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Carbon nanotubes magnetic hybrid nanocomposites for a rapid and selective preconcentration and clean-up of mercury species in water samples



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ABSTRACT

Hybrid nanocomposites based on Fe₃O₄ magnetic nanoparticles (MNPs) coated with different types of carbon nanotubes (CNTs) have been studied for the first time as sorbent materials for magnetic solid phase extraction (MSPE) for mercury speciation analysis. Monomethylmercury (MMHg) was the target mercury species in water samples and the adsorption and desorption processes were optimized based on this species. Single-walled CNT-MNP showed higher adsorption capacity than double-walled or multi-walled CNTs. Then, the magnetic sorbent was retrieved with an external magnet and MMHg was selectively desorbed from it with dichloromethane (DCM) in two steps with vortex agitation. Inorganic mercury was removed during the desorption stage. The rapid adsorption and desorption equilibrium, the magnetic separation of the sorbent, and the simple and fast synthesis of CNT-MNPs without any additional modification of the CNTs simplified and shortened the extraction procedure. The extract was submitted to derivatization of the mercury species by ethylation (with an optional nitrogen stream evaporation of the organic phase) and injection into a gas chromatograph coupled to an atomic fluorescence detector (GC-pyro-AFS). The overall procedure provides the preconcentration of MMHg up to 150 times and the removal of inorganic mercury at the same time. The procedural limits of detection (LOD) and quantification (LOQ) were 5.4 and 17.9 pg mL⁻¹, respectively. Moreover, magnetic nanocomposites can be reused at least 7 times without losing their efficiency. The methodology was validated in tap, dam and river water samples to evaluate the performance under real conditions with recoveries from 79% to 97% of spiked MMHg.

1. Introduction

Mercury is one of the most toxic elements and has a severe impact on the environment and human health [1]. The toxicity and availability of mercury are defined by the chemical form (species) in which it is found. Thus, organic species, namely monomethylmercury (MMHg) or dimethylmercury (DMHg), are more toxic than inorganic species [2]. Monomethylmercury has a high capacity of bioaccumulation, bioconcentration and biomagnification in the aquatic environment [3]. Therefore, the environmental risk assessment of mercury involves necessarily to carry out speciation analysis in water samples with special emphasis on MMHg.

A large number of analytical techniques has been proposed for the detection and quantification of mercury species but the chromatographic separation hyphenated to atomic fluorescence spectroscopy (AFS) or inductively coupled plasma mass spectrometry (ICP-MS) are the most widely used [4]. Among them, the separation by gas chromatography (GC) coupled to AFS via thermal pyrolysis (GC-pyro-AFS) is particularly advantageous in terms of sensitivity, selectivity and simplicity [5]. In spite of the significant developments in the analytical techniques, the mercury speciation analysis in water samples is still challenging. In these samples, the mercury species are found at ultratrace levels and the concentration of MMHg is much lower than that of inorganic mercury. Indeed, the proportion of organic mercury in marine waters is typically less than 5% of the total mercury concentration [6,7]. Therefore, preconcentration and/or clean-up steps are necessary to detect such low concentrations of MMHg in water samples regardless to the selected techniques used for separation and detection.

Purge and trap, distillation and other techniques have been traditionally used to preconcentrate mercury species, but they are time consuming and involve tedious processes [8,9]. Other preconcentration techniques like dispersive liquid-liquid micro-extraction (DLLME),

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cloud point extraction (CPE) and solid phase (micro-) extraction (SPE, SPME) have emerged as valuable alternatives [4]. Among them, SPE is a very interesting option because it is simple, provides high enrichment factors, requires little volume of organic solvent and, contrary to other traditional techniques, it has experienced a significant evolution in the last years thanks to the use of nanomaterials (NMs) [8,10]. Carbonbased materials and, particularly, carbon nanotubes (CNTs) are one of the most interesting options as sorbent material in SPE due to its structural, physical and chemical properties and also to their wide range of applications [11-13]. They have been widely used for the preconcentration of organic pollutants and heavy metals but in the field of trace element speciation the literature is still scarce [14]. In the case of mercury, most studies have focused on the removal of inorganic mercury from waters [15–17], but few studies have been devoted up to now to mercury speciation analysis [18,19]. Thus, as far as we know, there is only one paper reporting the use of CNTs for mercury species preconcentration [19]. In this work, CNTs were successfully used as sorbents in a continuous on-column preconcentration system after the derivatization of mercury species with sodium diethyldithiocarbamate (NaDDC). However, when the column dynamic extraction mode is used, the time limiting step is the large volume of sample to load to the cartridge. The alternative to the column mode would be the static batch mode but it is very difficult to separate the CNTs from aqueous solutions because of their little size [20]. To overcome these problems, a very interesting option is the new SPE mode based on the use of magnetic nanoparticles (MNPs) which is known as magnetic solid-phase extraction (MSPE) [21]. The extraction efficiency and time are greatly improved because the MNPs can be well dispersed into the samples by ultrasonication or vortex agitation, and then shortly isolated from sample solutions by the application of an external magnetic field. Magnetic-SPE has been previously used for mercury speciation analysis [14,22,23] but, to our best knowledge, the hybrid nanocomposite made up of MNPs and CNTs has never been used for this purpose in spite of the unique properties of CNTs as sorbents and the operational advantages of MSPE.

The aim of this work has been to develop and validate an analytical method for mercury speciation analysis in water using CNT-MNPs. The proposed analytical strategy is based on the simultaneous preconcentration of MMHg and clean-up of inorganic mercury. This preconcentration/clean-up procedure along with the analysis by GC-pyro-AFS meets the requirements of selectivity and sensitivity for the determination of mercury species in water samples.

2. Experimental

2.1. Chemicals and materials

Stock standard solutions of 1000 μ g mL⁻¹ of Hg²⁺ and MMHg were prepared by dissolving mercury (II) chloride (Panreac, Barcelona, Spain) in 5% HNO₃ (Merck, Darmstadt, Germany) and monomethylmercury chloride (Strem Chemicals, Newburyport, USA) in methanol. All stock solutions were stored in amber glass bottles at 4 °C. Working standards were prepared daily by proper dilution with ultrapure water.

Sodium tetraethylborate (NaBEt₄) and sodium thiosulfate were purchased from Sigma–Aldrich (Steinheim, Germany) and Panreac (Barcelona, Spain), respectively. Sodium acetate trihydrate and glacial acetic acid (Scharlab, Barcelona, Spain) were used to prepare the buffer (0.1 M, pH 3.9). Hydrochloric acid (37%) was purchased from Merck (Darmstadt, Alemania). Hexane, dichloromethane (DCM), isooctane and, acetonitrile (MeCN) were purchased from Scharlab (Barcelona, Spain). All chemicals were of analytical-reagent grade.

Iron (III) chloride hexahydrate, sodium acetate (Sigma-Aldrich, Steinheim, Germany) and ethylene glycol (Panreac, Barcelona, Spain) were used to synthesize the magnetic nanoparticles. Different types of CNTs were studied in this work. The main characteristics and Table 1

Main characteristics and manufacturer of CNTs used in this work.

Type of CNTs	Manufacturer	Length (µm)	Diameter (nm)
SWCNTs#1	Sigma-Aldrich	10-30	0.9-1.2
SWCNTs#2	Sigma-Aldrich	2–5	1.2-1.5
DWCNTs	XinNano Materials	2–6	1–3
MWCNTs	Nano-Lab	5-20	30 ± 15

(SW: single-walled; DW: double-walled; MW: multi-walled; CNTs: carbon nanotubes).

manufacturers of these nanocomposites are summarized in Table 1.

Ultrapure water (18.2 M Ω cm at 25 °C) was obtained from an Elga Purelab Ultra Analytic water purification system.

Helium C-50 was used as carrier gas, Argon C-50 was used as makeup at the transfer line and sheath gas at the AFS detector, and Nitrogen C-50 was used for preconcentration. All gases were from Carburos Metálicos (Barcelona, Spain).

2.2. Instrumentation

The mercury species were separated and detected in a GC (Shimadzu GC-2010) coupled to an AFS detector (Millennium Merlin 10025 P.S. Analytical, United Kingdom) via a pyrolysis unit. The optimized conditions of the hyphenated system have already been described in the literature [24].

A conductivity meter (Crison, microCM 2200) and a pH-meter (Crison, Basic 20) were respectively used for the characterization of real water samples. A ZX3 vortex stirrer (Velp Scientifica, Usmate, Italy) was used in the extraction procedure.

A heating module (Reacti-Therm; Pierce, Rockford, IL, USA) with an evaporating unit was used for preconcentration.

2.3. Synthesis of CNT-MNPs

The multiwalled (MW), single walled (SW #1 and #2) or double walled (DW) CNT magnetic composites were prepared according to a previously described procedure [25,26]. Briefly, this synthesis involves the addition of 0.014 g of FeCl₃·6H₂O and 0.004 g of either MW, SW or DW-CNTs. This mixture was suspended in 0.75 mL ethylene glycol in a glass vial. Then, 0.036 g of sodium acetate was added and dissolved. The solution was allowed to stand at room temperature for 30 min. Afterwards, the glass vial was heated in an oven at 200 °C for 24 h. After cooling, the synthetic product was washed for 5 times with 1 mL of deionized water and the CNT-MNPs were recovered by applying a magnetic field via a magnet placed on the outer wall of the glass vial. The CNT-MNPs obtained can be stored in ultrapure water (1 mL) or dried at 80 °C until needed. To confirm that the CNT-MNPs composite was obtained, the synthesized material was characterized by Transmission Electron Microscopy (TEM) [26].

2.4. Magnetic SPE procedure

An amount of 5 mg of magnetic nanocomposite was put in a vial. The material was vortexed for 1 min with 1 mL of MeCN and three times with 1 mL of ultrapure water for conditioning, as in previous works [13,26]. The solvents were discarded after each step. A volume of 10 mL of sample was added to 5 mg of activated nanocomposite and vortexed for 30 min. An external magnet was applied at the bottom of the vial and the separation of the supernatant from the composites was achieved in less than 2 min. Then, the desorption was carried out in two steps. Firstly, 5 mL of ultrapure water, 0.2 mL of hydrochloric acid (37%) and 1 mL of DCM were added and this mixture was vortexed for 10 min. The organic layer was collected and the aqueous phase was removed. Secondly, 5 mL of ultrapure water and 1 mL of DCM were added and vortexed again for 10 min. The organic layer was collected,

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