



# Determination of inorganic contaminants in carbon nanotubes by plasma-based techniques: Overcoming the limitations of sample preparation



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## ABSTRACT

In this work, sample preparation of carbon nanotubes (CNTs) for further determination of inorganic contaminants was investigated using a microwave-assisted wet digestion single reaction chamber system (MAWD-SRC). Analytes (Al, As, Ca, Cd, Co, Cr, Fe, La, Mg, Mo, Ni, Pb and Zn) were determined in CNTs by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS, except for Al, Ca, Fe and Mg). Method parameters were evaluated, as the mass of CNT (25–300 mg), the temperature (220–270 °C) and the time (35–75 min) of irradiation program. The accuracy was evaluated by using a certified reference material (CRM) of CNT and also by comparison of the results with those obtained using neutron activation analysis (NAA) and high resolution continuum source graphite furnace atomic absorption spectrometry with direct solid sampling (DSS-HR-CS-GF AAS). Quantitative recoveries for all elements were obtained using 275 mg of CNTs, 6 mL of 14.4 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.5 mL of 30% H<sub>2</sub>O<sub>2</sub> with an irradiation program of 65 min (35 min at 270 °C). No statistical difference was observed between the results obtained after the decomposition of CNTs by MAWD-SRC with those obtained by NAA and DSS-HR-CS-GF AAS. No difference was also observed for the results using the proposed method and the values for the CRM of CNT. The use of MAWD-SRC showed good performance for CNTs digestion using relatively high sample mass (up to 275 mg), contributing to low limits of quantification (LOQs) and overcoming the current limitations of sample preparation. To the best knowledge of the authors, this work reports the highest sample mass feasible to be decomposed using wet digestion for CNTs among the methods proposed in literature.

## 1. Introduction

Since their discovery and popularization in 1991 [1], carbon nanotubes (CNTs) have been investigated in many research areas as materials industry, electronics, medicine and also applications in analytical techniques [2–5]. A carbon nanotube is an allotropic form of carbon characterized by a tubular structure with a diameter in the nm range. This nanomaterial can be a single-wall carbon nanotube (SWCNT) or a multi-wall carbon nanotube (MWCNT) when additional graphene tubes are surrounding the core of a SWCNT [6].

Carbon nanotubes can be obtained by chemical vapor deposition, arc discharge or laser ablation with the use of a metallic catalyst (most common are nickel, cobalt, iron, lanthanum or their combinations) [4,6,7]. However, even after a purification process, which can be carried out by acid washing (e.g., 36 h at 80 °C using HNO<sub>3</sub>), many elements can be still present at relatively high levels because a significant part remains inside the CNT structure [8–10]. The presence of metal impurities can affect the physical, chemical and surface properties of

CNTs making difficult their use for industrial applications [2,7,11]. In addition to the risk of limiting their applications, the toxicity by inhalation and the risk assessment have been increasingly investigated due to the use of CNTs in medicine and related areas [12–15]. Thus, the quality control of CNTs is of great concern and the development of methods for the determination of inorganic contaminants is still required. However, there is only a few number of methods described for this kind of determination, mainly due to the high chemical resistance of this material.

The most common way to determine inorganic contaminants in organic matrices is by using atomic spectrometric techniques with sample introduction as aqueous solutions. However, CNTs like other carbon based structures, e.g., graphite, are very difficult to bring into solution [8,16]. Techniques allowing direct solid analysis, such as neutron activation analysis (NAA) [17,18] and the direct solid sampling graphite furnace atomic absorption spectrometry (DSS-GF AAS) [19,20] have been proposed for the determination of inorganic contaminants in CNTs. Some of them, particularly DSS-GF AAS, are prone to some

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drawbacks as the difficulty for calibration and the use of low sample mass that may raise issues regarding non homogeneity. Considering NAA, despite its advantages, a nuclear reactor is required and the necessary analysis time is relatively high making more difficult its use for routine analysis [21].

Some methods for CNTs digestion have been developed to overcome these limitations. A digestion method for metals determination by inductively coupled plasma mass spectrometry (ICP-MS) was proposed combining dry ashing and wet digestion with concentrated nitric acid and hydrogen peroxide [22]. However, despite the relatively good results obtained by this approach, only 20 mg of sample could be digested, after a relatively long time and using an open system that is prone to losses and contamination. In another work, [21] a comparison of extraction and digestion was proposed for further determination by inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-MS. However, only 5 mg of CNTs could be digested even using concentrated nitric acid and hydrogen peroxide, making difficult obtaining low limits of detection (LODs).

Recently, Grinberg et al. [23] proposed a method combining microwave-assisted wet digestion (MAWD), and dry ashing at 450 °C to determine trace metal impurities in SWCNT by ICP-MS. However, although the multi-step method has presented good performance, low recoveries for Cr were reported. In another work recently published [24], a combination of microwave-assisted fusion and MAWD was proposed but results using these methods were not in agreement. Nevertheless the authors have reported that results from both methods were complementary [24]. Other recent work proposed MAWD using concentrated nitric acid and hydrogen peroxide [25]. Even though digestion was applied to only 5 mg, authors reported particle residues after sample preparation demonstrating the difficulty to digest CNTs. Microwave-induced combustion (MIC) was an alternative to circumvent the poor efficiency of wet digestion for CNTs and has been successfully applied for the determination of halogens by ion chromatography and Fe, Co, Ni and Mo by plasma-based techniques [23,26,27]. However, its feasibility for elements in low concentration was not demonstrated.

Considering the difficulties reported for wet digestion of CNTs, combined with the limited availability of analytical methods for quality control of these materials, a new method is proposed in this work as an alternative to overcome the problems regarding sample preparation of CNTs. The conditions for microwave-assisted wet digestion (MAWD) using a single reaction chamber (SRC) equipment were investigated for the decomposition of CNTs for further determination of inorganic contaminants by ICP-MS and ICP-OES. The SRC system was recently proposed and is a feasible way to digest hard matrices using high temperature (up to 270 °C) and high pressure (160 bar) which are hard conditions not commonly available in most of microwave or conventional heating equipment. Conditions for the digestion and further determination of Al, As, Ca, Cd, Co, Cr, Fe, La, Mg, Mo, Ni, Pb and Zn were optimized. The analytes were chosen based on the works reported in the literature and taking into account the composition of the metallic catalysts and other contaminants that may be inserted by the materials and reagents used in the production of CNTs. The accuracy was evaluated by using a certified reference material (CRM) of SWCNT and also by comparison of the results with those by neutron activation analysis (NAA) and/or high resolution continuum source graphite furnace atomic absorption spectrometry with direct solid sampling (DSS-HR-CS-GF AAS).

## 2. Experimental

### 2.1. Instrumentation

Experiments were carried out using a microwave sample preparation system (Ultrawave™, Milestone, Sorisole, Italy) equipped with five quartz vessel (total volume of 40 mL) and a microwave cavity (1 L, Single Reaction Chamber, SRC) made of stainless steel with a

**Table 1**  
Operational parameters for the determination of inorganic contaminants by plasma-based techniques.

Parameter	ICP-MS	ICP-OES
RF generator frequency (MHz)	27	40
Power (W)	1300	1400
Plasma gas flow-rate (L min <sup>-1</sup> )	15	15
Auxiliary gas flow-rate (L min <sup>-1</sup> )	1.2	0.2
Nebulizer gas flow-rate (L min <sup>-1</sup> )	1.15	0.80
Spray chamber	Baffled cyclonic	Cyclonic
Nebulizer	Concentric	Concentric
View	–	Axial
Sample and skimmer cones	Pt	–
Ion lens	Auto lens	–
Dwell time (ms)	25	–
Analytes	<i>m/z</i>	Wavelength (nm)
Al	nd	396.153
As	75	189.042
Ca	nd	396.847
Co	59	238.892
Cd	111	214.438
Cr	53	205.552
Fe	nd	259.941
La	139	408.672
Mo	96	202.095
Mg	nd	280.270
Ni	60	221.648
Pb	208	168.215
Zn	64	213.856

nd: not determined using this technique.

polytetrafluoroethylene cover. Maximum operational temperature and pressure was set to 270 °C and 160 bar, respectively. Before microwave irradiation, chamber was sealed and pressurized with 40 bar of argon (99.996%, White Martins, São Paulo, Brazil) and vessels were irradiated with a maximum power of 1500 W. This method was referred as MAWD-SRC throughout this manuscript. For comparison of results, CNTs were decomposed by microwave-assisted wet digestion (MAWD) using a microwave system set at 280 °C and 80 bar, as maximum temperature and maximum pressure, respectively.

The determination of inorganic contaminants was performed using an inductively coupled plasma mass spectrometer (NexION 300×, PerkinElmer, Thornhill, USA) and an inductively coupled plasma optical emission spectrometer (Optima 4300 DV, Perkin Elmer, Shelton, USA). Operational parameters for measurements by ICP-MS and ICP-OES are shown in Table 1. The determination of dissolved carbon was carried out by ICP-OES at 193.030 nm and using yttrium (371.029 nm) as internal standard (1 mg L<sup>-1</sup>) [28].

The analysis of CNT-1 by NAA was performed at Institute of Energetic and Nuclear Research (IPEN, Laboratório de Análise por Ativação Neutrônica, São Paulo, Brazil) under a neutron flow at  $3 \times 10^{12}$  n cm<sup>-2</sup> s<sup>-1</sup> for 8 h. Gamma activity measurements were performed using a hyper pure Ge detector (GX 2020, Canberra) linked to a spectrometer. The radioisotopes were: <sup>75</sup>As at 559 keV, <sup>115</sup>Cd at 527.9 keV, <sup>60</sup>Co at 1332.4 keV, <sup>51</sup>Cr at 320.1 keV, <sup>59</sup>Fe at 1099.3 keV, <sup>140</sup>La at 1596.2 keV, <sup>96</sup>Mo at 140.5 keV and <sup>66</sup>Zn at 1115.5 keV.

Additionally, the accuracy for some elements was evaluated by comparison with high resolution continuum source graphite furnace atomic absorption spectrometry with direct solid sampling (DSS-HR-CS-GF AAS). A continuum source spectrometer (ContrAA 700, Analytik Jena, Jena, Germany) equipped with a manual solid sampling system (SSA 600, Analytik Jena) was used. The selected conditions were based on previous works [19,20]. Parameters for heating program are shown in Table S1 (Supplementary material). The wavelength used for measurements were: 394.4006 nm (Al), 242.4930 nm (Co), 425.4332 nm (Cr), 283.3060 nm (Pb) and 302.0639 nm (Fe).

An automatic titration system (836, Metrohm, Herisau, Switzerland) equipped with a module of automatic stirring (803 Ti Stand, Metrohm)

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