Journal of Hazardous Materials 182 (2010) 477–483

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Determination of toxic and other trace elements in calcium-rich materials using cloud point extraction and inductively coupled plasma emission spectrometry

Jolanta Borkowska-Burnecka, Anna Szymczycha-Madeja*, Wiesław Żyrnicki

Chemistry Department, Analytical Chemistry Division, Wroclaw University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland

ARTICLE INFO

Article history:
Received 27 October 2009
Received in revised form 14 June 2010
Accepted 14 June 2010
Available online 19 June 2010

Keywords:
Cloud point extraction
Matrix effects
Dolomites
Trace element analysis
ICP OES

ABSTRACT

A cloud point extraction (CPE) procedure for the simultaneous separation and preconcentration of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from materials rich in calcium prior to trace element analysis by inductively coupled plasma optical emission spectrometry (ICP OES) was developed. The method is based on the formation of hydrophobic complexes of the metal ions with PAN or 5-Br-PADAP, followed by their extraction into a surfactant-rich phase using Triton X-114 as the surfactant. The main variables affecting the extraction process, such as pH, concentration of surfactant and chelating agent were optimised. Under the optimum conditions the obtained limits of detection for Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were of 4.0, 4.3, 2.1, 1.9, 0.3, 5.6, 40 and 2.0 $\mu g\,L^{-1}$, respectively. The RSD values for 10 replicates were from 1.5% for Mn to 11% for Pb. The accuracy of the procedure was verified by analysis of certified reference material NIST 1400 (Bone Ash) and by recovery tests. The optimised method was successfully applied for the simultaneous determination of trace elements in dolomites used by different fertiliser factories.

1. Introduction

In addition to typical hazardous materials such as waste, sludge, many other materials can be a danger to people and the environment due to contamination with trace toxic chemicals, especially heavy metals. Trace elements incorporated in the structure of the materials can change their physical and chemical characteristics, and may limit their usefulness for many purposes. Bone meal, oyster shells, products formed from dolomite and other calcium minerals processed with inorganic compounds are commonly used as solid and liquid fertilisers [1–3] and can be potential sources of heavy metals in agricultural soils, increasing the risk of crop and food chain contamination. Hence, a control of heavy metal concentrations in fertilisers or their main components is very important considering the hazard of the accumulation of toxic metals in soil or their leaching into surface waters. On the other hand, materials such as shells, corals and other biogenic marine carbonates can serve as indicators of pollution and climate variation [4], and the trace element content of bone is used as an indicator of disease and/or long-term poisoning [5].

The determination of heavy metals in calcium-rich materials is not an easy task due to the low levels of concentration and strong matrix interferences. In atomic absorption spectrometry, the depression of analyte absorbance by up to 50% due to a calcium matrix has been observed [6,7]. A hydroxyapatite matrix was shown to cause significant signal suppression (from 17 to 54%) for most of the trace elements during ICP MS measurements [8]. In ICP OES, interferences caused by calcium and other alkali earth metals were observed to be considerable, and often led to over- or under-estimation of analyte concentrations [9–11]. To overcome or reduce matrix effects, different calibration methods such as external calibration, matrix matching calibration, standard addition or internal standards have been proposed. Matrix matching calibration is often not possible due to unknown or changing sample composition, as in the case of some minerals. The use of an internal standard should be specific for many analytes due to the dependence of matrix effect magnitude on spectral line properties, as in ICP OES [9,11].

Matrix separation methods based on derivatisation, extraction, co-precipitation, chromatographic and flotation processes are used in both on-line and off-line modes [12–16].

Cloud point extraction (CPE), successfully applied for the separation and preconcentration of species like metal ions, biomaterials or organic compounds [17–20] seems to be a promising and suitable procedure for the separation of analytes from calcium matrices. There are only a few works dealing with the application of CPE to the multielemental trace analysis of samples with complex matrices, and they concern water samples of high salinity or hardness [21–28].

Matrix effects and the separation of analytes from interfering elements have been previously investigated; however, to the best our knowledge, the separation of trace elements from calcium matrices by the CPE method has not been reported. It concerns both

---

* Corresponding author. Tel.: +48 71 3203807; fax: +48 71 3202494.
E-mail address: anna.szymczycha@pwr.wroc.pl (A. Szymczycha-Madeja).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.06.057

model solutions with high Ca concentrations, and natural samples such as dolomites and bones.

The main object of the present study was the development of an analytical method based on cloud point extraction separation that could be applied with the use of ICP OES and other spectroscopic methods to simultaneously determine trace elements (including hard toxic as Cd and Pb) in calcium-rich samples. Optimisation of the CPE procedure using Triton X-114 as a non-ionic surfactant and two pyridylazo chelating agents was performed to determine eight elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) in dolomites and bone tissues by means of ICP OES detection.

2. Experimental

2.1. Instrumentation

The concentrations of elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) were measured with the use of a Jobin Yvon sequential inductively coupled plasma emission spectrometer (JY 38S). The operating parameters and analytical line wavelengths used are shown in Table 1. The pH values were measured with a CP-401 pH meter (Elmetron) equipped with a combined glass electrode. A thermostatic bath maintained at the desired temperature was used for the cloud point experiments. A MPW-350 centrifuge (Med. Instruments) was used to accelerate the phase separation. Ultrasonic extraction of the samples was performed using an ultrasonic bath (UltrasonsH Selecta).

2.2. Reagents and standard solutions

All reagents used in this study were of analytical grade. The non-ionic surfactant Triton X-114 (10%) (Fluka GmbH, Switzerland) was used for the extraction experiments. The 1% solution of 5-Br-PADAP [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol] and 1% solution of PAN [1-(2-pyridylazo)-2-naphthol] (Sigma–Aldrich, Germany) were prepared by dissolving appropriate amounts of these reagents in ethanol (POCh S.A., Poland). A multielemental stock standard solution of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (100 mg L^{-1}) was prepared from the single element ICP OES standard solutions (1000 mg L^{-1}). Working standard solutions were prepared daily by suitable dilutions. Solutions of Ca and Mg were prepared from their nitrate salts (POCh). An ammonia buffer solution of pH 10 and 1% NaOH served for adjustment of the pH of samples.

For ultrasonic extraction, 1.0 M HCl (Merck KGaA, Germany) was applied as a leaching agent. With each set of extractions, a blank sample was simultaneously prepared through the complete procedure, analysed and then used for a correction of the analytical signals. All dissolutions and dilutions were performed with deionised water (18.3 MΩ cm^{-1}) obtained from EASYpure^{TM} (Baernstaed, Thermolyne Corporation, USA). All glassware was cleaned with 10% nitric acid in an ultrasonic bath and rinsed several times with deionised water.

Table 1
Instrumental and operating conditions for ICP-OES.

Generator	40.68 MHz
Rf power	1200 W
Injector i.d.	2.5 mm
Spray chamber	Cyclonic
Nebuliser	Burgener (MiraMist)
Monochromator	1 m with 4320/2400 grooves/mm grating
Plasma observation zone	12 mm above load coil
Ar flow rates	Plasma gas: 14 L min^{-1} Sheath gas: 0.2 L min^{-1} Carrier gas: 0.3 L min^{-1}
Sample uptake	0.9 mL min^{-1}
Lines (wavelengths in nm)	Cd II (228.80), Co II (238.89), Cr II (267.72), Cu I (324.75), Mn II (259.37), Ni II (221.65), Pb II (220.35), Zn I (213.86) I: atomic; II: ionic lines.

2.3. Samples and sample preparation

In our experiments, model solutions and two kinds of natural samples, dolomites and bone ash (NIST 1400 Bone Ash), were used. Dolomites were taken from different fertiliser factories.

About 0.5 g of bone ash or 2 g of dolomite were accurately weighted into a polyethylene tube, treated with 50 mL of 1 M HCl and placed into the ultrasonic bath for 40 min at 60 °C. After the extraction, the sample solutions were quantitatively transferred into 100 mL volumetric flasks and made up to volume with deionised water. Before CPE, all of the solutions were filtered through a hard filter paper.

2.4. Cloud point extraction procedure

An aliquot of 20.00 mL of the standard or sample solution was placed in a tube then 1 mL of buffer solution, 0.26–0.6 mL of Triton X-114 and appropriate amounts of 5-Br-PADAP or PAN solutions, were added. The sample solutions before buffer addition were neutralised by NaOH. The tubes were kept in a thermostatic bath at 50 °C for 40 min. The separation of the two phases was accelerated by centrifugation of the solution for 12 min at 3500 rpm. The tube was then placed in an ice bath for 30 min to increase the viscosity of the surfactant-rich phase. The aqueous phase was decanted by inverting the tube. In order to decrease the viscosity of the organic phase, 1 mL of HNO_3 was added and the solution was transferred to the flask and made up to 10.0 mL with deionised water. Blanks were submitted to the same procedure in parallel with the samples.

3. Results and discussion

3.1. Optimising the CPE procedure

The cloud point extraction procedure was optimised here using the synthetic solutions (aqueous standards) of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, simultaneously for the metal ions. The effects of pH, surfactant and chelating agent concentrations were examined and the

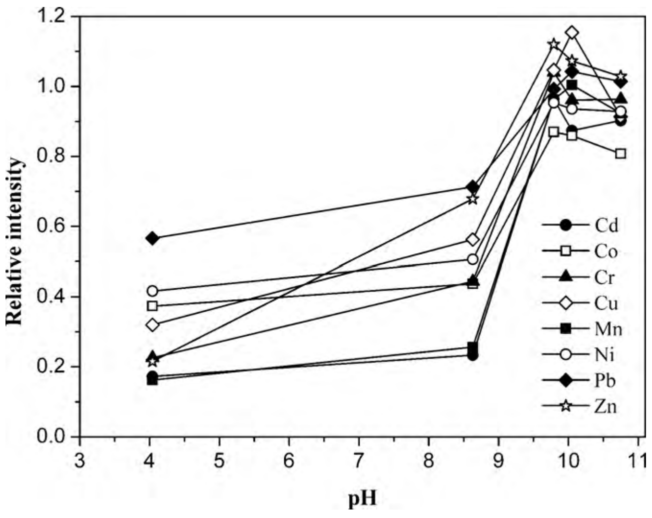

Fig. 1. Effect of pH on CPE efficiency using 5-Br-PADAP as chelating agent ($c_{\text{Triton X-114}} = 0.20\%$).