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Nanotechnologies — Characterization of volatile components in single-wall carbon nanotube samples using evolved gas analysis/gas chromatograph-mass spectrometry

Nanotechnologies — Caractérisation des composés volatils dans les nanotubes de carbone à simple paroi (SWCNT) utilisant l'analyse des gaz émis par chromatographie en phase gazeuse couplée à la spectrométrie de masse

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Foreword

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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).

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

This second edition cancels and replaces the first edition (ISO/TS 11251:2010), which has been technically revised.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Nanotechnologies — Characterization of volatile components in single-wall carbon nanotube samples using evolved gas analysis/gas chromatograph-mass spectrometry

1 Scope

This document specifies a method for the characterization of evolved gas components in single-wall carbon nanotube (SWCNT) samples using evolved gas analysis/gas chromatograph mass spectrometry (EGA/GCMS).

NOTE Some difference could appear between qualitative and quantitative results of emitted gas and gas content in the sample due to the heating and the possible presence of catalysts.

2 Normative references

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 — Vocaburlary — Part 3: Carbon nano-objects*

3 Terms and definitions

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

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

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

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

3.1
single-wall carbon nanotube
SWCNT
carbon nanotube consisting of cylindrical graphene layer

3.2
evolved gas analysis
EGA
technique in which the nature and/or amount of evolved gas product(s) released by a sample subjected to a controlled temperature program is(are) determined

Note 1 to entry: The method of analysis should always be clearly stated (Reference [1] in the Bibliography).

3.3
EGA/MS
evolved gas analysis/mass spectrometry
technique using mass spectrometry to analyse gaseous components evolved from a sample as a function of temperature

Note 1 to entry: Although the gases evolved at any particular temperature are detected simultaneously, it might not be possible to uniquely identify the different components using MS alone.

3.4
EGA/GCMS
evolved gas analysis/gas chromatography coupled to mass spectrometry
technique combining a gas chromatograph and a mass spectrometer to identify the chemical composition of gases evolved from a sample as a function of temperature

Note 1 to entry: The evolved gases are passed through a gas chromatograph (GC) to separate each component so that it can be identified in the MS unit.

3.5
volatile compounds
compounds that are evolved from a sample at the temperature under consideration

4 Principle

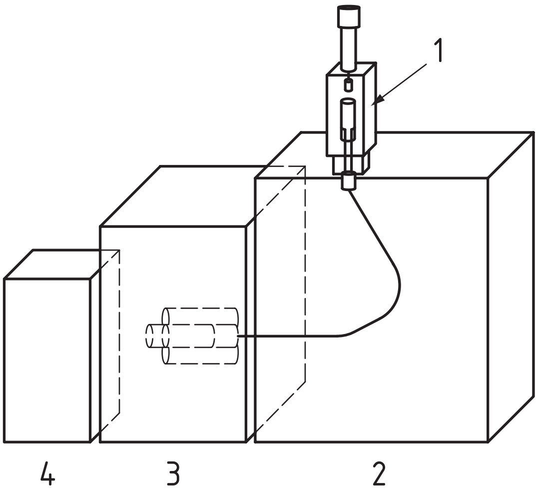
EGA/MS and EGA/GCMS are used to characterize evolved gas impurities in samples of SWCNT. Evolved gas compounds are identified by measuring the mass spectra of the gaseous component evolved from the heated samples in a furnace or other suitable heating device, such as that used for programmed temperature pyrolysis or thermogravimetric analysis. EGA/MS is used to determine the temperature range over which the release of evolved gas components occurs. EGA/GCMS analysis is used to identify each component separately by the use of a GC capillary column. Quantitative information can additionally be obtained by the sample mass loss in thermogravimetric analysis (TGA) and the peak area in EGA/MS.

NOTE Some details of the technique are described in References [2] to [6] in the Bibliography. EGA/GCMS plays a complementary role to TGA, which is mainly devoted to quantifying the mass of the evolved gas components.

5 Apparatus

Figure 1 shows a schematic diagram of EGA/MS which is composed of a furnace, a heating unit without a GC capillary column and a MS unit. In the EGA/MS, evolved gas from the furnace is led to the MS unit directly through a capillary tube without a separation process.

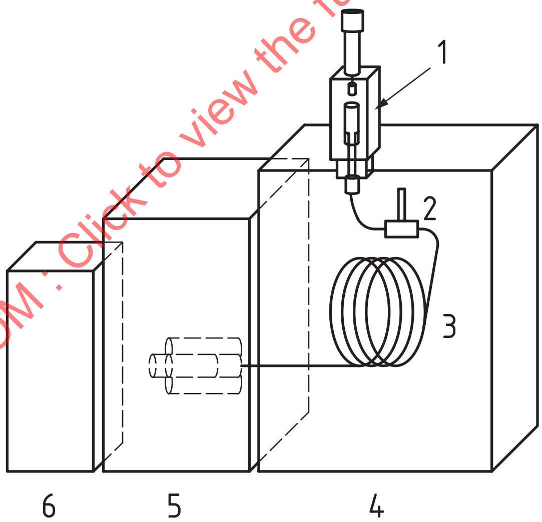
Figure 2 shows a schematic diagram of an EGA/GCMS which is composed of a furnace, a GC with a capillary column and an MS unit. In the EGA/GCMS, all compounds evolved from the sample within the furnace are captured by the cooling trap and are then introduced to the GC capillary column unit by heating the trap. The compounds are separated by the column in the GC unit.



Key

1 furnace
2 heating unit
3 MS unit
4 temperature controller of furnace

Figure 1 — Schematic diagram of EGA/MS



Key

1 furnace
2 cooling trap
3 capillary column
4 GC unit
5 MS unit
6 temperature controller of furnace

Figure 2 — Schematic diagram of EGA/GCMS

6 Sample preparation

Sample preparation, such as dissolution or dispersion, is not required. For a qualitative analysis, the sample shall be introduced into the EGA/MS or EGA/GCMS as it is. In order to avoid the vaporization of any evolved gas that might be present, samples shall not be exposed to temperature above 30 °C before analysis.

7 Measurement procedures for EGA/MS and EGA/GCMS

7.1 General

Load the SWCNT sample into the furnace and heat it up to identify the temperature range of gasification using EGA/MS measurement, and use the EGA/GCMS to identify each component at the designated temperature range.

7.2 Measurement procedure of EGA/MS

Weigh between 0,5 mg and 2 mg of the SWCNT sample, to the nearest 0,01 mg, using a calibrated mass balance.

Load the weighed sample into the furnace, including the sample cup used when weighing.

Heat the sample at a constant rate until gas evolution stops. Measure the total ions from evolved gas components. Determine the start temperature and the end-point of gasification using the EGA curve.

Compare the observed mass spectrum with the mass spectral database and determine each component in the evolved gas species. For appropriate comparison of mass spectra, ionization energy and tuning conditions used for the analysis shall match those in the spectral database.

Perform EGA/GCMS if the measured spectrum cannot be identified using the MS spectral database due to the mixture of components (see 7.3).

Weigh the sample after EGA/MS measurement, to the nearest 0,01 mg.

NOTE The rate of heating depends on the calorific capacity of the sample. Generally, a range of 10 to 25 °C/min is used for EGA/MS.

7.3 Measurement procedure of EGA/GCMS

Weigh between 0,5 mg and 2 mg of SWCNT from the same sample as that used in 7.2, to the nearest 0,01 mg.

Load the sample into the furnace.

Heat the sample at a constant rate to the lower temperature of either the end-point of the gasification or upper limit of the instrument.

Compare the electron ionization (EI) mass spectrum for each of the GC peaks with the mass spectral database and determine each component of the evolved gas species. For appropriate comparison of mass spectra, ionization energy and tuning conditions used for the analysis shall match those in the spectral database (typically 70 electron volts).

The mass analyser shall be calibrated manually or via the instrument's tuning algorithm by using a calibration reference material.

The rate of heating depends on the sample. Generally, a range of 45 to 65 °C/min is used for EGA/GCMS to shorten the analytical time. The temperature of the trap should be less than about −150 °C.

8 Data analysis and interpretations of results

8.1 Qualitative analysis

The qualitative analysis shall be based upon the standard spectral information of compounds. Components from evolved gas shall be determined by comparing the measured MS spectra with a mass spectral database.

a) Choose the component that needs to be identified.

b) Subtract the background from the analyte's mass spectra.

c) Search for similar spectra from within the spectral database.

d) Select the possible components in the sample from the candidates identified using the standard spectra.

NOTE 1 Many kinds of software for similarity searching and a mass spectral database are available, as an example, NIST/EPA/NIH Mass Spectral database with Similarity Search Program.

NOTE 2 Using this method, *n*-hexane, benzene and toluene were identified in the example shown in Annex A and Figure A.4.

8.2 Mass loss analysis

The evolved gas components in SWCNT samples are determined using the following formula:

$$P = \frac{W_0 - W_t}{W_0} \times 100$$

where

P is the evolved gas impurity content, expressed as a percentage;

W_0 is the sample mass, in milligrams, before heating;

W_t is the sample mass, in milligrams, after heating.

NOTE Normally, quantitative analysis by GC/MS needs calibration curves, which show the relationship of the signal intensity and the concentration of each component. It is impossible to prepare the calibration curves for all components of interest. For this reason, only mass loss by the EGA process is used.

9 Accuracy and uncertainties

Currently, the uncertainties in the evolved gas components characterizations for SWCNTs by EGA/GCMS come from

a) fluctuation of temperature in the oven or detector,

b) mis-calibration and/or drifting of the mass analyser, or

c) fluctuation of ionization energy.

10 Test report

The test report shall include the following information:

a) a reference to this document and its year of publication;

b) Identified components including gas chromatograph-mass spectrometry;

c) mass loss in percentage (%);

d) Instrumental conditions including heating conditions, start temperature and mass range.

Annex A
(informative)

Case study

A.1 General

An example of different analytical conditions is given in A.2.

A.2 Measurement parameters

The measurement parameters are as follows:

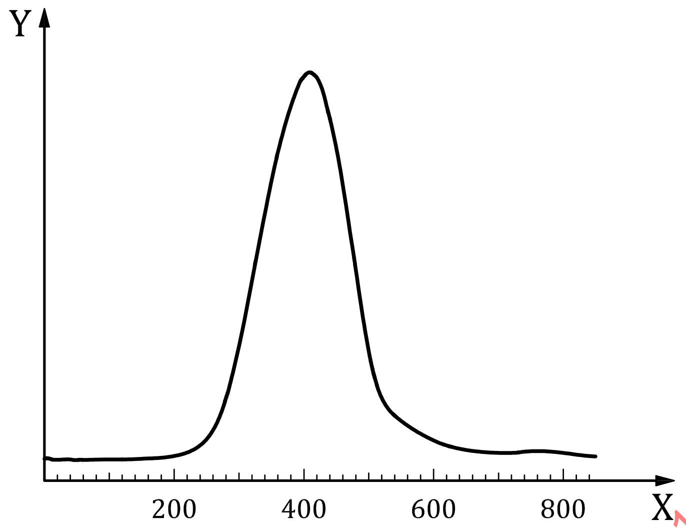
a) EGA/MS

EGA unit	
Furnace temperature	1) Hold sample at 40 °C for 2 min.
	2) Heat sample from 40 °C to 750 °C at 20 °C/min.
GC (Oven)	
Column	Deactivated capillary tube [2,5 m × 0,15 mm internal diameter (ID)]
Column temperature	300 °C (maintained temperature of GC oven)
Carrier gas	Helium (99,999 %)
Column head pressure	60 kPa
Injection temperature	230 °C
Injection method	Split 1:15
MS	
Ion-source temperature	200 °C
Interface temperature	300 °C
Ionization method	Electron ionization
Ionization energy	70 eV
Scan range	mass-to-charge ratio (*m*/*z*) 10 to 400
Scan interval	5 s

b) EGA/GCMS

EGA unit	
Furnace temperature	Heat sample from 150 °C to 600 °C at 60 °C/min
GC	
Column	capillary column (30 m × 0,32 mm (ID)
Column temperature	40 °C (1 min hold) to 200 °C at 40 °C/min to 250 °C at 25 °C/min, 250 °C (23 min hold)
Carrier gas	Helium (99,999 %)
Column head pressure	60 kPa
Injection temperature	230 °C
Injection method	Split 1:15
MS	
Ion-source temperature	200 °C
Interface temperature	260 °C
Ionization method	Electron ionization
Ionization energy	70 eV
Scan range	*m*/*z* 10 to 400
Scan interval	0,5 s

An EGA chromatogram from EGA/MS is shown in Figure A.1. For this SWCNT sample, the main evolved component was observed between 200 and 600 °C. In this evolved gas profile, the *m*/*z* of water, oxygen and nitrogen were subtracted to reduce interference.



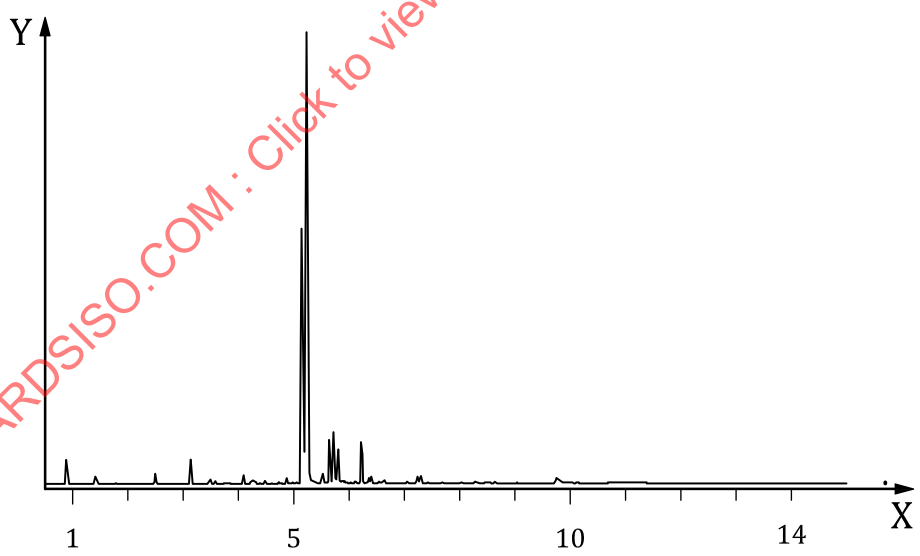
Key

X temperature, °C

Y abundance

Figure A.1 — Evolved gas profile by EGA/MS

Based on the result of the evolved gas profile, EGA/GCMS analysis was conducted to identify the evolved gas components. The total ion chromatogram (TIC) from the EGA/GCMS is shown in Figure A.2. The TIC is the chromatogram obtained by plotting the total electron current emitted from fragments as a function of the retention time.



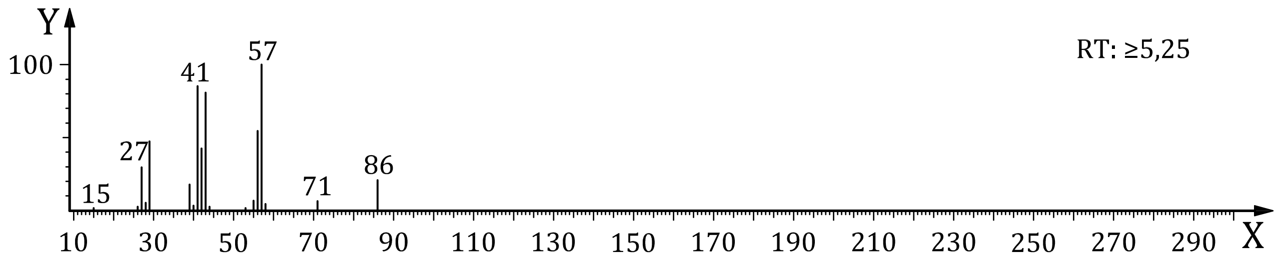
Key

X retention time, min

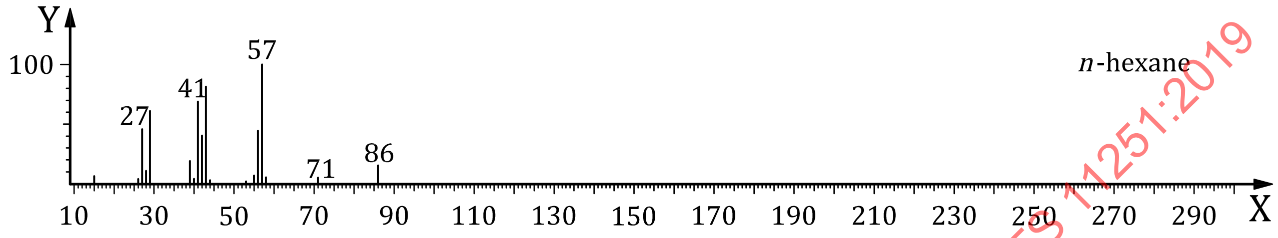
Y abundance

Figure A.2 — Total ion chromatogram of EGA/GCMS

By analysing the MS spectra of the peaks from this chromatogram, identification of each component was made. Several peaks were observed on the TIC. Figure A.3 shows a MS spectrum of the peak at about 5 min.



a) MS spectrum of the peak at about 5 min of retention time (RT)



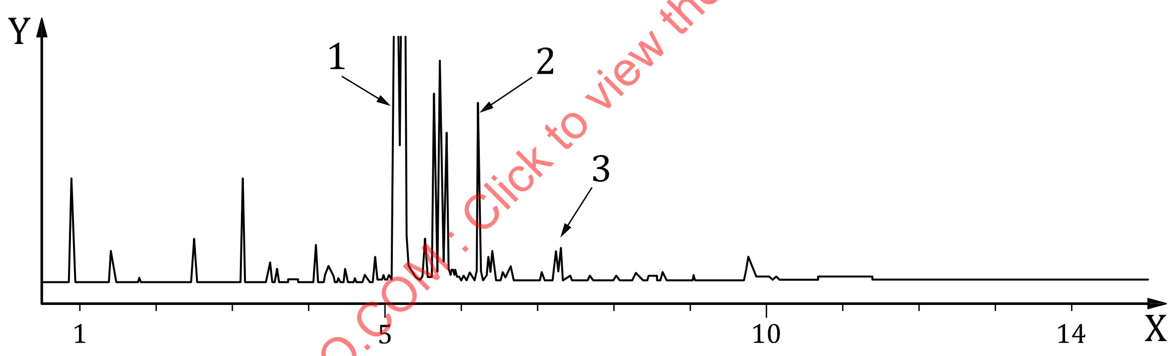
b) MS spectrum of *n*-hexane from standard library

Key

X *m*/*z*

Y relative abundance

Figure A.3 — Identification of MS spectrum



Key

1 *n*-hexane

2 benzene

3 toluene

Figure A.4 — Assignment of several components from a SWCNT sample

This compound was identified as *n*-hexane by comparison with reference spectra. By analysing the MS spectra, other peaks were assigned to benzene and toluene as shown in Figure A.4.

The mass reduction of the sample was approximately 0,055 mg from its original total mass 1,328 mg. This showed that 4 % of the total mass was due to evolved gas impurities including moisture in the SWCNTs.