



Simultaneous determination of nickel, cobalt and mercury ions in water samples by solid phase extraction using multiwalled carbon nanotubes as adsorbent after chelating with sodium diethyldithiocarbamate prior to high performance liquid chromatography



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ABSTRACT

Multiwalled carbon nanotubes (MWNTs) have been widely used for the enrichment of trace important pollutants in environment because of its large specific surface area, high extraction efficiency, and easy operation. In this study, a solid phase extraction method was established to determine nickel (Ni^{2+}), cobalt (Co^{2+}) and mercury (Hg^{2+}) ions using MWNTs as the adsorbent and sodium diethyldithiocarbamate (DDTC) as the chelating agent. The final analysis was performed on a high performance liquid chromatography (HPLC). The factors that may influence the extraction efficiency were optimized in detail including the type and volume of elution solvent, sample pH, volume of chelating agent solution, and volume of sample solution, etc. The experimental results indicated that good linear relationship between peak area and the concentration of the ions was achieved in the range of $0.1\text{--}100\ \mu\text{g L}^{-1}$, $0.1\text{--}50\ \mu\text{g L}^{-1}$, and $2.7\text{--}300\ \mu\text{g L}^{-1}$ for Ni^{2+} , Co^{2+} , and Hg^{2+} , respectively. The precision was determined by calculating the relative standard deviation (R.S.D.) values that were in the range of 6.2–11.7% under the optimal conditions. The detection limits of Ni^{2+} , Co^{2+} , and Hg^{2+} were in the range of $0.04\text{--}0.9\ \mu\text{g L}^{-1}$ ($S/N=3$). The presented method was applied for the determination of the metal ions mentioned above in real water samples, and satisfied results were achieved. All these indicated that proposed method will be a good alternative tool for monitoring the target ions in environmental samples in the future.

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1. Introduction

Heavy metals are important pollutants in environment due to their toxic effect on human health. Different from other kinds of pollutants, heavy metals cannot be eliminated from environment easily, and can always result in serious damage to human body. Nickel, cobalt and mercury are three typical metal ions in environmental samples. Although nickel is considered an essential trace element, its toxic effects are well known and it is also considered one of the most common causes of allergic contact dermatitis and respiratory system diseases [1–3]. Cobalt can produce toxicological effects including vasodilation, flushing and cardiomyopathy [4]. Mercury is also known as the most neurotoxic element [5] and can damage most of organs and tissues in human body. Since long times

ago, it is always a hot topic to develop simple, sensitive, cheap, and rapid determination methods for these metal ions.

Generally, there are many determination methods for the analysis of metal ions including flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma optical emission spectrometry (ICP-OES), ion trap mass spectrometry [6–9] and so on. As multielement analysis was concerned, there are also many methods developed with instruments mentioned above. For instance, Lin et al. determined the concentrations of mercury, lead, and cadmium with ICP-MS and arsenic with AFS in maternal blood [10]. Lagerström et al. established an automated on-line flow injection ICP-MS method for the determination of Mn, Fe, Co, Ni, Cu and Zn in open ocean seawater [11]. Qin et al. have developed a sensitive method for the heavy metals in *Indocalamus tesselatus* samples using inductively coupled plasma

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orthogonal acceleration time-of-flight mass spectrometry (ICP-oo-TOF-MS) [12]. Besides, ICP-OES is also an important tool for the measurement of heavy metal contamination [13]. ICP-MS, ICP-AES and ICP-OES could realize the simultaneous determination of heavy metals, but the cost for instruments and running is very expensive. GFAAS cannot match such requirement directly, and AFS generally realized the simultaneous determination of two elements by two channels. In order to solve these problems, liquid chromatography, ion chromatography, and their combination with ICP-MS, ICP-OES, UV and so on were reported [14–19]. These methods have provided some good merits for the analysis of heavy metals in environmental samples. Compared with these methods, high performance liquid chromatography has advantages such as good ability to separate and determine multiple analytes, low cost, and low limit of detection, and has been widely used in the determination of multiple components like polycyclic aromatic hydrocarbons, pesticides, metal chelates and so on [20–23]. It is expected that it will have great prospect in multielemental analysis.

Usually, the determination of heavy metals in environment cannot be conducted directly because the concentrations of heavy metal ions in environment samples are always at very low levels [24] and the sample matrices are very complex which would have impacts on the analysis of heavy metals. So separation and preconcentration procedures are always used before the determination of heavy metal ions such as dispersive liquid–liquid microextraction, ion-exchange, solid phase extraction with silica and activated carbons, and coprecipitation, flow injection and online mini-column preconcentration, etc. [14,25–29]. Among these methods, solid phase extraction (SPE) is one of the important pre-concentration methods in environmental analysis. Due to its simple operation, high enrichment factor, short extraction time, ability to deal with large volume of sample solution and low cost, SPE is widely used as an extraordinary pre-concentration method. Many kinds of new solid phase extraction material have been suggested for the enrichment of heavy metals from aqueous samples. Nowadays, the often used materials are activated carbon, C₁₈, silica gel, metallic oxide, carbon nanotubes and so on [24,27,28,30]. Among the materials, carbon nanotubes (CNTs) absorbed much more attention due to their high strength, high conductivity, high thermal conductivity and giant specific surface area. Since CNTs can be described as a sheet of graphite that has been rolled into a tube, and they can be divided into multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) [31]. Carbon nanotubes (CNTs) have been proposed as a magnificent solid phase adsorbent in many studies and have been applied to the pre-concentration and detection of trace environment pollutants including polycyclic aromatic hydrocarbons, pesticides, metal ions, nerve agents and so on [20–22,24,32–34]. However, no report was found on the simultaneous enrichment and determination of multielements with solid phase extraction using MWCNTs as the adsorbent coupled to HPLC.

In this study, the main goal is to investigate the potential of multi-walled carbon nanotubes as an adsorbent in extracting trace nickel, cobalt and mercury ions in environmental water samples. The potential factors affecting the SPE and subsequent HPLC separation of the analytes were optimized and discussed in detail.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade and were used without further purification. Purified water was purchased from local supermarket. Heavy metal ions stock solutions were prepared by diluting high purity compounds to a concentration of 1000 mg L⁻¹. The concentrations of the metal ions in working

solution were 0.5 mg L⁻¹, 0.5 mg L⁻¹, 3 mg L⁻¹ for nickel (Ni²⁺), cobalt (Co²⁺), and mercury (Hg²⁺), respectively. N-dimethyl dithiocarbamate (DDTC) was purchased from China National Biotec Group (Beijing, China), and its working solution with a concentration of 0.01 mol L⁻¹ was prepared for use. Multi-walled carbon nanotubes were purchased from Shenzhen Nanotech Port (Shenzhen, China), the average diameter was 20–40 nm, and the purity was over 95%.

2.2. Apparatus

MWNTs SPE cartridge was prepared by evacuating the C₁₈ packing from an Agilent SPE C₁₈ cartridge (0.2 g, 3 mL, and polypropylene) and adding 0.1 g MWNTs in the cartridge. The polypropylene upper frit was reset at the upper end of the cartridge to protect the nanotubes. Then the outlet tip of cartridge was connected to a SHZ-3(III) vacuum pump (Yuhua Instrument Co. Ltd., Zhengzhou, Henan), and the inlet part was connected to sample solutions with a polypropylene tube from infusion set.

An Agilent 1260 high performance liquid chromatography system with variable wavelength detector was used for analysis. The separation of the analytes was operated on an Agilent Eclipse XDB C₁₈ column (4.6 mm × 250 mm, 5 μm). The mobile phase was a mixture of methanol and water (80:20, v/v), and the flow rate was set at 1 mL min⁻¹. The column temperature was set at 25 °C, and the chromatographic data was acquired at the following setting of wavelength: 320 nm for 0–8 min, 270 nm for 8–14 min, and 280 nm for 14–18 min. The injection volume was 50 μL. Agilent Chem-Station software was used to control the chromatography units, acquire and process chromatographic data.

2.3. SPE procedure

The SPE cartridge was washed with 20 mL methanol, 20 mL acetonitrile and 50 mL purified water before the first use. Then water sample was spiked with three analytes (nickel ion, cobalt ion and mercury ion). After that the chelating agent and acid or alkali solution was added to adjust the pH of the solution. The reacting time was five minutes, and the solution was passed through the preconditioned cartridge at the highest flow rate. After the sample solution passed, the cartridge was washed with 10 mL purified water to remove co-absorbed materials from the cartridge. Subsequently the chelates retained on the SPE cartridge were eluted with an optimal volume of eluting solvent. The final eluent was blown to dryness with gentle N₂ flow at a temperature of 40 °C. Finally the extract was redissolved in 1 mL methanol and analyzed by HPLC.

2.4. Water samples

Three environmental water samples were collected from river, sewage canal and factory for validation. River water sample was taken from Tonghui River in Chaoyang District in Beijing. Sewage canal water sample was collected from the sewage canal in Chaoyang District. Factory water sample was taken from Chaoyang Electroplate Factory in Chaoyang City in Liaoning Province, China. Before being used, all the environmental water samples were stored in clean bottle at 4 °C.

3. Result and discussion

3.1. Optimization of SPE procedure

In SPE procedure, the enrichment performance could be influenced by several experimental conditions including eluent composition and its volume, sample pH, volume of chelating agent

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