends on the effectiveness of the pyrolysis stage and the use of chemical or matrix modification. Nevertheless, the application of a background corrector is mandatory in ETAAS, even for relatively “simple” matrices. In this context, the method reported by Smith and Hieftje (self-reversal method) has been recommended by different authors [8,9].

There are a variety of methods reported in the literature for Pb determination in environmental samples. Many of them use matrix separation to avoid interferences or to enhance sensitivity. However, potential risks of contamination or analyte losses may be expected [2,7,8,10–14]. On the other hand, procedures of mineralization and dissolution of solid environmental samples like soils, sediments, and sludges are prone to sample contamination. Besides these approaches are time consuming even when assisted by microwaves.

In this regard, slurry sampling (SS) has emerged as a reliable technique for trace metals determination by ETAAS. In general, the use of slurry sampling is faster and less subject to contamination or analyte losses. Pulverized solid samples are suspended in an acidic

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solution and subsequently sonicated. In order to assure that the slurry is homogeneous and stable, different dispersing agents such as glycerol or non-ionic surfactants are added [7,15,16].

However, the analysis of solid samples by slurry sampling-electrothermal atomic absorption spectrometry (SS-ETAAS) may imply spectral and chemical interferences caused by the large amount of concomitants introduced into the graphite furnace. In some circumstances they cannot be overcome even when using stabilized temperature platform furnace (STPF) conditions or typical approaches such as a previous sample ashing or the use of chemical modifiers [17].

In this work, the development of a robust analytical method for Pb determination in sediment, sludge, and soil samples by slurry sampling associated to ETAAS is presented. Two configurations for background correction namely, self-reversal (SR) and continuum source (CS) using the 283.3 nm and 217.0 nm analytical lines are evaluated. A systematic study is accomplished aiming to handle matrix effects and spectral interferences in order to reach accurate results. Despite the complexity of the samples analyzed, aqueous standards were successfully employed for calibration.

## 2. Experimental

### 2.1. Standards and reagents

All solutions were prepared with ultrapure water (18 M $\Omega$  cm) obtained from a Milli-Q, EASY pure RF (Barnsted, IA, USA). All glasses and other lab materials were cleaned by soaking in 10% HNO<sub>3</sub> (Fluka, Germany) and rinsing with ultrapure water. Synthetic standard stock solutions (1000 mg L<sup>-1</sup>) of Pb were from Fluka (Switzerland). Calibration standard solutions were prepared by step-wise dilutions of the stock solution in ultrapure water and acidified with nitric acid.

A Pd–Mg mixture (500  $\mu$ g g<sup>-1</sup>) was employed as chemical matrix modifier for Pb determination by ETAAS. The Pd–Mg solution was prepared by mixing stock standard nitrate solutions of the elements in a high purity nitric acid solution.

The non-ionic surfactant, Triton X-100, was obtained from Tokyo Kasei Industries (Chuo-Ku, Tokyo, Japan).

### 2.2. Instrumentation

Measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a GFA-EX7 electrothermal atomizer and an ASC-6100 autosampler. Pyrolytic graphite coated tubes with pyrolytic L'vov platforms from Shimadzu (Tokyo, Japan) were used throughout this work. A Pb high-intensity boosted discharge hollow-cathode lamp from Hamamatsu, Photonics (K.K., Japan) was used as the spectral radiation source. It uses the existing lamp current of 10 mA, but applies a second discharge at 300 mA within the lamp to increase the emission intensity. A conventional hollow-cathode lamp from Hamamatsu, Photonics (K.K., Japan) was also used and operated at 10 mA. The 217.0 nm and 283.3 nm analytical lines were used with 1.0 nm and 0.5 nm spectral bandpass, respectively. The continuum source background corrector was equipped with a deuterium lamp from Hamamatsu, Photonics (K.K., Japan). Argon was used as protective gas throughout.

An ultrasonic bath from Astrason Ultrasonic Clear, Farmingdale (NY, USA) was employed for preparing the slurries.

### 2.3. Sampling and pre-treatment procedure

Soil samples were collected from the surroundings of an energy plant that produces natural gas, petroleum, propane gas, gasoline, and diesel in an area located at 30 km southeast of the town of Colonia 25 de Mayo in the province of La Pampa, Argentina. The plant

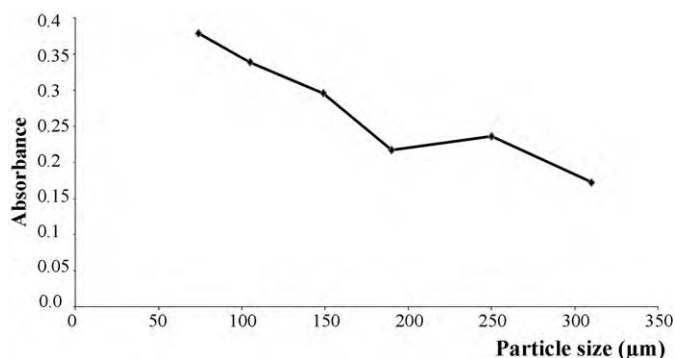


Fig. 1. Effect of particle size on Pb analytical response.

covers a total area of 834.36 km<sup>2</sup>. While Sample I and Sample II were taken from a potential contaminated area, Sample III was taken from a clean area. All samples were collected into polyethylene bags and stored in a dark, dry place. Before analysis, soil samples were grounded in a hand mortar and sieved to different mesh sizes.

A certified reference material, municipal sludge (QC MUNICIPAL SLUDGE A), and a reference sample, lake sediment (TRAP-LRM from IJS), were employed in method validation.

### 2.4. Slurries preparation

The mass of the weighed portion of the sample depends on the total content of Pb in it. Screening experiments showed that for slurry preparation aliquots from 50 mg to 200 mg were adequate for Pb determination. Samples were placed into 50 mL polyethylene vessels, and then a desired volume of concentrated HNO<sub>3</sub> and 0.1% of Triton X-100 were added. The mixtures were diluted to 50 mL with ultrapure water and placed into an ultrasonic bath for 30 min.

## 3. Results and discussion

### 3.1. Effect of particle size

Particle size is a mandatory variable to optimize owing to its influence on slurry stability, homogeneity, and measurement precision. Samples with different particle sizes; e.g. >250  $\mu$ m, 249–210  $\mu$ m, 209–150  $\mu$ m, 149–106  $\mu$ m, 105–75  $\mu$ m, and <74  $\mu$ m were used to prepare the slurries. It can be seen from Fig. 1 that smaller particle sizes improved the final result. This may be due to the fact that (1) larger particles may vaporize very slowly in the graphite furnace resulting in incomplete atomization of the analyte, and (2) these particles may be less efficiently pipetted from the stirred slurry as they are less likely to be held in a homogeneous suspension compared with smaller particles.

In order to evaluate the effect of particle sizes on slurries stability, different samples of diverse sizes were analyzed. From Fig. 2a and b, it can be inferred that the stability (repeatability) throughout the time was better when smaller particles were used.

In summary, it could be concluded that samples with sizes smaller than 74  $\mu$ m assured the better precision and trueness of the final results.

### 3.2. Effect of the nitric acid

Precision depends on sample homogeneity and analyte distribution between the liquid and the solid phase. Analyte extraction is facilitated by adding acid diluents and, in combination with the ultrasonic action; the solid particles become more flocculent helping the extraction process. Among the acids employed as diluents, HNO<sub>3</sub> showed an enhanced performance due to its oxidant properties.

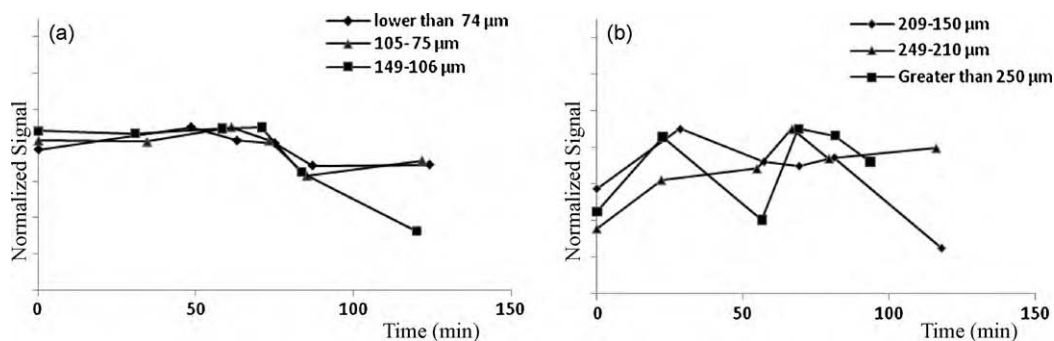


Fig. 2. Effect of particle size on slurries stability. Different samples of diverse particle size were analyzed in time. (a) >250  $\mu\text{m}$ , 249–210  $\mu\text{m}$ , 209–150  $\mu\text{m}$ ; (b) 149–106  $\mu\text{m}$ , 105–75  $\mu\text{m}$ , and <74  $\mu\text{m}$ .

In order to assure the homogeneity of slurries, the samples were previously ground to a particle size <74  $\mu\text{m}$ . In this study,  $\text{HNO}_3$  concentration was varied from 2.0 to 15.0% (v/v). When no evolution of fumes was observed, an aliquot of 50 mL solution containing 0.1% of Triton X-100 was added and the slurries were homogenized in an ultrasonic bath. From Fig. 3, it could be concluded that a 5.0% (v/v) acid concentration was at least necessary to reach the best analytical response. This acid concentration was close to that typically employed for slurry sampling in ETAAS [5].

### 3.3. Spectroscopic conditions

Lead determinations were carried out using alternatively two methods for background correction namely, continuum source (CS) and self-reversal (SR). In both cases, the slopes of the calibration curves as well as the dynamic calibration ranges obtained with the SR-method were slightly lower than those with the CS method. A reasonable explanation of these experimental observations is that this reduction in sensitivity and linearity occurred due to high stray light levels. This implies that the limiting absorbance values for the background measurements are smaller than those for the uncorrected signal. Thus, a small deep in the absorbance profile was obtained, inducing a decrease in the slope of the calibration curve at high concentrations.

### 3.4. Temperature program

Problems related to Pb determination in samples of different compositions by ETAAS may appear due to its volatility. However, the application of L'vov platform and chemical modifiers can be

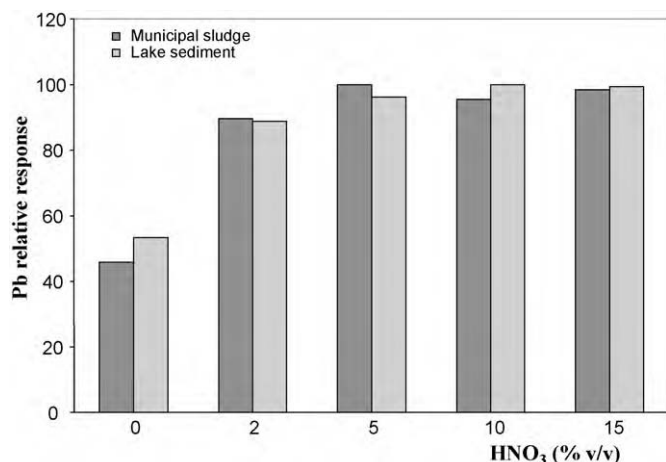


Fig. 3. Effect of added  $\text{HNO}_3$  on Pb signal.

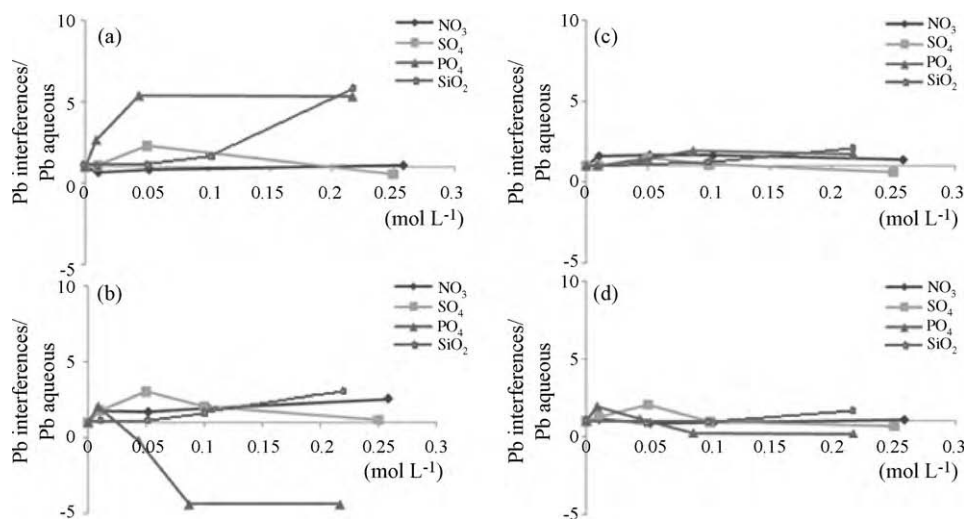
of some help to solve or minimize these difficulties. A systematic study was performed to optimize the temperature and time of the drying, pyrolysis, and atomization steps using Pd + Mg as chemical modifier. The conditions were optimized with samples prepared using the recommended procedure and compared with those obtained using aqueous standards of Pb. In all tests, drying was carried out in two stages (at 110  $^\circ\text{C}$  and 180  $^\circ\text{C}$ ) with the aim of achieving a complete removal of the liquid present in the sample. The use of these two drying steps helped to avoid some sputtering of sample.

Values of integrated absorbance were recorded between 300  $^\circ\text{C}$  and 1300  $^\circ\text{C}$  pyrolysis temperatures. The maximum temperature of pyrolysis without Pb loss was higher than 1100  $^\circ\text{C}$  in the slurries. This experimental observation demonstrated that a thermal stabilization of Pb occurred in the presence of Pd + Mg. Nevertheless, a temperature of 800  $^\circ\text{C}$  was selected for pyrolysis due to the fact that a similar behavior was observed for Pb when slurries and aqueous solutions were used at this temperature. The effect of the atomization temperature on Pb absorbance was studied in the range 1800–2600  $^\circ\text{C}$ . The optimum temperature of atomization in the presence of Pd + Mg modifier for Pb determination was 2200  $^\circ\text{C}$ . The same behavior was observed for the aqueous standards.

### 3.5. Spectral interferences

The most frequently background interferences caused in flames as well as in furnaces by the structured absorption of molecules are those originated by the pyrolysis products of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{SiO}_3^{2-}$  ions. Diatomic molecules such as NO, PO, SO, and SiO, show very sharp rotational structures in the ultraviolet region. It is very likely that a large number of these compounds can arise during the digestion of samples and during the sample pre-treatment (drying, ashing) in the furnace [18,19].

The effects of some anionic species ( $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{SiO}_3^{2-}$ ) were studied at the two analytical lines evaluated and with the two configurations selected for background correction. On the one hand, the effect of these species was firstly evaluated with the continuum source background corrector. While the presence of  $\text{NO}_3^-$  did not show a significant effect upon Pb absorbance at the two analytical lines, serious interferences were observed when  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{SiO}_3^{2-}$  ions were present. At the 283.3 nm line, Pb signal experienced a marked positive effect due to  $\text{PO}_4^{3-}$ . Lead signal showed a similar behavior in the presence of  $\text{SO}_4^{2-}$  or  $\text{SiO}_3^{2-}$ , though in a lower extent. Additionally, at the 217.0 nm line, Pb signal decreased to such an extent that it turned out to be negative, indicating an overcorrection due to the presence of  $\text{PO}_4^{3-}$ . The effect of  $\text{SO}_4^{2-}$  on Pb signal, when the 217.0 nm line was tested, showed the same tendency that was observed at 283.3 nm. The same trend was observed when  $\text{SiO}_3^{2-}$  was present (Fig. 4a and b).



**Fig. 4.** Effect of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SiO}_2$ , and  $\text{PO}_4^{3-}$  on Pb absorbance at both analytical lines. (a and b) At 283.3 nm and 217.0 nm, respectively, with continuum source background corrector; (c and d) at 283.3 nm and 217.0 nm, respectively, with the self-reversal background corrector.

**Table 1**

Determination of Pb in one certified, one reference, and three real samples.

Sample	Experimental values ( $\text{mg kg}^{-1}$ )	Confidence limits ( $\pm$ ) <sup>a</sup>	Certified values ( $\text{mg kg}^{-1}$ )	Confidence limits ( $\pm$ ) <sup>a</sup>
Municipal sludge	59.9	4.8	61	2.8
Lake sediment	1289	124.2	1373	38
Sample I <sup>b</sup>	88.2	2.1	–	–
Sample II <sup>b</sup>	44.9	3.7	–	–
Sample III <sup>c</sup>	30.2	4.1	–	–

<sup>a</sup>  $t_{95,2} \times \sigma / \sqrt{n}$ .

<sup>b</sup> Contaminated soils.

<sup>c</sup> Non-contaminated soil.

A further systematic study was undertaken, but employing the SR-corrector (Fig. 4c and d) this time. The outcome of those experiences indicated that those interfering effects that appeared as over- or under-corrected were reduced and even avoided when a boosted HCL was employed for self-reversal correction. The fact that the Pb signal was adequately corrected, even at high concentration of the interferences, was due to the SR-method was able to correct the background in the nearby of the analytical line, avoiding the effect of fine structured molecular bands.

### 3.6. Analytical performance

The figures of merit of the proposed method were evaluated at both analytical lines. The calibrations with aqueous standards covered a Pb concentration range from  $1 \mu\text{g L}^{-1}$  to  $30 \mu\text{g L}^{-1}$  for the 217.0 nm line and from  $5 \mu\text{g L}^{-1}$  to  $30 \mu\text{g L}^{-1}$  for the 283.3 nm line and were linear with correlation coefficients of 0.9992 and 0.9997, respectively. Following the  $3\sigma$  ( $n = 10$ ) criteria, the limits of detection were  $0.025 \mu\text{g g}^{-1}$  (217.0 nm) and  $0.1 \mu\text{g g}^{-1}$  (283.3 nm).

**Table 2**

Methods for Pb determination by slurry sampling associated to ETAAS.

Sample	Background correction	Limit of detection	RSD (%)	Reference
Biological and sediments	Z-ETAAS	$0.055 \mu\text{g g}^{-1}$	<7.7	[4]
Lake sediment	CS-ETAAS	$0.65 \mu\text{g g}^{-1}$	<5.5	[5]
Food	Z-ETAAS	$0.118 \mu\text{g L}^{-1}$	<10	[19]
Sediment	Z-ETAAS	$0.2 \mu\text{g g}^{-1}$	<8	[20]
Marine plankton	Z-ETAAS	$0.62 \mu\text{g L}^{-1}$	<10	[21]
Municipal sludge, lake sediment, and soils	SR-ETAAS	$0.025 \mu\text{g g}^{-1}$	<8.2	This work

Z-ETAAS, electrothermal atomic absorption spectrometry with Zeeman background corrector.

CS-ETAAS, electrothermal atomic absorption spectrometry with continuum source background corrector.

SR-ETAAS, electrothermal atomic absorption spectrometry with self-reversal background corrector.

Precision was evaluated as the relative standard deviation of five replicate determinations and, in all cases, was better than 8.2%.

While precisions and accuracies achieved with this method were comparable with those typically obtained in slurry sampling-ETAAS analysis even when the other approaches used the Zeeman background corrector; limits of detection were better than those previously reported (Table 2). Another feature of this method is that reliable results could be obtained in solid samples with different levels of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  or  $\text{SiO}_3^{2-}$ .

### 3.7. Application to real samples and validation

Lead was determined in soils with different characteristics following the proposed method (SS-SR-ETAAS). A certified reference municipal sludge (QC MUNICIPAL SLUDGE A) and a reference lake sediment (TRAP-LRM from IJS) were analyzed by using the recommended procedure to assess the accuracy. The average concentrations of Pb found in each sample as well as the certified values for this analyte are shown in Table 1. The results were compared

through a paired *t*-test and no significant differences were observed ( $n = 3$ ,  $p = 0.05$ ). In all cases the calibration was run against aqueous reference solutions.

#### 4. Conclusion

Lead could be determined in sediments, sludges, and soils with good accuracy using the proposed slurry sampling-ETAAS method. This procedure joined the excellent sensitivity attainable by ETAAS and the advantages of the slurry technique such as the reduction of reagent consumption and time of analysis. It was demonstrated that conventional background correction with a deuterium lamp led to serious errors. In contrast, interferences caused by structured background or absorption line overlapping were accurately compensated using the self-reversal method. Another feature of this method was that despite of the complexity of the samples analyzed, aqueous standards may be used for calibration showing that no matrix effects were observed after optimization. With minor modifications, this method may also be applied to other elements in these types of samples.

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