Available online at www.sciencedirect.com
SCIENCE DIRECT
Marine Chemistry 98 (2006) 286–294
MARINE CHEMISTRY
www.elsevier.com/locate/marchem

Sample treatment with focused ultrasound and bath sonication as a powerful tool for the evaluation of cadmium pollution in estuarine waters

R. Agapito [a], S. Alves [a], J.L. Capelo [b,*], M.L. Gonçalves [a], A.M. Mota [a]

[a] *Centro de Química Estrutural. Instituto Superior Técnico de Lisboa, Universidade Técnica de Lisboa, Torre Sul. 11° Andar. Avda. Rovisco Pais, 1049-001, Lisboa, Portugal*
[b] *REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal*

Received 11 April 2005; received in revised form 4 October 2005; accepted 21 October 2005
Available online 15 December 2005

Abstract

A new sample treatment was developed for the determination of dissolved cadmium in Tagus estuarine waters, based on focused ultrasound in conjunction with small volumes in the extraction steps for Cd pre-concentration. Cadmium was first pre-concentrated using a classical approach (APDC as the complexing agent and MIBK as the organic phase) and then back-extracted into HNO_3 with the aid of focused ultrasound, which reduced the acid concentration by more than one order of magnitude (from 4 to 0.1 mol L^{-3}). This sample treatment was accomplished in less than 5 min, using low sample volume (20 mL), and low-volume, low-concentration reagents. The pre-concentration factor used in this work was 25, but different sample/organic volume ratios may be used in order to increase that value. The limit of detection and the limit of quantification in Tagus water samples were 0.03 nmol L^{-1} and 0.1 nmol L^{-3}, respectively. Recoveries from spiked Tagus water were higher than 90%. The procedure was validated using the reference estuarine water NRC-SLEW-3. In the solubilization of Cd particulate, bath ultrasonication was used in conjunction with HNO_3+HCl, followed by H_2O_2, which took about 2 instead of the usual 12 h (cooling included) when high-pressure microwave digestion is used.

Keywords: Focused ultrasound; Bath sonication; Particulate cadmium; Dissolved cadmium; Tagus estuary; ET-AAS

1. Introduction

The physico-chemical forms in which the heavy metals occur in the aquatic medium, particularly in sea water, may strongly determine their bioavailability and toxicity. Cadmium is an insidious and widespread health hazard at trace levels. Today the challenge facing the scientific community and regulatory agencies is to assess the health risks of low-level exposure to heavy metals in the environment. Accordingly, new analytical procedures enabling the determination of trace and ultra-trace levels of analytes are needed (Buffle, 1988; Vasconcelos and Leal, 1997).

The heavy metals are present in the sea at trace levels, with normal concentration range of 0.1–100

* Corresponding author. Tel.: +351 212 949 649; fax: +351 212 948 550.
E-mail address: jlcapelom@dq.fct.unl.pt (J.L. Capelo).

0304-4203/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.marchem.2005.10.006

nmol L^{-1}. In the case of low metal levels, pre-concentration of the sample is often necessary in order to achieve the quantification limits of the most common techniques used in routine analysis for metal determination, such as Electrothermal Atomic Absorption Spectrometry (ET-AAS) or Flame Atomic Absorption Spectrometry (F-AAS). Recently, adsorptive stripping voltammetry coupled to ultrasound has been used to decrease the quantification limit, since mass transport during the deposition step is increased (Agra-Gutierrez and Compton, 1998; Saterlay et al., 1999; Banks and Compton, 2003).

In terms of separation and pre-concentration of metals from environmental matrices, several procedures have been developed, such as liquid–liquid extraction (Jan and Young, 1978; Capelo et al., 2004), APDC solvent extraction (Boyle and Edmond, 1975; Bruland et al., 1979; Danielsson et al., 1978), co-precipitation (Martinez-Jimenez et al., 1987), MgOH precipitation (Wu and Boyle, 1997), chelating ion exchange resins (Florence and Batley, 1976), electrolysis (Batley and Matousek, 1977) and solid phase extractions (Mahmoud et al., 2000).

In the liquid–liquid pre-concentration procedure, the analyte is transferred from an aqueous solution to an organic complexing phase with lower volume. Small-scale liquid–liquid single pre-concentration (Capelo et al., 2004; Carasek et al., 2002) is an approach that enables significant reduction of sample and reagent consumption with further advantages for the waste treatment and waste disposal. Small-extraction matches the requirements of the analytical minimalism, as outlined by Halls (1995).

In order to circumvent the problems raised by the analysis of organic solutions in ET-AAS (Capelo et al., 2004; Burrini and Cagnini, 1997; Volysnky et al., 1984; Tserovsky and Arpadjan, 1991), a second step of back-extraction can be performed where the metal content of the organic phase is transferred to an aqueous solution.

A feature to be taken into account in the application of an extraction procedure is the treatment time, which is usually too long; however, the overall time can be reduced using focused ultrasound. Recently, Tandem Focused Ultrasound (TFU) has been described as a powerful tool for sample treatment for the pre-concentration and back-extraction of mercury from human urine (Capelo et al., 2004). To the best of our knowledge, focused ultrasound has never been attempted in the pre-concentration and back-extraction procedures of metals from estuarine water. Furthermore, the information available in literature dealing with cadmium solid–liquid extraction from particulate matter by sonication with bath is still scarce. This manuscript presents results for Cd speciation in the Tagus estuary, where the samples were treated using (i) small-scale liquid–liquid pre-concentration and back-extraction procedures, with conventional (shaking) or ultrasonic probe and (ii) small-scale ultrasonic bath-assisted solid–liquid extraction (leaching) of particulate matter for cadmium determination by ET-AAS. The Tagus estuary receives the inflow of effluents from about 2.5 million inhabitants living in the Great Lisbon area, together with the effluents from its industries (chemicals, metallurgic and shipbuilding).

2. Experimental section

2.1. Apparatus

A Branson Sonifier 150 ultrasonic cell disruptor-homogeniser (150 W, 22.5 kHz, Branson Ultrasonics Corporation, USA) equipped with a 3-mm microtip was used. Ultrasonic energy irradiation was fixed at any desired level using a power setting in the 40–70% range with the 3-mm micro-tip. The Sonifier 150 has a digital LCD display which provides a continuous read-out of the watts delivered to the end of the probe (range 5–12 W in this work). A special auto-sampler cup (Capelo et al., 2004) was used in this work, with a conical-shaped bottom and a capacity of 2.5 mL. An ultrasonic bath, model Transonic 460 (35 kHz, 1L, Elma Germany) was used for cadmium leaching. Measurements of pH were made with an Orion model 720 A (Orion, UK) pH-meter equipped with an electrode model 9103SC (Orion).

Cadmium absorbance was measured with a Varian (Cambridge, UK) atomic absorption spectrometer model SpectrAA-300 plus equipped with a graphite furnace and an autosampler. Zeeman background correction was used. A cadmium hollow-cathode lamp operated at 6 mA was used as a radiation source. The cadmium analytical line at 228.8 nm and a slit width of 0.5 nm were used for measurements. Pyrolytic graphite-coated graphite tubes with L'vov platform were used. The electrothermal program is presented in Table 1. Palladium nitrate, 4.33×10^{-6} mol L^{-1}, was used as matrix modifier. Salinity was measured with a portable WTW LF 330/SET (Weilheim, Germany).

2.2. Reagents

Milli-Q ultrapure water was used throughout. All glassware and plasticware were twice decontaminated