TECHNICAL SPECIFICATION

ISO/TS 13278

Second edition
2017-11

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)

Reference number
ISO/TS 13278:2017(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies.*

This second edition cancels and replaces the first edition (ISO/TS 13278:2011), which has been technically revised.

Introduction

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 (see ISO/TS 10798), TEM (see ISO/TS 10797), and measurement methods for the characterization of multiwall carbon nanotubes (see ISO/TR 10929).

However, each method has its limitations for determination of elemental impurities. ICP-MS is 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 solubilized. 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][16][17][18].

The purpose of this document 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.

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

1 Scope

This document 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 document 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 references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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*

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

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, ISO/TS 80004-6 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

3.1.1
ICP-MS
inductively coupled plasma mass spectrometry method in which a high-temperature discharge generated in flowing argon by an alternating magnetic field induced by a radio-frequency (RF) load coil that surrounds the tube carrying the gas is detected using a mass spectrometer

Note 1 to entry: ICP-MS permits quantitative determinations of trace, minor and major elements in samples pertaining to almost every field of application of analytical chemistry.

3.1.2
elemental impurity
element other than carbon that is present in a carbon nanotube sample

Note 1 to entry: Such impurities are primarily remnants of metal catalysts used during large-scale production of CNTs.

Note 2 to entry: Amorphous carbon can be considered another type of impurity in samples containing SWCNTs and MWCNTs.

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
$C_\mathbf{s}$	expected concentration, in micrograms per litre, of spiked sample solution based on the added spike
CVD	chemical vapour deposition
DRC	dynamic reaction cell
EDX	energy dispersive X-ray analysis
EELS	electron energy loss spectroscopy
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
SEM	scanning electron microscopy
S_w	weight, in grams, of CNT sample
SWCNT	single-wall carbon nanotube
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
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

XPS X-ray photoelectron spectroscopy

XRF X-ray fluorescence spectrometry

4 Samples and reagents

4.1 General

CNT samples produced by various processes typically contain impurities consisting of amorphous carbon and other elements. ICP-MS allows the determination of major, minor and trace elements, providing quantitative information important for the characterization of the purity of CNT samples.

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, trace metal 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 at 298 K (25 °C) 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. 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.

The sample digest should be pre-tested in order to select appropriate internal standards, to ensure that the internal standard elements are not present in the samples.

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 1 10 µg/l of each internal standard is the final concentration used in calibration standards and samples.

NOTE 2 An alternative internal standard can be selected if Y is present in the carbon nanotube.

4.7 Stock standard tuning solutions

4.7.1 General

The operating parameters of the instrument shall be optimized daily using standard tune solutions. 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.

4.7.6 Standard tuning solution No. 5

1,6 mol/l HNO_3 containing 10 µg/l of Ce.

NOTE One multi-element tuning solution can 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][16][17][18][19] 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 [17] 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.