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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.

Keywords: Lead determination; On-line preconcentration; Polyurethane foam; USN-ICP-OES; Mate tea samples

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 Argentine. 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 MΩ 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