



## Analytical methodology

# A green and efficient procedure for the preconcentration and determination of cadmium, nickel and zinc from freshwater, hemodialysis solutions and tuna fish samples by cloud point extraction and flame atomic absorption spectrometry

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## ARTICLE INFO

## Article history:

Received 1 May 2013

Accepted 10 December 2013

## Keywords:

Metals ions

Cloud point extraction

Freshwater

Hemodialysis solutions

Tuna fish samples

## ABSTRACT

Cloud point extraction (CPE) was used to simultaneously preconcentrate trace-level cadmium, nickel and zinc for determination by flame atomic absorption spectrometry (FAAS). 1-(2-Pyridilazo)-2-naphthol (PAN) was used as a complexing agent, and the metal complexes were extracted from the aqueous phase by the surfactant Triton X-114 ((1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol). Under optimized complexation and extraction conditions, the limits of detection were  $0.37 \mu\text{g L}^{-1}$  (Cd),  $2.6 \mu\text{g L}^{-1}$  (Ni) and  $2.3 \mu\text{g L}^{-1}$  (Zn). This extraction was quantitative with a preconcentration factor of 30 and enrichment factor estimated to be 42, 40 and 43, respectively. The method was applied to different complex samples, and the accuracy was evaluated by analyzing a water standard reference material (NIST SRM 1643e), yielding results in agreement with the certified values.

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## Introduction

Cadmium, nickel and zinc are present in many samples, such as vegetables, food and water, and, with the exception of cadmium, are classified as micronutrients with specific functions. Nickel is a metal frequently used in industry and is also considered essential to plants [1]. Its bioavailability to organisms and related biochemical process is dependent on the compounds formed by nickel and such compounds are considered carcinogenic [2]. Inhaling vapors that contain nickel can cause asthma, bronchitis, lung cancer and other diseases related to the respiratory tract, as well as exposure to nickel can lead to skin dermatitis. The Brazilian Environmental regulation and World Health Organization (WHO) have established Ni threshold limits of 25 and  $70 \mu\text{g L}^{-1}$ , respectively, in water samples [3,4].

Zinc plays important roles in enzymes, is essential for the proper functioning of the immune, digestive and nervous systems and is present in a significant number of foods [5]. The symptoms of zinc deficiency lead to skin problems, slow healing of wounds, reduction in the senses of taste and smell, increased susceptibility to infections, decreased fertility, retardation of children's growth, mental lethargy and the loss of appetite and hair. Zinc is highly resistant to corrosion and has thus been widely used as a protective coating for

various products. The U.S. Environmental Protection Agency (EPA) has established that drinkable water should not contain amounts of Zn over  $5 \text{ mg L}^{-1}$  [6].

Cadmium is environmentally and toxicologically important due to its potential to generate carcinogenic damage if present at any level of exposure, with no tolerance threshold and primarily accumulates in the kidneys when ingested [7]. The main emissions of cadmium occur from waste incineration and fuel burning, but it is also used in foundry and metallurgic industries, batteries, plastics, fertilizers and other materials. Inhaling cigarette smoke has proven to cause exposure to cadmium [8].

Inductively coupled plasma optical emission spectrometry (ICP OES) [9], flame atomic absorption spectrometry (FAAS) [5], electrothermal atomic absorption spectrometry (ETAAS) [10,11], molecular spectrophotometry [12,13] and other atomic and molecular methods have all been used to quantify metals in many samples. Atomic absorption spectrometric techniques are preferred when quantifying elements at low concentrations due to their high sensitivity, good selectivity, high sample throughput and relative simplicity [14]. Analyte concentration and separation from the sample matrix are often required for trace analysis, aiming at increasing detectability and elimination of matrix effects and interferences [15,16]. This task has been carried out by time-consuming procedures that often generate large amounts of waste disposal (e.g., precipitation and solid-liquid extraction) [5,17]. In addition, conventional liquid-liquid extraction requires toxic solvents.

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Cloud point extraction (CPE) has emerged as an alternative to conventional liquid–liquid extraction due to its high preconcentration factors, smaller required sample size, lower toxic reagent use, elimination of large quantities of organic solvents, use of nontoxic surfactants and safer, simpler and more economical procedure [18–20]. Among the nonionic surfactants commonly used, Triton X-114 ((1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol) is the most feasible for the extraction and preconcentration cloud point.

In the determination of metals by CPE, a chelating agent is typically employed to form a hydrophobic complex with the metal ion [21]. 8-Hydroxyquinoline (8-HQ), 1-(2-pyridilazo)-2-naphthol (PAN), 1-(2-thiazolylazo)-2-naphthol (TAN), N-phenylbenzohydroxamic acid (PBHA), p-nitrophenylazoresorcinol (Magneson I), O,O-diethyldithiophosphate (DDTP) and di-2-pyridil ketone salicyloylhydrazine (DPKSH) have been used as chelating agents in CPE. Garcia et al. [22], using Triton X-114 as the surfactant and DPKSH as a complexing agent in CPE, developed a method for selective preconcentration of trace amounts of nickel by atomic and molecular spectrometry methods. Using Triton X-114 and TAN as surfactant and complexing agent, respectively, Mohamadi and Chapeyama [23] developed a method for preconcentration of trace amounts of cadmium, nickel, lead and zinc in fish samples by FAAS after CPE. An on-line CPE coupled with flow injection method was developed for preconcentration of lead and palladium using dimethylglyoxime as complexing agent and Triton X-114 as surfactant. After the CPE procedure, the surfactant rich-phase was retained in a minicolumn packed with animal wool, eluted and detected by FAAS [24]. Zhao et al. [25] developed a dual-cloud point extraction (d-CPE) procedure for determination of several metals in water by the ICP OES method. These authors also used 8-HQ and Triton X-114. After CPE, the surfactant rich-phase was treated by nitric acid, and the ions were back extracted into aqueous phase at the second CPE step.

PAN is often used as a colorimetric reagent in the determination of a variety of metal ions [26]. This chelating agent has low water solubility and a relatively high solubility in organic solvents, such as acetone and methanol, and in acidic or alkaline solutions. The fact that PAN is poorly soluble in aqueous solutions allows its use in extractions with suitable organic solvents and makes it widely used in the separation, extraction and determination of many metal ions [27,28].

In this context, the aim of this work was to develop a green – decreased consumption of the reagents and the sample reducing waste disposal as a result – efficient procedure, selective and sensitive spectrometric method for the determination of cadmium, nickel and zinc from freshwater, hemodialysis solutions and tuna fish samples using PAN as a complexing agent in CPE.

## Materials and methods

### Instrumentation

A pH meter model 713 Metrohm (Herisau, Switzerland) with a combined glass electrode was used for pH measurements. A stirring plate model BT 110 Biothec (São Paulo, Brazil) was used for heating to 60 °C, and a centrifuge model Q222TM Quimis (São Paulo, Brazil) was used to accelerate the phase separation.

For FAAS measurements, a ContrAA 300 high-resolution atomic absorption spectrometer Analytik Jena AG (Jena, Germany) equipped with a xenon short-arc lamp (XBO 301, 300 W, GLE) operating in hot-spot mode as a continuum radiation source was used for cadmium, nickel and zinc absorbance measurements at 228.80 nm, 232.00 nm and 213.86 nm, respectively. An air acetylene flame was used for the atomization and the sample aspiration

rate was fixed at 5.5 mL min<sup>-1</sup>. The instrumental parameters for atomic absorption spectrometry were adjusted according to the manufacturer's recommendations.

A UV-Vis 2450 spectrophotometer Shimadzu (Kyoto, Japan) was used for recording absorbance spectra with a 1-cm quartz cell.

Acid decomposition was carried out in closed quartz vessels in a microwave oven model Multiwave 3000 Anton Paar (Graz, Austria).

### Reagents and solutions

All solutions were prepared with analytical grade chemicals and deionized water obtained from Milli-Q system (Millipore, Bedford, U.S.). A  $2.0 \times 10^{-3}$  mol L<sup>-1</sup> PAN stock solution was prepared by dissolving appropriate amounts of reagent Sigma Aldrich (St. Louis, MO, U.S.) in ethanol Carlo Erba (Val de Reuil, France). Solutions of the nonionic surfactant Triton X-114 (Sigma Aldrich) were prepared at 5% (w/v) concentration. Buffer solutions were prepared from acetic acid (Sigma Aldrich) and sodium hydroxide Merck (Darmstadt, Germany) at pH 4.0, 5.0 and 6.0, ammonium acetate (Merck) at pH 7.0, hexamine (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>) at pH 8.0 (Sigma Aldrich), phosphoric acid and sodium hydroxide (Sigma Aldrich) at pH 8.0 and tris(hydroxymethyl)aminomethane (Sigma Aldrich) and hydrochloric acid (Merck) at pH 7.0, 8.0 and 9.0. Cadmium, nickel and zinc standard solutions were prepared by the appropriate dilutions of a 1000 mg L<sup>-1</sup> stock solution Ultra Scientific (North Kingstown, RI, U.S.).

### Sample pre-treatment and digestion

Analysis of a standard reference material (SRM) for Trace Elements in Water, supplied by the National Institute of Standards and Technology NIST 1643e, was used to assess method accuracy.

Freshwater samples were collected from Billings Dam, São Paulo, Brazil. All samples were acidified to pH 2.0 with nitric acid immediately after collection to prevent the adsorption of the metal ions onto the flask walls and filtered through 0.25 μm cellulose acetate membranes. Dialysate was prepared in the laboratory by salts solubilization, under shaker and heating. The samples present the following composition – Hemodialysis solution (A): 47.6 g NaCl; 41.6 g CH<sub>3</sub>COONa; 1.25 g MgCl<sub>2</sub>·6H<sub>2</sub>O; 1.54 g CaCl<sub>2</sub>·2H<sub>2</sub>O and 20.8 g C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> in 250 mL of water. Hemodialysis solution (B): 59.2 g NaCl; 1.13 g KCl; 0.775 g MgCl<sub>2</sub>·6H<sub>2</sub>O; 2.93 g CaCl<sub>2</sub>·2H<sub>2</sub>O and 22.1 g NaHCO<sub>3</sub> in 250 mL of water [16].

Tuna fish candidate reference material [29] was digested in a closed-vessel microwave oven. An accurate mass of the sample (300 mg) was transferred into quartz vessels and mixed with HNO<sub>3</sub> (65%), deionized water and H<sub>2</sub>O<sub>2</sub> (30%) at 1:3:2 mL. The heating program was executed in 4 steps: 1-ramp (140 °C/5 min), 2-ramp (180 °C/8 min), 3-ramp (220 °C/3 min) and 4-cooling to 25 °C (30 min). The obtained solution was transferred into a flask, and then a given volume (7 mL) of deionized water was added.

### General procedure

Different amounts of the sample or standard solutions (165 μL of 5%, w/v, Triton X-114, 861 μL of  $2.0 \times 10^{-3}$  mol L<sup>-1</sup> PAN and 500 μL of tris(hydroxymethyl)aminomethane 0.84 mol L<sup>-1</sup> (pH 8.0)) were transferred to 15 mL graduate tubes, which were then filled with water up to the mark. After complexation time of 15 min [30] the mixture was left to stand in a water bath at 60 °C for 10 min [12,22]. Phase separation was then achieved by centrifugation at 3600 rpm (centrifugal force estimated as 840 × g) for 10 min. The aqueous phase was removed with a Pasteur pipette, and the surfactant-rich phase was diluted to 500 μL with HNO<sub>3</sub> 0.1 mol L<sup>-1</sup> (in methanol medium) to reduce its viscosity. A blank solution subjected to the

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