

NICKEL AND COPPER EXTRACTION FROM LIQUID SAMPLES USING CARBON NANOTUBES

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Abstract

Novel carbon-based materials find nowadays increasing use in analytical science, mainly due to their unique properties. Carbon nanotubes (CNTs), one of the carbon-based materials, could possibly be used for the preconcentration and separation of trace amounts of heavy metal from liquid samples. Method called solid phase extraction (SPE) is used as extraction method for metal preconcentration, and carbon nanotubes (CNTs) are considered to be suitable solid sorbent material for this technique. Multiwalled carbon nanotubes were used as a solid phase extractor for Ni²⁺ and Cu²⁺ ions from liquid samples in this study. Experimental parameters including, pH of sample solution, oxidation technique of MWCNTs, amount of solid sorbent and analytes, concentration of eluent were investigated, focusing on the influence of these parameters on quantitative recoveries of the analytes. Analyte content in each sample or extract was determined by flame atomic absorption spectrometry (FAAS).

Keywords: nickel – copper - nanomaterial - carbon nanotubes - solid phase extraction

1 Introduction

Solid-phase extraction plays an important role in sample preparation process by replacing the classic liquid–liquid extraction in environmental and food analyses. The main objectives of sample preparation are the removal of potential interferences, analyte preconcentration, or converting the analyte into a more suitable form for detection or separation [1].

Carbon nanotubes are relatively new material, which, in the field of analytical chemistry, has obtained wide attention in recent years. Strong interactions of hexagonally grouped carbons in graphene sheets of CNTs, with other molecules and large specific surface area make this material a promising solid sorbent for preconcentration procedures [2]. In contrast to the activated carbon, CNTs have a well-defined structure at atomic scale, so reproducible results of metal preconcentration can be achieved [3]. Carbon nanotubes can be divided into two categories: singlewalled CNTs (SWCNTs) which look like hexagonal sheets of graphite rolled into cylindrical tubes and multiwalled CNTs (MWCNTs) consisting of several concentric SWCNTs [4, 5].

Usually metal ions in an aqueous medium are not capable of spontaneous adsorption on the surface of non-modified carbon nanotubes, and therefore it is necessary to modify them. The simplest form of modification of the carbon nanotube surface is by oxidation process. This process forms free oxygen functional groups on the surface of CNTs (for example -OH, -C=O, -COOH), and consequently causes their increased solubility in aqueous media [3]. These

functional groups containing oxygen radicals are capable of binding metal ions at a suitable pH. The oxidation of nanotubes can be carried out with acid reflux with HNO_3 , H_2SO_4 , HCl , or with oxidizing agents such as KMnO_4 and H_2O_2 [6]. The literary overview of carbon nanotubes oxidation methods, before utilizing them as a solid sorbent, is given in **Table 1**.

Table 1 Overview of CNTs oxidation processes

Oxidation reagent	V_{reagent} [cm^3]	m_{CNTs} [g]	Time [h]	Temperature [$^{\circ}\text{C}$]	Note	Reference
conc. HNO_3	-	-	1	25	reflux	[2]
conc. HNO_3	30	3	12	25	-	[7]
conc. HNO_3	-	-	1	25	reflux	[8]
conc. HNO_3	50	5	5	80	reflux	[9]
conc. HNO_3	25	1	6	100	-	[10]
HNO_3	-	-	5	80	reflux	[3]
$8 \text{ mol dm}^{-3} \text{HNO}_3$	50	2	12	25	-	[11]

The metal analytes adsorbed onto oxidized CNTs can be quantitatively desorbed with the aid of acidic eluting agents. Low pH of the eluent provides quantitative elution of analytes due to the competition between H^+ and metal ions [3]. Most commonly used elution agents and their concentrations are shown in **Table 2**.

As was mentioned above, nitric acid oxidation of carbon nanotubes leads to functionalization of the surface, and hence to the creation of functional groups containing oxygen radical. The surface charge of nanotube depends on the pH of surrounding electrolyte [2]. The sorption of metal ions on surface of the oxidized nanotubes increases in general with increasing pH. The surface of carbon nanotubes at higher pH is more deprotonated ($-\text{COOH} \rightarrow -\text{COO}^-$), which causes electrostatic interactions between metal ion Me^{2+} and oxygen functional group [9]. Sorption of the analyte onto surface of CNT varies with the metal ion to be sorbed. It was shown [2, 9], that within the range of pH 7 – 9, affinity of metal ion to CNTs surface is decreasing in this order: Cu^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} .

2 Experimental conditions

2.1 Reagents and materials

Synthetic aqueous solutions of copper, nickel and other accompanying metals were prepared from water stock solutions with certified content $1.000 \pm 0.002 \text{ g dm}^{-3}$ of given element in 2 % HNO_3 (ANALYTIKA®). Analytical grade salts ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CaCO_3 , Na_2SO_4 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, NaCl) were added to deionized water to create model solution containing main macro components of natural water at their average contents. The model solution content is listed in **Table 3**. A phosphate buffer solution was prepared by mixing of appropriate volumes of $0.2 \text{ mol dm}^{-3} \text{Na}_2\text{HPO}_4$ and $0.2 \text{ mol dm}^{-3} \text{KH}_2\text{PO}_4$ for pH = 6 – 9 and acetate buffer solution prepared by mixing of appropriate volumes of $0.2 \text{ mol dm}^{-3} \text{CH}_3\text{COOH}$ and $0.2 \text{ mol dm}^{-3} \text{CH}_3\text{COONa}$ for pH = 4 – 5.5. Multiwalled carbon nanotubes MWCNTs (> 95 % purity, 10 – 20 nm outer diameter, 10 – 30 μm length) used in experiments were purchased from Chengdu Organic Chemicals Co. Ltd.

Table 2 Overview of SPE-CNT experimental conditions

Element	Sample type	Sorbent type	Eluent	Detection technique	Reference
Au	geological samples, water	MWCNT	3 % thiourea in 1 mol dm^{-3} HCl	F-AAS	[2]
Au, Mn	water	MWCNT-NBHAЕ	0.1 mol dm^{-3} $\text{Na}_2\text{S}_2\text{O}_3$	F-AAS	[7]
Rare earth elements	lake water	MWCNT	1 mol dm^{-3} HNO_3	ICP-OES	[8]
Cu, Cd	food, water	MWCNT-APDC	HNO_3 + Acetone	F-AAS	[12]
Cu, Pb	sea, mineral water	MWCNT	3 mol dm^{-3} HNO_3	F-AAS	[13]
Cu	water	MWCNT	2 mol dm^{-3} HNO_3	F-AAS	[14]
Mn	water, aluminum alloy	MWCNT-PAN	0.1 mol dm^{-3} HNO_3	F-AAS	[15]
Cr, Pb	natural waters	MWCNT-EDA	1 mol dm^{-3} HCl	ICP-OES	[16]
Co, Ni, Hg	water	MWCNT	9 cm^3 Acetonitril	HPLC	[17]
Pb	water	MWCNT-PPy	10 cm^3 3 mol dm^{-3} HNO_3	F-AAS	[18]
Fe, Zn	sea, lake water	MWCNT	1 cm^3 1 mol dm^{-3} HNO_3	HR-CS GFAAS	[19]
Pb	urine	MWCNT	0.7 mol dm^{-3} HNO_3	ETAAS	[20]

APDC Ammonium pyrrolidine dithiocarbamate, EDA Ethylenediamine, ETAAS Electrothermal Atomic Absorption Spectrometry, HPLC High Performance Liquid Chromatography, HR-CSGFAAS High-resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry, NBHAЕ N,N'-bis (2-hydroxybenzylidene)-2,2'(aminophenylthio)ethane, PAN 1-(2-pyridylazo)-2-naphthol, F-AAS Atomic absorption spectrometry with flame atomization, ICP-OES Inductively coupled plasma optical emission spectroscopy

Table 3 Model solution content

Ion	Ca^{2+}	Mg^{2+}	Na^{2+}	Fe^{2+}	Cl ⁻	SO_4^{2-}	HPO_4^{2-}	HCO_3^-	$\text{Zn}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}$
Content [$\mu\text{g cm}^{-3}$]	100	40	30	0.2	50	50	0.2	150	0.5 - 5

2.2 Methods and apparatus

Extractions were carried out by mechanical shaking on shaker TS-400TD (M.R.C. Israel) in bath arrangement for 4 hours. Samples after adsorption onto CNTs were:

- filtered through filter paper for quantitative analysis, (medium filter speed, \varnothing 18.5 cm) and then analyzed by FAAS,
- centrifuged on CN-3100 (M.R.C. Israel) by 3000 RPM for 10 minutes, then the sample after extraction was separated from the solid residue by inverting the tube, 5 cm^3 of eluent was added to the solid residue, the suspension was shaken for 15 minutes on

laboratory shaker, the sample after elution was filtered through filter paper and analyzed by FAAS.

The determination of copper and nickel in samples after extraction and in samples after elution was carried out on Perkin Elmer 3030 atomic absorption spectrometer with flame atomization with these conditions: slit width: 0.7 nm, gas flow: 45 dm³ hour⁻¹ (air), 17 dm³ hour⁻¹ (acetylene), wavelength: 324.8 nm (Cu), 231.9 nm (Ni). The microwave-assisted and ultrasound-assisted oxidation process of CNTs was performed by high performance microwave digestion system (Ethos ONE, MILESTONE) and ultrasound probe (UZD 500, Person-Ultragen).

3 Results and discussion

The aim of this work was to optimize selected experimental conditions of novel and simple method of preconcentration for selected metal ions Cu²⁺ and Ni²⁺ using carbon nanotubes as a solid sorbent, before their determination by atomic absorption spectrometry with flame atomization.

3.1 pH of sample solution

First condition that needs to be optimized in SPE-MWCNTs extractions is the pH value of sample solution. Model distilled water solutions containing 2 µg cm⁻³ of Cu and Ni were prepared and their pH values were modified with appropriate buffer solution to achieve pH values from 4.0 to 9.0. Twenty milliliters of model solutions were then added to 200 mg of oxidized CNTs sorbents and shaken for 4 hours. The dependences of Cu and Ni recoveries on sample solution pH in pH range of 4.0 – 9.0 are shown in **Fig 1**. The highest recoveries were achieved by extracting metal ions at pH value of 9.0 in both cases. This pH was used as constant in our further experiments.

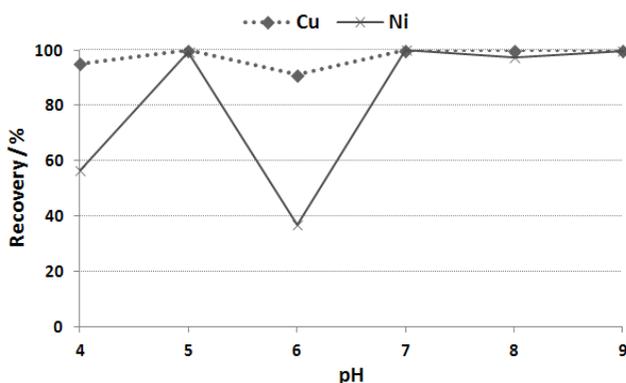


Fig. 1 The influence of sample solution pH on the extraction recoveries of Cu and Ni

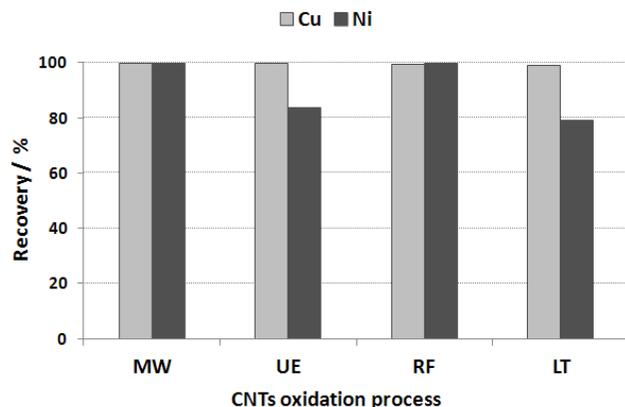
3.2 Oxidation of CNTs

Second most important parameter of SPE-MWCNTs extraction is the oxidation process of CNTs material. Four types of CNTs oxidation were chosen: microwave-assisted oxidation (MW), ultrasound-assisted oxidation (UE), oxidation using reflux (RF), and laboratory temperature oxidation (LT). Experimental properties of this four oxidation processes are given in **Table 4**.

Table 4 Experimental properties of CNTs oxidation

	Performance [W]	Time [min]	Temperature [°C]	Oxidation agent
MW	500	20	140	conc. HNO ₃
UE	350	10	-	conc. HNO ₃
RF	-	360	140	conc. HNO ₃
LT	-	720	20	conc. HNO ₃

The dependences of analytes recoveries according to the type of CNTs oxidation process used in SPE-CNT extractions are shown in **Fig. 2**. It is clear that microwave assisted oxidation of CNTs and their oxidation with reflux were two methods best suitable for CNTs treatment before their use in solid phase extraction of Cu and Ni from liquid solutions. The extraction efficiency of Ni was only around 80 %, by the use of other two methods. We have chosen oxidation with reflux for pretreatment of CNTs in our further studies. This was mainly due to the fact, that it was possible to oxidize higher amount of CNTs at once, than it was possible with the microwave technique.

**Fig. 2** The influence of CNTs oxidation process on the extraction recoveries of Cu and Ni

3.3 Amount of analyte

Next step was the determination of analytes amount that could be quantitatively adsorbed onto 200 mg of oxidized CNTs in the presence of other macro and micro components (components content are given in **Table 3**). Experimental conditions of these experiments were as follows: 40 cm³ of model solution containing from 0.5 to 5 µg cm⁻³ Cu and Ni + 2 cm³ of phosphate buffer (pH = 9) were shaken with 200 mg CNTs for 4 hours on laboratory shaker and then filtered through filter paper. The filtrates were measured for Cu and Ni contents that did not adsorb onto the solid sorbent. At the end, the recoveries were calculated. Results of these experiments are shown in **Fig. 3**. It is clear that 200 mg of oxidized CNTs were sufficient for quantitative retention of 20 - 200 µg Cu. In contrast, this amount of CNTs was not sufficient even for 20 µg Ni quantitative adsorption. The other accompanying components in model solutions could have been preferentially extracted instead of nickel ions at given pH. This resulted in the depleted sorption capacity of 200 mg of solid sorbent.

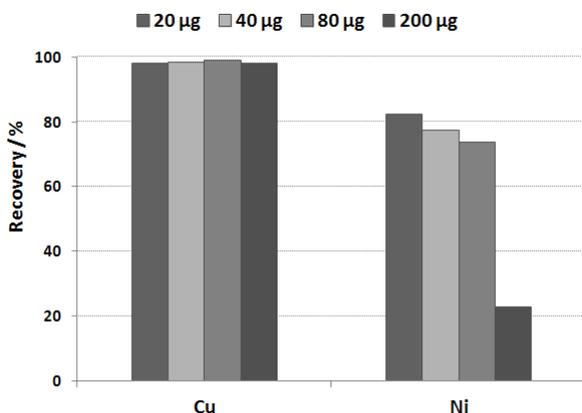


Fig. 3 The influence of analyte amount on the extraction recoveries of Cu and Ni

3.4 Amount of solid sorbent

According to the previous results, it was necessary to increase the amount of solid sorbent for quantitative extraction of Ni in further experiments. Therefore, the influence of solid sorbent amount onto the extraction recoveries of Cu and Ni was examined. For this purpose, 40 cm³ of model solution containing 1 µg cm⁻³ of Cu, 1 µg cm⁻³ of Ni and other components was applied onto 50 - 1000 mg of oxidized CNTs. The results showed that 50 mg of solid sorbent were enough for quantitative adsorption of Cu. On the other hand, more than 1000 mg of oxidized CNTs would be needed for quantitative adsorption of 40 µg Ni, in the presence of other macro and micro components in the sample. The results are graphically illustrated in **Fig. 4**.

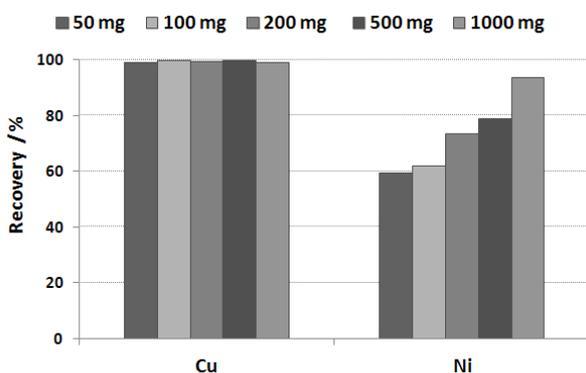


Fig. 4 The influence of sorbent amount on the extraction recoveries of Cu and Ni

3.5 Concentration of eluent

The influence of eluent concentration onto the elution efficiency of the analytes was evaluated by the preconcentration and subsequent elution of 40 µg Cu and 40 µg Ni from model aqueous solutions (Fig. 5). The analytes intercepted onto 200 mg of oxidized CNTs were eluted by 5 cm³ of nitric acid in concentration range 0.1 – 5 mol dm⁻³ HNO₃. The highest elution efficiencies were obtained by utilizing 5 cm³ of 0.5 and 5 mol dm⁻³ HNO₃ (around 60 %) for Cu and 5 mol dm⁻³ HNO₃ (around 50 %) for Ni. In any case, this maximum 60 % elution efficiency was not

sufficient and to increase the elution efficiency it is strongly recommended to test another type of eluent, increase the eluent volume or the eluent contact time with sample.

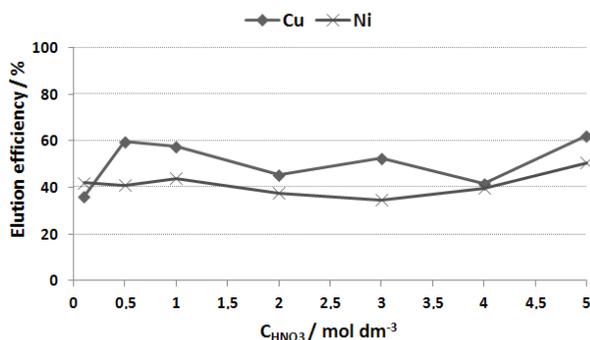


Fig. 5 The influence of eluent concentration on the elution efficiency of Cu and Ni

4 Conclusions

The impacts of chosen experimental conditions of SPE-CNT extraction on the recoveries of copper and nickel from model solutions were studied in this work. Based on the experimental results, the following conclusion can be stated:

- The experiments showed that the sorption efficiency of Cu^{2+} onto oxidized CNTs sorbent in the pH range 4.0 – 9.0 was stable and almost 100 %. The sorption efficiency of Ni^{2+} was unstable in the pH range 4.0 – 7.0 and stable from 7.0 – 9.0 and almost 100 %. The optimum pH for sorption of Cu^{2+} and Ni^{2+} was determined at pH = 9.0.
- The most suitable methods of CNTs oxidation are provided with the aid of microwave energy and with reflux. Reflux is more suitable for large amounts of CNTs to be oxidized.
- Two hundred milligrams of carbon nanotubes modified by oxidation were sufficient to adsorb up to 200 μg of copper from synthetic aqueous medium containing other macro and micro components with almost 100 % efficiency. In the case of Ni, 200 mg of CNT were not even sufficient for adsorption of 20 μg of Ni in the presence of other components.
- The experiments showed that 1000 mg of oxidized CNTs were with 93 % efficiency sufficient for adsorption of 40 μg of nickel.
- By using 0.1 - 5 mol dm^{-3} HNO_3 as eluent was the elution efficiency only around 50 % for Ni and cca 40 – 60 % for Cu. In further applications, it is strongly recommended, to try longer eluent contact time with sample or to use larger eluent volumes in the experiments.

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