

On-line preconcentration/determination of lead in *Ilex paraguariensis* samples (mate tea) using polyurethane foam as filter and USN-ICP-OES

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Abstract

The present paper proposes an on-line preconcentration procedure for lead determination in *Ilex paraguariensis* (St. Hilaire) samples by ultrasonic nebulization associated to inductively coupled plasma optical emission spectrometry (USN-ICP-OES). It is based on the precipitation of lead(II) ion on a minicolumn packed with polyurethane foam using 2-(5-bromo-2-pyridilazo)-5-diethylaminophenol (5-Br-PADAP) as precipitating reagent. The collected analyte precipitate was quantitatively eluted from the minicolumn with 20% (v/v) nitric acid. An enhancement factor of 225-fold was obtained (15 for USN and 15 for preconcentration). The detection limit (DL) value for the preconcentration of 10.0 ml of sample was 40.0 ng/l. The relative standard deviation (R.S.D.) was 3.0% for a Pb concentration of 1 µg/l, calculated from the peak heights obtained. The calibration graph using the preconcentration system for lead was linear with a correlation coefficient of 0.9997, at levels near the detection limits up to at least 100 µg/l. The preconcentration procedure was successfully applied to the determination of lead in mate tea samples.

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1. Introduction

For centuries, the dried leaves of a native South American arboreal crop, *Ilex paraguariensis* St. Hilaire (Aquifoliaceae), an evergreen holly, have been used to prepare mate, a stimulating and tonic beverage [1–3]. *Ilex paraguariensis* is either planted, or harvested from wild trees from the subtropical rainforests, at Brazil, Paraguay, Uruguay and Argentina. In this last country, the world's leading producer and consumer of mate, has been extensively planted since 1903, overcoming problems such as the natural low germination rates of its seeds.

The determination of heavy metals, especially some toxic metals which play important roles in biological mechanisms, has been receiving much attention. Even very low concentrations of some toxic metals can cause serious biological disorders that can lead to some serious diseases. It is well known that lead is a very abundant heavy metal; it represents a potential problem not only because of its widespread distribution throughout the environment, but also because of its toxicity. Lead enters the organism primarily via the alimentary and/or respiratory tract. The main sources of this metal intake are food, air and drinking water [4].

National and International regulations on food quality are lowering the maximum permissible levels of toxic metals in human food. Hence, the analytical control of lead in a beverage widely consumed as mate is becoming very important.

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Considering the low lead concentration levels in mate tea samples, sensitive analytical techniques are required to obtain adequate detection limits.

The contents of lead at low concentrations have been determined by several techniques, including flame atomic absorption spectrometry (FAAS) [5–7], electrothermal atomic absorption spectrometry (ETAAS) [8,9], inductively coupled plasma mass spectrometry (ICP-MS) [10], inductively coupled plasma optical emission spectrometry (ICP-OES) [11–13], and X-ray fluorescence (XRF) [14], among others.

Inductively coupled plasma optical emission spectrometry due to its excellent analytical performance is an optimum technique for the determination of Pb in mate tea samples. However, the low level of lead in mate is not compatible with the determination limit of this technique. In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are needed when the concentrations of analyte elements in the original material or the prepared solution are too low to be determined directly by ICP-OES. In addition, the use of an ultrasonic nebulizer can provide a 5–50-fold improvement in detection limits [15,16].

Polyurethane foam (PUF) was proposed as sorbent by Bowen [17] in 1970 and since then it has been used in many procedures for separation and preconcentration of a wide variety of inorganic and organic compounds [7,18–20]. Application of PUF in these produces smaller resistance for fluid passage than materials often employed for this proposal. Thus, it results low overpressure in the system reducing risk of leakage. PUF is easily disposable, very low cost and simple preparation. Moreover, this sorbent is resistant to rough changes on pH conditions, despite to swell when in presence of some organic solvents concentrated, as ethanol.

In procedures for lead determination, PUF has been employed several times [7,18,21–23]. However, in all of these works polyurethane foam has been used as a sorbent material. In this work, for first time, the use of polyurethane foam as a packed bed filter is proposed.

In the present study, a methodology for preconcentration and determination of lead in mate tea samples using polyurethane foam as a filter is proposed. Lead was retained as Pb–5-Br-PADAP precipitate at pH 9.0. The determination was performed using USN-ICP-OES associated with a FI methodology.

2. Experimental

2.1. Reagents

All reagents used were of the highest available purity and at least of analytical grade.

A solution of 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) 10^{-2} mol/l was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution in 17% (v/v) ethanol–water.

Working standard solutions were prepared by stepwise dilution from 1000 mg/l Pb stock standard solution immediately before use.

A buffer solution was prepared by diluting a 3.0 mol/l ammonium hydroxide solution adjusted to pH 9.0 with a hydrochloric acid solution.

Flexible polyurethane foam (PUF), commercial open-cell polyether-type polyurethane foam (by Mortimer of Argentina), was ground in a domestic blender with a large amount of ultrapure water, as previously described. Afterwards, PUF was filtered in a vacuum system and squeezed between clean sheets of filter paper. So, PUF was placed to dry in a stove at 80 °C for 1 h and stored in a dark bottle.

Ultrapure water (18 M Ω cm) was obtained from an EASY pure RF (Barnstedt, Iowa, USA).

2.2. Apparatus

The measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP2070]. The 1 m Czerny–Turner monochromator had a holographic grating with 1800 grooves/mm. The FI system used is shown in Fig. 1. An ultrasonic nebulizer, U 5000 AT [CETAC Technologies (Omaha, NE, USA)], with desolvation system was used. The ICP and ultrasonic nebulizer operating conditions are listed in Table 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France)] was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. A laboratory-made conical minicolumn (40 mm length, 4.5 mm internal upper-diameter and 1.5 mm internal lower-diameter) was used as the polyurethane foam holder. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent and eluent. The 220.353 nm spectral line was used, and FI system measurements were expressed as peak height emission, which was corrected against the reagent blank.

2.3. Sample preparation

We analyzed commercial samples of mate tea (10 samples). All samples were obtained from products that are widely consumed in Argentina.

Table 1
USN-ICP-OES instrumental parameters employed to lead determination

Forward power	1.0 kW
rf Generator	40.68 MHz
Coolant gas flow rate	8.5 l/min
Auxiliary gas flow rate	1.0 l/min
Carrier gas flow rate	0.5 l/min
Solution uptake rate	1.5 ml/min
Observation height (above load coil)	15 mm
Ultrasonic nebulizer conditions	
Heater temperature	140 °C
Condenser temperature	4 °C
Carrier gas flow rate	1 l/min

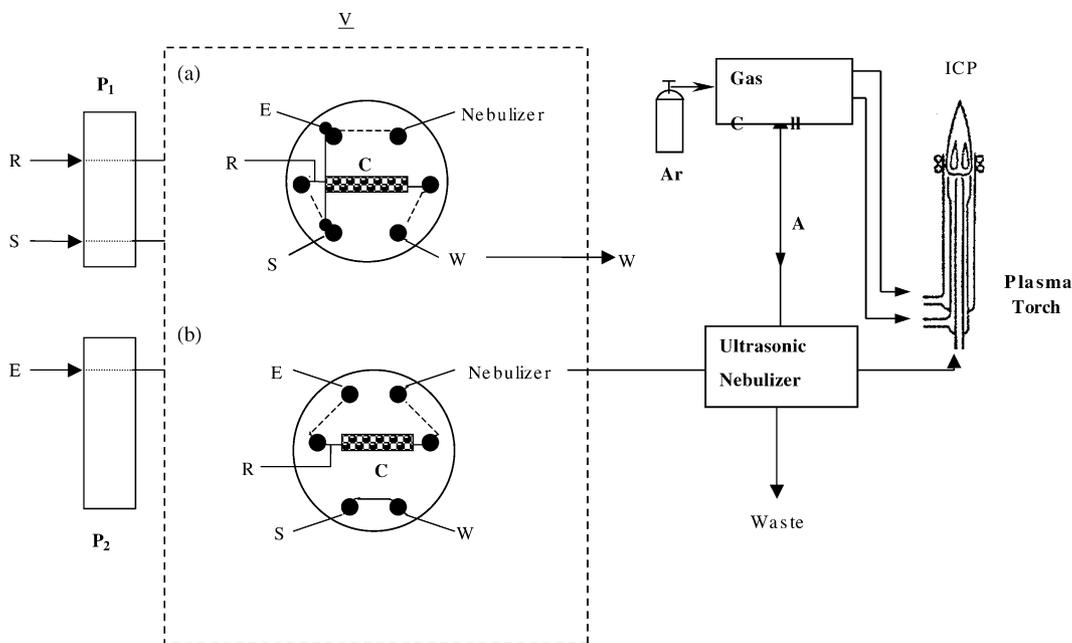


Fig. 1. Schematic diagram of the instrumental setup. S: sample (flow rate: 10 ml/min); R: reagent (flow rate 5.0 ml/min); E: eluent (flow rate: 1.5 ml/min); A: Ar (flow rate: 0.7 l/min); W: waste; P₁, P₂: peristaltic pumps; C: minicolumn packed with polyurethane foam; V: injection valve. Valve positions: (a) sample loading and (b) injection.

The procedure adopted for infusion preparation was as follows: 200 ml of boiling ultrapure water was poured onto 3 g of dried preparation, covered, left to infuse for 30 min, filtered, the moisture squeezed out, and the volume made up to 200 ml.

2.4. Preconcentration step

An aliquot of sample (10 ml) and the precipitating reagent (5-Br-PADAP 10^{-4} mol/l buffered at pH 9.0) at 10.0 and 5.0 ml/min loading flow rates, respectively, were loaded by means of peristaltic pump into the column. The sample and reagent streams merged at a point about 1 cm upstream of the column. The precipitate, which is formed instantaneously after the merging point, was collected on polyurethane foam; valve V in load position (a) (Fig. 1). Finally, the peristaltic pump was stopped, the injection valve V was switched to the injection position (b) and the retained precipitate was eluted with 20% nitric acid at a flow rate of 1.5 ml/min, directly in the ultrasonic nebulizer and ICP-OES. The operating conditions were established and the determination was carried out.

3. Results and discussion

The ultrasonic nebulization system, coupled to the preconcentration system, allowed the lowering of the ICP-OES detection limits to values compatible to the Pb content in mate tea samples.

3.1. Sample loading variables

In order to optimize the sorption conditions for the retention of the metal precipitates, the lead signal was monitored by measuring with ICP-OES while changing the pH of the solution that passes through the minicolumn. The Procedure was similar to describe in Preconcentration step section, the optimal pH values were in the 8.5–11.0. This phenomenon is understandable, since a better precipitation occurs within this range. According to these results, the selected pH was 9.0 (Fig. 2).

The sample flow rate through the minicolumn is a very important parameter, since this is one of the steps that controls the time of analysis. The influence of the sample loading rate on the analytical response obtained was studied between 1.0 and 15.0 ml/min. We could verify that the maximum response was constant up to a sample loading flow-rate of 10.0 ml/min (Fig. 3), which, under optimum conditions, allowed us to reach an enhancement factor value of 225-fold. At higher flow rates than 10.0 ml/min, the response decreased.

In order to avoid the precipitation of the complexing reagent 5-Br-PADAP in aqueous medium, the solution of the complexing reagent was prepared in presence of ethanol. It was observed that with 17% (v/v) of ethanol, 5-Br-PADAP remained in solution up to concentrations in the order of 10^{-4} mol/l. Subsequently, the influence of the ethanol concentration on the preconcentration of the precipitate Pb-5-Br-PADAP was assessed. The preconcentration decreases when ethanol concentrations above 25% (v/v) are used in the 5-Br-PADAP solution. This behaviour was to be expected since

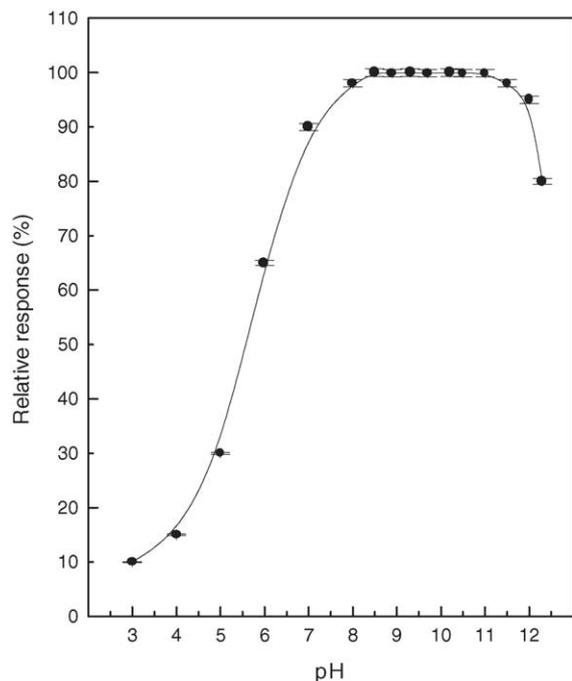


Fig. 2. Dependence of retention of Pb on pH of loading solutions. Preconcentration of 10 ml of Pb solution; lead concentration was $1.0 \mu\text{g/l}$; nitric acid concentration was 20% (v/v).

increasing solvent concentrations lead to higher solubility of the Pb–5-Br-PADAP precipitate, which hinders its precipitation and adsorption on the polyurethane foam. The 5-Br-PADAP concentration selected was 10^{-4} mol/l and the optimum load rate of it was 5.0 ml/min.

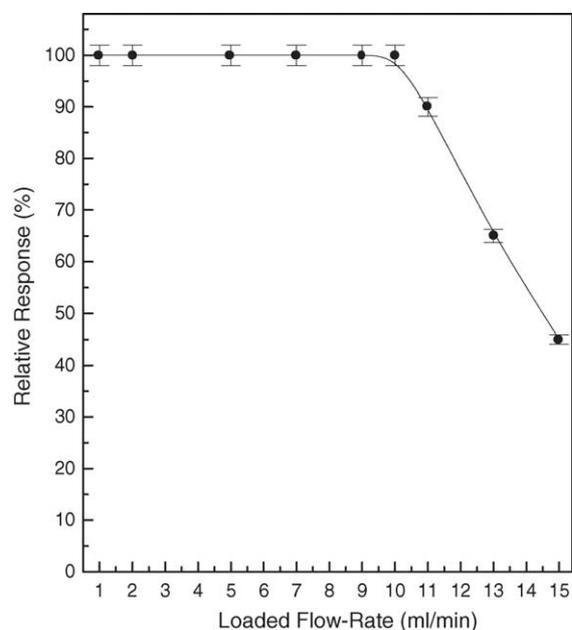


Fig. 3. Dependence of the response relative (%) on sample flow rate. Preconcentration of 10 ml of Pb at pH 9.0; lead concentration was $1.0 \mu\text{g/l}$; nitric acid concentration was 20% (v/v).

3.2. Optimization of the elution conditions

The selection of the eluent for the precipitates was critical. The use of organic solvents was not possible since they generate instability in the ICP, which can eventually lead to its extinction. Nitric acid turned out to be a good eluent for the Pb–5-Br-PADAP precipitate with 20% (v/v) as the minimum concentration to obtain the best response. A concentration of 20% (v/v) was adopted in this work. The effect of the flow rate of the eluent was studied and the best ICP-OES signal was achieved at 1.5 ml/min.

3.3. Interferences

The effects of representative potential interfering species (at the concentrations levels at which may occur in the sample under study) were also tested. Thus, Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} and Fe^{3+} could be tolerated up to at least $1000 \mu\text{g/l}$. Commonly encountered matrix components such as alkali and alkaline earth elements do not form stable complexes and are not retained on the polyurethane foam under the working conditions used for the system.

3.4. Analytical performance

The overall time required for preconcentration of 10 ml of sample (1.0 min, at flow rate of 10.0 ml/min), and elution (approximately 0.2 min, at flow rate of 1.5 ml/min) was about 1.2 min; the throughput was about 50.0 samples/h. A sensitive enhancement factor of 225-fold was obtained for lead, with respect to ICP-OES using pneumatic nebulization.

The precision for 10 replicate determinations was 3.0% relative standard deviation (R.S.D.) for a Pb concentration of $1 \mu\text{g/l}$. The calibration graph using the preconcentration system for lead was linear with a correlation coefficient of 0.9997 (relative response (%) = $99.9210 + 0.0195C_{\text{Pb}}$); at levels near the detection limits up to at least $100 \mu\text{g/l}$. The detection limit (DL) value was calculated as the concentration of lead required to yield a net peak that was equal to three times the standard deviation of the blank signal (3σ). The value of DL obtained for the preconcentration of 10 ml of sample solution was 40.0 ng/l .

3.5. Recovery and validation studies

The proposed method of digestion following USN-ICP-OES determination was applied to the quantification of trace amounts of lead in mate tea samples. Due to method of standard addition is considered as a validation method [24]; we used it in order to demonstrate the validity of our method. Ten portions of 3 g of mate tea sample were collected. Four of them were spiked with an appropriate volume of lead stock standard solution. All the samples were prepared following the proposed procedure (Section 2.3). The average quantity of Pb found in the six portions without addition was taken as the base value. The results obtained are reported in Table 2.

Table 2
Recovery study

Aliquots	Base value ($\mu\text{g/l}$)	Quantity of Pb ($\mu\text{g/l}$)		Recovery ^a (%)
		Added	Found	
1–6	–	0.0	7.6 ± 0.3	–
7	7.6	3.0	10.5	97.0
8	7.6	5.0	12.7	102.0
9	7.6	10.0	17.6	100.0
10	7.6	15.0	22.7	100.7

^a Recovery (%) = $100 \times [(\text{found} - \text{base})/\text{added}]$.

3.6. Application to mate tea samples

Finally, the proposed methodology was applied to mate tea samples. The concentrations of lead were in the range 7.6–8.9 $\mu\text{g/l}$. The average concentration of lead in commercial mate tea samples analyzed was 8.1 $\mu\text{g/l}$.

4. Conclusions

The main difficulty in the determination of lead in mate tea samples is its low concentration level. It has been shown that adequate sensitivity and accuracy can be attained using an on-line preconcentration system with an FI-NUS-ICP-OES method.

Additionally, the FI system increased the speed of the preconcentration and analysis process and reduced sample consumption and contamination risks.

The results in this work demonstrate the possibility of using 5-Br-PADAP for the preconcentration of lead, since the Pb–5-Br-PADAP precipitate was effectively retained on polyurethane foam, which can be used a long time without degradation of its performance. The recovery studies performed indicate that the determination shows good reproducibility and accuracy.

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