

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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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 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⁻¹. 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 2.0×10^{-3} mol L⁻¹ 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 (C₆H₁₂N₄) 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⁻¹ 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 CH₃COONa; 1.25 g MgCl₂·6H₂O; 1.54 g CaCl₂·2H₂O and 20.8 g C₆H₁₂O₆ in 250 mL of water. Hemodialysis solution (B): 59.2 g NaCl; 1.13 g KCl; 0.775 g MgCl₂·6H₂O; 2.93 g CaCl₂·2H₂O and 22.1 g NaHCO₃ 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 HNO₃ (65%), deionized water and H₂O₂ (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 2.0×10^{-3} mol L⁻¹ PAN and 500 µL of tris(hydroxymethyl)aminomethane 0.84 mol L⁻¹ (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 $840 \times g$) for 10 min. The aqueous phase was removed with a Pasteur pipette, and the surfactant-rich phase was diluted to 500 µL with HNO₃ 0.1 mol L⁻¹ (in methanol medium) to reduce its viscosity. A blank solution subjected to the

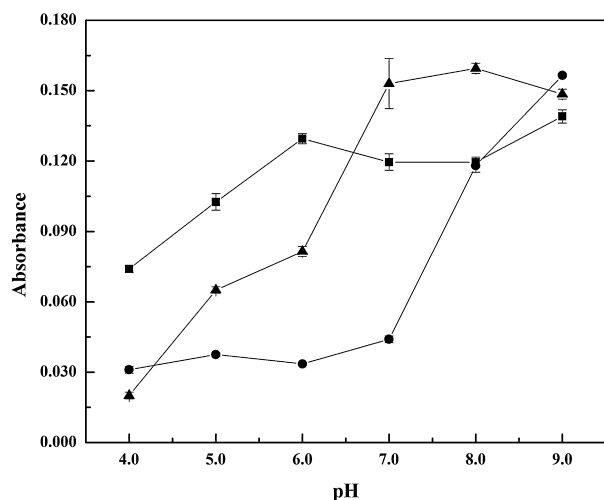


Fig. 1. Absorbance as a function of pH for the PAN complexes with cadmium (●), nickel (■) and zinc (▲). Experimental conditions: $281 \mu\text{g L}^{-1}$ Cd, $147 \mu\text{g L}^{-1}$ Ni, $163 \mu\text{g L}^{-1}$ Zn and PAN $62.5 \mu\text{mol L}^{-1}$. Wavelength: 552 nm (Cd), 568 nm (Ni) and 554 nm (Zn).

same procedure was measured in parallel with the samples or standard solutions.

A sliding-bar injector-commutator designed for flow injection analysis was employed to insert a $150 \mu\text{L}$ aliquot of the diluted surfactant-rich phase into the FAAS nebulizer as previously described [12].

Results and discussion

Optimization of the cloud point extraction procedure

The effects of pH, PAN concentration and Triton X-114 concentration were evaluated. The effect of pH and PAN concentration was evaluated by UV–vis spectrophotometry and the effect of Triton X-114 concentration was evaluated by FAAS. At pH 9.0 Cd(II), Ni(II) and Zn(II) form a complex with PAN with an absorption maximum at 552 nm, 568 nm and 554 nm, respectively. These maximum wavelengths were used at pH and PAN influence by the UV–vis spectrophotometric study.

Metal complexation with PAN is very dependent on the pH of the solution due to this complexing agent is an organic ampholyte, which can easily attract a proton to its pyridine nitrogen atom in acidic medium ($\text{pK}_a \text{ N}^+\text{H} = 3.35$ at 25°C) and can easily dissociate its o-hydroxy group in basic medium ($\text{pK}_b \text{ OH} = 2.60$ at 25°C) [31].

The optimization of pH solution from 4.0 to 9.0 for all PAN/metal complexes was evaluated with a Cd $281 \mu\text{g L}^{-1}$, Ni $147 \mu\text{g L}^{-1}$, Zn $163 \mu\text{g L}^{-1}$ and PAN $62.5 \mu\text{mol L}^{-1}$ concentrations. There was a significant increase in analytical signal from pH 7.0 to pH 8.0 for cadmium (approximately 2.7 times) and for nickel and zinc at the same pH range the analytical signal shows a slight difference, Fig. 1. Therefore, a pH 8.0 was chosen for subsequent experiments, aiming the more favorable complexation with PAN in relation of the hydrolysis of the metals.

Maintaining metals and PAN concentrations previously described, the influence of the buffer solution composition was evaluated using four different buffers at pH 8.0: Tris/HTris⁺ ($0.84/1.0 \text{ mol L}^{-1}$), $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ ($0.057/1.0 \text{ mol L}^{-1}$), $\text{C}_6\text{H}_{12}\text{N}_4$ (0.50 mol L^{-1}) and $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ ($0.64/0.10 \text{ mol L}^{-1}$). The analytical signals were slightly higher for Ni and Zn/PAN complexes using Tris/HTris⁺ compared to the $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer solution (ca. 16%). Therefore, a buffer solution of Tris/HTris⁺ was chosen for further experiments.

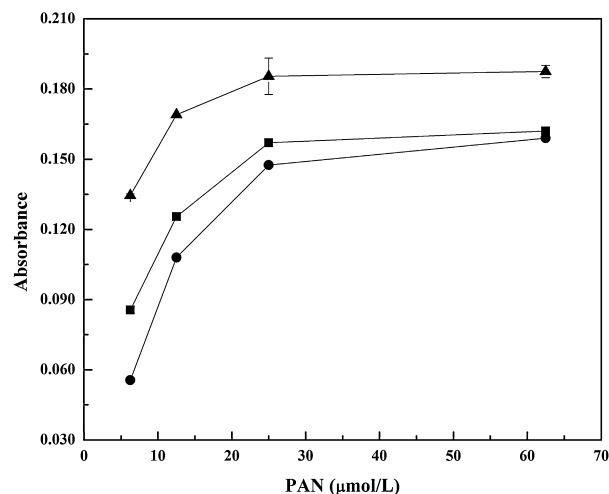


Fig. 2. Absorbance as a function of PAN concentration for complexes of cadmium (●), nickel (■) and zinc (▲). Experimental conditions: $281 \mu\text{g L}^{-1}$ Cd, $147 \mu\text{g L}^{-1}$ Ni, $163 \mu\text{g L}^{-1}$ Zn and pH = 8.0. Wavelength: 552 nm (Cd), 568 nm (Ni) and 554 nm (Zn).

The effect of PAN concentration was evaluated from 5 to $60 \mu\text{mol L}^{-1}$ to establish the minimum reagent concentration that yielded maximum sensitivity, with a Cd $281 \mu\text{g L}^{-1}$, Ni $147 \mu\text{g L}^{-1}$, Zn $163 \mu\text{g L}^{-1}$ concentrations and at pH 8.0 (Tris/HTris⁺). As shown in Fig. 2, the absorbance did not vary significantly for the three complexes at concentrations above $25 \mu\text{mol L}^{-1}$ PAN. In the CPE procedure, excess complexing reagent can compete with the complexes formed by surfactant micelles in solution [32]. A concentration of $25 \mu\text{mol L}^{-1}$ PAN (PAN:metal ratio of 10:1) was chosen for further studies avoiding any unnecessary consumption of reactants (93 mg per determination).

One of the most important parameters in cloud point extraction for the preconcentration of metal complexes is the surfactant concentration. There must be sufficient surfactant to guarantee a quantitative extraction (above surfactant CMC, critical micelle concentration). The volume ratio of the phases should also be noted: an increase in surfactant concentration can decrease the analytical signal due to dilution of the extract in the surfactant-rich phase volume [12,22,32].

The effect of surfactant concentration was evaluated from 0.50 to 8.0 mmol L^{-1} with a Cd $281 \mu\text{g L}^{-1}$, Ni $147 \mu\text{g L}^{-1}$, Zn $163 \mu\text{g L}^{-1}$, PAN $25 \mu\text{mol L}^{-1}$ concentrations and at pH 8.0 (Tris/HTris⁺). In this procedure, the final volume was adjusted to $500 \mu\text{L}$ (adding HNO_3 0.1 mol L^{-1} in methanol medium) before measurements, making the volume variation not influenced the preconcentration factor. At a concentration of 0.50 mmol L^{-1} a phase separation was difficult due to the low-volume rich phase. At Triton X-114 concentration equal 1.0 mmol L^{-1} the analytical signal increase for Zn and Cd, but a decrease was observed when the concentration is greater and equal to 2.0 mmol L^{-1} for Zn and Cd, respectively, as shown in Fig. 3. A 1.0 mmol L^{-1} Triton X-114 concentration (ca. 5-fold higher than CMC) was chosen as a compromise among the CPE efficiency, consumption (8.1 mg) and the effect on nebulization of the analyte extract in FAAS.

The effect of sample volume was evaluated by inserting discrete volumes of diluted surfactant-rich phase (HNO_3 0.1 mol L^{-1} in methanol medium) in the FAAS nebulizer. Transient signals were obtained, and it was observed that for a $150 \mu\text{L}$ sample volume, the analytical signal achieved 89% of the steady state value obtained by direct aspiration of the sample ($450 \mu\text{L}$). Therefore, a sample volume of $150 \mu\text{L}$ was then selected for further studies, which allowed the determination of all three analytes in the same extract.

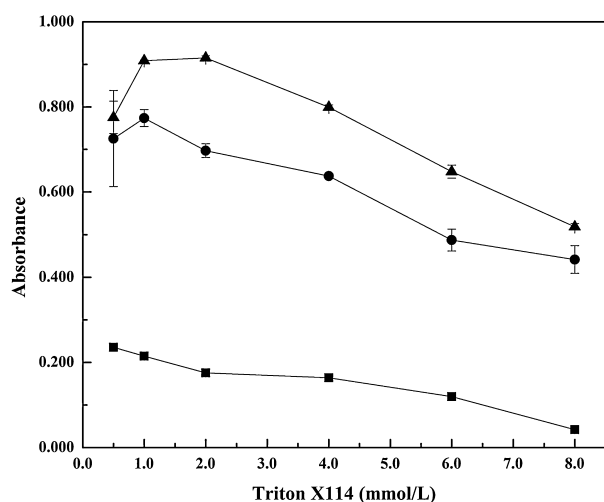


Fig. 3. Absorbance as a function of Triton X-114 concentration for complexes of cadmium (●), nickel (■) and zinc (▲) complexes. Experimental conditions: 281 $\mu\text{g L}^{-1}$ Cd, 147 $\mu\text{g L}^{-1}$ Ni, 163 $\mu\text{g L}^{-1}$ Zn, 25 $\mu\text{mol L}^{-1}$ PAN and pH = 8.0. Rich phase diluted to 500 μL using a 0.1 mol L^{-1} HNO_3 solution in methanol.

Analytical features of proposed method

Analytical curves were obtained in triplicate by preconcentration of 15 mL of samples containing known Cd^{2+} , Ni^{2+} and Zn^{2+} ions under optimized conditions. Table 1 shows the analytical features of the proposed method. Linear responses were observed and can be described by the following equations: $A = (-2.98 \pm 1.39) \times 10^{-3} + (5.03 \pm 0.06) \times 10^{-3} C_{\text{Cd(II)}}$, $r = 0.9993$; $A = (-1.0 \pm 0.0) \times 10^{-3} + (1.5 \pm 0.0) \times 10^{-3} C_{\text{Ni(II)}}$, $r = 0.9990$ and $A = (-2.00 \pm 0.02) \times 10^{-2} + (7.20 \pm 0.00) \times 10^{-3} C_{\text{Zn(II)}}$, $r = 0.9982$. The limits of detection (LOD) and quantification (LOQ) were estimated according to IUPAC recommendations at the 99.7% confidence level [33].

The preconcentration factor of 30 and enrichment factors (calculated from the ratio of the slopes of the calibration curves obtained with and without pre-concentration) of 42, 40 and 43 for Cd, Ni and Zn, respectively, were determined [12,22,32]. The relative standard deviations (precision) were estimated for 12 independent measurements with a 60.0 $\mu\text{g L}^{-1}$ Cd(II), Ni(II) and Zn(II) solution. The reagent consumption was 8.1 mg of Triton X-114 and 279 μg PAN per simultaneous metals preconcentration.

Selectivity of the proposed method

Under optimized conditions, experiments were carried out to evaluate the selectivity of the proposed method. The effect of selected cations and anions found in freshwater or hemodialysis solutions was evaluated based on the ratio between the species found in SRM NIST 1643e water (Table 2). The tolerance limit of a foreign ion was taken as the value that led to an error lower than $\pm 5\%$ in the analytical signal.

Table 1

Analytical characteristics of the proposed method for the cloud point extraction and determination of Cd, Ni and Zn by FAAS.

Parameters	Cd	Ni	Zn
Linear range ($\mu\text{g L}^{-1}$)	5.0–80	2.5–160	5.0–80
LOD 99.7% ($\mu\text{g L}^{-1}$)	0.37	2.6	2.3
LOQ 99.7% ($\mu\text{g L}^{-1}$)	1.2	8.8	7.7
Characteristic concentration ($\mu\text{g L}^{-1}$)	0.87	2.9	0.61
Coefficient of variation (%)	2.0	2.5	2.5

Table 2

Effect of foreign ions on the determination of cadmium, nickel and zinc.

Signal variation (%)				
Foreign ion	Concentration ($\mu\text{g L}^{-1}$)	Cd	Ni	Zn
Na^+	2.0×10^4	−3.3	+5.0	−0.5
K^+	1.9×10^3	−7.3	+14	+8.0
Ba^{2+}	531	−11	+7.0	+6.0
Ca^{2+}	4.0×10^3	−2.2	+8.0	−1.9
Sr^{2+}	315	−7.0	+5.0	−7.0
Mg^{2+}	7.8×10^3	−9.8	+1.0	+3.0
Co^{2+}	26	−10	+4.0	−8.0
Cu^{2+}	22	−5.5	−2.9	+5.0
Pb^{2+}	19	+9.0	−5.4	+4.0
Mn^{2+}	38	−9.8	+2.0	+4.0
Cr^{3+}	40	+3.0	+1.0	+8.0
Al^{3+}	20	+1.0	+3.0	−2.2
Fe^{3+}	96	+2.0	−5.7	+3.0

Concentration of Cd(II), 6.41 $\mu\text{g L}^{-1}$; Ni(II), 60.9 $\mu\text{g L}^{-1}$ and Zn(II) 76.5 $\mu\text{g L}^{-1}$. Experimental conditions: 15 mL sample volume, pH 8.0, 113 $\mu\text{mol L}^{-1}$ PAN and 1 mmol L^{-1} Triton X-114.

Some cations (Na^+ , Cu^{2+} , Al^{3+} and Fe^{3+}) do not interfere with cadmium, nickel and zinc determination by the proposed method, while Cr^{3+} , Mg^{2+} , Mn^{2+} , Pb^{2+} , Ca^{2+} , Sr^{2+} and Co^{2+} do not interfere or present a slight interference in cadmium and/or nickel and/or zinc determinations. Some anions ($\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , PO_4^{3-} , CO_3^{2-} , HCO_3^- , F^- and Cl^-) were studied at a 1:100 ratio of analyte:concomitant, and there was no significant interference.

Interferences with FAAS detection may be attributed to cations that react with PAN in the preconcentration step (e.g., Co(II)/PAN , $\log \beta_2$ 11.52; Zn(II)/PAN , $\log \beta_2$ 10.75 and Ni/PAN , $\log \beta_2$ 10.70 in methanol at 25 °C) [26].

Application of proposed method to freshwater, hemodialysis solutions, tuna fish samples and reference material

The proposed method was applied to determine Cd, Ni and Zn in a number of samples over a consumption range of 0.5–10 mL, including dam water, hemodialysis solutions, tuna fish and water reference material. Different amounts of cadmium, nickel and zinc were also spiked into the samples, and the resulting solutions were subjected to the cloud point extraction procedure.

Matrix interferences were observed by applying the proposed method in dam water sample, with recoveries below 75%. Therefore, to clean up dam water samples, a cloud point extraction procedure described previously (without PAN addition) was provided. An intense yellow coloration was observed in the rich-phase surfactant due to the presence of organic matter. After the separation of the two phases the cloud point extraction procedure was carried out again in the presence of PAN, the recovery of the metals in dam water sample ranged from 95.0% to 102%, indicating that the procedure was free of matrix effects, Table 3. Silva et al. [34] developed a method to determine nickel in plant reference materials and also have observed that a cleanup was necessary prior to cloud point extraction, even after sample digestion using a microwave system.

There are no reference materials for hemodialysis solutions and the WHO recommends a quality control of these solutions. Although the main problems in dialysis patients are attributed to aluminum, metals such as cadmium, lead and thallium may be present as contaminants in water used to prepare hemodialysis solutions and in the supplies [35]. The proposed method was applied in two hemodialysis solutions (A and B) with different dilutions. Recoveries from 90.8% to 119%, Table 3, were estimated, indicating that the proposed method is free from high saline matrix effects. For tuna fish sample, the recoveries from 98.0% to

Table 3Mean values and uncertainties for cadmium, nickel and zinc determination in different kinds of samples ($n = 3$).

Samples	Analyte amount ($\mu\text{g L}^{-1}$)				Recovery (%)		
	Added	Cd found	Ni found	Zn found	Cd	Ni	Zn
Dam water ^a	0.0	0.77 \pm 0.42	2.66 \pm 0.38	37.9 \pm 0.1	–	–	–
	15.0	15.8 \pm 0.3	17.6 \pm 1.2	51.3 \pm 2.3	101	99.0	98.1
	20.0	19.8 \pm 1.7	22.9 \pm 1.8	58.2 \pm 1.2	95.0	101	102
Hemodialysis solution A ^b	20.0	21.9 \pm 2.6	23.2 \pm 0.5	23.7 \pm 5.2	109	116	119
	50.0	50.8 \pm 1.6	44.8 \pm 2.9	51.8 \pm 1.6	102	99.5	104
	60.0	62.7 \pm 8.4	54.5 \pm 7.8	56.8 \pm 4.9	105	90.8	94.6
Hemodialysis solution B ^c	20.0	19.4 \pm 0.3	20.2 \pm 2.4	23.2 \pm 3.2	97.2	101	116
	50.0	52.2 \pm 1.0	51.1 \pm 3.6	51.7 \pm 6.3	104	102	103
	60.0	64.9 \pm 5.4	59.1 \pm 8.7	60.7 \pm 3.2	108	90.8	101
Tuna fish candidate reference material	10.0	9.80 \pm 0.3	9.90 \pm 0.7	9.83 \pm 2.0	98.0	99.0	98.3
	15.0	16.9 \pm 1.3	15.2 \pm 1.8	15.0 \pm 2.0	113	101	100
SRM NIST ^d 1643e	0.0	6.63 \pm 0.86	61.9 \pm 1.2	76.9 \pm 5.3	–	–	–

^a Extraction performed in two steps.^b Cd, Ni and Zn added to hemodialysis solution diluted to 10%.^c Cd, Ni and Zn added to hemodialysis solutions to 20%.^d Certified values: 6.57 \pm 0.07 $\mu\text{g L}^{-1}$ Cd, 62.41 \pm 0.69 $\mu\text{g L}^{-1}$ Ni and 78.5 \pm 2.10 $\mu\text{g L}^{-1}$ Zn.**Table 4**

Comparison of the proposed method with other methods after CPE extraction and FAAS detection.

Analyte	Complexing agent	EF	LOD ($\mu\text{g L}^{-1}$)	Sample volume (mL)	Precision (%)	References
Cd	DDTP ^a	23	0.62	10	–	[36]
Cd	BIMPI ^b	42.0	3.50	15	1.5	[37]
Zn	PBHA ^c	74.2	0.42	50	3.1	[38]
Zn	PAN	26	1.52	10	4–5	[39]
Ni	DPKSH	27	0.76	15	2.5	[22]
Ni:Mn	Magneson I ^d	17:19	2.7:2.9	25	1.8:1.3	[40]
Cu:Zn	PAN	36:32	0.1:0.15	50	1.3–2.7	[41]
Cd, Ni and Zn	PAN	40–43	0.37–2.6	15	2.0–2.6	This work

^a O,O-diethylthiophosphate.^b 2-((2-((1H-benzo[d]imidazole-2-yl)methoxy)phenoxy)methyl)-1H-benzo[d]imidazole.^c N-phenylbenzohydroxamic acid.^d p-Nitrophenylazoresorcinol.

113% contributed to the success of the proposed method showed by their applicability in a number of complex samples.

Accuracy was also assessed through the analysis of a water standard reference material (NIST 1643e) and results in agreement at the 99.7% confidence level (Table 3) was obtained.

Conclusions

The preconcentration and determination of Cd, Ni and Zn using PAN as complexation agent for cloud point extraction presented interesting features. The proposed method has the advantage of simultaneous extraction and cloud point preconcentration of cadmium, nickel and zinc ions with low reagent consumption and reduced waste disposal. The method was successfully applied to different types of complex samples with potentially interfering ions such as iron, aluminum and copper. Determining metals in a sample of freshwater required two extraction steps (i.e., in the absence and presence of PAN), but a significant improvement in the recovery was ultimately obtained. These results show the importance of the extraction and preconcentration steps in sample preparation for samples that may contain high concentrations of organic matter and lower concentrations of the analyte(s) of interest. Table 4 compares the analytical features of the proposed method with those reported in other procedures for the determination of cadmium, nickel and zinc after cloud point extraction [22,36–41]. The developed method has a good detection limit, higher enrichment factor – making it suitable for the trace analysis of these metal ions – better or comparable precision to those presented by other methods.

Conflict of interest statement

None declared.

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