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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 composants volatiles dans les nanotubes de carbone à paroi simple (SWCNT) utilisant l'analyse des gaz émis par chromatographie en phase gazeuse/spectrométrie de masse

Reference number
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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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ISO/TS 11251 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

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

1 Scope

This Technical Specification specifies a method for the characterization of volatile components in single-wall carbon nanotubes (SWCNTs) samples using evolved gas analysis/gas chromatograph mass spectrometry (EGA/GCMS).

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 27687, *Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 27687 and the following apply.

3.1
evolved gas analysis
EGA
technique in which the nature and/or amount of volatile product(s) released by a substance subjected to a controlled temperature program is(are) determined

NOTE The method of analysis should always be clearly stated (Reference [1] in the Bibliography).

3.2
evolved gas analysis/mass spectrometry
EGA/MS
technique using mass spectrometry to analyse gaseous components evolved from a sample as a function of temperature

NOTE 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.

3.3
evolved gas analysis/gas chromatograph mass spectrometry
EGA/GCMS
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 The evolved gases are passed through a gas chromatograph (GC) to separate each component so that it can be identified in the MS unit.

3.4
volatile compounds
compounds that are evolved from a sample at the temperature under consideration

4 Principle

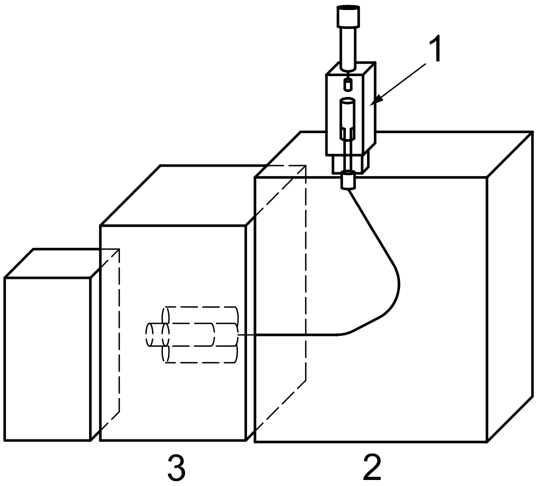
EGA/MS and EGA/GCMS are used to characterize volatile impurities in samples of SWCNT. Volatile compounds are identified by measuring the mass spectra of the gaseous component evolved from the heated samples in a furnace or other suitable heating device, such as that used for programmed temperature pyrolysis or thermogravimetric analysis. EGA/MS is used to determine the temperature range over which the release of volatile components occurs. EGA/GCMS analysis is used to identify each component separately by the use of a 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 volatile components.

5 Apparatus

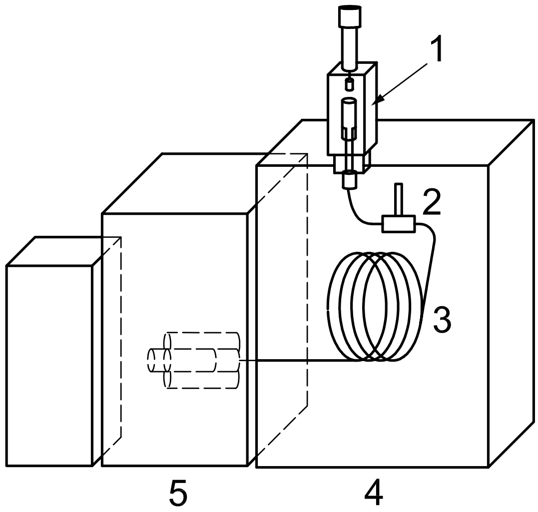
Figure 1 shows a schematic diagram of EGA/MS which is composed of a furnace, a heating unit without a separation column and a MS unit. In the EGA/MS, evolved gas from the furnace is led to the MS unit directly through a capillary tube without a separation process.

Figure 2 shows a schematic diagram of an EGA/GCMS which is composed of a furnace, a GC with a separation 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 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

Figure 1 — Schematic diagram of EGA/MS



Key

1 furnace
2 cooling trap
3 capillary column
4 GC unit
5 MS unit

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 volatiles that might be present, samples shall not be dried 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 volatile components. Determine the start temperature and the end-point of gasification using the EGA curve.

Compare the observed MS spectrum with the MS spectral database and determine each component in the evolved gas species. For appropriate comparison of MS spectra, an ionization voltage shall be in accordance with the voltage of the spectral database.

Perform EGA/GCMS if the measured spectrum cannot be identified using the MS spectral database due to its mixed 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 15 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 up 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 observed MS spectrum with the mass spectral database and determine each component of the evolved gas species. An ionization voltage shall be in accordance with the voltage of the standard spectra.

The MS detector shall be calibrated by using a calibration reference material.

NOTE 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.

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 targeted MS spectrum.

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

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

NOTE 1 Many kinds of software for searching and a mass spectral database are available, as an example, NIST/EPA/NIH Mass Spectral Library with 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 volatile components in SWCNT samples are determined using the following formula:

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

where

P is the volatile 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 Precision and uncertainties

Currently, the uncertainties in the volatile components characterizations for SWCNTs by EGA/GCMS comes from

a) fluctuation of temperature in the oven or detector,

b) mis-calibration of the MS detector, or

c) fluctuation of ionization voltage.

10 Test report

The test report shall include the following information:

a) a reference to this Technical Specification;

b) identified components;

c) mass loss in percentage (%);

d) heating conditions.