



Application of conventional and modified cloud point extraction for simultaneous enrichment of cadmium, lead and copper in lake water and fish muscles



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ABSTRACT

A new method based on modification of cloud point extraction for simultaneous enrichment of cadmium, lead and copper in water and fish muscle samples was proposed. The extraction efficiency by modified cloud point extraction (*m*-CPE) was compared with conventional cloud point extraction (*c*-CPE) method. The procedure for both CPE methods was comprised of formation of metal complexes with a hydrophobic chelating agent, dithizone, followed by entrapment of the chelates in a nonionic surfactant, Triton X-114. For *c*-CPE, the surfactant rich phase was treated with ethanolic solution of nitric acid and analyzed by flame atomic absorption spectrometer (FAAS). Whereas for *m*-CPE, aqueous nitric acid was used to back extract the metal ions from the surfactant rich phase and finally determined. The efficiency of the methods was tested by analyzing certified reference material and standard addition to a real sample. All the experimental parameters were optimized. At optimized experimental conditions, preconcentration and enhancement factors were 62.5 and 78.0 to 83.0 respectively for *m*-CPE, 25.0 and 56.0% higher than that of *c*-CPE. This improvement might be due to elimination of the effects of surfactant on the signal of analytes by FAAS. The developed method of *m*-CPE was applied successfully for analysis of the selected heavy metals in water and muscle tissues samples of fish of different lakes in Sindh, Pakistan.

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Introduction

Heavy metals are considered to be serious inorganic pollutants. They exist over a prolong period of time as environmental contaminants, having slow removal rate. Toxic metals have lethal effects on human health, animals, plants and life in aquatic environment especially fishes and populations eating them [1–5].

Cadmium (Cd) is one of the massive hazardous metals, it assembles in the body of human particularly in kidneys which leads to impairment in the operation of kidneys [6]. As a

consequence, it has been termed as a potential health threat. Moreover it is thought to be one of the major pollutants for assessment in most parts of the world and international organizations [7,8]. It has biological half-life of 10–30 years [9].

Lead (Pb), a naturally occurring element, has been in a strong relationship with human as an important metal over several thousands of years. Its nature of being flexible, resistant to corrosion and low melting, greatly enhances its strength and permanence has caused it to be used extensively. However, it is poisonous to humans, damaging the hemopoietic, nervous, cardiovascular, reproductive systems and the urinary tract [1–3,6,7]. So far, the reported data about it or its compounds does not reveal any health benefits to humans [10–14]. It causes numerous health consequences, particularly in children it is a universal issue [15,16]. It causes different neurological diseases and can accumulate in bones frame work, thus it can lead to behavioral deformities, retardation of judgment and brain power [17].

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Copper (Cu) is an essential element for both plants and animals. A plant yield decreases when its concentration is reduced. In humans and animals, it is part of more than 30 enzymes such as ceruloplasmin, superoxide dismutase, cytochrome oxidase or tyrosinase. But exposure to its high concentrations for long time can be fatal causing chronic effects. Its role in plants, animals and humans and effects caused by its insufficiency or overabundance have been mentioned in literature [18–21]. Bioavailable free Cu can cause severe toxicity even at the pico molar (10^{-12} M) concentration levels [22].

The widespread technological use of these metals e.g., in fertilizers, mining, pigments etc., their production from oil and coal being burnt, incineration of waste, farming, construction tools and electrical and electronic products bring about an extensive anthropogenic contamination of soil, air and water [23,24]. The maximum permissible level allowed by world health organization (WHO) in standard drinking water is 3, 10 and 2000 $\mu\text{g L}^{-1}$ respectively for Cd, Pb and Cu [25].

Many instrumental approaches, such as electroanalytical methods, flame (FAAS) and electrothermal atomic absorption spectrometry and inductively coupled plasma, hyphenated with optical emission and mass spectrometry are being widely employed for the analysis of trace quantity of heavy metal ions in different media [26–31]. Among these techniques, FAAS is being extensively used for the analysis of low levels of metal analytes, due to comparatively uncomplicated and low cost apparatus required [32–34].

The analysis of trace quantities of metals in different environmental and biological samples may be considered as a difficult analytical task, mostly due to their low concentration and complex sample matrix, which needs advance instrumental techniques or a pre-concentration method. Enormous number of analytical procedures for the pre-concentration of heavy metals were established, for instance, solid phase, liquid–liquid and cloud point extraction methods [34–38]. The pre-concentration step improves the analytical limit of detection, results accuracy, calibration of the method and uses common flame atomic absorption technique [39].

Several studies have been reported on preconcentration techniques based on cloud point extraction (CPE), declaring it as a green method [40]. In CPE, the behavior of non-ionic surfactants in aqueous solutions is utilized, which manifests separation of phases after reaching a specific temperature i.e. cloud point, and entrapping hydrophobic complexes of the metal analytes. The interactions, which cause the metal chelates to be entrapped in surfactant-rich phase, are purely hydrophobic. In conventional cloud point extraction (*c*-CPE) other hydrophobic species can be entrapped and may interfere with the determination of the analytes of interest [41,42]. That's why modification of CPE by back extraction of the metal analytes in acidic solution may improve the results [43,44].

The goal of this work is to establish a modified cloud point extraction method (*m*-CPE) for the simultaneous quantification of Cd, Pb and Cu at trace levels in water and muscle tissues of the fish, *Oreochromis mossambicus* collected from selected lakes. Diphenylthiocarbazone (dithizone) was used as a complexing agent for complexation of the metals and nonionic surfactant, polyethylene-glycol tert-octylphenylether (TX-114) for subsequent entrapment of the complexes formed. The metal analytes were back extracted with aqueous HNO_3 to overcome the surfactant unpropitious effects and to improve the selectivity and efficiency of the developed technique. In order to fully characterize the *m*-CPE technique, investigation and optimization of the related parameters, which influence the extraction efficiency of Cd, Pb and Cu in water and acid digested muscle tissues of fish, sampled from different lakes in Sindh, Pakistan, was carried out.

Experimental

Instrumentation

A Perkin-Elmer Model A Analyst 700 (Norwalk, CT) flame atomic absorption spectrophotometer was used to analyze the samples. For pH measurements a pH meter (Ecoscan Ion 6, Malaysia) was put to work. To Centrifuge the samples a WIROWKA Laboratory jna type WE-1, nr-6933 centrifuge (speed range 0–6000 rpm, timer 0–60 min, 220/50 Hz, Mechanika Pheczyjina, Poland) was used. The hollow cathode lamps of the elements under study were operated as suggested by the manufacturer. For each of the metals under study a single element hollow cathode lamp was put to work at the current of 7.0 mA and spectral bandwidth of 0.7 nm. The wavelengths for analysis were set at 228.8, 283.3 and 324.8 nm for cadmium (Cd), lead (Pb) and copper (Cu) respectively. The acetylene and air flow rates and the burner height were adjusted to obtain the maximum absorbance signal.

Chemical reagents and glass wares

All reagents used were of analytical reagent grade. All solutions were prepared in ultrapure water, obtained from ELGA, Lab water system, Bucks, UK. 0.6% (v/v) solution of surfactant polyethylene-glycol tert-octylphenylether (Triton X-114), acquired from Sigma (St. Louis, MO, USA), was prepared. Stock solution of Cd, Pb and Cu (1000 mg L^{-1}) were obtained from Fluka Kamica (Buchs, Switzerland). Successive dilutions of the stock solutions in $0.2 \text{ mol L}^{-1} \text{ HNO}_3$ (Sigma) was carried out to obtain working standard solutions. 0.5 g of diphenylthiocarbazone (dithizone) (Merck, Darmstadt, Germany) was dissolved in 100 mL ethanol (Sigma) to prepare 0.5% solution of the reagent. Acetate and phosphate buffers (Merck) were used to adjust the pH of the solutions, while $0.1 \text{ mol L}^{-1} \text{ HCl/NaOH}$ (Merck) was added to increase or decrease the pH. Certified reference material of water NIST SRM-1643e (Gaithersburg, MD, USA) and fish muscles DORM-2 (National Research Council of Canada, Ottawa, Ontario, Canada) were employed. All glass wares used for analyses were retained in 10% HNO_3 for a day and ultimately rinsed many times with ultrapure water, to avoid contamination.

Sample collection and pre-treatment

Lake water

The sampling frame work was extended over a wide range of key sites, which well represent the water quality of the selected four lakes in Sindh Pakistan. Water samples were collected from four different lakes namely Keenjhar Lake (KL), Pateji Lake (PL), Nareri Lake (NL) and Gadap Lake (GL) situated in districts Thatta and Badin of Sindh, Pakistan. To follow up the water quality of the four studied lakes, 10 sampling stations of each were chosen using Global positioning system (GPS). Sampling of both surface and bottom (>50 cm in depth) water was done by means of Van Dorn plastic bottles (1.5 L capacity) and kept in well stoppered polyethylene bottles which were previously dipped in 10% nitric acid for a day and rinsed with ultrapure water.

Fish muscles

The *Oreochromis mossambicus* (*O. mossambicus*) locally named as Tilapia (Dayoo) were caught with the help of nets from under study lakes. The 50 fish at size (20–25 cm) with weight (750–1000 g), were collected. All obtained fish samples were packed in polyethylene bags separately and assigned an identification number. Ten composite samples were established with five fish in each. The muscles were separated from other organs of fish and dried in an oven at 80°C for 48 h. Triplicate 200 mg of

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