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TECHNICAL SPECIFICATION

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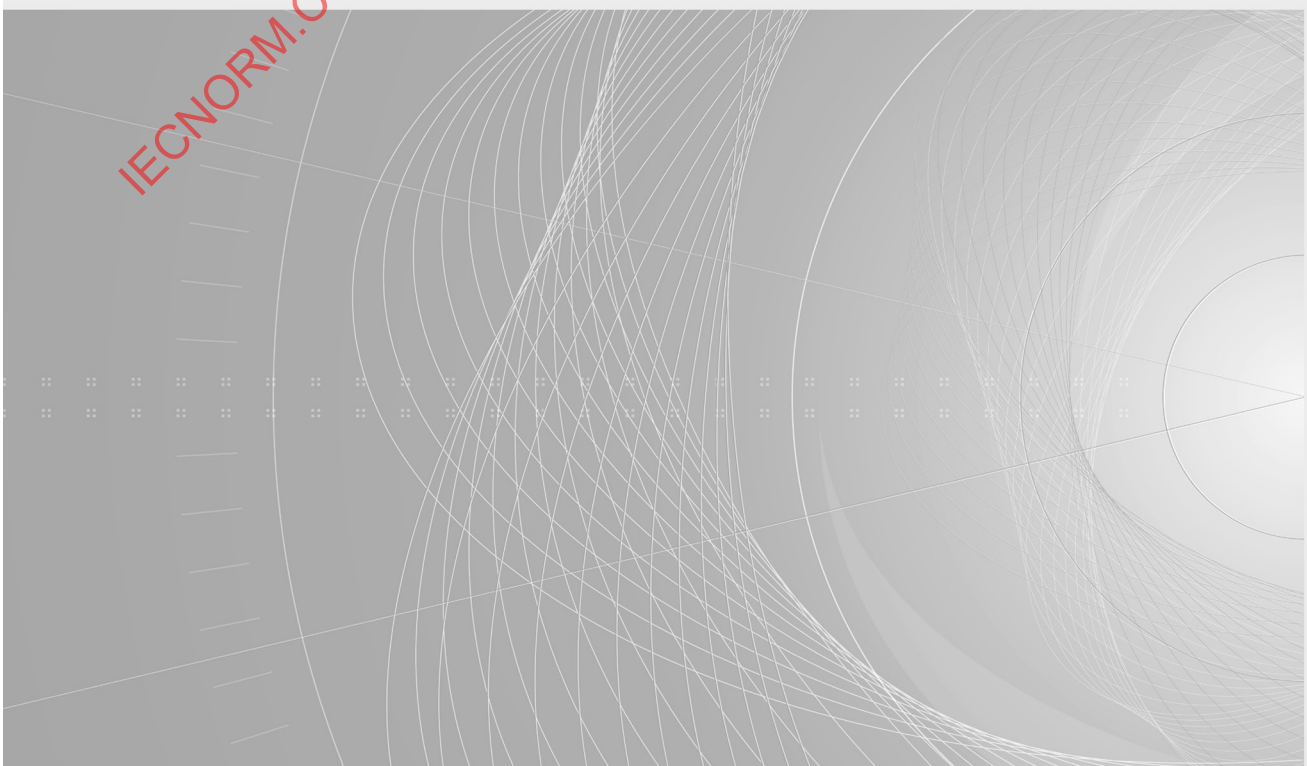
Nanomanufacturing – Key control characteristics – Part 6-20: Graphene-based material – Metallic impurity content: Inductively coupled plasma mass spectrometry



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

Draft	Report on voting
113/609/DTS	113/629/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.

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- withdrawn,
- replaced by a revised edition, or
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INTRODUCTION

Graphene-based materials have wide potential applications because of their unique electrical, thermal and mechanical properties, especially in the electronics industry: batteries, integrated circuits, high-frequency electronics, displays, etc. [1], [2], [3][1]. As industry uptake on graphene-based materials increases, international standardization is critical to enable the commercialization of graphene-based materials and related products. Metal impurities within graphene-based materials have significant impact on the electrical performance in the process of industrial application. Considering the multiple production routes and producers of graphene-based materials, in order to maintain product quality and reach a consensus between the supplier and the customer, there is no doubt that accurate, reliable and reproducible measurement methods for the key parameters of graphene-based materials need to be established.

Inductively coupled plasma mass spectrometry (ICP-MS) can carry out accurate detection of trace amounts of a variety of metal impurities simultaneously, obtain species and content of each metal impurity in graphene-based materials.

The purpose of this document is to enable accurate and quantitative determination of metal impurities using ICP-MS [4], through providing optimized digestion operation, preparation procedures for graphene-based materials in powder form, measurement method and data analysis. A similar document was published as ISO/TS 13278 for carbon nanotubes (CNTs) [5]; however, it is not suitable for graphene powder because of the noticeable difference between CNTs and graphene powder, especially in terms of sample preparation (including digestion technique and digestion procedure), the properties of test samples (many more species and much wider range of content of metal impurities in graphene powder), measurement procedure and so on. Therefore, this document has been developed for graphene powder; it is 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 6-20: Graphene-based material – Metallic impurity content: Inductively coupled plasma mass spectrometry
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1 Scope

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

– metallic impurity content

for powders of graphene-based materials by

– inductively coupled plasma mass spectrometry (ICP-MS).

The metallic impurity content is derived by the signal intensity of measured elements through MS spectrum of ICP-MS.

– The method is applicable for powder of graphene and related materials, including bilayer graphene (2LG), trilayer graphene (3LG), few-layer graphene (FLG), reduced graphene oxide (rGO) and graphene oxide (GO).
– The typical application area is in the microelectronics industry, e.g. conductive pastes, displays, etc., for manufacturers to guide material design, and for downstream users to select suitable products.

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 [6], 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 [6], 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 [6], 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 [6], 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 [6], 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 [6], 3.1.2.14]

3.2 Key control characteristics measured in accordance with this document

3.2.1
metallic impurity
metallic element present in graphene-based materials and not in the crystalline structure of graphene

Note 1 to entry: The content of most metallic impurities in graphene-based materials is usually trace, but for industrial products of graphene powder, the content of a few metal impurities can be higher, e.g. Na element coming from water used in rGO production, and Cu or Fe element coming from manufacturing equipment used in the production of FLG powder.

4 General

4.1 Chemical reagents

All reagents should be guaranteed reagents (GRs) at least, and the purity quotient should be no less than 99,99 %.

4.1.1 Ultra-pure nitric acid (HNO_3, MOS (metal-oxide-semiconductor) or higher, 70 % mass fraction), which is used as digestion solvent of graphene powder, to make up the control test sample, and blank solution for instrument self-checking and cleaning.

4.1.2 Hydrofluoric acid (HF, MOS or higher, 40% mass fraction), when necessary (e.g. Si or Ti element is a little higher in content), as a digestion solution together with nitric acid. However, HF is powerfully corrosive, and working with HF requires special precautions to avoid contact with skin. All operation should be carried out in fume hood with safe protection such as rubber gloves and work clothes, etc.

4.1.3 Ultra-pure water used as diluted solvent.

4.2 Description of measurement instrument and apparatus

4.2.1 Measurement instrument

ICP-MS should be used to measure metal impurities in graphene powder. ICP-MS instrument can be equipped with a quadrupole or sector field mass spectrometer, or another type of ICP-MS instrument operating with at least 1u (atomic mass unit) resolution for multi-elements determination.

4.2.2 Sample pre-treatment apparatus

4.2.2.1 Microwave digester used for digestion of graphene powder immersed in digestive solvent.

4.2.2.2 Pressure tank (acid proof and high temperature resistance) also used for digestion. The tank should be placed in an oven over 200 °C for more than 6 h.

4.2.2.3 Acid-driven processor used for acid-driving of the test samples after digestion.

4.2.3 Other

4.2.3.1 Static discharge gun used to neutralize the static charge while graphene powder is being weighed and transferred.

4.2.3.2 Analytical balance with a resolution of 0,000 1 g.

4.2.3.3 100 µL, 1 000 µL, 5 mL pipettes used to transfer liquid.

4.2.3.4 10 mL, 25 mL, 50 mL volumetric flasks used for constant volume.

4.2.3.5 10 mL, 15 mL, 50 mL, 100 mL centrifuge tubes used as container.

4.3 Calibration standards

4.3.1 Standard stock solutions

There are approximately 20 to 30 kinds of metal impurities in industrial graphene powder, so mixed standard solutions including Fe, Cr, Mn, W, Ti, Mo, Zn, Ni, Rb, Zr, Sr, Sb, Sn, Co, Pb, Ce, Ba, and Cu elements, etc, are recommended.

It is recommended to use simultaneously four kinds of mixed standard solution (available from commercial vendors), such as, but not limited to, the following.

a) Multi-element Solution No. 1: Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, and Zn.
b) Multi-element Solution No. 2: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y, and Yb.
c) Multi-element Solution No. 3: Au, Hf, Hg, Ir, Pd, Pt, Rh, Ru, Sb, Sn, and Te.
d) Multi-element Solution No. 4: B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, and Zr.

4.3.2 Internal standard (IS) solutions

Single-element internal standard (IS) solutions are available from commercial vendors. Alternatively, IS stock solutions can be prepared in-house giving due consideration to the purity of water and acids. Li, Sc, Ge, Y, Rh, In, Tb, Lu, Re, Bi, etc. are usually used as IS elements.

Prior to quantitative analysis, a preliminary scan should be conducted to select suitable IS elements.

The selection of IS elements should fulfil four criteria.

a) The IS element is not present in the test sample.
b) The IS element has similar molecular weight and ionization energy to the analytical element.
c) The IS element is not disturbed easily by other elements.
d) The signal intensity of the IS element is not affected by count statistics, that is, the concentration of the IS element is sufficiently high.

5 Sample preparation method

5.1 General

For the test sample of graphene powder, four to six parallel specimens should be treated simultaneously. According to the content of metal impurities measured, the standard recovery of several key elements should be measured, by adding the standard solution of metal elements selected into test specimens prior to digestion; at least two parallel specimens shall be prepared for spiked specimens.

5.2 Sample pre-treatment procedure

The pre-treatment procedure is as follows.

1) Select several PTFE digestion vessels, according to the microwave digester used and the number of parallel test specimens, spiked samples and control samples.

2) Weigh accurately 10,0 mg ± 0,2 mg graphene powder as one of test specimens in turn, put it into each vessel carefully.

3) Add an aliquot of 8,0 mL HNO_3 into each vessel slowly.

4) Pipette the appropriate stock standard solutions of several key elements selected into two test specimens, as spiked specimens used for the measurement of standard recovery.

5) Add 8,0 mL HNO_3 into each of two empty vessels as control specimens of solvent contrast.

NOTE 1 Thus far, a total of eight to ten specimens are subjected to the digestion process simultaneously, including four to six parallel test specimens, two spiked specimens and two control specimens.

6) Seal the digestion vessels, fit them into the microwave digester in accordance with the operation instructions.

7) Set and perform the microwave digestion programme. The digestion temperature should be higher than 190 °C, and the digestion pressure is set following temperature by microwave digester automatically.

NOTE 2 Running the microwave digester at higher temperatures (> 200 °C, 240 °C is better) or for longer digestion time (> 1 h) is advantageous for the complete digestion of test specimens of graphene powder.

8) At the end of the digestion procedure, remove the digestion vessels, let the vessels stand and cool to ambient temperature.

9) Release the sealing cap, check the situation of the digestion solution of all specimens. Check whether the digestion solution is clear and transparent, indicating that the test specimens of graphene powder have been digested completely. If not clear or a few suspended solids remain, the digestion procedure should be repeated following steps 6) and 7) until digestion is complete.

If the digestion temperature is less than 200 °C, the digestion procedure should be repeated three times in succession to achieve digestion as complete as possible.

NOTE 3 If the digestion is still not complete and there are white or greyish solids suspended in digestion solution after three repetitions, it is considered that there is Si or Ti element or both in test samples. If so, 2 mL HF can be added to facilitate the digestion, or the test specimens of graphene powder can be weighed and digested again, with 6 mL HNO_3 plus 2 mL HF as the digestion mixed-solvent.

WARNING — HNO_3 is a strong acid with powerful oxidation and corrosiveness; HF is a powerfully corrosive acid. The operation shall be carried out in a fume hood and with safety protection to avoid contact with the skin.

10) Evaporate HNO_3 or HF from the digestion solution of test specimens through acid-driven treatment under heating, until approximately 0,5 mL of concentrated digestion solution remains. Do not dry completely to avoid aggregation of digestion products.

11) Add 2 mL of HNO_3 with 2 % volume fraction into each vessel to dilute the concentrated digestion solution separately, and transfer into a 10-mL volumetric flask carefully. Repeat rinsing and transfer for three times, and then achieve constant volume of volumetric flask with 2 % volume fraction HNO_3. Referred to as A_s.

12) The control specimens of solvent contrast are treated equally following steps 10) and 11). Referred to as A_0.

13) A_s of test specimens may need to be diluted further to meet the concentration requirements of ICP-MS measurement and analysis.

NOTE 4 For ICP-MS instrumental analysis, the preferred concentration range of measured elements is from 50 µg/L to 200 µg/L, not too high or too low.

6 Measurement procedure

6.1 Calibration of ICP-MS instrument

The ICP-MS instrument's status shall meet the test requirements. Firstly, the ICP-MS instrument shall be optimized according to the instrument manufacturer's instructions. Then, calibrate the ICP-MS instrument by generating calibration functions using external calibration standard solutions. And then the suitable internal standard solution should be chosen to calibrate the testing procedure.

6.2 Quantitative measurement procedure

6.2.1 Whole element scanning

Prior to quantitative measurement, the qualitative and semi-quantitative whole element scanning shall be performed, to estimate the species of metal impurities and content range of each metal impurity in the test sample.

6.2.2 Quantitative measurement of metal impurities

Set up the test method and establish the standard calibration curve of measured elements. Each element should be measured three times to record the average value. Case study in Annex A.

The slope and intercept of the standard calibration curve and the correlation coefficient should be determined by linear regression, and the correlation coefficient should be no less than 0,95.

The measurement of most elements can be conducted using standard mode, but for several typical elements in industrial graphene powder, such as Co, Mn, Ni, Cu, Cr, Zn, some potential and unavoidable interferences exist (Table 1) and the collision mode or reaction mode is preferred.

Table 1 – Potential interferences for several typical elements in industrial graphene powder

Isotopes	Potential interference	ORS [a] mode
^{52}Cr	ArC, ClOH, ArO, ArN, ArNH	H_2
^{59}Co	ArOH, CaOH, CaO, NaAr	He
^{60}Ni	CaO, CoH, NaCl	He
^{63}Cu	ArAl, TiO, TiOH, ScO, NaAr, PO_2	He
^{66}Zn	S_2, ArMg, SO_2, TiO, TiOH, Ba^{++}	He
^{55}Mn	ArO, CaO, Cd^{++}, ArN, ArNH, ClOH	He
[a] Octopole reaction system.		

6.2.3 Method recovery measurement

Standard addition can be used to evaluate method recovery. Control specimens are measured along with the spiked and un-spiked solutions. The recovery is usually accepted between 90 % and 110 %.

6.2.4 Standard recovery measurement

Measure the spiked specimens (in Clause 5), calculate standard recovery of selected elements in test samples.

The standard recovery is usually accepted between 80 % and 120 % for industrial graphene powder, which contains many species of metal impurities, and the content range of metal impurities is very wide.

7 Data analysis

7.1 Content of metal impurities in test samples

The content of each metal impurity is measured and calculated according to the area of the measured peak. X_i represents the content using Formula (1):

$$X_i = \frac{C_{S,i} - C_{0,i} \times V_S \times I_d}{M_S} \quad * \tag{1}$$

where

$C_{S,i}$ is the concentration of any metal impurity i in the test sample solution (mg/L);

$C_{0,i}$ is the concentration of any metal impurity i in the control solution (mg/L);

V_S is the final volume of the test sample solution (L);

I_d is the dilution factor of the test sample solution, including all pre-treatment steps;

M_S is the mass of the test samples of graphene powder (g).

NOTE The test sample is dried under 105 °C prior to weighing.

7.2 Standard recovery

The standard recovery of several key elements of metal impurities contained in test samples should be measured. The elements measured should not be insensitive to external factors such as surroundings, digestion solvent or the diluent. The elements of Cr, Ba, Mo, Mn, W, Cu are recommended to measure standard recovery. Case study in Annex B.

The standard recovery R_i, in percent, of element i is calculated by Formula (2):

$$R_i = \frac{C_{S',i} - C_{S,i}}{C_i} \ \% \tag{2}$$

where

$C_{S',i}$ is the concentration of element i in the sample solution with standard addition (mg/L);

$C_{S,i}$ is the concentration of element i in the sample solution with no standard addition (mg/L);

C_i is the concentration of element i in the standard solution added (mg/L).

8 Measurement uncertainty estimation

Measurement uncertainty is estimated following the principles of ISO/IEC Guide 98-3 [6] and referenced paper [8]. For this measurement, the main sources of measurement uncertainty are the following:

a) homogeneity of test samples;

b) sample weighting;

c) sample pre-treatment, such as digestion process, acid evaporation, and dilution process. The effect of different pre-treatment methods is significant, see the comparison study in Annex C;

d) blank solution or control solution, digestion solvent, and calibration standards;

e) measurement instrument, including instrument calibration, measurement precision. Both ICP-MS and ICP-OES can be used for the measurement of metal impurities in graphene powder, but they have different measurement capacity and different demands for test samples, see Annex D.

All components of measurement uncertainty sources should be combined and converted to an expanded uncertainty at a specified level of confidence.

The final expanded uncertainty U is obtained by Formula (3):

$$U = k \times u_c(y) \tag{3}$$

where

U is the expanded uncertainty;

k is the coverage factor – usually the value is assigned as 2 or 3 according to the distribution type of measurement data and confidence interval [7], [8];

$u_c(y)$ is the combined standard uncertainty of the final result.

9 Measurement report

9.1 General

The measurement results shall be documented as a measurement report. The measurement report should include but not be limited to the following entries.

9.2 Product or sample identification

The report should contain all information to identify the test sample and trace back the history of the sample.

– General procurement information.

– General material description, including a technical drawing.

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

9.3 Measurement conditions

The ambient conditions during the measurement.

– Temperature range: ambient temperature.

– Range of relative humidity: ambient humidity.

9.4 Measurement specific information

– Instrument type, ICP-MS.

– Calibration status of instrument.

– Carrier atmosphere.

– Blank solution.

– Digestion solution.

– Analytical method.

9.5 Measurement results

Results of metal impurities measured.

– Measurement conditions, including internal standards, standard solutions, etc.

– Standard calibration curve information.
– Digestion conditions, including digestion solvent, digestion temperature and time, etc.
– Species of metal impurities in test samples.
– Species and concentration of metal impurities in control solvent contrast.
– Content and standard deviation of each metal impurity in test samples.
– Measurement mode (standard mode, collision mode, or reaction mode).
– Limit of detection (LOD) or limit of quantitation (LOQ) or both for each metal impurity in test samples.
– Standard recovery of typical metal impurities in test samples.

Annex A
(informative)

Case study for FLG powder

A.1 Test sample

An industrial product of few-layer graphene (FLG) with four to six layers synthesized through CVD method was used as test sample. The test sample of very low density is easy to float, so the static discharge gun should be used while weighing and transferring.

A.2 Sample pre-treatment

Four parallel test specimens, approximately 10 mg each, were pre-treated using microwave-assisted digestion; the digestion solvent consisted of 6 mL HNO_3 (MOS, 65 % mass fraction) and 2 mL HF (MOS, 40 % mass fraction). Through programmed temperature, the highest digestion temperature was reached up to 220 °C and maintained for 30 min, recycling three times in succession to obtain a clear digestion solution.

A.3 Instrument information

ICP-MS instrument, Agilent 7700X[2], was used as measurement instrument. The operation status of the instrument was calibrated using standard elements through daily self-checking. The carrier atmosphere is argon (Ar).

A.4 Standard calibration curve

A.4.1 Standard stock solutions

Name or code [a]	Concentration (mg/L)	Elements	Solvent	Uncertainty
Agilent #8500-6940	10,0	Ag Al As Ba Be Ca Cd Co Cr Cs Cu Fe Ga K Li Mg Mn Na V Zn Ni Pb Rb Se Sr Tl U	5 % HNO_3	±0,5 %
GSB 04-1768-2004	100	Zr Hf W Mo Ta Nb Ti	c(HNO_3) = 1,0 mol/L c(HF) = 1,0 mol/L	±1,4 %
GSB 04-1765-2004	100	As Sb Bi Pb Sn Cd	c(HCl) = 3,0 mol/L	±1,4 %
Agilent #8500-6944	10,0	Ce Dy Er Eu Gd Ho La Lu Nd Pr Sm Sc Tb Th Tm Y	5 % HNO_3	±0,5 %

[a] Trade names are given for the convenience of users of this document and do not constitute an endorsement by IEC of the products named.

2 Agilent 7700X is the trade name of a product supplied by Agilent Technologies Co., Ltd. This information is given for the convenience of users of this document and does not constitute an endorsement by IEC of the product named.

A.4.2 Standard calibration curve

Name or code[a]	Concentration gradient (μg/L)	Correlation coefficient
Agilent #8500-6940	5,0, 10,0, 20,0, 50,0, 100, 200 K, Na, Mg, Fe: 200, 500, 1 000, 2 000, 5 000	0,999 4 to 1,000 0
GSB 04-1768-2004	10,0, 20,0, 50,0, 100, 200	0,999 0 to 1,000 0
GSB 04-1765-2004	10,0, 20,0, 50,0, 100, 200	0,999 9 to 1,000 0
Agilent #8500-6944	5,0, 10,0, 20,0, 50,0, 100	0,999 9

[a] Trade names are given for the convenience of users of this document and do not constitute an endorsement by IEC of the products named.

A.5 Measurement procedure

The quantitative measurement is conducted using He collision mode for all metal impurities measured in test samples.

A.6 Measurement results

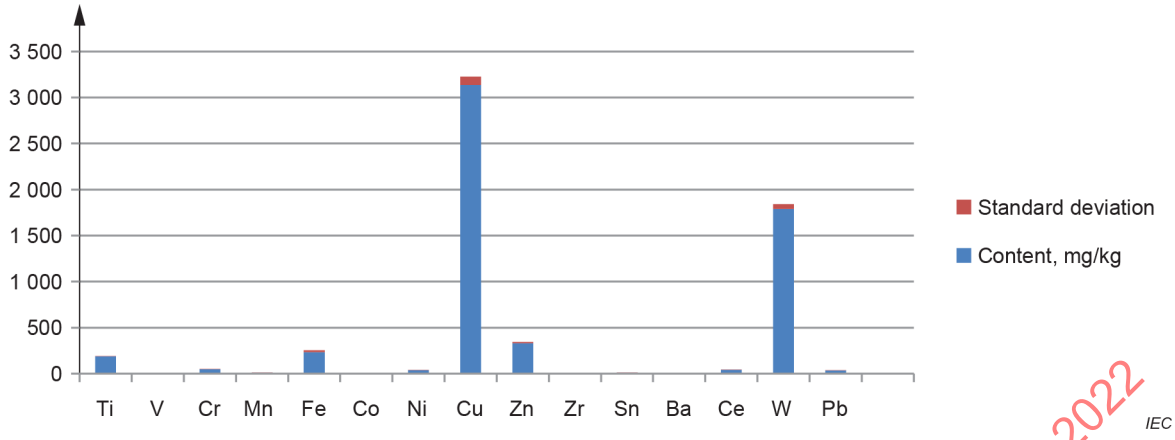
The species and content of all metal impurities detected in test samples are filled in Table A.1, and the content distribution of each metal impurity is shown as Figure A.1.

From the content of each metal impurity in Table A.1, it is shown that there are 15 species of metal impurities in FLG test samples; among them, the content of copper (Cu) impurity is the highest, up to 3 136,6 mg/kg, and the second is tungsten (W) impurity with 1 790,4 mg/kg. The contents of titanium (Ti), iron (Fe) and zinc (Zn) are 187,6 mg/kg, 233,2 mg/kg, and 330,6 mg/kg, respectively; other impurities have much lower content, even below 1 mg/kg.

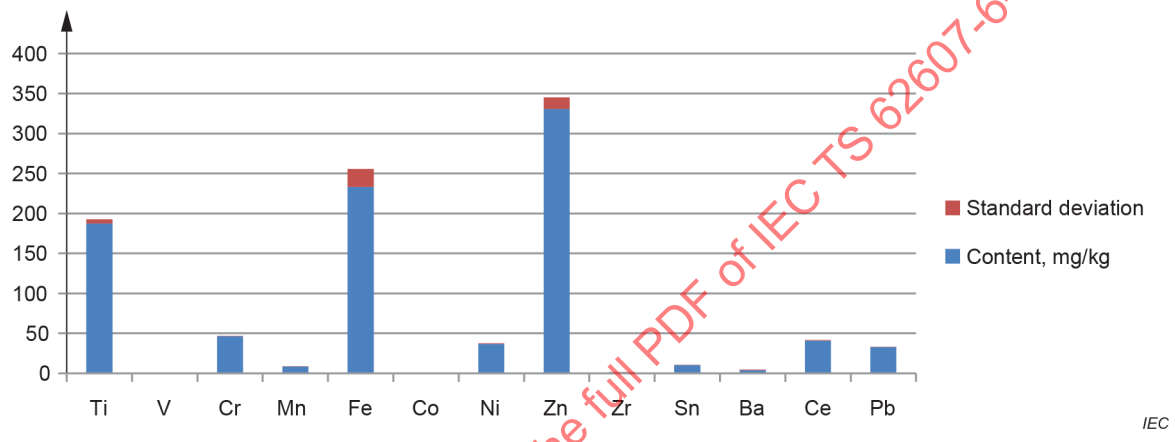
Table A.1 – Content of all metal impurities detected in FLG test sample

No.	Element	Mass number	Content (mg/kg) Four parallel test samples				Average content (mg/kg)	Standard deviation (mg/kg)	Relative standard deviation (%)
1	Ti	47	186,8	191,2	191,8	180,8	187,6	5,082	2,71
2	V	51	0,445	0,459	0,503	0,422	0,457	0,034	7,46
3	Cr	52	46,27	46,96	46,05	46,69	46,49	0,409	1,11
4	Mn	55	8,456	8,181	8,499	8,360	8,374	0,141	1,69
5	Fe	56	244,3	216,3	259,3	212,8	233,2	22,407	9,61
6	Co	59	0,560	0,588	0,537	0,475	0,54	0,048	8,91
7	Ni	60	35,88	36,30	37,33	37,53	36,76	0,797	2,17
8	Cu	63	3 183,9	3 040,2	3 238,1	3 084,4	3 136,6	90,475	2,88
9	Zn	66	319,0	325,1	352,0	326,1	330,6	14,640	4,43
10	Zr	90	1,128	1,044	1,275	1,213	1,165	0,101	8,64
11	Sn	118	9,77	10,80	9,91	10,80	10,32	0,557	5,40
12	Ba	137	3,505	4,006	5,073	3,982	4,142	0,662	16,0
13	Ce	140	41,79	39,97	41,36	40,08	40,80	0,913	2,24
14	W	182	1 845,6	1 752,4	1 741,2	1 822,3	1 790,4	51,411	2,87
15	Pb	208	33,30	32,96	33,14	32,84	33,06	0,202	0,611

It is thus clear that not only are there many species of metal impurity, but also a very wide range of contents of metal impurities, which can be found directly from Figure A.1.



a) total of 15 species of metal impurities detected



b) 13 species of metal impurities excluding Cu (the highest content) and W (the second highest content) elements

Figure A.1 – Content distribution of metal impurities detected in FLG test sample

Annex B
(informative)

Case study for rGO powder

B.1 Test sample

A rGO industrial product in the form of black powder was used as test sample.

B.2 Sample pre-treatment

Four parallel test specimens, approximately 10 mg each, were pre-treated using microwave-assisted digestion; the digestion solvent was 6 mL HNO_3 (MOS, 65 % mass fraction). Through programmed temperature, the highest digestion temperature was reached up to 220 °C and maintained for 30 min, recycling three times in succession to obtain a clear digestion solution.

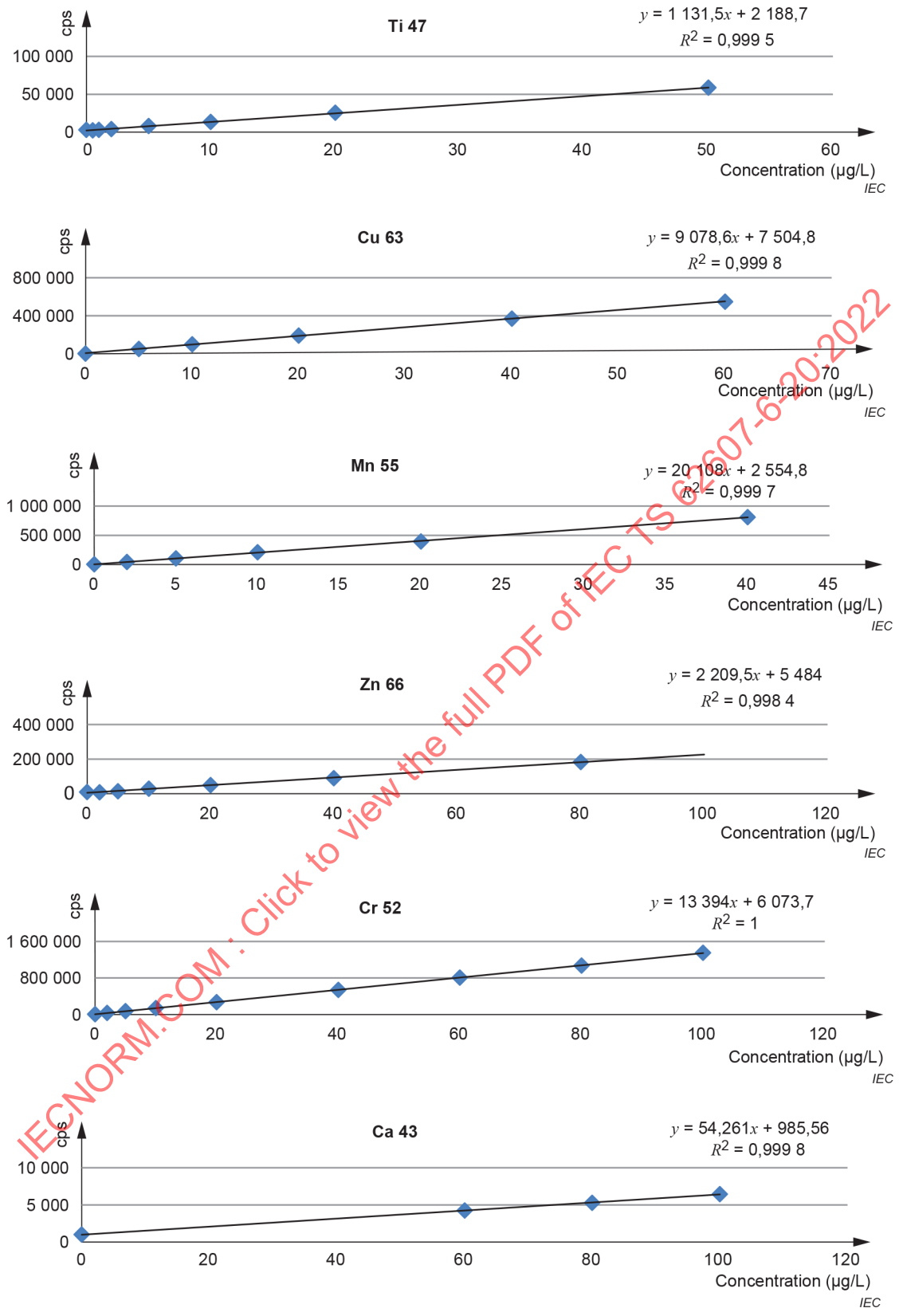
B.3 Measurement instrument

The measurement instrument model is NexION® 300 [3] ICP-MS instrument. Prior to measurement, the operation parameter was optimized by self-checking and the operation status was calibrated using standard stocks. The carrier atmosphere was Ar.

B.4 Standard calibration curve

Prior to the quantitative measurement, the whole scanning was conducted first, and the standard calibration curve, obtained through linear regression, of each metal impurity selected following whole scanning was obtained. The calibration curves and the correlation coefficients of several elements are shown in Figure B.1. It can be seen that all of the correlation coefficients are better than 0,999.

[3] NexION® 300 is the trade name of a product supplied by Perkin-Elmer, Inc. This information is given for the convenience of users of this document and does not constitute an endorsement by IEC of the product named.



Key

cps counts per second.

Figure B.1 – Standard calibration curves of several metal elements contained in rGO test sample

B.5 Measurement results

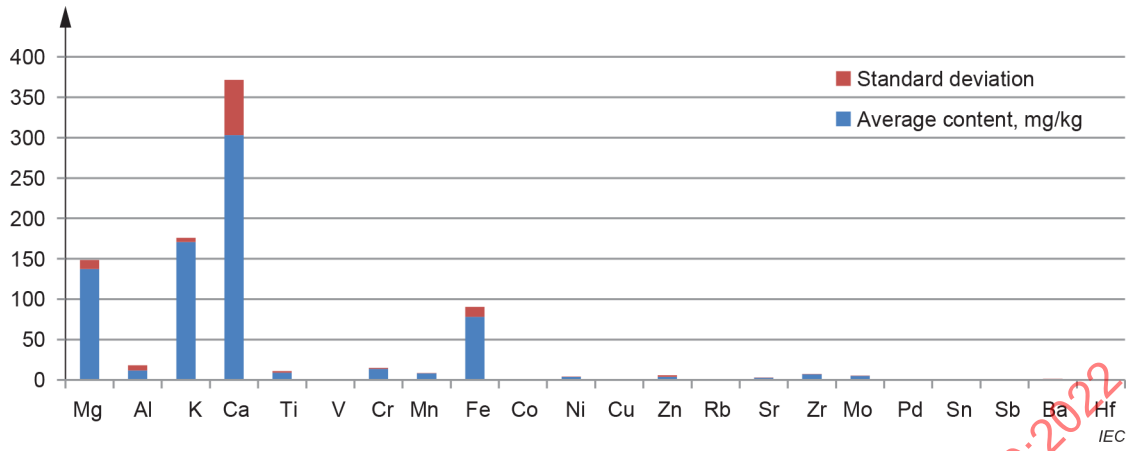
The quantitative measurement was conducted using standard mode.

The species and content of metal impurities in rGO test sample are filled in Table B.1. It is shown that there are 23 species of metal impurities detected; among them, the content of sodium (Na) is the highest, up to 5 700 mg/kg. Additionally, three species of metal impurities – magnesium (Mg), potassium (K) and calcium (Ca) – have much higher content too, the high content of these four species of metal impurities being attributed to water used for washing rGO products.

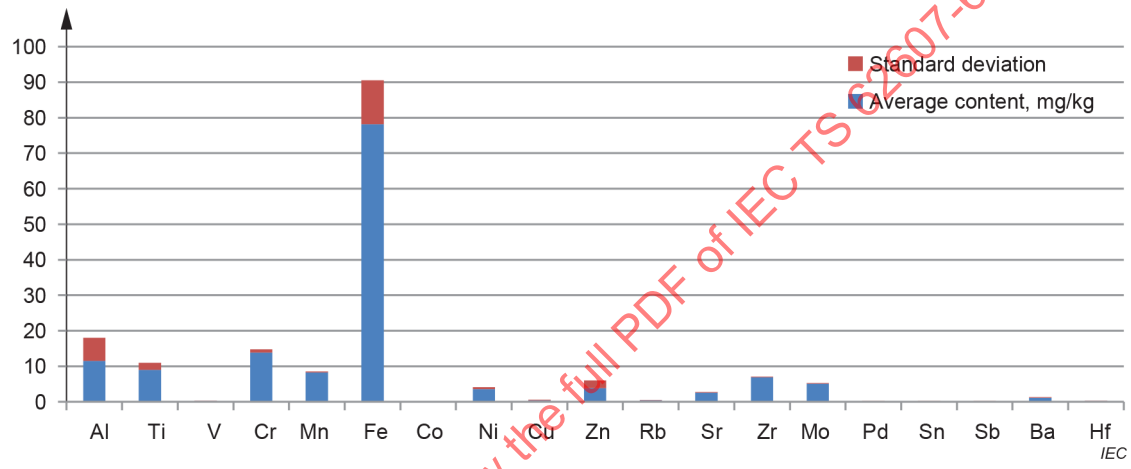
Table B.1 – Content of all metal impurities detected in rGO test sample

No.	Element	Mass number	Content (mg/kg)						Average content (mg/kg)	Standard deviation (mg/kg)
			Six parallel test specimens							
1	Na	23	5 375	5 478	5 014	5 941	6 210	6 183	5 700	485,18
2	Mg	24	126,06	141,72	137,34	136,92	155,6	127,24	137,48	10,79
3	Al	27	5,16	21,81	5,37	8,7	15,56	12,68	11,55	6,48
4	K	39	168,02	179,28	169,16	173	170,12	163,98	170,59	5,17
5	Ca	43	339,85	410	228,35	258,7	326,9	254,6	303,07	68,20
6	Ti	47	6,75	11,18	8,36	7,57	11,75	8,13	8,96	2,03
7	V	51	0,23	0,28	0,25	0,22	0,22	0,22	0,24	0,02
8	Cr	52	13,91	15,55	14,05	12,89	13,55	13,05	13,83	0,96
9	Mn	55	8,28	8,79	8,14	8,06	8,11	8,34	8,29	0,27
10	Fe	57	68,68	91,5	74,76	65,98	95,62	72,52	78,18	12,36
11	Co	59	0,08	0,1	0,07	0,07	0,07	0,08	0,08	0,01
12	Ni	60	3,67	3,71	4,38	3,01	3,72	3,08	3,60	0,50
13	Cu	63	0,22	0,79	0,35	0,26	0,49	0,35	0,41	0,21
14	Zn	66	3,71	6,84	2,58	1,83	6,02	2,09	3,85	2,12
15	Rb	85	0,36	0,43	0,36	0,36	0,37	0,37	0,38	0,03
16	Sr	88	2,42	2,94	2,34	2,53	2,46	2,74	2,57	0,23
17	Zr	90	6,97	7,22	6,58	6,94	6,86	6,93	6,92	0,21
18	Mo	98	4,86	5,32	5,06	5,16	5,22	5,08	5,12	0,16
19	Pd	106	0,2	0,18	0,16	0,18	0,16	0,18	0,18	0,02
20	Sn	118	0,11	0,12	0,09	0,09	0,11	0,09	0,10	0,01
21	Sb	121	0,11	0,21	0,11	0,22	0,14	0,2	0,17	0,05
22	Ba	138	0,9	1,41	0,97	0,97	1,21	1,19	1,11	0,19
23	Hf	180	0,27	0,19	0,16	0,17	0,17	0,17	0,19	0,04

It is thus clear that not only are there many species of metal impurities, but also a very wide range of contents in the rGO test sample, which can be found directly from Figure B.2.



a) total of 22 species of metal impurities detected excluding Na element (the highest content)



b) 19 species of metal impurities excluding Na (the highest content), Mg, K and Ca (three species with higher content)

Figure B.2 – Content distribution of metal impurities detected in rGO test sample

B.6 Standard recovery

The standard recovery of most species of metal impurities in rGO test samples was measured, as shown in Figure B.3. It is shown that all standard recovery is between 80 % and 120 %, which exhibits that the measurement method is reliable.

NOTE The high standard recovery of nickel (Ni) element is abnormal, which is attributable to the Ni sampling cone of the ICP-MS measurement instrument.

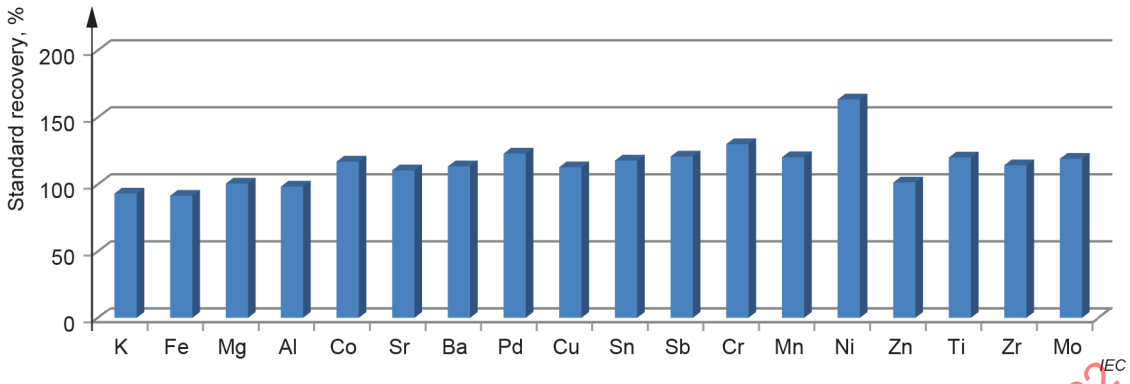


Figure B.3 – Standard recovery of most species of metal impurities in rGO test sample