

# Determination of non-steroidal anti-inflammatory drugs in urine by combining an immobilized carboxylated carbon nanotubes minicolumn for solid-phase extraction with capillary electrophoresis-mass spectrometry

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## Abstract

Last years, the usefulness of the use of carbon nanotubes (CNTs) as sorbent material have been demonstrated for a wide variety of compounds. In this work, it has been demonstrated for first time that immobilized carboxylated single-walled carbon nanotubes (c-SWNTs) offer clear advantages over the use of CNTs. The higher adsorption capacity has been attributed to the special orientation of c-SWNTs molecules on the glass surface. The potential of this new sorbent was evaluated for the preconcentration of non-steroidal anti-inflammatory drugs (NSAIDs) from urine samples. Purified samples were analysed by capillary electrophoresis-mass spectrometry detection allowing the determination of 1.6 to 2.6  $\mu\text{g/L}$  of NSAIDs with only 5 mL of sample. The precision of the method for the determination of real spiked urine samples ranged from 5.4 to 7.4% and the recoveries from 98.6 to 102.2%.

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## 1. Introduction

Carbon nanotubes (CNTs) are widely recognized as an essential nanomaterial in the developments of nanotechnology. Last years especial attention has been made to the chemical aspects of CNTs sciences. In Analytical Sciences, this attention has resulted in the use of CNTs as sorbent material among other uses, such as the development of sensors, biosensors or probes.

There are several examples in the literature of the use of CNTs for preconcentrating trace analytes. In this way, multi-walled carbon nanotubes (MWNTs) have been characterized for removing dioxins [1], endocrine disruptors, such as bisphenol A, 4-*n*-nonylphenol and 4-*tert*-octylphenol [2], chlorobenzenes [3], phthalate esters [4]. In addition to CNTs, carboxylated-carbon nanotubes (c-CNTs) which are obtained after oxidation treatment with nitric acid have also been used as SPE sorbent. For example, it has been used for removing  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{F}^-$  from aqueous solution [5], or Cd, Mn, Ni [6]. In this sense, the

study of kinetic curves of adsorption of  $\text{Cu}^{2+}$  point out that not only outer surface, but also inner cavities and inter-layers in the structure of c-CNTs are responsible for sorption of  $\text{Cu}^{2+}$  ions [7].

As an alternative, we propose to use c-CNTs immobilized on inert porous glass as a sorbent material. In literature, the incorporation of CNTs on different matrices has been described. For example, MWNTs immobilized on silica glass surfaces via laser treatment was made for reinforcement in robust composites and for conducting fillers in polymers [8]. Alternatively, Plenet et al. made carbon nanotubes silica glass composites in thin films by sol-gel technique [9]. The aim of these incorporations, as well as improvement the mechanical properties for CNT polymer composites, is the interest for developing new photonic applications and optical devices. Another immobilization strategy used in the development of sensors is the spraying of CNTs or surfactant coated-CNTs onto glass or plastic [10].

But not only electrochemical applications are possible when the CNTs are retained on glass. By way of example, single-walled carbon nanotubes (SWNTs) are physically adsorbed to the inner wall of fused silica capillaries to change its surface properties and perform the electrophoretic separation of aniline derivatives [11]. According to the authors, the interaction of the solutes with the modified capillary wall occurs via a dual

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mechanism: ionic interactions with the charged moieties of c-CNTs and hydrophobic interactions between the benzene ring and the surface of the c-CNTs.

In this work we study the capabilities of c-SWNTs to adsorb organic analytes. In order to increase the time of life of c-SWNT and to avoid problems of pressure due to compacting of minicolumn or even losses of c-SWNT due to its small dimensions, c-SWNTs were chemically immobilized on controlled porous glass. The immobilization results in c-SWNT aligned and perpendicular to glass surface. This is a consequence of the coupling reaction which takes place selectively with the carboxylic groups located at the ends of the SWNTs. Non-steroidal anti-inflammatory drugs were selected as a target compounds due to their particular chemical structure in which an aromatic group and a carboxylic group can be identified. The aromatic group can interact with the c-CNTs through  $\pi$ - $\pi$  stacking interaction, whereas the carboxylic group can establish hydrogen bonding with the carboxylic groups of the c-CNTs. To the best of our knowledge, this is the first study on the analytical potential of this type of CNTs to perform SPE purifications.

## 2. Materials and methods

### 2.1. Chemicals

Single-walled carbon nanotubes (0.7–1.2 nm  $\times$  2–20  $\mu$ m), controlled-pore glass (120–200 mesh, 240 Å nominal diameter), 1,3-dicyclohexylcarbodiimide, pentachlorophenol (PCP), activated carbon, 3-amino propyl triethoxy silane, glutaraldehyde, phosphoric acid, ketoprofen, tolmetin, indomethacin, citric acid and ammonium acetate were purchased from Sigma (Barcelona, Spain). HPLC-grade methanol, dimethylformamide (DMF), nitric acid (60%) and hydrochloric acid (35%) were obtained from Panreac (Barcelona, Spain) and sodium hydroxide was supplied by J.T. Baker (Deventer, the Netherlands). Standards solutions of the individual anti-inflammatory drugs and the internal standard, pentachlorophenol, were prepared at a concentration of 1000 mg/L in methanol. Working standard solutions were prepared by appropriate dilution of the standard solution with 50 mM citric acid. Background electrolyte and sheath liquid were made in purified water (18 M $\Omega$ ) from a Millipore Milli-Q water purification system.

### 2.2. Equipments

An Agilent HP3D capillary electrophoresis system equipped with a diode array detector (Waldbronn, Germany) was used to separate the analytes. The CE equipment was coupled to an Agilent 1100 Series LC/MSD (equipped with a quadrupole analyser) via an electrospray atmospheric pressure ionization (API) interface. The make-up flow of sheath liquid was delivered by the Agilent 1100 isocratic pump, which was operated at a split ratio of 1:100. Control of the CE-MS system, data acquisition and processing was performed using the Agilent ChemStation software. Fused silica capillary 60 cm long (50  $\mu$ m I.D.  $\times$  375  $\mu$ m O.D.) was used to accomplish the separation. New capillaries were sequentially conditioned by flushing at 200 mbar 1 M HCl,

Milli-Q water, 0.1 M NaOH and Milli-Q water for 5 min each, and finally with running buffer for 10 min. Between runs, the capillary was flushed at 200 mbar with 0.1 M NaOH for 2 min and run buffer for 3 min.

### 2.3. On-line coupling of the flow system to the capillary electrophoresis equipment

The continuous SPE configuration designed for the on-line preconcentration of NSAIDs from biological matrices was the same described in a previous work developed the preconcentration of tetracycline residues [12]. The system consists of a peristaltic pump, an injection valve to introduce the eluent in the system, a minicolumn containing the immobilized c-SWNTs, and two selection valves. One for selecting sample or cleaning solution and the other one to select the waste or to direct the purified sample to the CE-MS equipment.

The minicolumn was constructed by packing 15 mg of the controlled-pore glass containing the c-SWNT immobilized on its surface in a PTFE tube of 1.2 mm I.D. Cotton upper frit and lower frit were inserted at each end of the cartridge to hold the sorbent. Before preconcentration, the minicolumn was preconditioned with Milli-Q water and methanol for 2 min of each it (flow rate: 2 mL/min). In the preconcentration step, 5 mL of standard or sample was aspirated into the system at a flow rate of 1.15 mL/min. Analytes were retained on the column and then the matrix was washed with water for 1 min. In the elution step, the injection valve with the 200  $\mu$ L loop filled with methanol was switched and methanol was pumped with an air stream and passed through the sorbent column to elute the retained NSAIDs. The extract was collected in a vial and transferred to the CE-MS instrument for analysis. The CNTs sorbent column was washed by passing water during 2 min at a flow rate of 2.31 mL/min, after which the column was ready for a new analysis. This purified solution containing the analytes, was inserted in a minivial of the CE autosampler through the replenishment system [13,14].

### 2.4. Synthesis of c-SWNT and immobilization on glass particles

*Synthesis of carboxylic carbon nanotubes:* c-CNTs were prepared by adding in a glass beaker 100 mg of SWNTs to 20 mL of H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> mixture (3:1). The mixture was ultrasonicated (50 W, 60 Hz) during 90 min. Afterwards, the mixture was highly diluted with water (2 L) and filtered through 0.45  $\mu$ m cellulose acetate filter. The obtained residue was then washed with water and treated with 25 mL of 1 M HCl. In this case, the mixture was sonicated only for 45 min. Finally, c-CNTs were filtered washed and dried to air.

*Activation of glass:* initially the controlled-pore glass (120–200 mesh, 240 Å nominal diameter, Sigma-Aldrich, Barcelona, Spain) was suspended in HNO<sub>3</sub> (5% v/v) for 45 min. After this clean-up, 200 mg of cleaned and dried glass was mixed with 0.2 mL of 3-amino propyl triethoxy silane and 6 mL of ammonium acetate 0.05 M (pH 5.0). The mixture, protected from light, was heated at 80 °C in a water bath during 2 h. After this reac-

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