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BSI Standards Publication

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

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National foreword

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It is being issued in the Draft for Development series of publications and is of a provisional nature. It should be applied on this provisional basis, so that information and experience of its practical application can be obtained.

Comments arising from the use of this Draft for Development are requested so that UK experience can be reported to the international organization responsible for its conversion to an international standard. A review of this publication will be initiated not later than 3 years after its publication by the international organization so that a decision can be taken on its status. Notification of the start of the review period will be made in an announcement in the appropriate issue of *Update Standards.*

According to the replies received by the end of the review period, the responsible BSI Committee will decide whether to support the conversion into an international Standard, to extend the life of the Technical Specification or to withdraw it. Comments should be sent to the Secretary of the responsible BSI Technical Committee at British Standards House, 389 Chiswick High Road, London W4 4AL.

The UK participation in its preparation was entrusted to Technical Committee NTI/1, Nanotechnologies.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Compliance with a British Standard cannot confer immunity from legal obligations.

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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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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

ISO/TS 13278 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

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 10797[1]), and measurement methods for the characterization of multiwall carbon nanotubes (ISO/TR 10929[2]).

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.

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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

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 $\mathrm{d}f/\mathrm{d}x_i$
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
$u_\mathrm{c}(y)$	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. HNO_3, 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. H_2O_2, 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% HNO_3 (1,6 mol/l HNO_3) 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 HNO_3 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 HNO_3 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 HNO_3 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 HNO_3 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 HNO_3 containing 10 mg/l of Sc in ultrapure water.

4.6.3 Internal standard No. 2

1,6 mol/l HNO_3 containing 10 mg/l of Y in ultrapure water.

4.6.4 Internal standard No. 3

1,6 mol/l HNO_3 containing 10 mg/l of Rh in ultrapure water.

4.6.5 Internal standard No. 4

1,6 mol/l HNO_3 containing 10 mg/l of In in ultrapure water.

4.6.6 Internal standard No. 5

1,6 mol/l HNO_3 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 HNO_3 containing 1 µg/l of Be.

4.7.3 Standard tuning solution No. 2

1,6 mol/l HNO_3 containing 1 µg/l of Co.

4.7.4 Standard tuning solution No. 3

1,6 mol/l HNO_3 containing 1 µg/l of In.

4.7.5 Standard tuning solution No. 4

1,6 mol/l HNO_3 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 HNO_3 and one part by volume 3 % mass fraction H_2O_2.

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) 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 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 HNO_3.

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 HNO_3 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.

The ICP-MS instrument shall be set up according to the instrument manufacturer's instructions. To ensure optimum instrument performance, it is recommended that the following instrument parameters be optimized before analysis:

— plasma flow rate;

— auxiliary argon flow rate;

— nebulizer argon gas flow rate;

— forward RF power;

— dwell time.

NOTE Optimization of instrument parameters will vary between manufactured instruments.

7.2 Interferences in ICP-MS

The ICP-MS instrument measures intensity at each atomic mass unit (u or Daltons; more accurately, the ratio of the mass of the ion to its charge is displayed, and labelled m/z) in the mass region 3 to 250 u. Spectral interferences can arise from the argon that supports the plasma, the acid used, as well as the sample matrix. A polyatomic or isobaric interference occurs when a given species has a similar m/z to that of the analyte and the resolution of the spectrometer is insufficient to resolve the two peaks, e.g. $^{58}Ni^+$ on $^{58}Fe^+$, $^{40}Ar^+$ on $^{40}Ca^+$, $^{40}Ar^{16}O^+$ on $^{56}Fe^+$, $^{40}Ar^{12}C^+$ on $^{52}Cr^+$, or $^{40}Ar_2^+$ on $^{80}Se^+$. The resolution of a quadrupole ICP-MS instrument is generally around 0,8 u.

NOTE HCl, $HClO_4$, H_3PO_4 and H_2SO_4 can cause considerable spectral problems. Polyatomic interferences are caused by Cl^+, P^+, and S^+ ions in conjunction with other plasma/matrix ions, such as Ar^+, O^+, and H^+. Examples of such isobaric interferences include $^{35}Cl^{40}Ar^+$ on $^{75}As^+$, and $^{35}Cl^{16}O^+$ on $^{51}V^+$. For this reason, the avoidance of HCl, $HClO_4$, H_3PO_4 and H_2SO_4 in ICP-MS is recommended, whenever possible.

7.3 Isotope selection

Of the 70 elements that can be scanned using ICP-MS, only a few are usually found in measurable concentrations in CNT samples. Based on potential interferences and isotopic abundances, the following isotopes should be analysed for ICP-MS analysis: $^{53}Cr^+$, $^{55}Mn^+$, $^{54}Fe^+$, $^{57}Fe^+$, $^{59}Ni^+$, $^{60}Co^+$, $^{63}Cu^+$, $^{65}Cu^+$, $^{66}Zn^+$, $^{68}Zn^+$, $^{95}Mo^+$, $^{172}Yb^+$, $^{182}W^+$, and $^{184}W^+$. Isotopes for analytes not contained in this list, as well as alternative isotopes for analytes that are contained in this list, may be selected by the analyst, based on laboratory-specific, instrument-specific, and/or sample-specific factors. When available, the CCT or DRC method may be employed for the elimination of argon-based polyatomic interferences for the detection of $^{54}Fe^+$, $^{60}Ni^+$, $^{63}Cu^+$, and $^{52}Cr^+$, while matrix desolvation systems may be employed to reduce oxide species. Sector field instruments may be used to resolve isobaric interferences by means of higher spectral resolution. The polyatomic interference of ArC^+ is a major problem for Cr^+ detection. Optimization should be carried out daily with a standard tuning solution (1 µg/l each of Be, Co, In, and U, referred to in 4.7). Raw data are usually collected on a personal computer using proprietary software. The peak areas of elemental signals should be used for quantitative analysis.

7.4 Standard calibration curve

Calibration standards having concentrations that span the range of 1 µg/l to 100 µg/l shall be used to provide appropriate calibration curves. Working standards shall be prepared daily by dilution from the stock solutions described in 4.4. Use at least four calibration standards.

Plot the calibration curve as a function of relative response versus concentration; determine the slope, intercept and correlation coefficient of the calibration curve by the linear regression method. The correlation coefficient shall be $\geq 0{,}95$; if not, the instrument shall be re-calibrated. The concentration of a particular sample can be further confirmed through analysis of certified reference materials. The ICP-MS response can be matrix dependent. Therefore, the standards and samples should be matrix-matched, meaning primarily that the acidic compositions of the standards and samples should be approximately the same.

7.5 Method recovery evaluation using standard addition

Standard addition can be used to evaluate method recovery. Blank solutions are measured along with the spiked and unspiked solutions prepared for analysis.

a) Measure the intensity of a blank solution.

b) Measure the intensity of the unspiked sample solution.

c) Measure the intensity of the sample solution which is spiked with known concentrations of each element.

d) Calculate the recovery for each element for which a spike has been added (see 8.2).

e) The recovery is usually acceptable between 90 to 110 %.

NOTE 1 The sensitivity of measurement of the blank could be different from that of the spiked solution for many elements and care is required to ensure an accurate blank correction (i.e. not as a raw intensity correction).

NOTE 2 Standard addition can also be used as a means of calibrating an ICP-MS analysis, but is not covered in this Technical Specification.

7.6 The use of internal standards in ICP-MS

a) Add the internal standard quantitatively to the digested samples (see 4.6).

b) Use five stock solutions, Internal Standard No. 1, Internal Standard No. 2, Internal Standard No. 3, Internal Standard No. 4 and Internal Standard No. 5 for analytes in the atomic mass ranges of <61 u, 63n to 88 u, 95 to 137 u, and 205 to 209 u, respectively, and throughout the experiment.

c) The analyte and internal standard isotopes shall be sampled and measured as nearly simultaneously as possible.

NOTE 1 The aim of step c) is to compensate most effectively for sample introduction-based and plasma-based noise and achieve optimum precision.

NOTE 2 True simultaneous measurements are only possible when a multicollector instrument is available, otherwise the closest approach to this is achieved using time of flight platforms. Single detector sector field and quadrupole instruments are sequential, not simultaneous.

8 Data analysis and interpretation of results

8.1 Calculation of elemental impurity mass fraction in test sample

The decision whether to use peak height or peak area for signal quantitation should be made by the analyst, though measurement of peak area is recommended.

Calculate the mass fraction of an elemental impurity in the CNT sample (mg/kg) using the following equation:

$$X_i = \frac{M_\mathrm{c} \times V \times I_\mathrm{d}}{S_\mathrm{w}} \tag{1}$$

where

M_c is the concentration obtained from the calibration curve, in micrograms per litre, of the analysed sample solution;

V is the final volume, in litres, of the analysed sample solution;

I_d is the dilution factor of the analysed sample solution, accounting for all sample preparation steps;

S_w is the weight, in grams, of the CNT sample.

8.2 Calculation of the spike (method) recovery

The spike recovery in the sample is used to determine whether a result is quantitative and accurate. Spike recoveries from 90 % to 110 % are considered acceptable. Calculate the spike recovery, $R\%$, using the following equation:

$$R\% = \frac{M_\mathrm{s} - M_\mathrm{c}}{C_\mathrm{s}} \times 100 \tag{2}$$

where

M_s is the average measured concentration in the spiked sample solutions, in micrograms per litre, after blank correction;

M_c is the average measured concentration of the (unspiked) sample solutions, in micrograms per litre, after blank correction;

C_s is the expected concentration of spiked solution based on the added spike, in micrograms per litre.

9 Uncertainty estimation

In accordance with international requirements, the uncertainty associated with measurement results shall also be calculated and reported. It is recommended that this be done following the principles of the ISO *Guide to the Expression of Uncertainty in Measurement* (GUM) (see also Reference [10]). Components of uncertainty shall be included for all significant sources of uncertainty in the measurement process. Important sources of uncertainty in the case of ICP-MS analysis include, for example, sample preparation steps such as weighing, digestion (particularly important in the case of refractory samples such as CNTs), the assigned values of the calibration standards, instrument calibration, measurement precision, and method bias. Once the individual standard uncertainties for the significant sources of uncertainty have been determined, these shall be combined and converted to an expanded uncertainty at a specified level of confidence.

An elemental mass fraction value, y, determined using ICP-MS is a function of N input quantities, x_i, where $i = 1, 2, \ldots, N$ [i.e., $y = f(x_1, x_2, \ldots, x_N)$]. Using the GUM approach, the combined standard uncertainty associated with the determined mass fraction value, $u_\mathrm{c}(y)$, is found by combining the individual standard uncertainties according to the law of propagation of uncertainty:

$$u_\mathrm{c}\left(y\right) = \sqrt{\sum_i \left[c_i \times u(x_i)\right]^2} \tag{3}$$

where

c_i is sensitivity coefficient for input quantity, x_i, defined as $\mathrm{d}f/\mathrm{d}x_i$;

$u(x_i)$ is standard uncertainty associated with input quantity, x_i.

Equation (3) ignores the covariance terms in the law of propagation of uncertainty. This simplification usually has negligible consequences in terms of the estimated value of $u_\mathrm{c}(y)$.

The final expanded uncertainty, U, is obtained by multiplying the combined standard uncertainty, $u_\mathrm{c}(y)$, by a coverage factor, k.

$$U = k \times u_\mathrm{c}\left(y\right) \tag{4}$$

where

U is the expanded uncertainty;

k is the coverage factor;

$u_\mathrm{c}(y)$ is the combined standard uncertainty of the final result.

The value of k can be calculated for a specific level of confidence based on the effective degrees of freedom associated with $u_\mathrm{c}(y)$. The effective degrees of freedom can be estimated using the Welch-Satterthwaite formula or other methods. However, it is usually acceptable to just assume that $k = 2$, because this approach typically results in a level of confidence of approximately 95 %.

10 Test report

The test report shall include the following:

a) identification of tested CNT samples, including the manufacturer's code, catalogue or formulation number, batch number or date of manufacture, trade-name, etc.;

b) identification of all equipment and instrumentation used, e.g. manufacturer's model or catalogue number, serial number or date of manufacture, brand-name, etc.;

c) a brief description of sample pretreatment procedures, including the type of acid, digestion method, temperature, and other conditions for wet digestion, etc.;

d) a brief description of experimental ICP-MS procedures;

e) all results of the measurements and their uncertainty estimates;

f) all supporting information developed during preparation and throughout tests;

g) the use of the appropriate units of the International System of Units (SI).

Annex A
(informative)

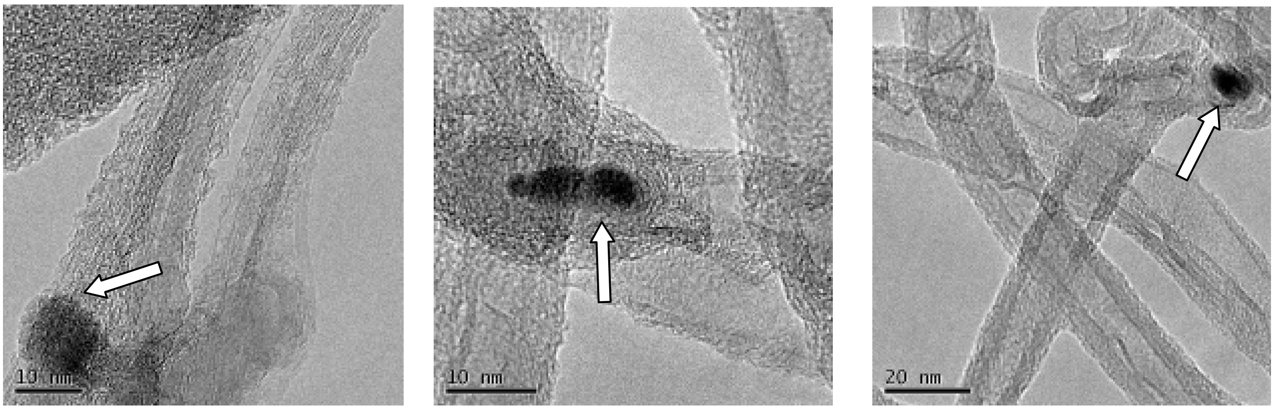
Example of determination of elemental impurities in carbon nanotubes

A.1 SWCNT and MWCNT samples

The main techniques for the production of CNTs include electric arc discharge, laser evaporation, and catalytic decomposition of hydrocarbons. These techniques have been successfully developed to synthesize CNTs. The catalyst employed in synthesizing CNTs can be a single element from Group V, VI, VII or VIII, a lanthanide, or a transition metal or combinations thereof. Table A.1 gives selected parameters of SWCNTs and MWCNTs supplied by several vendors. Figure A.1 shows TEM images of SWCNTs and MWCNTs from several vendors. The dark regions identified by arrows indicate metal impurities.

Table A.1 — Parameters of SWCNTs and MWCNTs supplied by different vendors

Sample	Outer diameter	Length	Purity	Ash	Specific surface area	Electrical conductivity	Thermal conductivity	Amorphous carbon
	nm	µm	wt %	wt %	m^2/g	S/cm	W/m K	wt %
1-SWCNT	1 to 2	5 to 30	>90	<1,5	>407	$>10^2$		
2-SWCNT	<2	<20	>90	<3	>450		~4 000	<5
4-MWCNT	20 to 30	10 to 30	>95	<1,5	>110	$>10^2$		
5-MWCNT	10 to 20	0,5 to 2	>95	<1,5	>350	$>10^2$		
6-MWCNT	10 to 20	~50	>95	<1,5	>180	$>10^2$		
7-MWCNT	10 to 30	5 to 15 or 1 to 2	>95	<0,2	40 to 300		~2 000	<3
8-MWCNT	10 to 30	5 to 15 or 1 to 2	>95	<0,2	40 to 300		~2 000	<3
9-MWCNT	10 to 20	5 to 15 or 1 to 2	>95	<0,2	40 to 300		~2 000	<3
	20 to 40	5 to 15 or 1 to 2	>95	<0,2	40 to 300		~2 000	<3
11-MWCNT	40 to 60	5 to 15 or 1 to 2	>95	<0,2	40 to 300		~2 000	<3
12-MWCNT	60 to 100	5 to 15 or 1 to 2	>95	<0,2	40 to 300			
13-SWCNT	1,3	0,5 to 3	50 to 70				~2 000	<3
14-SWCNT	1,3	0,5 to 3	>90					



3-SWCNT 7-MWCNT 8-MWCNT

NOTE Dark regions (highlighted by arrows) indicate metal impurities[13].

Figure A.1 — TEM images of as-purified SWCNTs and MWCNTs from various vendors

The as-purified CNTs received further purification by vendors.

A.2 Equipment

ICP-MS with a hexapole collision cell (Thermo Elemental X7)3) was used. The plasma and auxiliary argon flow rates were 13 and 0,75 l/min, respectively. The nebulizer argon gas flow rate was 0,75 l/min for the glass concentric nebulizer. The forward rf power was 1 200 W. The dwell time was 200 ms.

A.3 Detailed description of sample pretreatment procedures

Before ICP-MS analysis, CNTs were digested completely in accordance with the method of wet digestion under high pressure given in 6.2. This method involves placing the PTFE vessel containing 10 to 20 mg samples and a 4 ml mixture of three parts $\mathrm{HNO_3}$ to one part $\mathrm{H_2O_2}$ into an oxygen combustion bomb. The latter was then heated at 180 °C and at a gauge pressure of 4 MPa for 12 h in an oven. If digestion was incomplete, more of the acid mixture was added and the digestion procedure was repeated. When digestion was over, the remaining acid was driven off and the final solution was adjusted to a fixed volume using 2 % nitric acid and then diluted, centrifuged, and analysed by ICP-MS[12].

A.4 ICP-MS analysis

The final digestion solutions were first screened for the presence of elements using ICP-MS with a hexapole collision cell. Isotopes such as $^{53}\mathrm{Cr}$, $^{55}\mathrm{Mn}$, $^{54}\mathrm{Fe}$, $^{57}\mathrm{Fe}$, $^{59}\mathrm{Ni}$, $^{60}\mathrm{Co}$, $^{63}\mathrm{Cu}$, $^{65}\mathrm{Cu}$, $^{66}\mathrm{Zn}$, $^{68}\mathrm{Zn}$, and $^{95}\mathrm{Mo}$ were monitored. The collision cell technique (CCT) was employed for the elimination of the polyatomic interferences of $^{40}\mathrm{Ar}$, $\mathrm{ArO^+}$, $\mathrm{Na_2O^+}$, $\mathrm{NaAr^+}$, and others in the detection of $^{54}\mathrm{Fe}$, $^{59}\mathrm{Ni}$, $^{63}\mathrm{Cu}$, $^{52}\mathrm{Cr}$, and so on. Optimization was carried out daily with a normal tuning solution (1 ng/ml, Be, Co, In, U). Raw data were collected using a personal computer. The peak areas of elemental signals of ICP-MS were used for quantitative analysis online[12].

Two spiking experiments were performed to determine the accuracy of the ICP-MS method. In the first, mixed elemental standard solutions of known concentrations were added to the final digested solutions of CNT samples after pretreatment in order to evaluate the accuracy of the ICP-MS measuring system. For the second, mixed elemental standard solutions of known concentrations were added to the original CNT samples prior to acid pretreatment, through which the accuracy of the whole procedure was evaluated. Several single elemental standard stock solutions were mixed to prepare mixed standard solutions. Then, 100 µl of mixed

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3) Thermo Elemental X7 is the trade name of a product supplied by Thermo Electron Co. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

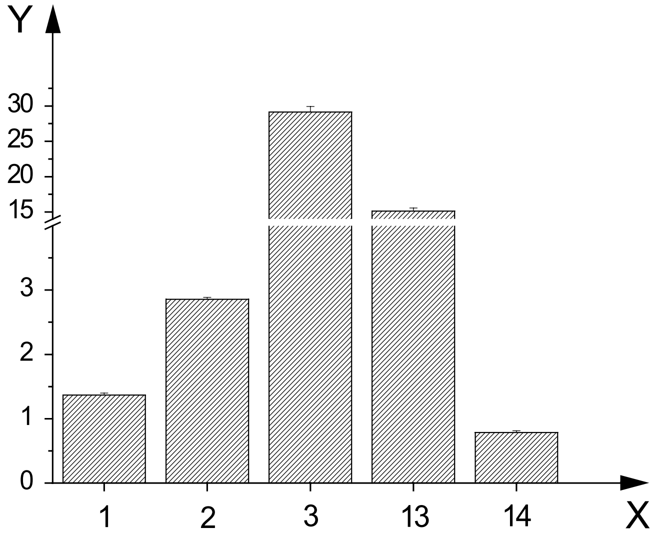
elemental standard solutions of known concentrations were added to 10 mg of original CNT samples prior to acid pretreatment; the ratio of addition for each element was 1:1 in the final solution for ICP-MS. The spiked and unspiked CNT samples were subjected to the same pretreatment procedure as for wet digestion at high pressure and were finally determined by ICP-MS[12].

A.5 NAA analysis

20 mg samples were enclosed in polyethylene capsules. The samples were irradiated for 8 h at a thermal neutron flux of 5,88 × 10^{13} n cm^{-2} s^{-1} using a heavy water nuclear reactor of the Chinese Institute of Atomic Energy, Beijing. The gamma spectra were acquired using a spectrometer equipped with an HPGe detector. Its energy resolution is 1,96 keV for the 1 332 keV peak of ^{60}Co and its relative detection efficiency is 25 % and the peak-to-Compton ratio was 48:1. Some well-prepared mixed chemical solutions were used as the comparators, which contained the elements of interest in the known concentrations[12][13].

A.6 Example results of ICP-MS analysis

Figures A.2 and A.3 summarize the mass percentages of impurity elements determined by ICP-MS in SWCNT and MWCNT samples, respectively, obtained from various suppliers[13]. The results show that these commercial CNTs contain significant quantities of residual metals despite the use of post-processing by the manufacturers to reduce metallic and amorphous carbon contents.



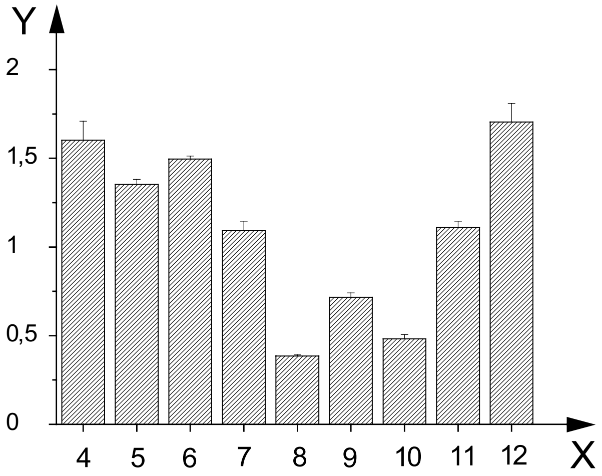
Key

X sample number

Y content of metal impurities (wt %)

Figure A.2 — Total mass percentages of metal impurities in five SWCNT samples provided by various manufacturers

The data for each sample represent the mean and standard deviation of three independent determinations[13].



Key

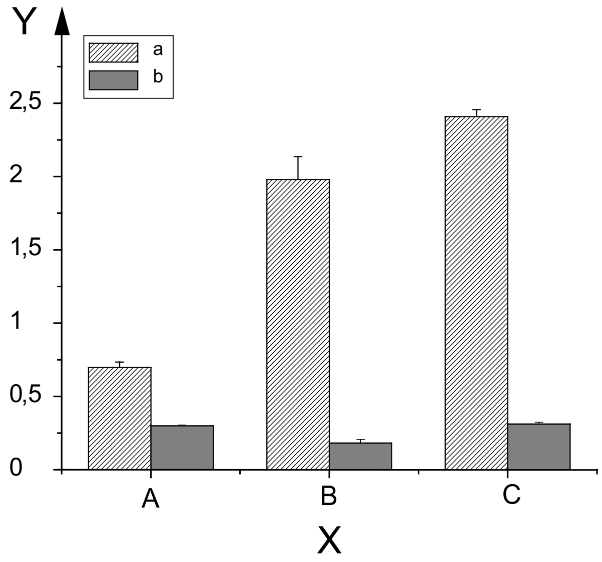
X sample number

Y content of metal impurities (wt %)

Figure A.3 — Total mass percentage of metal impurities in MWCNT samples provided by various manufacturers

The data for each sample represent the mean and standard deviation of three independent determinations[13].

Figure A.4 shows the total mass percentages of metal impurities determined using ICP-MS in MWCNT samples before and after further purification using a mixed acid reflux procedure[13]. The outer diameters of the MWCNTs were different for each of the three samples. The samples as received from the vendors were refluxed in a concentrated mixture of sulfuric and nitric acids, followed by washing with distilled water. Figure A.4 shows that the residual metal impurities contained in the CNTs could not be removed completely, even after employing this rigorous purification step.



Key

X sample number

Y content of metal impurities (wt %)

a Before further purification.

b After further purification.

Figure A.4 — Total mass percentages of metal impurities determined using ICP-MS in MWCNT samples before and after further purification using mixed acid reflux procedure

The data for each sample represent the mean and standard deviation of three independent determinations.

A.7 Comparison of results obtained by ICP-MS and NAA methods

Table A.2 compares the mass fractions of impurity elements in SWCNT and MWCNT samples determined by ICP-MS and NAA. The results obtained using the two methods compare favourably, with mean and median observed relative differences of less than 4 %. NAA was employed as a reference technique in the absence of CNT reference materials.

Each value is expressed as the mean, plus or minus one standard deviation of three independent determinations (µg/g)[13].

Table A.2 — Comparison of the mass fractions of impurity elements in CNT samples determined by ICP-MS and NAA

Sample	SWCNT		MWCNT	
	NAA µg/g	ICP-MS µg/g	NAA µg/g	ICP-MS µg/g
Cr	1 180 ± 42	1 143 ± 54	146 ± 9,7	159 ± 12
Fe	20 000 ± 10	19 585 ± 57	7 750 ± 396	8 323 ± 20
Co	6,92 ± 0,1	6,5 ± 0,25	1,21 ± 0,03	1,3 ± 0,3
Ni	959 ± 17	910 ± 31	954 ± 55	971 ± 25
Zn	28,1 ± 2,54	30 ± 7	584 ± 30	518 ± 24
Mo	6 030 ± 212	5 803 ± 6	1 307 ± 3,9	1 306 ± 25
La	1,1 ± 0,1	0,8 ± 0,01	1,61 ± 0,04	1,4 ± 0,05
W	5,35 ± 0,7	4,7 ± 0,04	2,25 ± 0,08	2,05 ± 0,09

NAA has several merits, including high accuracy and high sensitivity. It is also non-destructive, requiring no destructive pre-treatment of the nanotubes prior to the analysis. However, NAA is not readily available in most laboratories. In contrast, ICP-MS is usually available in many analytical laboratories. As there are no standard reference materials for CNTs available yet in which the identities and mass fractions of metallic impurities are known, use of NAA as an accurate method for quantification and ICP-MS as a practical analytical method is evident.

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