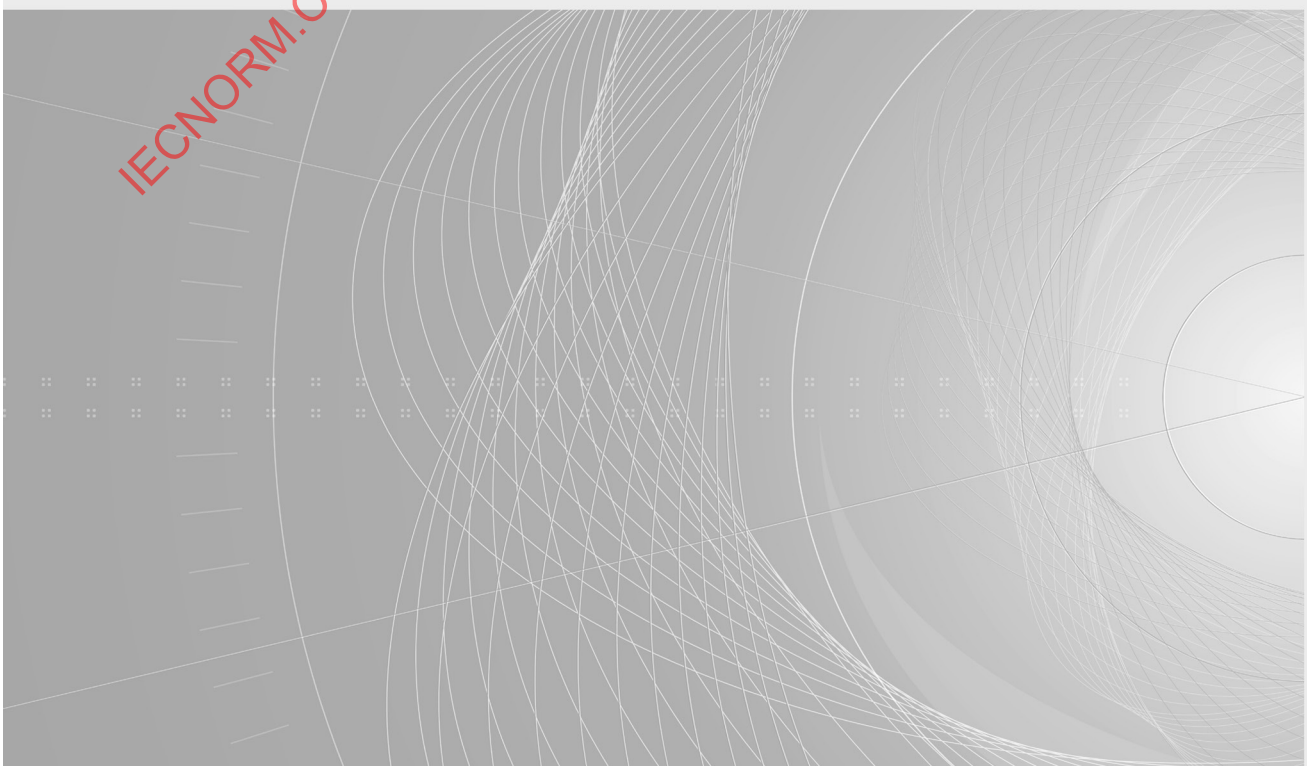
IEC TS 62607-6-21

Edition 1.0 2022-09

TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 6-21: Graphene-based material – Elemental composition, C/O ratio: X-ray photoelectron spectroscopy



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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-21: Graphene-based material – Elemental composition, C/O ratio: X-ray photoelectron spectroscopy

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The text of this Technical Specification is based on the following documents:

Draft	Report on voting
113/607/DTS	113/630/RVDTS

Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this Technical Specification is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available

at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/standardsdev/publications.

A list of all parts of the IEC TS 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

Graphene has unique electrical, thermal and mechanical properties and has wide potential industrial application, especially in the electronics industry: batteries, integrated circuits, high-frequency electronics, displays, etc. [1], [2], [3], [4], [5][1]. The content of main elements, especially oxygen element and the ratio of carbon to oxygen are the significant parameters influencing the electronic and thermal application performance of graphene materials [3]. The main elements in graphene materials include carbon (C), oxygen (O), nitrogen (N), sulfur (S), chloride (Cl), and silicon (Si). The C/O ratio is a key parameter to identify the type of graphene or graphene-oxide (GO), and reflects directly the degree of reduction and product quality of reduced graphene oxide (rGO). Because of multiple different production processes and manufacturers for graphene powder, the main elemental composition and C/O ratio are also different. For the development of industrial application, a standard measurement method with reliability, accuracy and reproducibility needs to be established. The X-ray photoelectron spectroscopy (XPS) technique can measure multiple elements simultaneously and obtain accurately the relative abundance of each element in a test sample [6], [7].

The purpose of this document is to provide an optimized preparation, measurement and analysis procedure for graphene powder, to enable accurate and quantitative determination of the C, O, N, S, Cl, Si elements and C/O ratio using the XPS technique.

This document has been developed based on study in VAMAS Technical Working Area 41 (TWA 41).

[1] Numbers in square brackets refer to the Bibliography.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-21: Graphene-based material – Elemental composition, C/O ratio: X-ray photoelectron spectroscopy

1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the chemical key control characteristics

– elemental composition, and
– C/O ratio

for powders of graphene-based materials by

– X-ray photoelectron spectroscopy (XPS).

The elemental composition (species and relative abundance) is derived by the elemental binding energy and integral peak area at corresponding portion of XPS spectrum.

– The elemental composition refers to main elements in graphene powders, typically including carbon (C), oxygen (O), nitrogen (N), sulfur (S) , chloride (Cl) and silicon (Si).
– This document is applicable to graphene powders consisting of graphene, bilayer graphene (2LG), trilayer graphene (3LG), few-layer graphene (FLG), graphene nanoplate (GNP), reduced graphene oxide (rGO), graphene oxide (GO), and functionalized graphene powders.
– Typical application areas are the microelectronics and thermal management industries, e.g. batteries, integrated circuits, high-frequency electronics. This document can be used by manufacturers in research and development and by downstream users for product selection.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions 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 http://www.iso.org/obp

3.1 General terms

3.1.1
graphene
graphene layer
single-layer graphene
monolayer graphene
single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure

Note 1 to entry: It is an important building block of many carbon nano-objects.

Note 2 to entry: As graphene is a single layer, it is also sometimes called monolayer graphene or single-layer graphene and abbreviated as 1LG to distinguish it from bilayer graphene (2LG) and few-layer graphene (FLG).

Note 3 to entry: Graphene has edges and can have defects and grain boundaries where the bonding is disrupted.

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.1]

3.1.2
graphene-based material
GBM
graphene material
grouping of carbon-based 2D materials that include one or more of graphene, bilayer graphene, few-layer graphene, graphene nanoplate and functionalized variations thereof as well as graphene oxide and reduced graphene oxide

Note 1 to entry: "Graphene material" is a short name for graphene-based material.

3.1.3
bilayer graphene
2LG
two-dimensional material consisting of two well-defined stacked graphene layers

Note 1 to entry: If the stacking registry is known, it can be specified separately, for example, as "Bernal stacked bilayer graphene".

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.6]

3.1.4
trilayer graphene
3LG
two-dimensional material consisting of three well-defined stacked graphene layers

Note 1 to entry: If the stacking registry is known, it can be specified separately, for example, as "twisted trilayer graphene".

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.9]

3.1.5
few-layer graphene
FLG
two-dimensional material consisting of three to ten well-defined stacked graphene layers

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.10]

3.1.6
graphene oxide
GO
chemically modified graphene prepared by oxidation and exfoliation of graphite, causing extensive oxidative modification of the basal plane

Note 1 to entry: Graphene oxide is a single-layer material with a high oxygen content, typically characterized by C/O atomic ratios of approximately 2,0 depending on the method of synthesis.

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.13]

3.1.7
reduced graphene oxide
rGO
reduced oxygen content form of graphene oxide

Note 1 to entry: rGO can be produced by chemical, thermal, microwave, photo-chemical, photo-thermal, microbial or bacterial methods, or by exfoliating reduced graphite oxide.

Note 2 to entry: If graphene oxide was fully reduced, then graphene would be the product. However, in practice, some oxygen containing functional groups will remain and not all sp^3 bonds will return back to sp^2 configuration. Different reducing agents will lead to different carbon to oxygen ratios and different chemical compositions in reduced graphene oxide.

Note 3 to entry: It can take the form of several morphological variations such as platelets and worm-like structures.

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.14]

3.1.8
graphene nanoplate
graphene nanoplatelet
GNP
nanoplate consisting of graphene layers

Note 1 to entry: GNPs typically have thickness of between 1 nm to 3 nm and lateral dimensions ranging from approximately 100 nm to 100 µm.

[SOURCE: ISO/TS 80004-13:2017 [8], 3.1.2.11]

3.1.9
X-ray photoelectron spectroscopy
XPS
method in which an electron spectrometer is used to measure the energy distribution of photoelectrons and Auger electrons emitted from a surface irradiated by X-ray photons

Note 1 to entry: X-ray sources in common use are unmonochromated Al Kα and Mg Kα X-rays at 1 486,6 eV and 1 253,6 eV, respectively. Modern instruments also use monochromated Al Kα X-rays. Some instruments make use of various X-ray sources with other anodes or of synchrotron radiation.

[SOURCE: ISO/TS 80004-6:2021 [9], 5.19]

3.1.10
relative elemental sensitivity factor
coefficient proportional to the absolute elemental sensitivity factor, where the constant of proportionality is chosen such that the value for a selected element and transition is unity

Note 1 to entry: Elements and transitions commonly used are C 1s or F 1s for XPS and Ag $M_{4,5}VV$ for Auger electron spectroscopy.

Note 2 to entry: The type of sensitivity factor used should be appropriate for the analysis, for example, of homogeneous samples or segregated layers.

Note 3 to entry: The source of the sensitivity factors should be given in order that the correct matrix factors or other parameters have been used.

Note 4 to entry: Sensitivity factors depend on parameters of the excitation source, the spectrometer, and the orientation of the sample to these parts of the instrument. Sensitivity factors also depend on the matrix being analysed and in secondary-ion mass spectrometry, this has a dominating influence.

[SOURCE: ISO 18118:2015 [10], 3.2]

3.2 Key control characteristics measured in accordance with this document

3.2.1
elemental composition
species and relative abundance of main elements in the test sample of graphene powder

3.2.2
C/O ratio
carbon to oxygen ratio
ratio of relative abundance (atomic fraction) of carbon element to oxygen element in the test sample of graphene powder

4 General

4.1 Measurement instrument

A modern XPS instrument equipped with monochromated X-rays is required, in order to measure the relative abundance of each element detected on the surface of a solid test sample. The sampling depth, D_s (normal to the surface of the test sample, $D_s = 3\lambda$), is decided by inelastic mean free path, IMFP(λ). The actual values for the IMFP of electrons in matter are a function of the energy of the electrons and nature of the sample through which they travel [11]. For organics and polymers, IMFP of C 1s is about 4 nm to 10 nm. Annex B provides a detailed discussion.

4.2 Calibration of measurement instrument

The XPS instrument should be calibrated prior to measurement. For the calibration of X-ray photoelectron spectrometers with monochromated Al X-ray sources, use reference materials (RMs) of Cu, of Au and of Ag. The RMs shall be polycrystalline and of at least 99,8 % purity metals which, for convenience, are usually in the form of foils typically of an area 10 mm by 10 mm, and 0,1 mm to 0,2 mm thick. The test samples of RMs for instrumental calibration shall be clean.

The energy resolution of the system should be specified by use of the full width at half maximum (FWHM) of the silver Ag $3d_{5/2}$ peak, and the accuracy of the binding energy scale calibration as a function of time should also be specified at the energy for the Cu 2p 3/2 or Au 4f 7/2 peaks from RMs [12], shown in Table 1.

Table 1 – Reference values for the peak positions on the binding-energy scale, $E_{\text{ref }n}$

Peak number, n	Assignment	$E_{\text{ref }n}$ (eV)		
		Al Kα	Mg Kα	Monochromatic Al Kα
1	Au $4f_{7/2}$	83,95	83,95	83,96
2	Ag $3d_{5/2}$	(368,22)	(368,22)	368,21
3	Cu L_3VV	567,93	334,90	/
4	Cu $2p_{3/2}$	932,63	932,62	932,63
NOTE The Ag data included in parentheses are not normally used for calibrations.				

4.3 Charge control

In some cases, charge control (the effort to control the buildup of charge at a surface or to minimize its effect) is needed [13]. The amount and distribution of surface and near-surface charge for a specific experimental system are determined by many factors, including specimen composition, homogeneity, magnitude of bulk and surface conductivities, photo-ionization cross-section, surface topography, spatial distribution of the exciting X-rays, and availability of neutralizing electrons. Charge buildup occurs along the specimen surface and into the material. The presence of particles on or different phases in the specimen surface can result in an uneven distribution of charge across the surface, a phenomenon known as differential charging. Charge buildup can also occur at phase boundaries of interface regions within the specimen that is

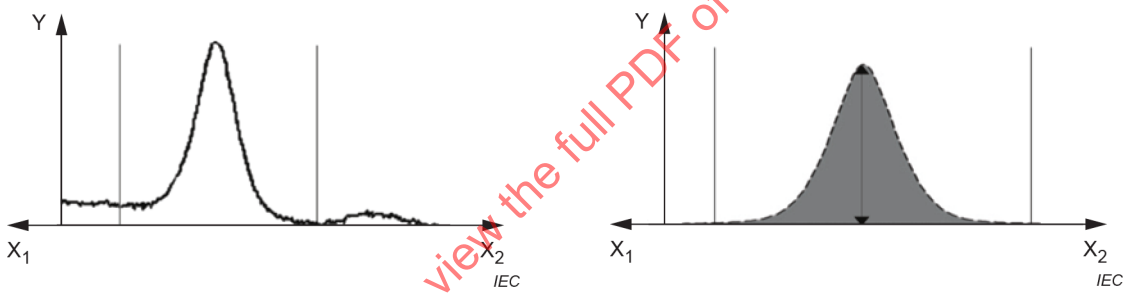
irradiated by X-ray. Some specimens undergo time-dependent changes in the amount of charging because of chemical and physical changes induced by electrons, X-rays or heat.

For charge control, peak shape is one of the most important parameters to consider in assessing the effectiveness of the method used. For the measurement of graphene powder defined in this document, if initial spectrum without any charge control treatment shows peak shift and broadening, the charge compensation shall be done using an electron flood gun. Low electron energies (usually 10 eV or less) are used to maximize the neutralization effect and reduce the number of electron-bombardment-induced reactions.

4.4 Quantitative analysis

The quantitative mass fraction can be analysed from peak area of each element using relative sensitivity factor (RSF), S. Take the RSF of C 1s as reference, equal to 1, RSFs of other elements can be calculated in accordance with Annex A. Usually, RSFs of many elements are readily available within most XPS analysis software packages or from the literature [14], [15]. The peak area of each element can be obtained from integration of the peak defined by the end points and fitting the peak with an appropriate analytical function after the subtraction of inelastic background to a measured spectrum by computer software, as in Figure 1.

NOTE The fitting method of C 1s peak on XPS spectrum can be selected appropriately in accordance with test purpose and test conditions.[7]



a) b)

In a) the vertical lines indicate suitable limits for the construction of a Shirley background, and in b) the shaded area indicates the area of XPS peak to be measured following the subtraction of the inelastic background.

Figure 1 – Illustration of XPS peak measured

If the test sample consists of n elements, the atomic mass fraction X_i of element i can be obtained from Formula (1).

$$X_i = \frac{\frac{I_i}{S_i}}{\sum_{j=1}^{n}\left(\frac{I_j}{S_j}\right)} \quad (1)$$

where

X_i is the atomic mass fraction of element i in the test sample containing n elements;

I_i is the measurement intensity of element i in the test sample;

I_j is the measurement intensity of element j in the test sample;

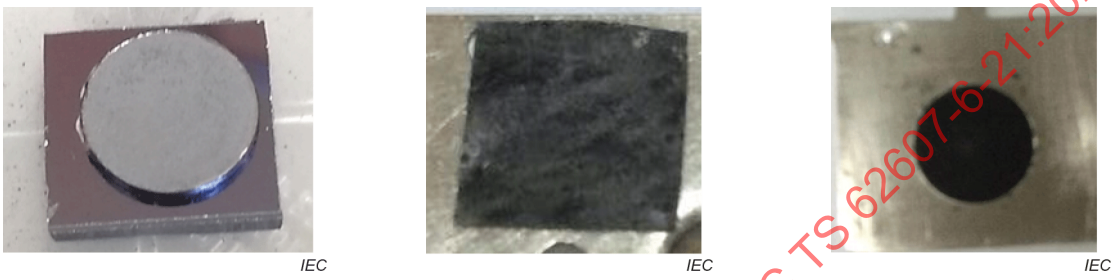
S_i is the relative sensitivity factor for element i;

S_j is the relative sensitivity factor for element j.

5 Measurement procedure

5.1 Sample preparation

The test sample (graphene powder, case study for GNP in Annex C and for GO in Annex D) should be measured after pressing of the powders into pellets directly. Figure 2 shows an example of a pressed pellet, no thicker than 1 mm, mounted on a silicon wafer or on the sample stage of XPS. If a pellet cannot be produced, a similar continuous sample should be prepared so as to avoid any signal from the mounting substrate. The contamination of test samples shall be avoided during sample preparation. Disposable laboratory gloves and masks should be used. The sample preparation can refer to ISO 18117:2009, Clause 8 (Sources of specimen contamination in handling). [16]



a) on silicon wafer

b) on conductive tape adhered on XPS sample stage

c) on XPS sample stage with specimen tank specially designed

Figure 2 – Digital photos of test samples as pressed pellet of graphene powder on different substrates

5.2 Measurement conditions

The prepared test sample is transferred to the XPS preparation chamber quickly. Vacuum pumping is carried out until the vacuum pressure is low enough to transfer the test sample into the analytical chamber. If achievable, the vacuum pressure should be lower than 5×10^{-8} mbar. Ideally, the instrumental vacuum should be better than 1×10^{-9} mbar during data acquisition. However, if not achievable, a suitable vacuum pressure for measurement should be maintained and recorded.

The basic instrumental performance parameters can be selected, refer to ISO 15470:2017 [17]. For the test samples of graphene powder, some key parameters should be set as given in 5.3.

5.3 Measurement procedure

Firstly, the survey scan (wide scan) is performed over an energy range of 0 to 1 000 eV, the counts per second (CPS) value at C 1s peak should be no less than 1×10^5. And then the high-resolution scan (narrow scan) is performed at the range of C 1s, O 1s, N 1s, Cl 2p, and S 2p peaks, respectively (suggested pass energy of 40 eV). The scanning step should be set as 0,05 eV to 0,1 eV. To obtain good signal with high quality, the test samples should be scanned until the peak intensity of greater than 2×10^4 counts is recorded for the C 1s peak. All other peaks should be scanned for the same scanning number as the C 1s at least, to carry out peak area fitting. A total energy window of at least three times the width of the main peak should be used, with particular consideration given to ensure capture of the carbon and sulfur oxide peaks where present. Two or three parallel test specimens should be measured for each test sample, and the measurement should also be conducted from five different positions on each parallel test specimen. The acquisition conditions should be recorded.

6 Data analysis

For the test samples of graphene powder, the peak of main elements is single, so the peak intensity using peak area should be determined directly in the XPS spectrum measured.

a) Select the integral range of the detected elements, conduct background subtraction for high-resolution spectrogram of each element, and report the subtraction method.

   A linear or Shirley background should be applied to the O 1s, N 1s, S 2p and Cl 2p peaks, and a background capable of capturing the change in background (e.g. Tougaard or Werner background) for the C 1s peak.

b) In the integral range selected, fit the peak using any suitable analytical function used to describe peak shapes (e.g. Gaussian, Lorentzian and various combination functions) and inelastic background. Obtain the integral peak area using the computer software.

   The integral energy interval should be no less than 12 eV for C 1s, 8 eV for O 1s, 10 eV for N 1s, 12 eV for Cl 2p, and 12 eV for S 2p.

c) Calculate the quantitative mass fraction of each element based on the peak intensity of peak area using relative sensitivity factors method.

7 Uncertainty estimation

a) Uncertainty derived from instrumental effects:

   1) whether the observed intensities for the spectral regions of interest are linearly dependent on the incident X-ray flux on the sample or not, if this needs to be corrected;

   2) the varying intensity response of the electron spectrometer.

b) Uncertainty derived from peak intensity of peak area fitting and calculation, e.g. the shape and fitting function.

c) Uncertainty derived from background subtraction method.

d) Uncertainty derived from the test samples, e.g. the homogeneity, stability, etc.

e) Uncertainty derived from the repeatability of measurement results.

8 Measurement report

8.1 General

The measurement results shall be recorded in a measurement report, including the date and time of the measurement as well as the name and signature of the person responsible for the accuracy of the report.

8.2 Test sample identification

The report shall contain all information to identify the test sample and trace back the history of the sample:

– General procurement information.

– General material description.

NOTE A blank detail specification for graphene is under development (IEC 62565-3-1).

8.3 Ambient conditions

The laboratory ambient conditions during the test.

– Temperature range: ambient temperature.

– Range of relative humidity: ambient humidity.

8.4 Instrumental information

– Instrument type.
– Instrument calibration.
– X-ray source.
– Power.
– Energy range.

8.5 Measurement specific information

– Vacuum.
– Count rate of C 1s in survey.
– Measurement conditions of high-resolution spectrum collection (pass energy, scanning step, count rate, etc.).
– Sample preparation method.
– Number of parallel specimens.
– Sampling positions on each specimen.

8.6 Measurement results

Results of main elements and C/O ratio measured in accordance with this document:

– Species of elements detected.
– Relative sensitivity factors of each element measured.
– Subtraction method.
– Analytical method.
– Relative abundance and standard deviation of each element measured.
– C/O ratio.

Annex A
(informative)

Relative sensitivity factors

A.1 Overview

The atomic fraction of an element i in an unknown material containing n elements can be evaluated through relative sensitivity factors from Formula (A.1):

$$X_i^{\text{unk}} = \frac{\left(\frac{I_i^{\text{unk}} F_i}{S_i}\right)}{\sum_{j=1}^{n}\left(\frac{I_j^{\text{unk}} F_j}{S_j}\right)} \tag{A.1}$$

where

X_i^{unk} is the atomic fraction of element i in the unknown sample containing n elements;

I_i^{unk} is the measured intensity of element i in the unknown sample containing n elements;

I_j^{unk} is the measured intensity of element j in the unknown sample containing n elements;

F_i is the matrix correction factor for element i;

F_j is the matrix correction factor for element j;

S_i is the relative sensitivity factor for element i;

S_j is the relative sensitivity factor for element j.

If, for simplicity, the matrix correction factors are neglected, Formula (A.1) becomes Formula (A.2):

$$X_i^{\text{unk}} = \frac{\left(\frac{I_i^{\text{unk}}}{S_i}\right)}{\sum_{j=1}^{n}\left(\frac{I_j^{\text{unk}}}{S_j}\right)} \tag{A.2}$$

where

X_i^{unk} is the atomic fraction of element i in the unknown sample containing n elements;

I_i^{unk} is the measured intensity of element i in the unknown sample containing n elements;

I_j^{unk} is the measured intensity of element j in the unknown sample containing n elements;

S_i is the relative sensitivity factor for element i;

S_j is the relative sensitivity factor for element j.

A.2 Elemental relative sensitivity factors

A.2.1 General

Elemental relative sensitivity factors (ERSFs) can be obtained from measurements made with pure elements or with compounds containing the desired element.

A.2.2 Pure-element relative sensitivity factors

The pure-element relative sensitivity factors (PERSFs), S_i^{Ep}, can be obtained from measurements of I_i^{ref} for the selected element and a measurement of the peak intensity for the selected key material, I_{key}, as given in Formula (A.3):

$$S_i^{\mathrm{Ep}} = \frac{I_i^{\mathrm{ref}}}{I_{\mathrm{key}}} \tag{A.3}$$

where

I_i^{ref} is the measured intensity of element i in the reference sample.

A.2.3 Elemental relative sensitivity factors from measurements with compounds

The elemental relative sensitivity factor for element i in a specified compound, S_i^{Ec}, can be obtained from measurement of I_i^{ref} for the selected element in that compound and of I_{key} for the particular key material as given in Formula (A.4):

$$S_i^{\mathrm{Ec}} = \frac{I_i^{\mathrm{ref}}}{X_i^{\mathrm{ref}} I_{\mathrm{key}}} \tag{A.4}$$

where

X_i^{ref} is the atomic fraction of element i in the compound.

A.2.4 Set of elemental relative sensitivity factors

Measurement of S_i^{Ep} and S_i^{Ec} for a particular instrument and for particular experimental conditions have often been combined to yield a set of elemental RSFs, S_i^{E}.

NOTE Instrument suppliers can provide a set of elemental RSFs.

Annex B
(informative)

Discussion about the influence of surface contamination

B.1 Sampling depth

For XPS measurement, what should be concerned is the sampling depth, D_s, which is the detection depth and is decided by inelastic mean free path, IMFP(λ).

According to the definition in [18], D_s is calculated using Formula (B.1):

$$D_s = 3\lambda \tag{B.1}$$

The sampling depth is the average distance that an electron with a given energy travels between successive inelastic collisions. The actual values for the IMFP of electrons in matter are a function of the energy of the electrons and nature of the sample through which they travel. The schematic diagram is shown in Figure B.1.

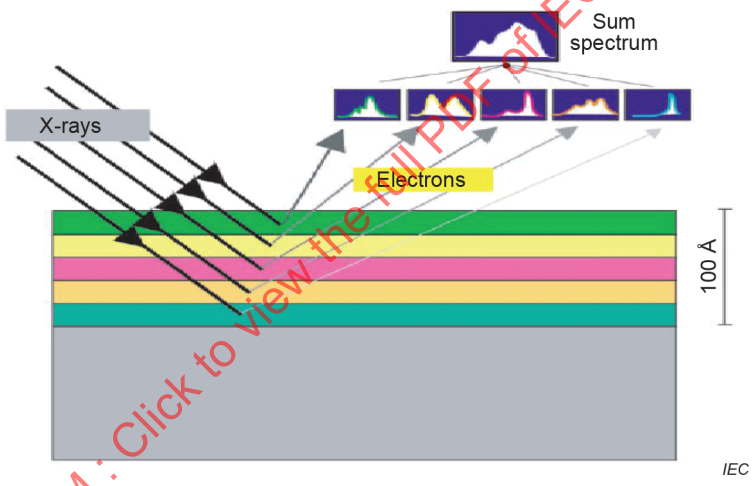


Figure B.1 – Schematic diagram of sampling depth and XPS spectra

As shown in Figure B.1, electron spectroscopy for chemical analysis (ESCA) or XPS spectra are convolutions of the information from each depth within the sampling depth. In this model material, each coloured layer represents material of a different composition. Overlayers attenuate the intensities of photoelectrons emitted from deeper layers and so contributions from the underlying layers to the final spectrum will be lower [11].

According to Einstein equation (B.2),

$$E_B = hv - E_K \tag{B.2}$$

where

E_B is the binding energy of the electron in the atom (a function of the type of atom and its environment);

hv is the energy of the X-ray source (a known value);

E_K is the kinetic energy of the emitted electron that is measured in the ESCA or XPS spectrometer.

A higher energy X-ray source will liberate higher E_K photoelectrons. These more energetic photoelectrons have a greater IMFP and, consequently, an increased sampling depth.

Equations that relate IMFP to electron energy and the type of material through which the electron is traversing have been developed [11] as Formula (B.3)

$$\text{IMFP} = \lambda_d = 49E_K^{-2} + 0{,}11E_K^{0,5} \text{ (for organic compounds)}, \quad \text{(B.3)}$$

where

E_K is the electron kinetic energy, eV.

If different X-ray sources of Al Kα (1 487 eV), Ag Lα (2 984 eV), and Cr Kα (5 415 eV) are each used to generate ESCA spectra of the same sample, the C 1s electron sampling depths, calculated using Formula (B.3), can be estimated as 10,8 nm, 16,2 nm, and 22,4 nm, respectively.

Usually for organics and polymers, the IMFP of C 1s is about 4 nm to 10 nm, so the sampling depth of C 1s is no less than 10 nm, the thickness of single-layer graphene is 0,3 nm, thus the sampling depth of graphene-related materials is no less than 30 layers. So the measurement results of XPS are not too sensitive to the surface contamination.

B.2 Test study of surface contamination

In order to investigate the influence of surface contamination for the measurement results of graphene powder test samples using XPS measurement, two treatment methods were conducted: long-time vacuum desorption treatment and vacuum thermal-desorption treatment.

Vacuum desorption is the usual method to remove the surface contamination of test sample in high-vacuum conditions, and vacuum thermal-desorption is based on vacuum desorption plus thermal treatment of high temperature and has stronger capability to remove contaminations. The measurement results of test sample through treatment mentioned above are shown in Figure B.2 and Table B.1, Figure B.3 and Table B.2.

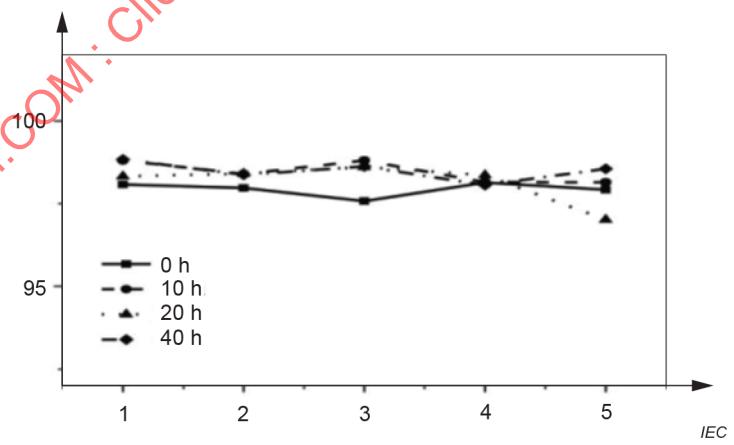
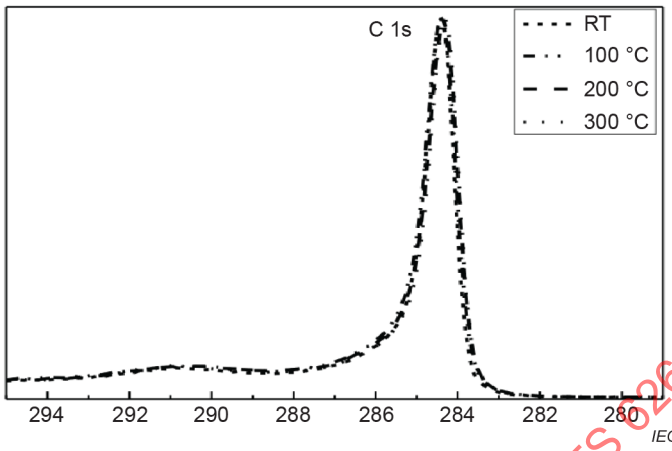


Figure B.2 – Data distribution of relative abundance of C 1s at five test positions through long-time vacuum desorption treatment

Table B.1 – Relative abundance of C 1s at different times of vacuum desorption

Desorption time (h)	0	10	20	40
Relative abundance	97,94	98,46	98,34	98,49
Standard deviation	0,22	0,33	0,21	0,29



Key

RT room temperature

Figure B.3 – XPS spectra of C 1s through thermal desorption of different temperatures for 1 h

Table B.2 – Relative abundance of C 1s through vacuum desorption under different temperatures for 1 h

Desorption temperature (°C)	0	100	200	300
Relative abundance	98,39	97,66	97,93	98,23
Standard deviation	0,40	0,54	0,34	0,41

It is shown that the relative abundance of C 1s has no distinct change neither during long-time vacuum desorption nor vacuum thermal-desorption treatment, so the influence of surface contamination can be neglected.

Contamination should be avoided as much as possible during sample preparation; for example, the test sample preparation should be done with clean utensils, and all operation should be conducted in clean surroundings.

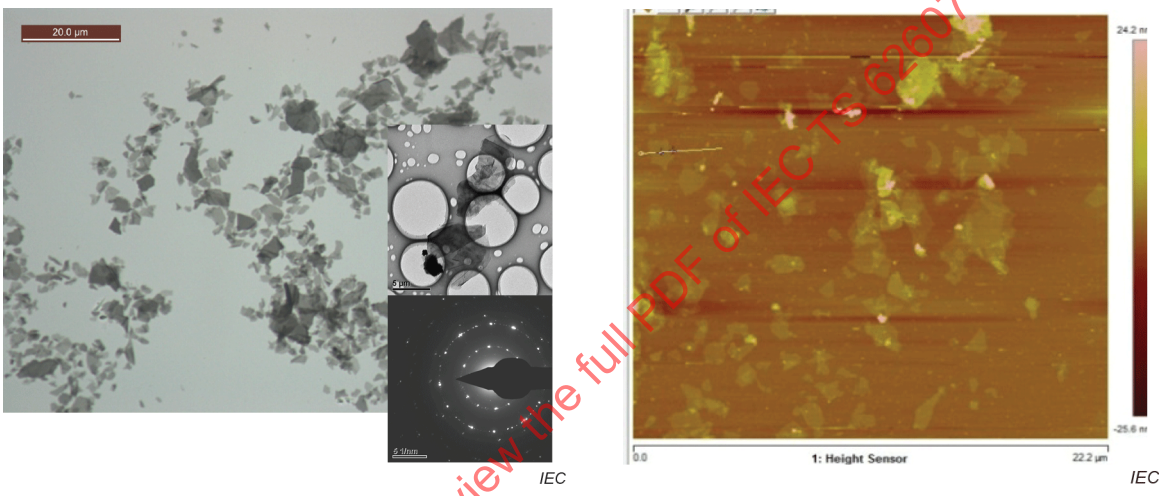
Annex C
(informative)

Case study for GNP

C.1 Test sample

The test sample is industrial graphene nanoplate (GNP) manufactured using mechanical exfoliation, in the form of black powder; the morphologies are characterized with atomic force microscopy (AFM) and transmission electron microscopy (TEM), shown in Figure C.1.

The TEM and AFM images exhibit that the lateral size distribution is wide, from several hundreds of nanometres to approximately 8 μm, and the height distribution is approximately from 2 nm to 10 nm.



a) TEM morphology and selection area electronic diffraction pattern

b) AFM lateral size and height distribution

Figure C.1 – Morphologies of GNP sample

C.2 Measurement results using XPS

The black powder of GNP test samples is pressed into round pellets with less than 1 mm thickness. Three parallel test specimens are prepared and mounted on the samples stage of XPS instrument at the same time.

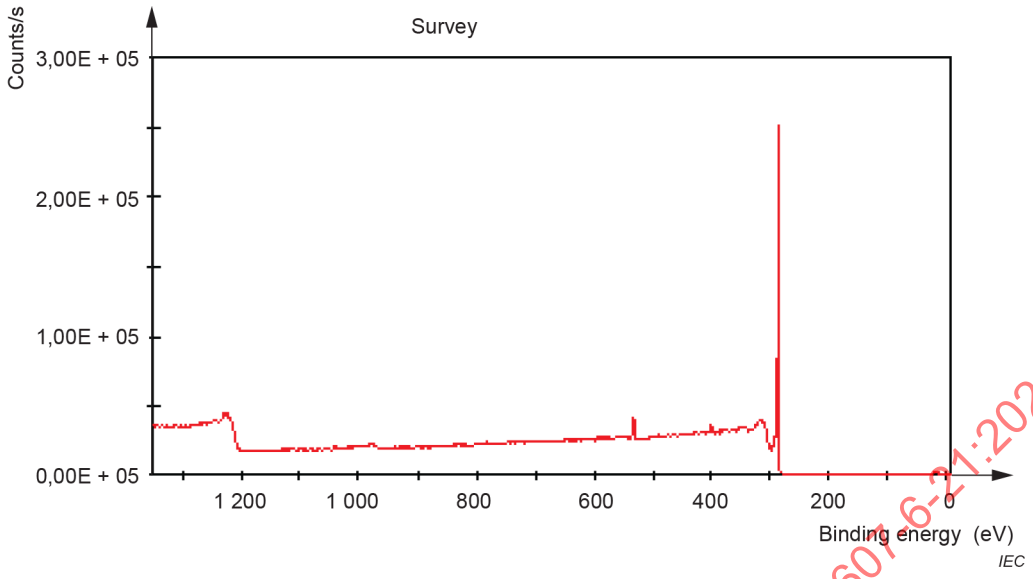


Figure C.2 – Survey spectrum of GNP test sample

A total of eleven different test positions on three parallel test specimens were selected to conduct measurements. Firstly, the survey scan is performed over an energy range of 0 to 1 300 eV; the survey spectrum of one of eleven positions is shown in Figure C.2. Then the high-resolution scan is performed at the C 1s, O 1s, N 1s, Cl 2p and S 2p peaks. The XPS spectra of one of eleven positions obtained are shown in Figure C.3. The spectra show that the signal of three elements of C 1s, O 1s and N 1s is obvious to be fitted and calculated, and the signal of Cl 2p and S 2p is too weak to obtain valuable measurement results.

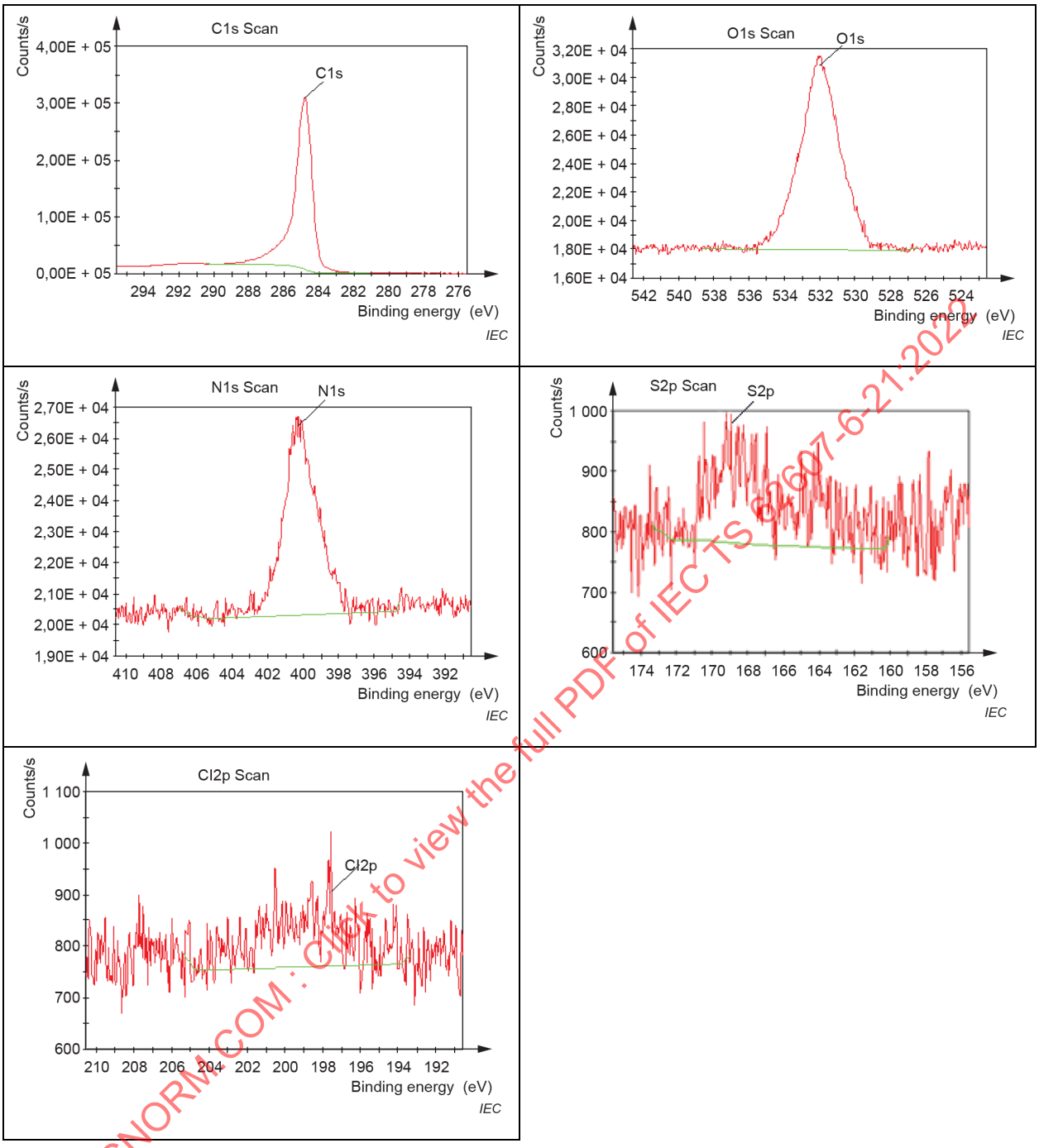


Figure C.3 – XPS spectra of the main elements of C 1s, O 1s, N 1s, Cl 2p and S 2p peaks in GNP test sample

The XPS measurement results of relative abundance of C 1s, O 1s and N 1s from eleven test positions are listed in Table C.1 and Figure C.4. It is shown that relative abundance of C, O and N elements is 95,865 %, 2,612 %, 1,454 %, respectively, and the C/O ratio is 37,31. The standard deviation value is small: 0,48, 0,35 and 0,22 for relative abundance of C, O and N elements, respectively. In other words, the measurement results of eleven test positions have good consistency. The homogeneity of the test samples is very good.

Table C.1 – Relative abundance of main elements and C/O ratio in GNP test sample

Test position	PA of C 1s	At% of C 1s	PA of O 1s	At% of O 1s	PA of N 1s	At% of N 1s	C/O
1	86 380,67	96,045	5 845,51	2,325	2 587,07	1,630	41,31
2	87 525,1	96,369	5 743,74	2,263	2 192,7	1,368	42,58
3	77 606,28	95,552	6 396,79	2,818	2 336,54	1,630	33,90
4	87 863,1	96,691	5 338,9	2,102	1 935,11	1,206	45,99
5	84 921,73	95,892	5 995,52	2,422	2 635,26	1,686	39,59
6	82 479,23	95,255	6 976,44	2,883	2 666,98	1,745	33,04
7	76 526,32	95,410	7 224,35	3,223	1 781,29	1,258	29,60
8	82 888,71	96,133	6 158,85	2,556	1 812,5	1,191	37,61
9	81 022,88	95,765	5 873,86	2,484	2 419,54	1,620	38,55
10	83 429,84	96,181	6 274,18	2,588	1 768,14	1,155	37,16
11	79 763,47	95,166	7 180,82	3,066	2 233,88	1,510	31,04
Average value	/	95,860	/	2,612	/	1,454	37,31
Standard deviation	/	0,48	/	0,35	/	0,22	5,04

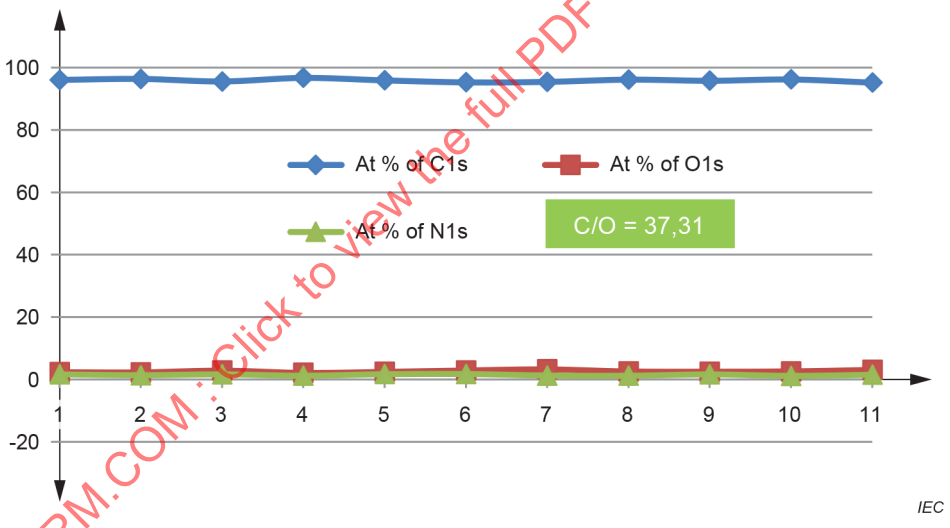


Figure C.4 – Data distribution of relative abundance of C, O, and N elements and C/O ratio of eleven test positions in GNP test sample