Nederlandse praktijkrichtlijn

NPR-ISO/TS 13278

(en)

Nanotechnologies - Determination of elemental impurities in samples of carbon nanotubes using inductively coupled plasma mass spectrometry
(ISO/TS 13278:2011,IDT)

ICS 07.030

december 2011

Als Nederlandse praktijkrichtlijn is aanvaard:

- ISO/TS 13278:2011,IDT

Normcommissie 342229 "Nanotechnologie"

NEN

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NPR-ISO/TS 13278:2011

TECHNICAL SPECIFICATION

ISO/TS 13278

First edition
2011-11-01

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 13278:2011(E)

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Published in Switzerland

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.

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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order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn.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again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.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.

1) Under preparation.

2) Under preparation.

TECHNICAL SPECIFICATION **ISO/TS 13278:2011(E)**

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 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. 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.

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