
**Nanotechnologies — Determination of
elemental impurities in samples of carbon
nanotubes using inductively coupled
plasma mass spectrometry**

*Nanotechnologies — Dosage des impuretés dans les nanotubes en
carbone (CNTs) par spectroscopie de masse à plasma induit (ICP-MS)*

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

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An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is a well-established multi-element analytical technique used for fast, precise and accurate determinations of trace elements. ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and ICP atomic emission spectrometry (ICP-AES). The ability to handle both simple and complex matrices with a minimum of matrix interferences is due to the high temperature of the ICP source. ICP-MS also has high sensitivity and superior detection capability.

Owing to their unusual physical and chemical properties, and potential applications in a number of areas, interest in carbon nanotubes (CNTs) has shown tremendous growth in the past decade. Metal particle catalysts are essential in the mass production of nanotubes by chemical vapour deposition (CVD)^{[1][2][3]}. Removal of these residual catalysts (typically Fe, Co, and/or Ni) after CNT production is one of the key challenges for the application of CNTs in many fields^[4]. After complicated purification steps, the concentration of such catalysts is measured. It is of great concern that the results of toxicological and ecological impact studies of carbon nanotubes could be misinterpreted due to the presence of impurities in the test materials^{[5][6][7]} and that the metals could be released into the environment during disposal of the product by means of combustion or other ways. Additionally, the actual desired performance of nanotube materials might depend on these impurities, which is the reason why it is so crucial to use reliable techniques to determine their content in these materials.

Currently available methods for analysis of the purity of CNTs include neutron activation analysis (NAA), transmission electron microscopy (TEM) with electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and X-ray fluorescence (XRF) spectrometry^{[8][9][10][11][12]}. A number of these techniques for the characterization of single-wall and/or multiwall carbon nanotubes are the subject of standardization within ISO/TC 229, including SEM (ISO/TS 10798), TEM (ISO/TS 10797¹⁾), and measurement methods for the characterization of multiwall carbon nanotubes (ISO/TR 10929²⁾).

However, each method has its limitations for determination of elemental impurities. TGA can only provide a gross estimation of metal content. NAA is a quantitative and qualitative method based on nuclear reactions between neutrons and target nuclei. This method provides high efficiency for the precise and simultaneous determination of a number of major, minor and trace elements in different types of samples in the parts per billion (10^{-9}) to parts per million (10^{-6}) range. Moreover, due to the superior figures of merit, including high accuracy, good precision and no matrix blank requirement, NAA is widely used in the certification of reference materials. NAA is, however, not a technique that is readily available, being not only a highly specialised field of analysis, but also requiring access to a nuclear reactor. ICP-MS, on the other hand, is also capable of providing highly accurate and precise results, while being widely available in most commercial laboratories. However, using conventional solution sample introduction ICP-MS, the sample has to be completely solubilised. Digestion of some types of samples requires thorough pretreatment schemes. Standard sample preparation procedures are available for routine matrix types, including soils, rocks and biological specimens. In the case of carbon nanotubes, because of their extremely stable structure and possible encapsulation of metals in structural defects, it is necessary that the materials go through special destructive pretreatments before analysis by ICP-MS^{[12][13][14][15]}. ICP-MS offers better sensitivity than graphite furnace atomic absorption spectrometry with the multi-element speed of ICP-AES.

The purpose of this Technical Specification is to provide guidelines for optimized sample pretreatment methods for single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) to enable accurate and quantitative determinations of elemental impurities using ICP-MS. An example of the determination of elemental impurities in commercially produced carbon nanotubes, using the methods described, is given in Annex A.

1) Under preparation.

2) Under preparation.

Nanotechnologies — Determination of elemental impurities in samples of carbon nanotubes using inductively coupled plasma mass spectrometry

1 Scope

This Technical Specification provides methods for the determination of residual elements other than carbon in samples of single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) using inductively coupled plasma mass spectrometry (ICP-MS).

The purpose of this Technical Specification is to provide optimized digestion and preparation procedures for SWCNT and MWCNT samples in order to enable accurate and quantitative determinations of elemental impurities using ICP-MS.

2 Normative reference

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004-3, *Nanotechnologies — Vocabulary — Part 3: Carbon nano-objects*

3 Terms, definitions, symbols and abbreviations

3.1 Terms and definitions

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For the purposes of this document, the terms and definitions given in ISO/TS 80004-3 and the following apply.

3.1.1

inductively coupled plasma source

device used to generate a plasma sustained in argon gas at atmospheric pressure by radiofrequency electromagnetic fields

3.1.2

ICP-MS

inductively coupled plasma mass spectrometry

analytical technique comprising a sample introduction system, an inductively coupled plasma source for generation of ions of the material(s) under investigation, a plasma/vacuum interface, and a mass spectrometer comprising an ion focusing, separation and detection system

NOTE ICP-MS permits quantitative determinations of trace, minor and major elements in samples pertaining to almost every field of application of analytical chemistry.

3.1.3

elemental impurity

element other than carbon that is present in a sample and not in the form of carbon nanotubes

NOTE 1 Such impurities are primarily remnants of metal catalysts used during large-scale production of CNTs.

NOTE 2 Amorphous carbon can be considered another type of impurity in samples containing SWCNTs and MWCNTs, but is outside the scope of this Technical Specification.

3.2 Symbols and abbreviations

CCT	collision cell technology
c_i	sensitivity coefficient for input quantity, x_i , defined as df/dx_i
CNT	carbon nanotube
C_s	expected concentration, in micrograms per litre, of spiked sample solution based on the added spike
CVD	chemical vapour deposition
DRC	dynamic reaction cell
ICP-MS	inductively coupled plasma mass spectrometry
ICP-AES	inductively coupled plasma atomic emission spectrometry
k	coverage factor
I_d	dilution factor of the analysed sample solution, accounting for all sample preparation steps
MWCNT	multiwall carbon nanotube
M_c	measured concentration, in micrograms per litre, of the analysed sample solution
M_s	measured concentration, in micrograms per litre, in the spiked sample solution
NAA	neutron activation analysis
OD	outer diameter
PTFE	polytetrafluoroethylene
S_w	weight, in grams, of CNT sample
SWCNT	single-wall carbon nanotube
U	expanded uncertainty
$u_c(y)$	combined standard uncertainty of the final result
$u(x_i)$	standard uncertainty associated with input quantity, x_i
V	volume, in litres, of the analysed sample solution
wt %	weight percentage

4 Samples and reagents

4.1 General

CNT samples produced by various processes typically contain impurities consisting of amorphous carbon and other elements if they are not specifically separated. ICP-MS allows the determination of major, minor and trace elements, providing quantitative information important for the characterization of the relative purity of CNT samples. By acquiring the mass spectrum of the plasma, data can be obtained for almost the entire periodic table in just minutes, with detection limits below 0,1 µg/l for most elements.

4.2 Samples

Samples shall be used that contain either SWCNTs or MWCNTs, or both.

4.3 Reagents

4.3.1 General

All reagents should be prepared and stored in polytetrafluoroethylene (PTFE) containers precleaned by nitric acid and ultrapure water. Precleaned containers made from polypropylene, quartz, or other materials may also be suitable.

4.3.2 Purity of acids

Ultra high purity acids (e.g. HNO₃, guaranteed reagent or equivalent grade) shall be used for sample dissolution and preparation of calibration standards.

4.3.3 Purity of reagents

Guaranteed grade chemicals (99,99 % or higher than 99,99 %) shall be used in all tests (e.g. H₂O₂, guaranteed reagent or equivalent grade). Certified reference materials should be used whenever available.

4.3.4 Purity of water

Ultrapure water having a resistivity of at least 18 MΩ cm shall be used in all tests.

4.4 Stock solutions

4.4.1 General

Stock solutions may be obtained directly as multi-element standards from accredited commercial vendors or national metrology institutes as certified reference materials. They may also be prepared from single element standards or suitable starting materials in-house, although this can be difficult due to problems with cross-contamination. The following stock solutions shall be available for calibration of the instrument. The purity of starting materials should be assessed.

4.4.2 ICP-MS calibration standard stock solution No. 1

1 000 mg/l of each element (Ca, Ce, Gd, Ge, Hg, La, Li, Sb, Sm, Ti, W, Yb) in 10 vol% HNO₃ (1,6 mol/l HNO₃) in water.

4.4.3 ICP-MS calibration standard stock solution No. 2

100 mg/l of each element (As, B, Be, Fe, Se, Zn) in 1,6 mol/l HNO₃ in water.

4.4.4 ICP-MS calibration standard stock solution No. 3

10 mg/l of each element (Ag, Al, Ba, Bi, Cd, Co, Cr, Cu, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sr, Te, Tl, U, V) in 1,6 mol/l HNO₃ in water.

NOTE The working standard should be prepared daily.

4.5 Stock spike solutions

4.5.1 General

Multi-element spike standards are available from commercial vendors and national metrology institutes. Alternatively, stock solutions of multi-element spike standards may be prepared in-house giving due consideration to the purity of water and acids. The following stock spike solutions shall be available.

4.5.2 Stock spike solution No. 1

10 mg/l each of As, Ca, Co, Cr, Cu, Fe, Mn, Ni, Se, V, and Zn in 1,6 mol/l HNO₃ in water.

4.5.3 Stock spike solution No. 2

20 mg/l each of Be, Cd, Fe, Ni, Gd, Ge, Sr, V, W, Yb, and Pb in 1,6 mol/l HNO₃ in water.

4.6 Stock internal standard solutions

4.6.1 General

Single element internal standard solutions are available from commercial vendors and national metrology institutes. Alternatively, internal standard stock solutions may be prepared in-house giving due consideration to the purity of water and acids. The following stock internal standard solutions shall be available for calibration of the instrument.

4.6.2 Internal standard No. 1

1,6 mol/l HNO₃ containing 10 mg/l of Sc in ultrapure water.

4.6.3 Internal standard No. 2

1,6 mol/l HNO₃ containing 10 mg/l of Y in ultrapure water.

4.6.4 Internal standard No. 3

1,6 mol/l HNO₃ containing 10 mg/l of Rh in ultrapure water.

4.6.5 Internal standard No. 4

1,6 mol/l HNO₃ containing 10 mg/l of In in ultrapure water.

4.6.6 Internal standard No. 5

1,6 mol/l HNO₃ containing 10 mg/l of Tb in ultrapure water.

NOTE 10 µg/l of each internal standard is the final concentration used in calibration standards and samples.

4.7 Stock standard tuning solutions

4.7.1 General

Tuning of the instrument shall be carried out daily. Single element standard tuning solutions are available from commercial vendors and national metrology institutes. Alternatively, standard tuning solutions may also be prepared in-house, giving due consideration to the purity of water and acids. The following standard tuning solutions should be available for optimization of the instrument.

4.7.2 Standard tuning solution No. 1

1,6 mol/l HNO₃ containing 1 µg/l of Be.

4.7.3 Standard tuning solution No. 2

1,6 mol/l HNO₃ containing 1 µg/l of Co.

4.7.4 Standard tuning solution No. 3

1,6 mol/l HNO₃ containing 1 µg/l of In.

4.7.5 Standard tuning solution No. 4

1,6 mol/l HNO₃ containing 10 µg/l of Bi.

NOTE One multi-element tuning solution may be used in place of single-element tuning solutions. Such multi-element tuning solutions are commercially available.

5 Apparatus

Use an ICP-MS instrument with a quadrupole or sector field mass spectrometer, or another type of ICP-MS instrument operating with at least 1 u (atomic mass unit) resolution for multi-element determinations. It is recommended that CCT or DRC technology^{[12][13][14][15][16]} be used, if available, to efficiently remove or minimize spectral interferences.

6 Sample pretreatment

6.1 Sample preparation for ICP-MS analysis

Harmonizing sample preparation procedures by using a protocol such as that described in References [12] and [14] contributes to the quality of measurements by improving repeatability, reproducibility and reliability. This in turn ensures that measurement results can be compared with those generated in other laboratories. Given that different laboratories might have different types of sample preparation equipment, it is helpful to provide more than one option for pretreatment of CNTs. Three different sample pretreatment methods, which can be found in Reference [12], are described here. These include wet digestion under high pressure, a combination of dry ashing with wet digestion, and a microwave-assisted sample preparation for dissolution of elemental impurities in the CNT samples before ICP-MS analysis. These methods have been shown to provide reliable and reproducible measurement results using ICP-MS^[12]. They are all equivalent. Among the three procedures described, the appropriate choice for a particular laboratory can be made on the basis of the available equipment or other laboratory-specific factors, as well as a consideration of possible sample effects. If elements of high volatility that are subject to thermal losses, such as Hg, Se, and As, are to be determined, then samples shall be digested using closed microwave-assisted acid digestion systems or sealed PTFE vessels under high pressure.

In each of the following procedures, a selected number of “spiked” samples shall be prepared with each batch of “unspiked” samples. The number of spiked samples shall be at least 10 % of the number of unspiked samples. The purpose of the spiked samples is to allow analyte recovery to be calculated. Spike recovery is described in 8.2.

6.2 Wet digestion under high pressure

- a) Select the desired number of PTFE digestion vessels, taking into account the fact that each vessel will be used to prepare one sample, as well as the desired number of spiked samples. Label the vessels that will contain spiked samples with the word “spiked”, the other vessels are labelled with the word “unspiked”.
- b) Weigh 10 mg to 20 mg of the CNT sample into each vessel.

NOTE 1 PTFE vessels typically have a static charge, making it difficult to accurately weigh mg samples directly into the vessel. The accurate weight of a 10 mg to 20 mg sample in PTFE vessels is calculated from the weight difference between the absence and presence of CNT sample.

NOTE 2 If 10 mg of CNT material might not be sufficient to provide a homogenous and representative sample, the CNT material is homogenized in advance.

- c) Add to each vessel 4 ml of a mixture containing three parts by volume concentrated HNO₃ and one part by volume 3 % mass fraction H₂O₂.
- d) Pipette 0,1 ml or more of the appropriate stock spike solution(s) into each vessel labelled “spiked”.

NOTE 3 One or both spike solutions are used, depending on the impurities remaining in the samples of carbon nanotubes.

- e) Seal the PTFE vessels inside oxygen combustion bombs (one vessel per bomb).
- f) Heat the bombs in an oven at 180 °C and at a gauge pressure of 4 MPa for 12 h; then remove the bombs and allow them to cool to room temperature.
- g) Open the bombs to see if digestion is complete, as indicated by the absence of any black residue. If it is complete, proceed to step h). If it is incomplete, add a 4 ml to 6 ml aliquot of the same mixture used in step c) to each vessel and repeat steps e) to g) until digestion is complete. Three or four heating cycles are typically necessary.
- h) Evaporate each digested solution to incipient dryness (almost dryness). Then add 2 % (volume fraction) HNO₃ to a fixed volume (e.g. 3 ml). Dilute further using 2 % (volume fraction) HNO₃ if necessary for ICP-MS analysis.

NOTE 4 Since evaporation necessitates an open vessel, care should be taken to minimize the potential for contamination, e.g. using HEPA-filtered environment.

6.3 Combined dry ashing and acid digestion

- a) Select the desired number of quartz crucibles, taking into account the fact that each crucible will be used to prepare one sample, as well as the desired number of spiked samples. Label the crucibles that will contain spiked samples with the word “spiked.”
- b) Weigh between 25 mg and 50 mg of the CNT sample into each quartz crucible.
- c) Pipette 0,1 ml of the appropriate stock spike solution(s) into each vessel labelled “spiked.”

NOTE 1 One or both spike solutions are used, depending on the impurities remaining in the samples of carbon nanotubes.

- d) Place the crucibles in a muffle furnace for more than 5 h at a temperature that is appropriate for the composition of the samples being ashed.

NOTE 2 The burning temperature of amorphous carbon is 350 °C. SWCNTs decompose at a temperature of about 500 °C or higher, while MWCNTs decompose at a temperature between 600 °C and 700 °C, under the above mentioned conditions. When the composition of an unknown sample is not well-characterized, a temperature of 750 °C should be used.

NOTE 3 When spiked samples are to be ashed, care should be taken to ramp the temperature to slowly evaporate the solvent; otherwise the spike can sputter, resulting in analyte loss.

- e) Remove the crucibles from the muffle furnace to a desiccator and allow them to cool to room temperature. Then completely transfer the resultant ashes into PTFE vessels using 3 ml to 4 ml hot (50 °C) concentrated HNO₃.
- f) Seal the PTFE vessels inside oxygen combustion bombs (one vessel per bomb).
- g) Heat the bombs in an oven at 180 °C and at a gauge pressure of 4 MPa for 4 h; then remove the bombs and allow them to cool to room temperature.
- h) Open the bombs to see if digestion is complete, as indicated by the absence of any black residue. If it is complete, proceed to step i). If it is incomplete, add 3 ml to 4 ml hot (50 °C) concentrated HNO₃ to each vessel and repeat steps f) to h) until digestion is complete.

- i) Evaporate each digested solution to incipient dryness (almost dryness). Then add 2 % (volume fraction) HNO_3 to a fixed volume (e.g. 3 ml). Dilute further using 2 % (volume fraction) HNO_3 if necessary for ICP-MS analysis.

NOTE 4 The combination of dry ashing with high pressure wet digestion consumes lower quantities of acid reagents and requires a shorter digestion time than the direct high pressure wet digestion method (see 6.2).

6.4 Microwave-assisted digestion

- a) Select the desired number of PTFE digestion vessels for the available microwave sample preparation system, taking into account the fact that each vessel will be used to prepare one sample and the desired number of spiked samples. Label the vessels that will contain spiked samples with the word “spiked.”
- b) Weigh 10 mg of the CNT sample into each vessel.
- c) Add to each vessel an aliquot of concentrated HNO_3 , 5 ml for SWCNT samples or 10 ml for MWCNT samples.

NOTE 1 The amount of acid used is significantly larger than the amount typically used for microwave digestion of other sample types, such as biological and environmental samples.

- d) Pipette 0,1 ml of the appropriate stock spike solution(s) into each vessel labelled “spiked.”

NOTE 2 One spike solution or both spike solutions are used, depending on the impurities remaining in the samples of carbon nanotubes.

- e) Seal the digestion vessels and perform microwave digestion using the following parameters:

- microwave power = 800 W;
- maximum digestion temperature = 200 °C;
- time at maximum temperature = 30 min for SWCNTs or 60 min for MWCNTs.

A higher wattage can be used depending on the number of vessels. After the microwave program has ended, remove the digestion vessels and allow them to cool to room temperature.

- f) Open the vessels to see if digestion is complete, as indicated by the absence of any black residue. If it is complete, proceed to step g). If it is incomplete, add 4 ml to 6 ml concentrated HNO_3 to each vessel and repeat steps e) and f) until digestion is complete. Two or three heating cycles are typically necessary.
- g) Evaporate each digested solution to incipient dryness (almost dryness). Then add 2 % (volume fraction) HNO_3 to a fixed volume (e.g. 3 ml). Dilute further using 2 % (volume fraction) HNO_3 if necessary for ICP-MS analysis.

NOTE 3 There are now potentially more efficient systems available for dissolution/decomposition of carbon nanotubes using oxygen assisted microwave combustion^{[12][15]}, but these are beyond the scope of this Technical Specification.

7 Experimental procedures

7.1 ICP-MS

Submit the ICP-MS instrument to a Performance Qualification process. Calibrate the ICP-MS instrument by generating calibration functions using external calibration standard solutions. An alternative calibration scheme such as standard addition or internal standard, may be undertaken to calibrate the ICP-MS.

If generation of calibration functions using external calibration standard solutions is selected as the calibration method, then the concentrations of elements of interest shall be determined following calibration of the ICP-MS instrument using the calibration standards referred to in Clause 4.