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Cloud-point extraction, preconcentration and spectrophotometric determination of trace quantities of copper in food, water and biological samples

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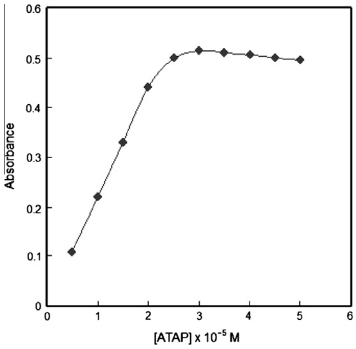
HIGHLIGHTS

- New sensitive cloud point extraction method for determination of Cu(II) in various samples.
- Beer's law is obeyed in the concentration range 4.0–115 ng mL^{-1}.
- The detection limit of 1.20 ng mL^{-1} with preconcentration factor of 125.

GRAPHICAL ABSTRACT



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ABSTRACT

A new, simple and sensitive cloud point extraction procedure was presented for the preconcentration and determination of copper(II) ion in food, water and biological samples. The analyte was complexed with a new synthesized reagent, 2-amino-4-(*m*-tolylazo)pyridine-3-ol (ATAP) as a new complexing agent and Triton X-114 as the surfactant. After centrifugation, dilution of the surfactant-rich phase with 0.4 mL of ethanol acidified with 1.0 M HNO_3 was performed after phase separation, and the copper contents were measured by spectrophotometry at λ_{max} 608 nm. The influence of analytical parameters including concentration of complexing agent, Triton X-114, pH, equilibration temperature and time, centrifuge rate and time were optimized. The analytical characteristics of the method (e.g. linear range, molar absorptivity, Sandell sensitivity, optimum Ringbom concentration ranges limits of detection and quantification, preconcentration factor, and improvement factors) were obtained. Linearity was obeyed in the range of 4.0–115 ng mL^{-1} of Cu(II) ion. The detection and quantification limits of the method were 1.20 and 3.94 ng mL^{-1} of Cu(II) ion, respectively. The interference effect of some anions and cations was also tested. The method was applied for determination of copper in food, water and biological samples.

Introduction

In recent years, the toxicity and the effect of trace elements on human health and the environment are receiving increasing attention in pollution and nutritional studies. Copper is one of the most widespread heavy metal contaminants in environment. It is an important element for most life forms as a micronutrient, but is also toxic at high concentrations [1]. Copper has a biological action at low doses and a toxic effect when ingested in larger quantities. A concentration more than 1.0 μg mL^{-1} of copper can impart a bitter taste to water. Large oral doses can cause vomiting and may eventually cause liver damage. Copper concentration in potable water is usually very low ($\leqslant$20 μg L^{-1}) [2]. A high concentration

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of copper in foods originates mainly from fungicide residues containing this metal used in agriculture and from water plumbing. The determination of trace levels of copper is important because it could catalyze oxidation of fatty acid chains, exerting a deleterious influence on shelf life and nutritional value [3].

Therefore, sensitive, reproducible and accurate analytical methods are required for the determination of trace copper in environmental biological and water samples. Although inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) [4,5] are among the most widely used methods for trace metal determination, they are usually insufficient due to the matrix interferences and the very low concentration of metal ions. For these reasons, an efficient separation and preconcentration procedure is often required prior to the measurement step.

Currently, the most widely used preconcentration methods are liquid phase microextraction [6], liquid–liquid extraction [7], ion-exchange [8], resins chelation [9], fiber chelation [10], solid-phase extraction (SPE) [11,12], electrochemical deposition [13] and cloud point extraction (CPE) [14]. CPE technique has become increasingly popular in comparison with the classical liquid–liquid extraction method because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection.

Micelles and other organized amphiphilic assemblies are increasingly utilized in analytical chemistry especially in separation and preconcentration procedures. Their unique micro heterogeneous structures capable of selective interaction with different solute molecules can strongly modify solubility, chemical equilibrium, kinetics and the spectroscopic properties of analytes and reagents [15,16]. Compared with other extraction methods such as liquid–liquid extraction, cloud point extraction (CPE) exhibits much more environmentally friendly properties, and it is safer because small volumes of noxious surfactants are used instead of toxic organic solvents. CPE is an attractive technique that reduces the consumption and exposures to a solvent and it also reduces disposal costs and extraction time that has been used for preconcentration of metal ions after the formation of sparingly water-soluble complexes [17–19]. Triton X-114 was chosen as the non-ionic surfactant because of its low cloud point temperature and high density of the surfactant-rich phase as well as its low cost commercially and lower toxicity. The efficiency of the cloud point extraction depends on the hydrophobicity of the ligand and of the complex formed, on the apparent equilibrium constants in the micellar medium and on the formation kinetics of the complex and on the transference between the phases.

In the present work, a new reagent, 2-amino-4-(*m*-tolylazo) pyridine-3-ol (ATAP) was synthesized, characterized and used for preconcentration and determination of copper(II) by spectrophotometry based on cloud-point extraction (CPE) of the copper(II) complexed with ATAP using Triton X-114 as surfactant. The proposed method was also applied to the determination of copper in food, water and biological samples.

Experimental

Apparatus

All Absorption spectra and absorbance measurements were recorded and measured with a Perkin-Elmer λ3B double beam UV–VIS spectrophotometer with 5.0 mm quartz cuvettes. An Orion research model 601A/digital ionalyzer fitted with a combined glass–calomel electrode was used for pH adjustment and checking the pH value of buffer solutions. An inductively coupled plasma (ICP) model Varian Liberty 150AX Turbo was used for copper concentration determination. A Hettich, EBA 21 model centrifuge with 50 mL calibrated centrifuge tubes were used to achieve and accelerate the phase separation process, respectively. A thermostated water bath with a good temperature control within ±1.0 °C was used for cloud point temperature experiments.

In order to characterize the synthesized reagent, the IR spectrum was recorded as KBr discs using Matson FTIR spectrophotometer in the 4000–200 cm^{-1} range. The ^1H-NMR spectrum of the reagent was performed using a varian EM 390-90 NMR spectrometer in d^6-DMSO as solvent using tetramethylsilane (TME) as an internal standard. The microanalysis of C, H and N of this compound was performed in the Microanalytical Center of Cairo University.

Chemicals and reagents

High-purity ethanol, methanol, isopentyl alcohol, chloroform, nitric acid, hydrochloric acid, and ammonia solution all from Merck (Darmstadt, Germany) were used without any further purification. Analytical-grade cupric nitrate, mercuric chloride, sodium molybdate, sodium tungstate, sodium acetate, hydroxylamine hydrochloride and nitrate salts of sodium, potassium, lithium, calcium, barium, beryllium, magnesium, manganese, strontium, cobalt, iron, lead, and nickel all from Merck were of the highest purity available and used without any further purification. Doubly distilled and deionized water was used throughout.

A standard stock copper solution (1000 mg L^{-1}) was prepared by dissolving 0.3802 g of $Cu(NO_3)_2 \cdot 3H_2O$, (Merck) in water and diluting to 100 mL. This solution was standardized by iodimetric titration. Working solutions were prepared by appropriate dilution of the stock solution. A 2.0% (v/v) Triton X-114 from Merck was prepared by dissolving 2.0 mL of Triton X-114 in bidistilled water in 100 mL volumetric flask with stirring. Cloud point of Triton X-114 in aqueous solution is 24 °C [20].

Thiel buffer solutions of pH 2.0–12 were prepared by mixing different proportions of two successive solutions in the following list to obtain the required pH-value:

(a) 0.05 M oxalic acid +0.20 M boric acid;
(b) 0.20 M boric acid +0.05 M succinic acid +0.05 M sodium sulphate;
(c) 0.05 M sodium tetraborate;
(d) 0.05 M sodium bicarbonate; resulting in a + b (pH 1.5–2.5), b + c (pH 3.0–9.0), and c + d (pH 9.5–12) [21].

Synthesis of 2-amino-4-(m-tolylazo)pyridine-3-ol (ATAP) reagent

The azo dye under investigation was prepared by the common way used for preparing azo dye derivatives of aromatic amines. A 0.01 mole of *p*-toluidine was converted to the hydrochloric form by adding the least amount of 1:1 HCl then diluting with water and cooling at −2.0 °C. A cooled solution of $NaNO_2$ (0.01 mole) is added gradually with continuous stirring to the amine salt. The resulting diazonium salt solution is allowed to stand in ice bath for 15 min with stirring at −2.0 °C and added gradually to a solution of 0.01 mole of 2-amino-3-hydroxypyridine dissolved in 10% NaOH which cooled at −2.0 °C. The resulting solution is allowed to stand for 15 min with constant stirring until the azo dye completely formed. The obtained azo compound is filtered off, dried and recrystallized in ethanol. The purity of the resulting azo compound is checked by measuring the melting point constancy. The chemical structure of the synthesized reagent (ATAP) (Fig. 1) was detected by elemental analysis (C, H, N), IR and ^1H-NMR spectra.

A 5.0×10^{-4} M solution of the ATAP reagent was prepared by dissolving an appropriate weight of reagent in 10 mL ethanol and