



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⁻¹ HNO₃ and 0.5 mL of 30% H₂O₂ 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 HNO₃), 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 ⁻¹)	15	15
Auxiliary gas flow-rate (L min ⁻¹)	1.2	0.2
Nebulizer gas flow-rate (L min ⁻¹)	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⁻¹) [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 3×10^{12} n cm⁻² s⁻¹ for 8 h. Gamma activity measurements were performed using a hyper pure Ge detector (GX 2020, Canberra) linked to a spectrometer. The radioisotopes were: ⁷⁵As at 559 keV, ¹¹⁵Cd at 527.9 keV, ⁶⁰Co at 1332.4 keV, ⁵¹Cr at 320.1 keV, ⁵⁹Fe at 1099.3 keV, ¹⁴⁰La at 1596.2 keV, ⁹⁶Mo at 140.5 keV and ⁶⁶Zn 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)

and a combined pH electrode (6.0262.100, Metrohm) were used for the determination of acidity in digests. All statistical evaluations were performed using GraphPad InStat software (GraphPad InStat Inc, Version 3.06, 2007) with a confidence level of 95%.

2.2. Reagents and samples

All the reagents were of analytical grade (Merck, Darmstadt, Germany). Ultrapure water (resistivity of 18.2 MΩ cm) from a Milli-Q system (Millipore Corp., Bedford, USA) was used for dilution and preparation of all standards and solutions. Concentrated HNO₃ (65%, Merck, Darmstadt, Germany) was distilled using a sub-boiling system (model DuoPur, Milestone, Sorisole, Italy). Hydrogen peroxide (30%, Merck, Darmstadt, Germany) was also used for MAWD-SRC. A 10 mg L⁻¹ multi-element reference solution (PlasmaCal calibration solution, SCP33MS, SCP Science, Quebec, Canada) was used for preparation of analytical standards (0.01–1 µg L⁻¹ for ICP-MS and 2.5–100 µg L⁻¹ for ICP-OES) in 5% HNO₃.

Three commercial MWCNT samples (named CNT-1, CNT-2 and CNT-3) were used in this work. Samples CNT-1 and CNT-2 have 95% of minimum purity, 50–80 nm of outside diameter and 10–20 µm of length and CNT-3 has 95% of minimum purity, 20–40 nm of outside diameter and 5–15 µm of length. Samples were dried at 105 °C in an oven (Nova Ética, Vargem Grande Paulista, Brazil) and stored at room temperature before analysis. For MAWD-SRC, samples were directly weighed inside the digestion vessel. For DSS-HR-CS-GF AAS, 0.05–7 mg were weighed directly onto the graphite platform and transferred to the graphite tube using the commercial manual device for solid sample introduction. The accuracy was evaluated by using a certified reference material (CRM) of SWCNT (2LV-BIO-SWCNT-1), provided by National Research Council Canada.

2.3. Digestion procedures

The following parameters were evaluated for the proposed method using MAWD-SRC: the mass of CNT, temperature and time of irradiation program. The SRC chamber was previously filled with 120 mL of water, 2 mL of H₂O₂ and 2 mL of HNO₃ and was pressurized with argon up to 40 bar before the microwave irradiation. The maximum pressure and power were set at 160 bar and 1500 W, respectively. Sample masses in the range of 25–300 mg were directly weighed into quartz vessels and were digested using 6 mL of 14.4 mol L⁻¹ HNO₃ + 0.5 mL of 30% H₂O₂. Maximum temperature achieved during digestion (temperature up to 220, 250 and 270 °C) and the irradiation program (35, 45, 55, 60, 65 and 75 min) were evaluated. Finally, digests were diluted with water up to 25 mL for further determination by ICP-MS and ICP-OES. Residual acidity was evaluated by determining the acid amount in final digests by titration with KOH. It was expressed as a percentage of acidity in final digests in relation to the initial amount (6 mL of 14.4 mol L⁻¹ HNO₃).

For comparison, a wet digestion method based on a previous protocol reported by Grinberg et al. [23] was also used. Briefly, 6 mL of 14.4 mol L⁻¹ HNO₃ and 0.5 mL of 30% H₂O₂ were used for decomposition of 25 mg of CNTs. The operational conditions were: maximum

pressure of 80 bar and maximum temperature of 280 °C (during digestion, maximum temperature was 215 °C because maximum pressure was reached). Microwave program was: i) 700 W for 25 min, ii) 1000 W for 15 min, iii) 1400 W for 20 min and iv) 0 W for 20 min (cooling step).

3. Results and discussion

3.1. General optimization of MAWD-SRC

When developing a digestion method the evaluation of irradiation temperature and time to assure an efficient digestion is important. As higher as the sample mass that can be digested, lower limits of detection can be reached. The optimization of these parameters depends on the sample composition and instrumentation. Particularly, CNTs are very difficult to bring into solution in view of their stable structure. In addition, a method development is difficult due to the wide variation in the type and concentration of inorganic contaminants present in CNTs. This means that the accuracy is difficult to be ensured under the same conditions for all samples.

Recently (2011), a new digestion system (SRC, Ultrawave™ system, single reaction chamber, SRC) was developed that allows operating at temperature and pressure up to 270 °C and 160 bar, respectively [29,30]. This system has been applied for several matrices, such as milk powder, bovine liver and kidney, nuts [31], active pharmaceutical ingredients [32], polymeric waste from electrical and electronic equipment [33], polymers (PVC) [34] and heavy crude oil [35] for further metals and metalloids determination by plasma-based techniques (ICP-OES and ICP-MS). In these works, low values of residual carbon and residual acidity were obtained. However, no works were found in the literature regarding the feasibility of this system for the decomposition of CNTs and further inorganic contaminants determination. In this sense, the evaluation of digestion parameters was performed.

3.1.1. Optimization of digestion temperature

Experiments were performed to evaluate the temperature required for the decomposition of CNT-1. In this sense, maximum temperatures of 220, 250 and 270 °C were evaluated. This maximum operating temperature (270 °C) was defined according to the recommendation of manufacturer [30] for longer time of irradiation. The irradiation program was: i) hold of 15 min at 180 °C (ramp of 10 min), ii) hold of 35 min at 220, 250 or 270 °C (ramp of 5 min) and iii) 40 min of cooling.

First, the irradiation program with a temperature limit of 220 °C (in the second step) was performed. After the end of irradiation program, it was possible to observe that the decomposition was not complete (Fig. 1A). When using 250 °C, it was possible to observe that the decomposition was better (Fig. 1B) when compared to the aspect of the digests obtained using 220 °C. Using 270 °C it was possible to observe a complete decomposition of CNT (Fig. 1C). It is important to emphasize that the limit temperature was chosen taking into account the complete decomposition of CNTs based on the residual mass of CNT. Although the determination of residual carbon can be generally used to evaluate the decomposition efficiency for organic matrices [36,37], such as food [38] and biological materials [39], it was not an efficient strategy in this study. Digests presented always carbon content lower than

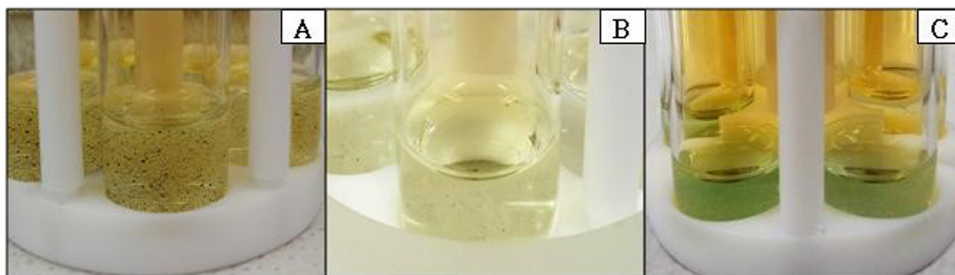


Fig. 1. Aspects of the digests after decomposition of 25 mg of CNT-1 by MAWD-SRC with temperature limit of A) 220 °C, B) 250 °C and C) 270 °C. Experimental conditions: 6 mL of 14.4 mol L⁻¹ HNO₃ and 0.5 mL of 30% H₂O₂, irradiation program was: i) hold of 15 min at 180 °C (ramp of 10 min), ii) hold of 35 min at 220, 250 or 270 °C (ramp of 5 min) and iii) 40 min of cooling, with maximum pressure of 160 bar and 1500 W of maximum power.

10 mg L⁻¹, for all conditions. However, it was possible to observe that for lower temperatures, CNTs matrix remained practically unchanged. Probably, it was not possible to detect the presence of dissolved carbon in solution because no soluble carbon-based compounds were produced during digestion. Thus, the absence of visible amount of non digested CNT and negligible mass of sample were used to choose the more suitable condition for digestion. Based on this study, a subsequent experiment was performed using 270 °C as temperature limit. It should be noticed that this parameter can be considered the main difference of this system, which was decisive for the decomposition of CNTs. Using 270 °C as temperature limit, the maximum pressure was 150 bar. By allowing pressures up to 160 bar, the SRC allowed temperatures as high as 270 °C and this allowed for a better digestion.

3.1.2. Evaluation of sample mass

In order to evaluate the maximum amount of sample that can be decomposed using MAWD-SRC, masses of CNT-1 from 25 mg to 300 mg were evaluated. Six milliliters of 14.4 mol L⁻¹ HNO₃ plus 0.5 mL of H₂O₂ were used for digestion and the limit temperature was 270 °C. Using these conditions, it was possible to observe digestion for masses up to 275 mg. When 300 mg of CNT-1 were decomposed it was possible to observe the presence of non digested CNT in the final solution (Fig. S1 Supplementary material). In this way, the digestion of 275 mg of CNT was considered feasible, which is an important improvement for sample preparation of CNTs. The MAWD-SRC method allowed for lower LODs in comparison to previous wet digestion methods described in literature. Table 2 summarizes the main conditions of those methods.

It is possible to observe that the reported digestion methods with conventional or microwave heating involve the use of concentrated acids and relatively long times for sample decomposition. In some cases, even a previous ashing step is required [22,27]. A high volume of reagents is generally necessary and sometimes, procedures using very long time (even higher than 6 h) have been reported [22,27]. In addition, most of protocols are not performed in a single step, requiring successive heating steps [22,27]. Moreover, due to the high stability of

CNTs, available methods are able to digest only a very few sample amount, 5 mg [21], 20 mg [22], 50 mg [20] or 100 mg [27]. Combustion methods, as dry ashing [22,27] and microwave-induced combustion [26,27] demonstrated to be able to digest higher masses (up to 500 mg) and were proposed for the determination of catalyst residues, [27] metals [23] and halogens [26].

Due to the wide spread use of wet digestion in routine laboratories, the development of a method to overcome the current limitations for CNTs is desirable. The suitability to digest a relatively high sample mass contributes to the lower limits of quantification (LOQs) as will be further discussed. The conditions described in Table 2 show that the proposed method allows the digestion of a considerably high amount of CNT in comparison to the previously reported wet digestion methods [20–22,27]. Moreover, the proposed method overcome the main limitation of sample preparation of CNTs using wet digestion: limited sample mass, tedious sample preparation and use of large amounts of reagents [40].

3.1.3. Effect of microwave irradiation time

In order to check the effect of irradiation time, experiments were performed using 275 mg of CNT-1, 6 mL of 14.4 mol L⁻¹ HNO₃ plus 0.5 mL of H₂O₂ as digestion mixture and 270 °C. Irradiation times were evaluated by using 5, 15, 25, 30, 35 and 45 min as hold time in the second step. The aspects of the final solutions for those irradiation program are shown in Fig. 2A.

It was possible to observe that the amount of CNT remaining in the solution decreases with the use of higher hold time in the second step. In this way, the digestion of CNT was obtained using at least 35 min (a total irradiation program of 65 min considering all steps). In addition, the residual acidity in digests was determined. As can be seen in Fig. 2B the residual acidity decreases as the time increases up to 35 min. It is due to the higher consumption of acid during digestion using these conditions. Using this condition, the residual acidity was about 7 ± 1% (corresponding to a 0.2 mol L⁻¹ acid solution in final digest, considering the initial amount of HNO₃) which is suitable for sample

Table 2

Reported methods for wet digestion of CNTs and determination of contaminants by plasma-based techniques.

Analytes	Digestion method	General conditions	Ref.
Ni and La	Dry ashing + wet digestion	100 mg; ashing at 550 °C for 3 h. Dissolution with 5 mL of 12 mol L ⁻¹ HCl and heating at 80 °C for 2 h (this procedure was repeated three times).	[27]
Co, Cr, Cu, Fe, Mn, Mo, Ni and Zn	i) Dry ashing + acid extraction ii) Wet digestion in open and closed system iii) Microwave-assisted wet digestion	i) 10 to 20 mg Dissolution with 2% HNO ₃ Decomposition procedure: a) Ashing in a muffle furnace at 700 °C; b) Resultant ashes were extracted twice using 2% diluted nitric acid at room temperature or by concentrated HNO ₃ in a heating bath at 80 °C. i) 10 to 20 mg 4 mL of a mixture of HNO ₃ + H ₂ O ₂ (3+1) Heating program: 120 °C for 8 h (open system) and 180 °C for 12 h (closed system). i) 10 mg 5 to 10 mL of HNO ₃ Irradiation program: 800 W for 45 min up to 200 °C.	[22]
Co, Cr, Cu, Fe, Mo, Ni and Zn	i) Water extraction ii) Acid extraction iii) Microwave-assisted wet digestion	i) 5 mg 25 mL of distilled-deionized water. i) 5 mg 25 mL of 1% HNO ₃ . i) 5 mg 2 mL of HNO ₃ + 4 mL of H ₂ O ₂ Irradiation program: a) 25 min at 170 °C (ramp of 20 min) and b) 20 min at 185 °C (ramp of 5 min).	[21]
Al, Cd, Co, Cr, Cu, Mg, Mn and Pb	Microwave-assisted wet digestion	50 mg 6 mL of HNO ₃ Irradiation program: a) 1000 W for 60 min (ramp of 10 min), b) 0 W for 20 min (cooling step); up to 280 °C and 80 bar.	[20]
Al, As, Ca, Cd, Co, Cr, Fe, La, Mg, Mo, Ni, Pb and Zn	MAWD-SRC	275 mg 6 mL of 14.4 mol L ⁻¹ HNO ₃ + 0.5 mL of 30% H ₂ O ₂ Irradiation program: a) hold of 15 min at 180 °C (ramp of 10 min), b) hold of 35 min at 270 °C (ramp of 5 min) and c) 40 min for cooling; up to 160 bar	Proposed method

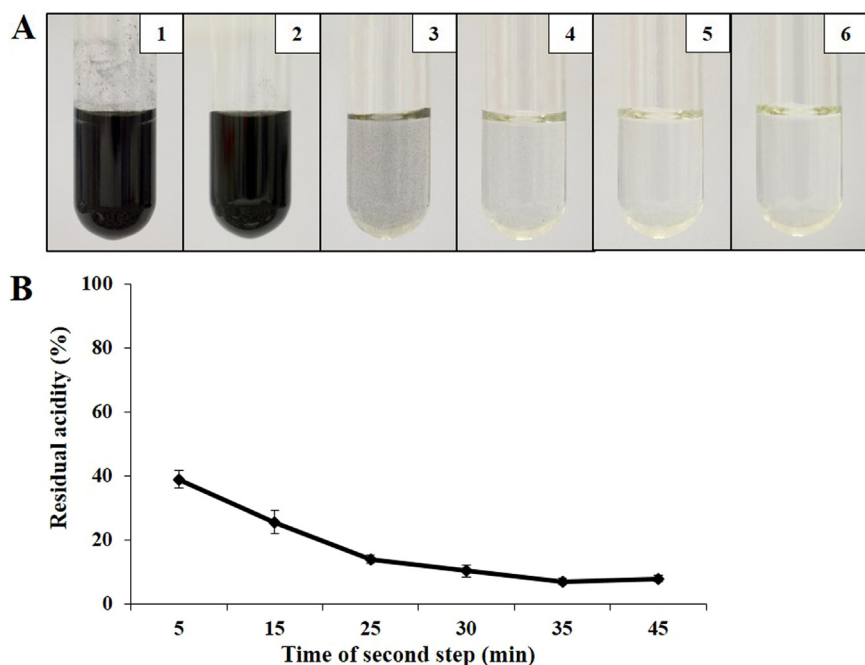


Fig. 2. A) Aspects of the digests obtained after decomposition by MAWD-SRC using irradiation times of 1) 5 min, 2) 15 min, 3) 25 min, 4) 30 min, 5) 35 min and 6) 45 min as the hold time of the second step and B) effect of microwave irradiation time (second step) on the residual acidity in final digests of CNT-1 after decomposition by MAWD-SRC. Experimental conditions: 275 mg of CNT-1, 6 mL of 14.4 mol L⁻¹ HNO₃ and 0.5 mL of 30% H₂O₂, irradiation program was: i) hold of 15 min at 180 °C (ramp of 10 min), ii) hold of 5–35 min at 270 °C (ramp of 5 min) and iii) 40 min of cooling, maximum pressure of 160 bar and 1500 W of maximum power.

introduction in ICP equipment without additional dilution.

Furthermore, the agreement of results using 5–45 min of irradiation in the hold step was evaluated by comparing the results with those obtained by the reference method [23]. The results are shown in Fig. 3.

According to Fig. 3, the results for Al, Ca, La, Mg, Pb and Zn presented no statistical difference (*t*-test, 95% of confidence level) for all evaluated irradiation times when compared with those obtained using the reference method. The results obtained were lower and presented statistical difference (*t*-test) for other analytes depending on the time used. Lower results were obtained for As and Co using 5–25 min. For La, results presented statistical difference using 5 and 15 min. For Fe and Ni, no statistical difference was observed using at least 30 min as hold time in the second digestion step. In addition, Cr and Mo presented no statistical difference only when 35 and 45 min were evaluated. The results obtained for Cd were lower than the LOQ (0.007 µg g⁻¹) for all evaluated conditions.

Taking into account the quantitative recoveries for analytes (Fig. 3), it was possible to observe that a leaching step could be suitable for some elements (Al, Ca, Mg, Pb and Zn) and thus lower times can be used in these cases. On the other hand, for some elements, particularly Co, Cr, Fe, La, Mo, and Ni, it was observed that longer digestion times (at least 35 min) at higher temperature (270 °C) must be applied. This fact may be associated with the way in which the elements can be present in the CNTs. Studies have reported that metallic contaminants may be present inside the CNTs structure [8,9,27]. In this way, to ensure the quantitative recoveries for all elements, a complete decomposition of CNTs is important, which also minimizes problems in the determination step. Thus, the irradiation time of 65 min (35 min at higher temperature, in the second step) was chosen for further experiments. In addition, using these conditions, no statistical difference was observed between the results obtained for all elements using MAWD-SRC with those obtained using the reference method [23].

3.2. Accuracy and analytical figures of merit

Accuracy of the proposed method was evaluated by comparing the results by MAWD-SRC with those by other methods. The determination by NAA was carried out for CNT-1 and the results were used for comparison. In the same way, the accuracy for some elements was evaluated by comparison with the results by DSS-HR-CS-GF AAS. Table 3

shows the results for sample CNT-1 for all methods.

In general, no statistical difference (ANOVA) was observed between the results obtained using the proposed method (MAWD-SRC) with those using the reference method [23] and using NAA or DSS-HR-CS-GF AAS. Taking into account the results obtained using the proposed method, the relative standard deviation (RSD) ranged from 5% to 10% for all analytes and was considered as acceptable taking into account the low concentration for some elements and the difficulties for CNTs digestion. To evaluate the accuracy of the proposed method for Cd, a spike recovery experiment was performed by adding 20 µg of Cd previously to digestion. In this experiment, a recovery of 96% was obtained.

For Cr and Fe no statistical difference (ANOVA) was observed between the results using MAWD-SRC, the reference method [23], NAA and DSS-HR-CS-GF AAS. For Al and Pb, the results obtained using MAWD-SRC presented no statistical difference (*t*-test) when compared with those by DSS-HR-CS-GF AAS. For La and Mo, the results by MAWD-SRC presented no difference (*t*-test) when compared with the results by NAA.

It is important to emphasize that no difference was observed between the results obtained by ICP-MS and ICP-OES when the concentration of inorganic contaminants was higher than the LOQ by both techniques. This shows that the digests obtained by MAWD-SRC are suitable for plasma-based determination free from interferences. This can be considered a consequence of the complete digestion and the low acidity of digests.

Additionally, the decomposition of CRM 2LV-BIO-SWCNT-1 was also performed. Results are shown in Table 4.

No statistical difference (*t*-test) was observed between the results obtained by MAWD-SRC and the certified or informed value for all elements, except for Cr. Particularly for Cr, a significant difference was also observed in a study previously developed by Grinberg et al. [23]. In that study, results were 226 ± 11 µg g⁻¹, 201 ± 16 µg g⁻¹ and 147 ± 10 µg g⁻¹, for MAWD, microwave-induced combustion and dry ashing, respectively [23]. The authors attributed the difficulty for Cr recovery to the presence of Cr refractory compounds [23]. The result obtained by the proposed MAWD-SRC is in agreement with that obtained by those authors. It is important to emphasize that the RSD obtained for some analytes were unusually high (up to 23%) but were considered acceptable once they are also relatively high (6–28%) for

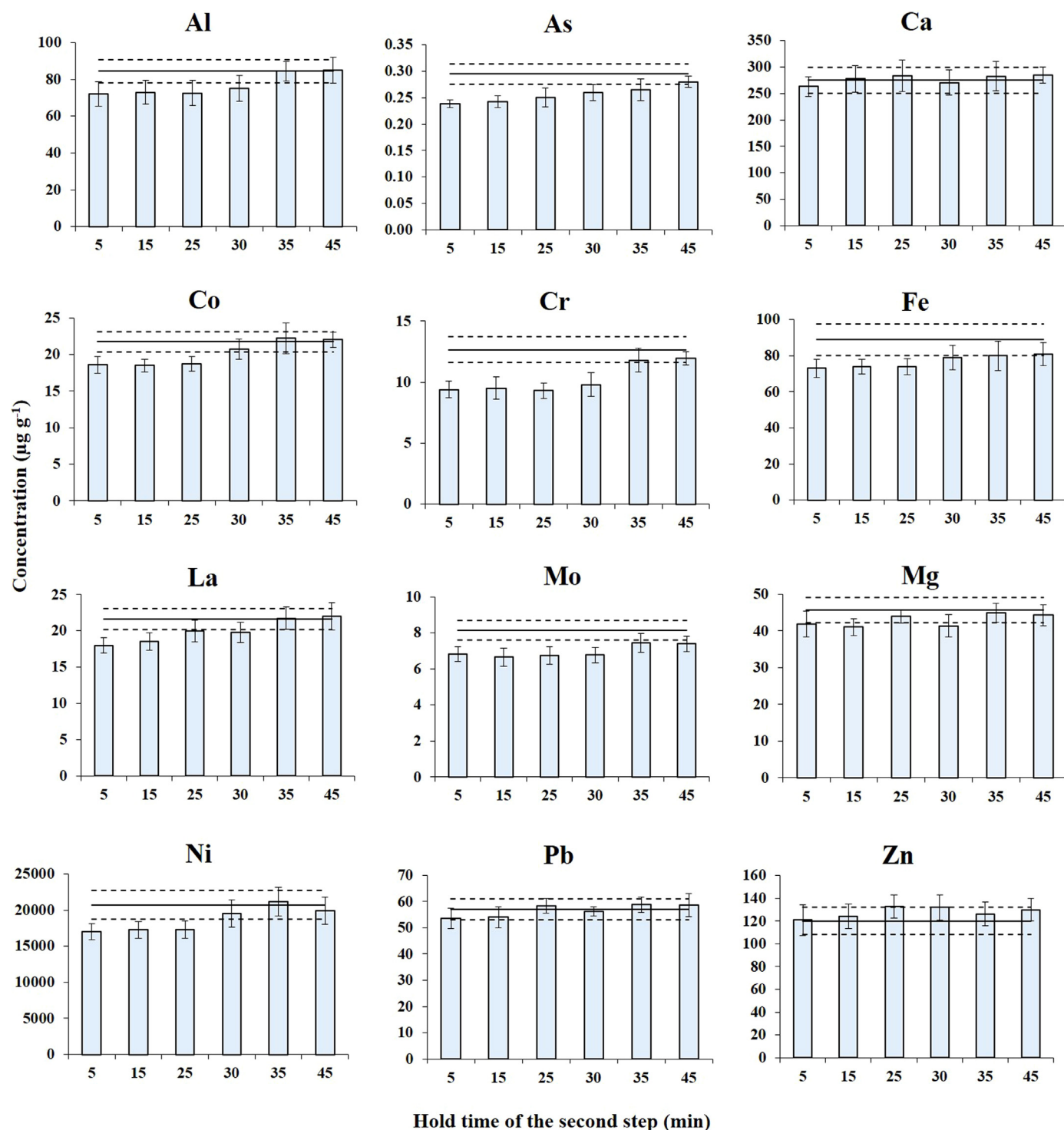


Fig. 3. Results for inorganic contaminants in CNT-1 ($n = 3$) using MAWD-SRC with 5, 15, 25, 30, 35 and 45 min as hold time of the second step of irradiation program. Continuous horizontal lines are the mean values (reference method) and the dashed lines represent the standard deviation. Conditions: 275 mg of CNT-1, 6 mL of 14.4 mol L⁻¹ HNO₃ plus 0.5 mL of 30% H₂O₂, maximum temperature and pressure of 270 °C and 160 bar, respectively, 1500 W of maximum power.

the certified values.

Other CNT samples were digested by MAWD-SRC and the results are shown in Table S2 (Supplementary material). It is possible to observe that the concentration of elements is variable for each sample and can be related to the reagents and catalyst metals used during the synthesis of CNTs. It is important to mention that some elements, e.g. Ni, are present at high concentration (> 1.5%). For all analytes no statistical difference (t -test) was observed between the results by MAWD-SRC and

reference method [23]. This suggest that the method can be extended to other CNTs regardless its purity and size/length.

Using MAWD-SRC method, the LOQ obtained was better than those obtained by other methods from the literature. Table 5 summarizes some analytical figures of merit for MAWD-SRC method.

Using MAWD-SRC system, five samples can be simultaneously digested in 65 min for each run. Most important, the sample mass that can be digested was 275 mg is the highest reported in literature for wet

Table 3

Results for inorganic contaminants in CNT-1 after decomposition by MAWD-SRC and by the reference method [23] and further determination by ICP-OES or ICP-MS, NAA and DSS-HR-CS-GF AAS (results in $\mu\text{g g}^{-1}$, mean \pm standard deviation, $n = 3$).

Elements	MAWD-SRC ^c	Reference method ^d	NAA	DSS-HR-CS GF AAS
Al ^a	84.4 \pm 5.3	84.5 \pm 6.2	–	89.4 \pm 8.3
As ^b	0.265 \pm 0.020	0.295 \pm 0.019	–	–
Ca ^a	283 \pm 28	275 \pm 25	–	–
Cd ^b	< 0.007	< 0.009	< 2	–
Co ^a	22.2 \pm 2.0	21.8 \pm 1.4	25 \pm 1	17.6 \pm 1.8
Cr ^a	11.8 \pm 1.0	12.7 \pm 1.0	14.0 \pm 2.0	10.7 \pm 1.4
Fe ^a	83.3 \pm 8.2	89.0 \pm 8.8	< 69	71.9 \pm 8.0
La ^a	21.8 \pm 1.6	21.6 \pm 1.4	24.3 \pm 0.3	–
Mg ^a	45.0 \pm 2.6	45.8 \pm 3.4	–	–
Mo ^a	7.93 \pm 0.51	8.14 \pm 0.55	8.3 \pm 0.3	–
Ni ^a	21,212 \pm 1820	20,725 \pm 1950	–	–
Pb ^a	58.8 \pm 3.0	57.0 \pm 4.0	–	58.0 \pm 3.9
Zn ^a	126 \pm 11	120 \pm 12	–	–

^a ICP-OES.

^b ICP-MS.

^c 275 mg, 6 mL of 14.4 mol L⁻¹ HNO₃ + 0.5 mL of 30% H₂O₂, 65 min of irradiation program + 40 min for cooling.

^d microwave-assisted wet digestion: 25 mg, 6 mL of 14.4 mol L⁻¹ HNO₃ + 0.5 mL of 30% H₂O₂, 65 min of irradiation + 20 min for cooling.

Table 4

Results for inorganic contaminants in CRM of SWCNT after decomposition using MAWD-SRC (determination by ICP-OES, mean \pm standard deviation, $n = 3$).

Analytes	CRM 2LV-BIO-SWCNT-1	
	Found value	Certified value
Al ($\mu\text{g g}^{-1}$)	470 \pm 97	494 \pm 94 ^a
Ca ($\mu\text{g g}^{-1}$)	2722 \pm 323	2650 \pm 300 ^a
Co (mg g ⁻¹)	15.3 \pm 1.6	15.9 \pm 1.0
Cr ($\mu\text{g g}^{-1}$)	205 \pm 24	285 \pm 26 ^a
Fe (mg g ⁻¹)	2.1 \pm 0.2	2.2 \pm 0.2
La ($\mu\text{g g}^{-1}$)	1.15 \pm 0.26	0.96 \pm 0.27 ^a
Mo (mg g ⁻¹)	7.0 \pm 0.8	7.3 \pm 1.1
Ni (mg g ⁻¹)	14.5 \pm 0.9	14.4 \pm 0.8
Pb ($\mu\text{g g}^{-1}$)	6.2 \pm 0.7	6.8 \pm 0.9

^a Informed value.

Table 5

Summary of analytical figures of merit obtained for inorganic contaminants using MAWD-SRC for CNTs digestion.

Parameter	MAWD-SRC	
Sample mass, mg	275	
Reagents	6 mL of 14.4 mol L ⁻¹ HNO ₃ + 0.5 mL of 30% H ₂ O ₂	
Digestion time, min	65	
Replicates per run	5	
LOQs ^a	ICP-OES	ICP-MS
Al	2.50	nd
As	3.30	0.01
Ca	8.30	nd
Cd	0.37	0.19
Co	0.32	0.01
Cr	0.52	0.01
Fe	0.71	nd
La	0.49	0.01
Mg	0.70	nd
Mo	0.51	0.01
Ni	0.41	0.09
Pb	3.57	0.010
Zn	0.88	0.69

nd: not determined.

^a Limits of quantification ($\mu\text{g g}^{-1}$).

digestion of CNTs. In comparison to previous works for wet digestion of CNTs, sample mass ranged from 5 to 100 mg and digestion time was typically from 45 min to 12 h [20–22,27]. In this way, the proposed MAWD-SRC method can be considered as an alternative for the decomposition of CNTs and further determination of inorganic contaminants by plasma-based techniques. The relatively high sample mass that can be digested allowed to reach very low LOQs and the method provided suitable digests, thus overcoming the limitations of sample preparation of CNTs.

4. Conclusions

The determination of inorganic contaminants in CNTs is important due to the increasing use of this kind of material, especially in the industry and medicine. The proposed MAWD-SRC method showed to be suitable for this purpose, overcoming the capabilities of sample preparation methods with regard to the sample mass. Using the proposed method it was possible to decompose up to 275 mg of CNTs using 6 mL of 14.4 mol L⁻¹ HNO₃ plus 0.5 mL of 30% H₂O₂ and 65 min of irradiation program (65 min of total irradiation time, 35 min at 270 °C). The results obtained after decomposition by MAWD-SRC and determination of inorganic contaminants by ICP-MS and ICP-OES presented no difference when compared with the results obtained using a reference method, NAA and DSS-HR-CS-GF AAS. The use of MAWD-SRC showed good performance for CNTs allowing to digest relatively high sample mass (up to 275 mg), contributing to very low LOQs. Taking into account the lack of methods and the difficulty of bringing this material into solution, MAWD-SRC can be considered as an alternative for the decomposition of CNTs for routine quality control of inorganic contaminants using plasma-based techniques.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.talanta.2018.09.050](https://doi.org/10.1016/j.talanta.2018.09.050).

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