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# Determination of Pb in river water samples by inductively coupled plasma optical emission spectrometry after ultrasound-assisted co-precipitation with manganese dioxide☆

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**Abstract**

A simple and efficient procedure for separation and pre-concentration using ultrasound-assisted co-precipitation with manganese dioxide was developed for Pb determination by inductively coupled plasma optical emission spectrometry (ICP OES). The optimization process was carried out using a two-level factorial design and a Doehlert matrix. Three variables (i.e. concentration of oxidizing solution—$KMnO_4$, concentration of $MnSO_4$ solution and time of ultrasonic irradiation) were used as factors in the optimization. The recoveries, based on the analysis of spiked samples, were between 90% and 105%, and the precision was ≤5%. The detection limit and quantification limit for Pb determination were 3.2 and 10.7 μg $L^{-1}$, respectively. The proposed method was applied for the determination of Pb in water samples from a river heavily polluted by industrial effluents. The recovery measured by analyte addition technique showed that the proposed pre-concentration method had good accuracy.


*Keywords:* Lead; Co-precipitation; Ultrasonic irradiation; Pre-concentration

## 1. Introduction

Determination of Pb in environmental samples is a subject of considerable interest because its toxicity for humans is well-known, and it is a serious cumulative body poison. The main Pb sources for humans are food and water. Hence, rapid and sensitive methods must be accessible for Pb determination in natural water samples.

However, a major analytical difficulty in the determination of trace metals in natural waters is the pre-concentration step that is often required due to low environmental levels [1–3]. Various separation/pre-concentration procedures have been proposed to allow the quantification of trace metals in this kind of samples, including liquid–liquid extraction, ion exchange, solid phase extraction (SPE) and co-precipitation procedures [1,4–6].

Co-precipitation is one of the most efficient separation/enrichment techniques for trace heavy metal ions. The co-precipitation technique has several advantages: it is simple, several analyte ions can be pre-concentrated and separated from the matrix simultaneously and inorganic or organic co-precipitants can be used as efficient collectors of trace elements [7]. Manganese dioxide is a well-known good

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inorganic precipitant; freshly precipitated manganese dioxide has been used to pre-concentrate different metals. However, the process is slow and sometimes samples have to be kept overnight for complete co-precipitation [8].

Laboratories are using ultrasonic waves mainly for cleaning purposes. However, ultrasound has been employed for sample preparation in order to increase the interaction of solvent with the solid surface. The chemical effects induced by high power ultrasonic irradiation (>1 W $cm^{-2}$) in liquids can be explained by acoustic cavitation and mass transport processes [9]. The ultrasonic irradiation of a heterogeneous system increases the interaction between liquid and solid phases due to the disruption of solid particles, forced by the impact of solvent microjets, which propagated toward the solid (ca. 100 m $s^{-1}$), increasing the solid surface area and demanding solid agglomeration process [10].

In this work, a simple, rapid, and sensitive pre-concentration and separation method was developed for Pb determination in river water samples, using ultrasound-assisted co-precipitation with manganese dioxide with subsequent quantification of this element by inductively coupled plasma optical emission spectrometry (ICP OES). In the proposed method performed under ultrasonic field, the co-precipitation procedure employed manganese dioxide produced by the reaction between manganese sulfate and potassium permanganate, as collector. The optimization of experimental variables was carried out using two-level full factorial design and Doehlert matrix [11,12]. Three variables were regarded as factors in the optimization: concentration of oxidizing agent—$KMnO_4$, concentration of $MnSO_4$ and ultrasonic irradiation time.

## 2. Experimental

### 2.1. Apparatus

An Applied Research Laboratories model 3410 minitorch sequential inductively coupled plasma optical emission spectrometer (Valencia, USA), equipped with an IBM PC-AT computer (Armonk, USA) was used for Pb determination. The emission intensity measurements were made at 220.353 nm.

A Digimed DM-20 digital pH meter (S. Paulo, Brazil) was used to measure the pH values.

Table 1
Factors and levels used in factorial design

| Variables | (−) | Central point | (+) |
|---|---|---|---|
| Sonication time (s) | 60 | 210 | 360 |
| Concentration of $KMnO_4$ (mol $L^{-1}$) | $3.2\times10^{-4}$ | $8.0\times10^{-4}$ | $1.28\times10^{-3}$ |
| Concentration of $MnSO_4$ (mol $L^{-1}$) | $4.0\times10^{-4}$ | $6.6\times10^{-4}$ | $9.2\times10^{-4}$ |

Table 2
Factorial design and results of Pb recovery

| Experiment | $MnSO_4$ concentration | Irradiation time | $KMnO_4$ concentration | Pb recovery (%) |
|---|---|---|---|---|
| 1 | + | + | + | 74 |
| 2 | + | + | − | 107 |
| 3 | + | − | + | 52 |
| 4 | + | − | − | 101 |
| 5 | − | + | + | 62 |
| 6 | − | + | − | 106 |
| 7 | − | − | + | 67 |
| 8 | − | − | − | 110 |
| 9 | 0 | 0 | 0 | 89 |

A sonicator Aquasonic 75D (VWR, N. York, USA) was employed for ultrasound-assisted co-precipitation. The batch processes were carried out using a 400 mL borosilicate vessel covered with PVC film for irradiation.

### 2.2. Reagents and solutions

All reagents were of analytical grade unless otherwise stated. Ultrapure water from Milli-Q water purification system (Millipore, Bedford, USA) was used to prepare all solutions. The laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution. Before use, the glassware was washed with deionized water and dried in a dust-free environment.

The Pb stock solution was prepared from Merck reference solutions (Merck, Darmstadt, Germany) to a final concentration of 1000 μg $mL^{-1}$. The working solutions were obtained by dilution of the stock solution with deionized water, and the pH of the working solutions was adjusted to 3.0 with nitric acid.

The $KMnO_4$ and $MnSO_4$ solutions were prepared from the respective salts (Merck, Darmstadt, Germany).

### 2.3. Procedure

Surface water samples from a river heavily polluted by industrial effluents were collected in Subaé River, BA, Brazil, around the Santo Amaro municipality. The samples were filtered through a membrane of 0.45 μm pore size and stocked in polypropylene bottles. Aliquots of 200 mL of river water samples were acidified with concentrated $HNO_3$ to a pH of 3.0 and appropriate aliquots of $KMnO_4$ and $MnSO_4$ were added. The sample was exposed to ultrasonic irradiation for an appropriate time. The sonication process was always conducted in a central position above one of the piezoelectric ceramics of the ultrasonic bath. This way, the Pb(II) was quantitatively co-precipitated with the $MnO_2$ formed in the reaction. The precipitate was filtered through Whatman 541 filter paper and finally, the precipitate was dissolved with 7.0 mL of $HNO_3$ (6.0 mol $L^{-1}$) and 3.0 mL of $H_2O_2$ by rinsing the paper with these solutions. The concentration of Pb in the resulting clear solution was determined by ICP OES at 220.353 nm. Procedural blank solutions were prepared in a