ELSEVIER

# Extraction and preconcentration of nickel, cadmium, cobalt, and lead cations using dispersive solid phase extraction performed in a narrow-bore tube

Mir Ali Farajzadeh*, Adeleh Yadeghari

*Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*

A B S T R A C T

A new version of DSPE in a narrow-bore tube followed by HPLC-DAD was proposed for the analysis of $Ni^{2+}$, $Cd^{2+}$, $Co^{2+}$, and $Pb^{2+}$ cations. 2-Propanol is mixed with $C_{18}$ sorbent and used for dispersing the sorbent into solution containing the cations oxinate complexes. The sorbent passes through the solution in a short time versus passing the solution from the cartridge which is done in the conventional SPE in a long time. In comparison to SPE, the active surface area is larger because of preventing sorbent clogging. EFs and LODs were obtained in the ranges of 831–1073 and 0.05–0.40 $\mu g\,L^{-1}$, respectively.

© 2017 Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

## Introduction

Over the past decades, industrialization and mining activities led to emergence and dispersal of various pollutants in ecosystems. Among these contaminants, most heavy metal cations as a hazardous class of environmental pollutants can be harmful to human health even at low concentrations due to the formation of complex compounds within the cell [1,2]. For example, lead may cause brain damage, kidney injury, seizures, and anemia. Also, it is harmful to plants and animals [3,4]. Human exposure has risen dramatically as a result of global industrial revolution and plethora of their use in several industrial, agricultural, domestic, and technological applications [5–7]. Heavy metal cations cannot be biodegraded, so they persist in the environment and cause pollution of air, soil, and water ecosystems [8]. Therefore, the development of efficient, inexpensive, safe, and environmentally friendly methods for the identifying, limiting, and determination of metallic cations pollutions is earnestly required.

There are many established analytical techniques, such as atomic absorption spectroscopy (AAS) [9–13], inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [14,15], and ICP-mass spectrometry (ICP-MS) [16–18] for determination of metallic cations. ICP-optical emission spectrometry [19–21], atomic fluorescence spectrometry [22], X-ray fluorescence

spectrometry [23], and neutron activation analysis [24] are other methods used in this field. High-performance liquid chromatography (HPLC) [25,26] and electrochemical methods [27], in particular, stripping voltammetry techniques are other established methods for metallic cations determination.

However, the analysis of heavy metal cations in environmental matrices has been a problem due to their low concentrations in real samples as well as the samples matrix complication. Also, on the basis of the green chemistry rules the introduction of analytical methods with a minimal impact on the environmental is required. Sample preparation procedures are typically the most resource-intensive component of analytical methods in terms of material consumption and disposal requirements. So, the trend of analytical chemistry studies is replacing the traditional sample preparation methods with new ones that are less toxic. Solid phase extraction (SPE) [28–30] and liquid–liquid extraction (LLE) [31] are two traditional methods of sample preparation. The main drawbacks of LLE include large volumes of organic solvents usage and emulsion formation [32]. Moreover, clogging of cartridges, the necessity of pretreatment of sorbents before extraction procedure, the requirement of pumping or suction, and low extraction efficiency are some of SPE drawbacks [33,34]. Also in SPE, active surface area due to aggregation of particles is reduced, hence extraction efficiency is disturbed [35]. Batch SPE such as matrix solid-phase dispersion extraction (MSPDE) [36,37], magnetic solid phase extraction (MSPE) [38], solid-phase microextraction (SPME) [39–41], and dispersive solid phase extraction (DSPE) [42] have

been proposed to resolve the mentioned drawbacks. Despite providing an enhanced surface area in MSPDE for extraction of the analytes from solid, semi-solid, and highly viscous samples, it cannot resolve the many disadvantages of SPE like the requirement of pumping and suction [43,44]. The prevention of column packing and the easy and rapid phase separation are the fundamental benefits of MSPE [45]. But the synthesis of magnetic cores, coating of them, and immobilization processes are time-consuming and optimization of these steps is difficult. In the case of SPME, the used fibers are expensive and fragile, also there is the possibility of memory effect [46]. In spite of simplicity and low cost of DSPE, an additional step is required to transfer of the analytes from solid or aqueous samples into an organic solvent like methanol or acetonitrile [42].

In this study, a new version of SPE using a large volume of the sample has been proposed to achieve a high sensitive analytical method that could be used for the extraction and preconcentration of trace concentrations of some heavy metal cations in different aqueous samples followed by their determination with HPLC-diode array detector (HPLC-DAD). In the proposed method a water-miscible organic solvent will be used for dispersing of a sorbent into an aqueous solution placed into a narrow-bore tube. It is expected that during passing the sorbent through the solution, the contact between the active surface of the sorbent and analytes will be increased, extraction time reduced, and extraction efficiency improved. By this method, clogging of the cartridge, the requirement of pumping or suction, and necessity of pretreatment of sorbents which are time-consuming and consume organic solvent can be resolved.

## Experimental

### Reagents and standard solutions

Analytical-grade nitrate salts of nickel, cobalt, lead, and cadmium cations were from Merck (Darmstadt, Germany). HPLC-grade water and methanol were supplied by Caledon (Canada). Deionized water was from Ghazi Company (Tabriz, Iran). 8-Hydroxyquinoline (oxine) as a chelating reagent, sodium hydrogen carbonate, ammonia, ammonium acetate, sodium chloride, hydrochloric acid, and sodium hydroxide were obtained from Merck. Acetonitrile (ACN), methanol, acetone, and 2-propanol tested as the dispersion agents for the sorbent and the elution solvents of the analytes from the sorbent were from Caledon. The used sorbents including amino propyl ($NH_2$), cyano propyl (CN), diol, octadecyl ($C_{18}$), and octyl ($C_8$) were from Merck. Individual stock solutions of Ni (II), Co (II), Pb (II) and Cd (II), ($1000 \, mg \, L^{-1}$ of each) were prepared by dissolving the related nitrate salts in deionized water. Working solution was prepared daily by appropriate dilutions of the stock solutions with deionized water ($100 \, \mu g \, L^{-1}$ of nickel and cobalt, $200 \, \mu g \, L^{-1}$ of cadmium, and $400 \, \mu g \, L^{-1}$ of lead cations). A solution of 0.5 M oxine was prepared in methanol to chelate the target cations. A carbonate buffer (C = 1 M, pH = 11) was prepared for pH adjusting of solutions.

### Instrumentation

Chromatographic experiments were performed using a Hewlett Packard 1090-II HPLC system (Palo Alto, CA, USA) equipped with a DAD, an oven, and a 10-$\mu$L injection loop. Chromatographic separation of the target analytes was achieved using a reversed-phase Eurospher $C_8$ column (25 cm × 4.6 mm i.d.) with a particle size of 5 $\mu$m (Knour, Berline, Germany). ChemStation software was employed to acquire and process the chromatographic data and controlling the HPLC system. The mobile phase was a mixture of $H_2O$: methanol (30:70, *v/v*) containing $20 \, mmol \, L^{-1}$ oxine at a flow rate of $0.5 \, mL \, min^{-1}$. The column temperature was thermostated at 50 °C. The detection wavelength was set at 380 nm in the cases of Ni (II), Cd (II), and Pb (II), and 400 nm for Co (II). A Metrohm pH meter model 654 (Herisau, Switzerland), a Labinco vortex model L46 (The Netherlands) and a D-7200 Hettich centrifuge (Kirchlengern, Germany) were used. An LBS2 ultrasonic bath (FALC Instruments, Treviglio, BG, Italy) was used to degas the mobile phase prior to use.

### Samples

The wastewater samples were collected from Rajaee Industrial Region (Tabriz, Iran) and Songon Mine (Varzeghan, Iran) Refineries (input and output in each case) and were diluted at ratios of 1:4 and 1:1 to eliminate matrix effect, respectively, before analysis. Also, a tap water sample collected from our laboratory was analyzed without dilution.

### Extraction and preconcentration procedure

The pH of 50 mL deionized water spiked with $100 \, \mu g \, L^{-1}$ of Ni (II) and Co(II) (each cation), $200 \, \mu g \, L^{-1}$ of Cd(II), and $400 \, \mu g \, L^{-1}$ of Pb(II) or sample solution (see Section "Samples") was adjusted at 11 by adding 2.5 mL carbonate buffer. A 100 $\mu$L oxine solution (0.5 M in methanol) was added into the solution to chelate the target cations. This solution was transferred into a home-made set-up consists of a narrow-bore glass tube (90 × 0.8 cm i.d.) which its head was the funnel shaped and its end was connected to an ground glass joint. The ground glass joint end was connected to a ground glass joint test tube with the conical bottom. It is noted that the narrow and long tube led to move the sorbent through whole parts of the tube with high contact with the analytes. Then, 50 mg of $C_{18}$ sorbent immersed in 1 mL 2-propanol as a dispersive solvent was injected into the solution using a 2-mL syringe. By this action, the sorbent particles were rapidly dispersed into the upper section of the aqueous solution and moved down through the tube under gravity force. After 10 min nearly all particles of the sorbent were sedimented. After this step, the test tube was disconnected and centrifuged for 3 min at 604 × g. By a 5-mL syringe, the supernatant solution was removed carefully. In the next step, for eluting the analytes from the sorbent, 300 $\mu$L methanol was added to the tube. Then, it vortexed for 1 min. The elution solvent was transferred into a home-made microtube (2 × 0.5 cm i.d.) using a 500-$\mu$L micro-syringe. To access the high enrichment factors (EFs) and low limits of detection (LODs), the solvent was evaporated to dryness under a stream of nitrogen at room temperature. The residue was dissolved in 30 $\mu$L of methanol and injected into the HPLC system for analysis. The extraction procedure and the used set up are illustrated schematically in Scheme 1.

## Results and discussion

In order to obtain high extraction recovery (ER) and EF, improved analytical signals, good repeatability, and high sensitivity, the effect of different parameters including type and amount of sorbent, type and volume of dispersive solvent, pH, sorbent conditioning, extraction time, etc. must be studied and the optimum conditions to be selected. In this study a narrow bore tube was chosen to hold the aqueous solution. This configuration has some advantages over the test tube along with agitation. Using a disperser solvent is necessary in this study due to hydrophobic property of the sorbent used. In the absence of disperser solvent, the used sorbent is aggregated and clogged in the upper of the solution and associated around the rim of the tube. Also by passing the sorbent through the long tube much equilibria are achieved similar to conventional SPE mode whereas in test tube only one