Development of novel simultaneous single step and multistep cloud point extraction method for silver, cadmium and nickel in water samples

Naeemullah [a,b], Tasneem Gul Kazi [b], Mustafa Tuzen [a,c,*]

[a] Gaziosmanpaşa University, Faculty of Science and Arts, Chemistry Department, Tokat 60250, Turkey
[b] National Centre of Excellence in Analytical Chemistry University of Sindh, 76080 Jamshoro, Pakistan
[c] King Fahd University of Petroleum and Minerals, Center for Environment and Water, Dhahran 31261, Saudi Arabia

ABSTRACT

A novel, simple and rapid single and multi-step cloud point extraction procedure was developed for the selective and simultaneous preconcentration of silver, cadmium and nickel in real samples prior to their determination by flame atomic absorption spectrometry. Dithizone was used as neutral hydrophobic complexing agent. Separation of understudy metals can be achieved by controlling the pH value of the extraction system. Evaluation of the two CPE methods was checked by paired t-test, which indicated a non-significant difference. It was successfully applied to the real water sample. Certified reference materials were used for the accuracy of the green extraction methods. The regression equation for the calibration curve was linear in the range of 10–150 μg L^{-1} for Ag, 5–100 μg L^{-1} for Cd, 10–200 μg L^{-1} for Ni. Relative standard deviation (RSD%) values were found to be lower than 2.5% for all elements. Enhancement factor (EF) and limit of detection (LOD) values were found in the range of 41–58 and 0.27–1.12 μg L^{-1}, respectively.

Introduction

Silver has an important role in modern industry [1,2]. Due to excessive use in modern industry, increased silver content might cause a potential risk as a water pollutant and pose a toxic effect on human health [3,4].

Nickel has an important role in modern industries which induced overexposure to the environment. Overexposure to nickel can create sever impact on human health [5,6]. Toxicity of the nickel is the leading hazardous threat to the environment specially to human being in low concentrations can provoke allergic reactions and might be responsible for carcinogenicity [7]. Nickel enters waters through natural process from dissolution of rocks and soils, biological cycles, atmospheric fallout, and anthropogenicly mainly through activities industrial activity [8,9].

Cadmium is a highly toxic and one of the most dangerous trace elements and responsible for a number of health problems [10]. A prolonged intake of cadmium leads to calcium regulation in biological systems, which induces cell injury and death. It also inhibits the action of zinc enzymes by substitution. Cadmium is also considered a teratogenic and carcinogenic agent [11]. The maximum level of cadmium allowed by the American Environmental Protection Agency in drinking water is 10 μg L^{-1} for protection of human health [12].

A number of methods including flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry, inductively coupled plasma mass spectroscopy has been extensively used for trace element determination in different samples [13–17]. Direct analysis of trace quantity of target analytes in real samples by FAAS might be difficult due to their low quantity and their lower sensitivity. On the bases of these facts, a great effort has to be play to develop highly sensitive and selective methods for simultaneously and selective separation of these metals in water samples. Thus, preconcentration procedures are often required. There are a number of methods have been used for sample preparation such as solid-phase extraction (SPE) [18–20], liquid–liquid microextraction (LLME) [21,22], single drop microextraction [23], cloud point extraction (CPE) [24–26]. Mostly the desire methods must be simple, sensitive, high extraction capability and environmental friendly [27,28].

* Corresponding author. Tel.: +90 3562521616; fax: +90 3562521585.
E-mail address: mustafa.tuzen@gop.edu.tr (M. Tuzen).

Recently a great efforts put forward in miniaturization of sample preparation [29]. Among them cloud point extraction (CPE) is considered to very simple separation technique [21,30–33] couple with ETAAS to achieve good sensitivity and selectivity. Several CPE methods for silver and other heavy metals (cobalt, lead, nickel and cadmium) determination have been described in the literature. Ligands such as dithizone [30,34–36], 1-(2-pyridylazo)-2-naphthol [37], ammonium pyrrolidinedithiocarbamate [38], 1-nitroso-2-naphthol [39] and 2-amino-cyclopentene-1-dithiocarboxylic acid [40] have been employed for cloud point extraction in several procedures for under study metals. Separation and preconcentration of several elements such as copper, cadmium, nickel, silver in CPE by using their dithizone complex have been reported [30,34,35]. These ligands are widely employed due several advantages obtained, such as capacity to form complexes with a large variety of metals and low solubility in water. Dithizone is a classical reagent used for complexing purposes in preconcentration procedures [41].

The aim of this work is to introduced novel approach that reduced solvent consumption, effort, time, reagent and opening-up a new horizon for selective and simultaneous preconcentration of silver, cadmium and nickel in fresh and industrial waste water samples. We used dithizone firstly as a complexing agent for selective and simultaneous separation of silver, cadmium and nickel by single step (SS-CPE) and multi step (MS-CPE) at different pH.

Experimental

Instrumentation

A Perkin–Elmer Analysis 700 model (Norwalk, CT, USA) atomic absorption spectrometer, equipped with hollow cathode lamps and an air–acetylene burner was used for elements. Nuve NF 800 model centrifuge was used for centrifugation. The pH was measured by pH meter (720-pH meter, Metrohm).

Reagents

All reagents used were of analytical reagent grade and all solutions were prepared with ultrapure water. The non-ionic surfactant Triton X-114 was obtained from Sigma (St. Louis, MO, USA). Stock solution of Ag, Cd and Ni ($1000 \, \mu g \, L^{-1}$) were obtained from (Merck, Darmstadt, Germany). A solution of $1 \times 10^{-3} \, mol \, L^{-1}$ dithizone (Merck, Darmstadt, Germany) was prepared by dissolving appropriate amounts of this reagent in ethanol. The $0.1 \, mol \, L^{-1}$ acetate, phosphate and borate buffer solutions were used to control the pH of the solutions. Certified reference material of water NIST SRM-1643e (Gaithersburg, MD, USA) was used.

Sample collection and preparation procedure

The fresh surface water samples (canals) and industrial waste water were collected on different sampling sites of Turkey. All water samples were filtered through a 0.45 μm membrane filter to remove suspended particulate matter and were stored at 4 °C for further analysis.

Design of (SMS-CPE) for simultaneous and selective extraction of Ag, Cd and Ni

Multi-step cloud point extraction (MS-CPE) procedure

MS-CPE experiment is quite simple. A specific volume (10 mL) of the duplicate sample or standard solution having target metals (4–200 μg L^{-1}) was added with 0.05–0.5% (v/v) Triton X-114 (2.5–5 mL from 0.25% (v/v) solution) and dithizone ($2.5 \times 10^{-5} \, mol \, L^{-1}$). Subsequently the pH was adjusted to the true value of (1.5) with
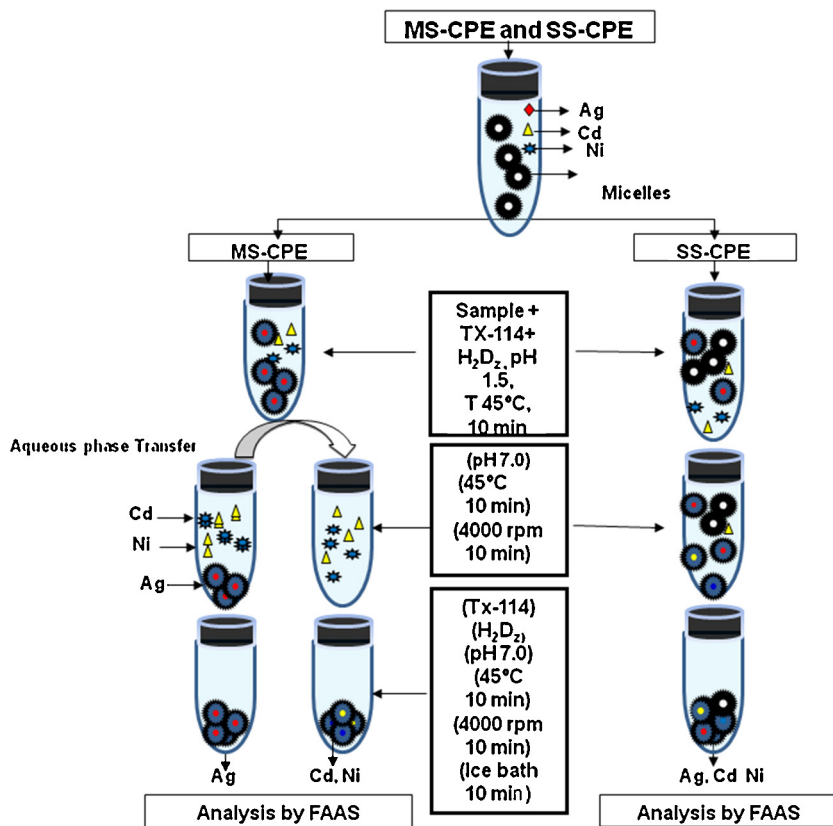

Fig. 1. Schematic diagram of single step (SS–CPE) and multi step (MS–CPE).