Original article

Simultaneous extraction and preconcentration of copper, silver and palladium with modified alumina and their determination by electrothermal atomic absorption spectrometry

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A B S T R A C T

In the present work, an easy solid phase extraction method using alumina modified with polyethylenimine as a new adsorbent was applied to the simultaneous extraction of copper, silver, and palladium ions prior to their determination with electrothermal atomic absorption spectrometry. The analytical procedure involved the complex formation of these cations with polyethylenimine as a chelating agent in buffer media of pH 7.0. Under the optimum conditions, a preconcentration factor of 200, 150, and 200, precision of $\pm 5.4\%$, $\pm 4.7\%$, and $\pm 5.2\%$ and linear calibration ranges of 15.0–140, 4.0–93, and 7.5–125 ng/L (in original solution) for Cu, Ag, and Pd were obtained, respectively. Also detection limits of 3.9, 1.1, and 2.0 ng/L were obtained for Cu, Ag, and Pd, respectively. The proposed method was applied to the determination of copper, silver, and palladium in some real samples with satisfactory results.

1. Introduction

Presently, determination of trace heavy and precious metals in environmental samples is essential, because they have negative effects on human health [1,2].

Copper is one of the most widely distributed elements in the environments of industrialized countries. It is present in all organisms, land and marine. It has been shown that copper is an essential element in many biological processes, such as blood formation and the function of many important enzymes. Copper is classified as a biogenic element, playing a significant role in photosynthesis, metabolism of nitrogen compounds, or regulation of RNA and DNA transcription process [3].

Silver is an industrially important element. The widespread use of silver compounds and silver-containing procedures in industry, medicine, jewelry, cloud seeding, and in the disinfection of drinking water has resulted in increasing silver content of environmental samples. It is used for the preparation of corrosion-resistant alloys, and its compounds are extensively used in

the processing of foods, drugs, beverages, and in filters and other equipment to purify water [4].

The importance of palladium has grown in recent years due to its increasing use in the production of dental and medical devices, jewelry, and catalytic converters. Although the benefits of car catalysts are indisputable, the emission of Pd into the environment is largely associated with the production and recycling of catalytic converters in the metal finishing industry as well as the operation of vehicle catalysts [5].

All of these issues emphasize the importance of identifying and quantifying Cu, Ag, and Pd to provide comprehensive information about their properties and human health relevance. For this purpose, several analytical methods have been developed to measure these ions in clinical, environmental, industrial, and pharmaceutical samples including: spectrophotometry, flame atomic absorption spectrometry (FAAS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and electrochemical methods.

Electrothermal atomic absorption spectrometry (ETAAS) is a good technique for the determination of ultra-trace amounts of heavy metals in several types of samples due to its sensitivity [6]. But by reason of ultra-low concentration of metals and high concentration of interfering matrix components in most real samples, ETAAS often requires a suitable pretreatment step.

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Various techniques have been used for the separation and preconcentration of Cu, Ag, and Pd, such as dispersive liquid–liquid microextraction (DLLME), solidified floating organic drop microextraction (SFODME), and cloud point extraction (CPE).

To the best of our knowledge, there was no previous literature on the application of modified Al_2O_3 and ETAAS for simultaneous column preconcentration and determination of ultra-trace amounts of copper, silver, and palladium. In this work, the adsorption behavior of Cu, Ag, and Pd on modified Al_2O_3 with polyethylenimine (PEI) as a novel solid phase extractor was studied. Experimental parameters affecting the column preconcentration and determination of metals, such as ETAAS temperature program, pH, eluent type, sample and eluent flow rates, sample volume, and interfering ions were studied and optimized. The proposed method has been applied for the determination of trace amounts of Cu, Ag, and Pd in sea water, synthetic samples, and standard reference materials with satisfactory results.

2. Experimental

2.1. Apparatus

Copper, silver, and palladium measurements were performed with a Varian Spectra AA 220 atomic absorption spectrometer (Varian, Australia) with a deuterium lamp background correction and equipped with a graphite furnace (GTA-110 series). Optimum operating parameters for ETAAS are given in Table 1. A Metrohm 713 pH meter (Metrohm, Switzerland) was used for pH measurements with a combined glass calomel electrode. Thermogravimetric analysis (TGA) was accomplished with a Perkin-Elmer TGA-USA (pyris) (Perkin-Elmer, USA). Also a mechanical shaker with speed control was used for preparation of the adsorbent. A Thermo Finnigan Flash EA1112 microanalyzer (Finnigan, Germany) was used for determination of C, H, N percentage.

2.2. Reagents

All chemicals were of analytical reagent grade, and deionized water was used in all experiments. Stock solutions of copper (1000 mg/L) and silver (1000 mg/L) were prepared by dissolving the appropriate amount of copper nitrate ($Cu(NO_3)_2$, Merck, Germany) and silver nitrate ($AgNO_3$, Merck, Germany) in deionized water, respectively. A stock solution of Pd^{2+} (1000 mg/L) was prepared by dissolving a proper amount of palladium chloride ($PdCl_2$, Merck, Germany) in 10.0 mL of HCl (1.0 mol/L) and diluted to 250.0 mL in a standard flask. Solutions of lower concentrations were prepared daily by a suitable dilution of the stock solutions with deionized water. Also, a solution of polyethylenimine (5%) (Molecular weight: 600,000–1,000,000) (Fluka, Switzerland) was prepared in deionized water. Al_2O_3 (Fluka, Switzerland) was used as an adsorbent. A 1.0 mol/L solution of thiourea (Merck, Germany) was prepared by dissolving a proper amount of thiourea in deionized water. Buffer solution was prepared from 0.1 mol/L of KH_2PO_4/K_2HPO_4 (Merck, Germany) for pH7. HCl, HNO_3, and $NaNO_3$ were purchased from Merck (Germany).

2.3. Preparation of modified adsorbent

The modified alumina with PEI (PEI/Al_2O_3) was prepared as following: 1.0 g of alumina, 0.5 g of $NaNO_3$, and 5.0 mL of PEI (5%) was mixed, and the pH was adjusted to about 7.0. The obtained suspension was shaken for 24 h. Then, the adsorbent was filtered, washed several times with deionized water and finally dried in a desiccator. It was characterized by elemental analysis (C, H, N) (Table 2) and TGA. The thermogravimetric analysis curve of the PEI/Al_2O_3 adsorbent shows four mass loss steps. The 1.7% mass loss up to 88.6 °C in the first step is due to adsorbed water. In the second step, the mass loss is 3.9% up to 296.4 °C. In the third step, mass loss is 3.9% up to 506.5 °C, and in the fourth step, mass loss is 1.53% up to 723.1 °C. The mass losses in the second, third and fourth steps correspond with PEI.

2.4. Preparation of column

A total of 50.0 mg of modified adsorbent (PEI/Al_2O_3) was slurred in water and then poured into a funnel-tipped glass tube (length: 80 mm, diameter: 5 mm). Before use, the column was conditioned with the buffer solution at pH 7.0. Cotton was placed at the bottom and the top of the column to allow the adsorbent to settle properly.

2.5. Recommended procedure

100.0 mL of the standard multi-element solution containing 100.0 ng of Cu, Ag, and Pd and 10.0 mL of buffer solution (pH = 7) was passed through the column with the desired flow rate (2.0 mL/min). Then, the formed metal chelates that settled on the column were desorbed with two 5.0 mL of eluent solution at the flow rate of 4.0 mL/min. Each 5.0 mL of eluent contains 3.0 mL of thiourea (1.0 mol/L) and 2.0 mL of HCl (1.0 mol/L). Finally, 20.0 μL of each 5.0 mL of eluate solution was automatically injected by the autosampler into the graphite tube and then the absorbance of Cu, Ag, and Pd were measured under the operating conditions summarized in Table 1.

2.6. Samples preparation

2.6.1. Sea water

The selected water sample (Caspian Sea water) was filtered through a Millipore filter to remove suspended particulate matter.

Table 1
Instrumental parameters and thermal programs of ETAAS for determination of Cu, Ag and Pd.

(a) Instrumental parameters			
Parameter	Cu	Ag	Pd
Wavelength (nm)	327.4	328.1	244.8
Spectral bandwidth (nm)	0.5	0.5	0.2
Lamp current (mA)	4	4	5
Signal measurement	Peak height	Peak height	Peak height
Sample volume (μL)	20	20	20

(b) Temperature programs			
Step	Furnace temp. (°C)	Time (s)	Argon flow rate (L/min)
Drying	85	5	3.0
Drying	95	40	3.0
Drying	120	10	3.0
Ashing	800[a],400[b], 1000[c]	5	3.0
Ashing	800[a], 400[b], 1000[c]	1	3.0
Ashing	800[a],400[b], 1000[c]	2	3.0
Atomization	2300[a], 2000[b], 2500[c]	1.1[a], 0.9[b], 1.2[c]	0
Atomization	2300[a], 2000[b], 2500[c]	2	0
Cleaning up	2400[a], 2100[b], 2600[c]	2	3.0

[a] Cu.
[b] Ag.
[c] Pd.

Table 2
Elemental analysis (C, H, N) for two kinds of adsorbent.

Adsorbent	Element (%)		
	Nitrogen	Carbon	Hydrogen
PEI + alumina[a]	1.34594	1.74820	0.81426
PEI + alumina + NaNO$_3$[a]	1.47334	1.95490	0.84415

[a] Average of two measurements.