



**International
Standard**

ISO 5861

**Surface chemical analysis — X-ray
photoelectron spectroscopy —
Method of intensity calibration for
quartz-crystal monochromated Al
K α XPS instruments**

**First edition
2024-06**

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 document 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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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

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.

Introduction

X-ray photoelectron spectroscopy is routinely used to measure the elemental composition of surfaces and the depth distribution of those elements. The translation of peak intensities into elemental compositions and depth distributions in the absence of reference materials relies upon comparison of the relative peak intensities to external reference data. The kinetic energies of the peaks being compared are different and therefore it is important to know the relative transmission and detection efficiency of electrons at different kinetic energies to achieve a meaningful comparison to the external reference data. International interlaboratory studies demonstrate that XPS instruments display markedly different transmission characteristics. Consistent intensity scale calibration enables the direct comparison of XPS results and enables international trade through trust in measurements throughout the supply chain and in the comparability of data from analytical service providers.

This document provides a method to determine the relative response of X-ray photoelectron spectrometers which utilise quartz-crystal-monochromated Al K α radiation as the excitation source. Clean low-density poly(ethylene) is employed as a reference material. Measured intensities from clean low-density poly(ethylene) are compared to reference intensities at specific electron kinetic energies to determine the relative response of electrons to the detector. The resulting relative response function is traceable to accurate reference spectra for copper, silver and gold held by the National Physical Laboratory, UK.

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Surface chemical analysis — X-ray photoelectron spectroscopy — Method of intensity calibration for quartz-crystal monochromated Al K α XPS instruments

1 Scope

This document specifies a procedure by which the intensity scale of an X-ray photoelectron spectrometer that employs a concentric hemispherical analyser can be calibrated using low-density poly(ethylene). This document is applicable to instruments using quartz-crystal-monochromated Al K α X-rays and is suitable for all instrument geometries. The intensity calibration is only valid for the specific settings of the instrument (pass energy or retardation ratio, lens mode, slit and aperture settings) used during the calibration procedure. The intensity calibration is applicable at kinetic energies higher than 180 eV. The intensity calibration is suitable for instruments that do not have an ion gun for the purpose of cleaning metal specimens in-situ (i.e. Au, Ag, Cu), or exhibit detector saturation when these specimens are measured using standard instrument parameters.

This document is not applicable to XPS instruments which do not have a system of charge compensation, or instruments that have a non-linear intensity response. This document is not applicable to instruments and operating modes which generate significant intensity from electrons scattered internally in the spectrometer (i.e. >1 % contribution of scattering intensity to the total spectral intensity).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115-1 and the following apply.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

relative throughput

ratio of measured signal rate to the known intensity from a reference sample as a function of electron kinetic energy

Note 1 to entry: Relative throughput is related to the spectrometer response function and is distinguished in this document as the experimentally determined response.

4 Symbols and abbreviated terms

For the purposes of this document the following abbreviations apply.

ISO 5861:2024(en)

LDPE low density poly(ethylene), or low density polyethylene, CAS RN¹⁾ 9002-88-4

XPS X-ray photoelectron spectroscopy

For the purposes of this document the following symbols apply.

A	XPS peak area	eV s^{-1}
a	an exponent	
b	an exponent	
β	detection angle between incoming X-rays and outgoing electrons	
C	count rate from reference material	s^{-1}
D	noise rate	s^{-1}
E	analyser kinetic energy	eV
F	correction for angular emission	
g	instrument geometry factor	
h	magnitude of the slope of the survey spectra intensity ratio	keV^{-1}
I	angle-averaged reference intensity	I_A
K	reference kinetic energy, equal to $E + q$	eV
M	number of independent parameters in a functional description of T	
Q	relative throughput: ratio of signal rate, S , to the reference intensity, R	$I_A^{-1} \text{s}^{-1}$
q	electric potential energy of reference material relative to spectrometer	eV
R	reference intensity for the XPS instrument	s^{-1}
S	signal rate: the difference between count rate, C , and noise rate, D	s^{-1}
s	average matrix relative sensitivity factor	
σ_C	standard uncertainty of count rate	s^{-1}
σ_Q	standard uncertainty of relative throughput Q	$I_A^{-1} \text{s}^{-1}$
σ_q	mean standard uncertainty of relative throughput Q	$I_A^{-1} \text{s}^{-1}$
σ_S	standard uncertainty of signal rate S	s^{-1}
σ_T	standard uncertainty of relative response T	$I_A^{-1} \text{s}^{-1}$
T	relative response of a spectrometer	$I_A^{-1} \text{s}^{-1}$
W	X-ray anode power	W
W_r	X-ray anode power used during LDPE reference material analysis	W

1) CAS Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

X	root mean square error of a functional description of T relative to Q	
x	relative atomic concentration	at. %
ξ	dihedral angle between X-ray anode-monochromator-sample plane and monochromator-sample-electron analyser plane	
Y	XPS signal rate from a sample	s^{-1}
Z	calibrated XPS intensity from a sample	I_A

5 Requirements

5.1 General

Annex A.1 shows a flow chart (Figure A.1) for instrument set-up and the acquisition of data and summarises the steps to be taken in Clause 5.

5.2 X-ray photoelectron spectrometer

5.2.1 Operating requirements

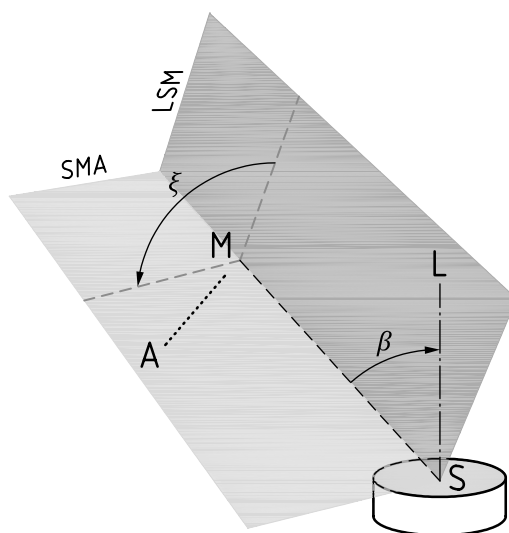
The XPS instrument requires a monochromated Al $K\alpha$ X-ray source and a charge compensation system such as a low energy electron flood source or low energy ion source. The XPS spectrometer shall be operated in a pulse-counting mode. Count rates that are used for calibration following the procedures in this document shall be within the linear operating regime of the detector. The pass energy and slit widths of the spectrometer shall be set to minimise the contribution of electrons scattered within the analyser to the recorded count rate. In the case that analyser internal scattering can be measured, the contribution shall comprise less than 1 % of the count rate.

NOTE Linearity of the intensity scale can be confirmed using methods described in other documents^[1,2].

Scattering in electron spectrometers can be diagnosed and minimised^[3,4], but significant scattering intensity shall be reported to the instrument manufacturer for corrective action. For concentric hemispherical analysers, higher pass energies and smaller entrance slit widths reduce the effect of scattering. A pass energy of 50 eV or higher is usually sufficient to ensure that the major scattering contributions are significantly less than 1 %.

5.2.2 Instrument geometry

The geometry of the XPS spectrometer shall be known. The geometry is characterised by two angles: the detection angle β which is the angle between the incoming X-rays from the monochromator and the outgoing electrons directly toward the electrostatic lens column; and ξ , the dihedral angle between the plane defined by the centres of the X-ray anode, the monochromator, and the sample (which is assumed to be in the focal point of the X-ray spot and analyser defined analysis spot) and the plane defined by the centres of the monochromator, sample and electrostatic lens column. Figure 1 provides a schematic of the XPS instrument geometry used in this document to help identify the angles β and ξ . The instrument manufacturer will know the exact angles of β and ξ from chamber design schematics.

**Key**

A	centre of X-ray anode	M	centre of quartz-crystal monochromator
S	analysis point on sample	L	centre of analyser lens
β	angle between lines MS and SL	ξ	dihedral angle between planes LSM and SMA

Figure 1 — Schematic of XPS instrument geometry showing the angles β and ξ

From these two angles, the geometry factor of the instrument shall be calculated using [Formula \(1\)](#).

$$g = [(2,990 - 0,765 \cos \beta)(0,500 - 0,042 \cos 2\xi) \sin^2 \beta] - 0,995 \quad (1)$$

where

g is the instrument geometry factor;

β is the detection angle;

ξ is the dihedral angle.

NOTE 1 [Formula \(1\)](#) contains numerical values that arise from the nearly identical angular emission distributions of C 1s and C 2s electrons and the X-ray polarisation induced by the monochromator [\[5\]](#).

NOTE 2 Most commercial spectrometers have a coplanar dihedral angle, $\xi = 180^\circ$, and a detection angle, β , between 45° and 60° . Useful numerical values of g are: $-0,434\ 2$ for $\beta = 45^\circ$; $-0,217\ 7$ for $\beta = 54,7^\circ$; $-0,099\ 3$ for $\beta = 60^\circ$ and; $+0,374\ 4$ for $\beta = 90^\circ$.

NOTE 3 Exact angles of β and ξ can be obtained from the instrument manufacturer.

5.3 Reference material

The reference material shall be LDPE sheet of approximately 1 mm thickness free from obvious polymer damage or discolouration. Cut the LDPE sheet to a size suitable for analysis using clean metal scissors and affix to a sample holder. Use a brand-new disposable scalpel, or a scalpel cleaned with an isopropanol alcohol-soaked tissue, to uniformly scrape the surface immediately prior to inserting it into the XPS instrument. A visual inspection of the XPS survey scans should exhibit no peaks other than those due to carbon. If this condition is met, then the LDPE sheet is suitable as a reference material for use with this document. At the conclusion of this protocol, the reference LDPE should be stored in the dark, avoiding exposure to humidity and high temperatures or proximity to volatile solvents or fumes, until required.

If peaks due to elements apart from carbon are observable in the LDPE X-ray photoelectron spectrum, the sample shall be removed and cleaned again by additional scraping using a different clean metal scalpel. If

repeated cleaning does not remove the non-carbon elemental peaks, then an alternative source of LDPE shall be sought.

In subsequent uses of this document, stored and previously used LDPE reference samples shall be scraped before use.

NOTE 1 Contamination can also arise from the XPS instrument and sample holder. Failure to obtain clean LDPE can also indicate that the XPS instrument requires baking or sample holders require cleaning.

NOTE 2 Clean, uncoated razor blades without a lubricant coating such as PTFE can be used in place of a scalpel.

5.4 Frequency of intensity scale calibration

Intensity calibration shall be performed at a maximum interval of one year, or more frequently if changes in intensity response are identified and occur over a shorter period. Intensity calibration is also required after maintenance, alteration of instrument configuration, or a bake-out.

NOTE ISO 24237, repeatability and constancy of intensity scale, ISO 16129, procedures for assessing the day-to-day performance of an X-ray photoelectron spectrometer and other documents provide methods for identifying changes in instrument response^[6-8].

6 Data acquisition

6.1 General

Annex A.1 shows a flow chart (Figure A.1) for instrument set-up and the acquisition of data that summarises the steps to be taken in Clause 6. Additionally, A.2 shows a flow chart (Figure A.2) for the inspection of data and determining $Q(E)$ that summarises the steps to be taken in Clause 6.

6.2 Preparation

6.2.1 XPS Instrument

Operate the instrument in accordance with the manufacturer's instructions. Turn on the XPS instrument control and high voltage power supplies at least three hours before proceeding. Set the instrument to the required operating mode, pass energy or retardation ratio, slit widths and aperture settings for which the intensity calibration is required.

6.2.2 LDPE reference sample

Prepare the LDPE reference sample by mounting on a sample holder and scraping with a scalpel described in 5.3. Immediately place the reference sample in the instrument load lock, evacuate the load lock chamber and transfer it to the analysis chamber as soon as possible. Position the reference sample away from the analysis position so that it will not be exposed to X-rays during X-ray source warm up, see 6.2.3.

6.2.3 X-ray source and electron flood source

Turn on the X-ray source at a normal operating power. Turn on the electron flood source and set it to typical operating parameters. Wait for at least 30 min for the X-ray source and electron flood source to equilibrate before proceeding. The X-ray power used for acquiring the reference spectra, W_r , shall be recorded.

Similar to instrument parameters described in 6.2.1, the resulting intensity calibration obtained from this procedure is also a function of the X-ray source energy, optics, and spot size. Multiple calibrations shall be obtained for different X-ray source parameters except for W_r .

6.2.4 Noise spectrum

Ensure that neither the LDPE sample, nor any part of the manipulator is in, or in proximity to, the analysis position. This is achieved by moving them as far away from the analysis position as the instrument will allow. Acquire a survey spectrum from 175 eV to 1 500 eV kinetic energy. The acquisition time shall be greater than 10 minutes to ensure statistical relevance. The data shall be plotted and visually inspected for any kinetic energy dependent structure. If there is no evidence of kinetic energy dependent structure in the noise spectrum then the noise rate, D , will be determined from the LDPE spectra, see [6.3.2.2](#).

If there is evident structure in the noise spectrum, then the measurement shall immediately be repeated to ensure that it is reproducible. If the noise spectrum is reproducible and can be described using a simple energy-dependent function, such as a power law or polynomial, then the noise spectrum shall be fitted. The fit shall be used to establish the kinetic energy dependent value of the noise rate, D .

If the noise spectrum is not reproducible then this document is not applicable. If the noise spectrum cannot be described by a simple energy-dependent function, then this document is not applicable.

NOTE 1 Typically XPS spectrometers will have energy independent and low noise count rates, less than 10 s^{-1} . A high noise count rate indicates that the discriminator setting is incorrect and requires adjustment.

NOTE 2 A reproducible energy-dependent noise spectrum indicates that there is a fault with the spectrometer. An irreproducible energy-dependent noise spectrum indicates that there is interference from other equipment or an unstable power supply.

6.3 LDPE intensity measurement

6.3.1 Spectra

6.3.1.1 Initial survey spectrum

Move the LDPE reference sample into the analysis position with the sample normal directed toward the analyser and optimise the position according to the manufacturer's instructions or local procedures. Optimise the electron flood source to achieve a stable surface potential. Acquire a survey spectrum from 175 eV to 1 500 eV kinetic energy. The acquisition time and number of sweeps shall be set to achieve at least 5 000 counts at 1 000 eV kinetic energy to ensure statistical relevance. The spectrum shall be inspected to confirm the absence of peaks due to elements other than carbon. If other peaks are observed then the LDPE shall be removed and cleaned again, see [5.3](#).

NOTE The C 1s peak is normally between 1 200 eV and 1 206 eV kinetic energy with low energy electron flood compensation.

6.3.1.2 High kinetic energy region spectrum

Without moving the sample or adjusting the instrument in any way, acquire a spectrum from 1 195 eV to 1 500 eV kinetic energy. The acquisition time and number of sweeps shall be set to achieve at least 10 000 counts at 1 350 eV kinetic energy to ensure statistical relevance.

NOTE The total acquisition time for the high kinetic energy region will typically be more than ten times that of the initial survey spectrum.

6.3.1.3 Final survey spectrum

Without moving the sample or adjusting the instrument in any way, acquire a final survey spectrum from 175 eV to 1 500 eV kinetic energy using the same acquisition parameters as the initial survey spectrum [6.3.1.1](#).

6.3.1.4 Data inspection

Ensure that the intensities in the spectra have not been modified by the software, for example using the manufacturer's intensity calibration procedure. Plot all spectra as count rate against kinetic energy and

ensure that, in an overlay, there are no significant differences in count rate for the inelastic background beyond the range of the spectral noise. If this condition is not met, then the data shall not be used for intensity calibration.

If there are any elemental peaks observed in the spectra which are from elements other than carbon then the data shall not be used for intensity calibration and the LDPE cleaning procedure revisited, see [5.3](#).

Divide the intensity of the final survey spectrum by the corresponding intensity in the initial survey spectrum at each kinetic energy across the range from $E = 180$ eV to $E = 1\,480$ eV. Calculate the mean ratio and ensure that this value is within 5 % of unity. Perform a linear regression on the ratio and ensure that the magnitude of the slope of the ratio, h , is less than $0,033\text{ keV}^{-1}$. If these conditions are not met, then the data shall not be used for intensity calibration.

NOTE 1 The ratio of the final survey spectrum to the initial survey spectrum could display a slope. This is indicative that there was insufficient equilibration time before acquiring the first spectrum or a problem with the electron detector.

NOTE 2 The ratio of the final survey spectrum to the initial survey spectrum can display sharp deviations near the peaks in the spectrum. This is indicative that the charge compensation was not stable.

NOTE 3 The maximum slope criteria is calculated using a maximum ratio deviation of 0,05 divided by 1 500 eV. Conforming to both the maximum slope and mean ratio criteria ensures that the linear intensity ratio cannot deviate more than 7,5 % from unity.

6.3.2 Data preparation

6.3.2.1 Calculation of LDPE potential, q

The analyser kinetic energy position of the C 1s peak maximum in the final survey spectrum shall be subtracted from 1 201 eV and the result shall be assigned as the electric potential of the reference material relative to spectrometer, q .

NOTE 1 The error in relative response associated with an incorrect measurement of LDPE potential is small, typically less than 0,2 % per eV.^[2] The primary importance of ensuring kinetic energy alignment with the reference data is to prevent unintended overlap of peaks into the background regions used for intensity calibration.

NOTE 2 The sign of q is typically negative if a low-energy electron flood source is used for charge compensation.

6.3.2.2 Determination of noise rate, D

If the intensity of the noise spectrum was constant with kinetic energy, see [6.2.4](#), then the noise rate, D , shall be calculated as the average count rate from 1 495 eV to 1 500 eV in the high kinetic energy region spectrum and this value used at all kinetic energies, $E = K - q$. Otherwise, the kinetic energy dependent function determined in [6.2.4](#) shall be used and shall be calculated at the kinetic energies, $E = K - q$. The values of K are listed in [Table B.1](#).

NOTE In an interlaboratory study^[5], the noise rate determined at kinetic energies higher than the X-ray energy was generally, but not always, identical to the noise rate with no sample at the analysis position. Consistency with other calibration methods was best achieved through the method described here.

6.3.2.3 Signal rate, S

The count rate, C , shall be determined in relation to the reference kinetic energies, K , which are listed in [Table B.1](#). Each of the reference kinetic energies are associated with a range in the spectra with a lower bound in E of $(K - q - 5\text{ eV})$ and an upper bound of $(K - q + 5\text{ eV})$. At each reference energy, the mean count rate across this range shall be calculated using the mean of the initial and final survey spectra for kinetic energies less than 1 201 eV and using the high kinetic energy region spectrum for kinetic energies greater than 1 201 eV. These mean count rates shall be the count rate, C , at kinetic energies, $E = K - q$.

The standard deviation of the count rates within each range shall be calculated and recorded as an estimate of the standard uncertainty, σ_C . The signal rate, S , shall be calculated at each kinetic energy region E

using [Formula \(2\)](#) and the uncertainty in the signal rate, σ_S , shall be calculated for each region of E using [Formula \(3\)](#).

$$S(E) = C(E) - D(E) \quad (2)$$

$$\sigma_S(E) = \left(1 + \frac{D(E)}{C(E)} \right) \sigma_C(E) \quad (3)$$

where

$S(E)$ is the average signal rate at E ;

$C(E)$ is the average count rate in the region $(K-q-5 \text{ eV})$ to $(K-q+5 \text{ eV})$;

$D(E)$ is the average noise rate at E ;

E is the analyser kinetic energy;

$\sigma_S(E)$ is the standard uncertainty of S at E ;

$\sigma_C(E)$ is the standard uncertainty of C at E .

NOTE [Formula \(3\)](#) assumes Poisson statistics in the count rate.

6.3.2.4 The reference intensity, R

The reference intensity, R , shall be calculated at each kinetic energy, E , using [Formula \(4\)](#) and the angle-averaged reference intensity, I , the instrument geometry factor, g , and the correction for angular emission, F . The values of I and F for each value of reference kinetic energy K are listed in [Table B.1](#) along with precalculated values of R for common instrument geometries. The assignment accounts for the charge on the reference materials, noting that $E = K - q$.

$$R(E) = I(K)[1 + gF(K)] \quad (4)$$

where

$R(E)$ is the reference intensity at E ;

E is the analyser kinetic energy;

$I(K)$ is the angle-averaged reference intensity at K ;

$F(K)$ is the angular emission correction at K ;

K is the reference kinetic energy;

g is the instrument geometry factor from [Formula \(1\)](#).

6.3.2.5 Relative throughput, Q

The relative throughput, Q , shall be calculated using [Formula \(5\)](#) and the standard uncertainty of the relative throughput, σ_Q , shall be calculated using [Formula \(6\)](#)

$$Q(E) = \frac{S(E)}{R(E)} \quad (5)$$

$$\sigma_Q(E) = \frac{\sigma_S(E)Q(E)}{S(E)} \quad (6)$$

where

- $Q(E)$ is the relative throughput at E ;
- $S(E)$ is the average signal rate at E ;
- $R(E)$ is the reference intensity at E ;
- E is the analyser kinetic energy;
- $\sigma_Q(E)$ is the standard uncertainty of Q at E ;
- $\sigma_S(E)$ is the standard uncertainty of S at E .

6.3.2.6 Mean uncertainty contribution of Q

The mean uncertainty contribution of Q , σ_Q , shall be calculated as the arithmetic mean of all $\sigma_Q(E)$.

7 Relative response

7.1 General

Annex A.2 shows a flow chart (Figure A.2) for inspection of data and determining $Q(E)$ that summarises the steps to be taken in Clause 7. Also, A.3 shows a flow chart (Figure A.3) for fitting $Q(E)$ to obtain $T(E)$ that summarises the steps to be taken in Clause 7.

7.2 Calculation of relative response, T

7.2.1 Relative throughput inspection

The values of Q shall be plotted against E , using error bars of size $2\sigma_Q$. The graph shall be inspected for inconsistencies. The values are expected to form a continuous curve within the bounds of the error bars. Particular attention shall be given to the continuity of the region below $E = 1\,201$ eV and the region above $E = 1\,201$ eV. Discontinuity between these regions and any single points that are outliers should be investigated further and the cause established and corrected before continuing or restarting the calibration procedure from the beginning.

NOTE Discontinuity between the lower kinetic energy and higher kinetic energy regions can usually be traced to one of the following causes: failure to express signal correctly as rates; incorrect instrument geometry factor, g ; inconsistent or erroneous noise rate, D and; unaccounted internal scattering in the spectrometer.

7.2.2 Extension of throughput data

7.2.2.1 Interpolation

The set $Q(E)$ contains points which are spaced in E by 32 eV from $E = (180-q)$ eV to $E = (1\,428-q)$ eV with gaps where the C KLL and C 1s peaks appear. Additional points shall be included in the set $Q(E)$ using Formula (7), Formula (8), Formula (9) and Formula (10).

$$Q(276-q) = \frac{Q(244-q) + Q(308-q)}{2} \quad (7)$$

$$Q(1\,172-q) = \frac{3Q(1\,140-q) + Q(1\,268-q)}{4} \quad (8)$$

$$Q(1\,204-q) = \frac{Q(1\,140-q) + Q(1\,268-q)}{2} \quad (9)$$

$$Q(1\ 236-q) = \frac{Q(1\ 140-q) + 3Q(1\ 268-q)}{4} \quad (10)$$

where $Q(E)$ is the relative throughput at E .

7.2.2.2 Extrapolation

7.2.2.2.1 Low energy extrapolation

The set $Q(E)$ does not cover the full range of electron kinetic energies used in XPS analysis and requires extension. One additional point shall be included at low kinetic energy in the set $Q(E)$ at $E = (148-q)$ eV using [Formula \(11\)](#).

$$Q(148-q) = 2Q(180-q) - Q(212-q) \quad (11)$$

where $Q(E)$ is the relative throughput at E .

7.2.2.2.2 High energy extrapolation

Extrapolation to energies higher than the photon energy is required to assist in the stability of some fitting functions. The five values of $Q(E)$ for $E = (1\ 300-q)$ eV and higher shall be used to calculate the parameters for a power-law extrapolation using [Formulae \(12\)](#) and [\(13\)](#).

$$a = \frac{(\sum (\log E_i)^2 \sum \log Q_i) - (\sum \log E_i \sum (\log E_i \log Q_i))}{5 \sum (\log E_i)^2 - (\sum \log E_i)^2} \quad (12)$$

$$b = \frac{5 \sum (\log E_i \log Q_i) - (\sum \log E_i \sum \log Q_i)}{5 \sum (\log E_i)^2 - (\sum \log E_i)^2} \quad (13)$$

where

a is an exponent;

b is an exponent;

E_i are the 5 values: $(1\ 300-q)$, $(1\ 332-q)$, $(1\ 364-q)$, $(1\ 396-q)$ and $(1\ 428-q)$;

Q_i are the 5 values of $Q(E_i)$ at the values of E_i .

Extrapolated values of $Q(E)$ shall be calculated using [Formula \(14\)](#) at values of E equal to $(1\ 460-q)$, $(1\ 492-q)$, $(1\ 524-q)$, $(1\ 588-q)$ and $(1\ 620-q)$ in units of eV and included in the set $Q(E)$.

$$Q(E) = 10^a E^b \quad (14)$$

where

a is an exponent;

b is an exponent;

$Q(E)$ is the relative throughput at E ;

E is the analyser kinetic energy.

NOTE [Formulae 12](#) and [13](#) represent simple linear regression of the logarithm of $Q(E)$ against the logarithm of E .

7.2.3 Relative response determination

7.2.3.1 Choice of method

The relative response of the spectrometer, $T(E)$ shall be determined directly from $Q(E)$. There are two methods that can be used:

- Linear interpolation between the two closest values of $Q(E)$.
- Fitting a smooth descriptive curve of $T(E)$ to the discrete values of $Q(E)$.

The first method is described in 7.2.3.2 and is the simplest. It has the disadvantages of including the experimental noise in $Q(E)$ and having a discontinuous slope. The second method of fitting is described in 7.2.3.3, with additional information in Annex C. It does not have the disadvantages of the first method but can introduce significant error if the functional form chosen for the curve does not describe $Q(E)$ sufficiently well. Examples of relative response determination using both the linear interpolation and fitting methods are shown in Annex D.

7.2.3.2 Linear interpolation

For a given value of kinetic energy E_1 , the two closest values of kinetic energy, E_0 equal or lower than E_1 , and E_2 , larger than E_1 , in the set $Q(E)$ shall be found. Formula (15) shall be used to calculate the relative response at energy E_1 .

$$T(E_1) = \frac{(E_2 - E_1)}{(E_2 - E_0)} Q(E_0) + \frac{(E_1 - E_0)}{(E_2 - E_0)} Q(E_2) \quad (15)$$

where

$Q(E)$ is the relative throughput at E ;

$T(E)$ is the relative response at E ;

$R(E)$ is the reference intensity at E ;

E_0 is the first kinetic energy value ($K-q$) lower than E_1 ;

E_1 is the analyser kinetic energy at which the relative response is required;

E_2 is the first kinetic energy value ($K-q$) higher than E_1 .

7.2.3.3 Fitting

A continuous, differentiable function $T(E)$ shall be selected to fit the values of $Q(E)$. It shall have M independent parameters where the value of M is less than 12. The root mean square error, X , shall be calculated using Formula (16) and the M independent parameters iteratively varied from initial values to minimise X .

$$X = \sqrt{\frac{\sum_i (Q(E_i) - T(E_i))^2}{47 - M}} \quad (16)$$

where

- $Q(E_i)$ is the relative throughput at E_i ;
- $T(E_i)$ is the relative response function at E_i ;
- E_i are the 47 kinetic energy values from $(148-q)$ eV to $(1\,620-q)$ eV;
- M is the number of independent parameters in the function T ;
- X is the root mean square error of the fit.

After minimising the value of X , the residuals of the fit, $Q(E_i) - T(E_i)$, shall be plotted with error bars of size $2\sigma_q$. If there are more than 2 deviations of the residual from zero of a size similar to, or larger than, the error bars are observed then either:

- a) the iterative fit shall be tried again using different initial values for the M independent parameters in T ;
- b) a different functional form of T shall be used;
- c) the linear interpolation described in 7.2.3.2 shall be used.

7.2.4 Error in relative response

The relative error in relative response, σ_T , shall be estimated using Formula (17) if linear interpolation, 7.2.3.2, was employed and Formula (18) if fitting, 7.2.3.3, was employed. The highest kinetic energy, E_2 , and lowest kinetic energy, E_1 , in eV in the range being considered is required.

$$\sigma_T = \sqrt{\sigma_q^2 + (h^2 + 0,001) \left(T \left[\frac{E_2 - E_1}{1\,000} \right] \right)^2} \quad (17)$$

$$\sigma_T = \sqrt{X^2 + (h^2 + 0,001) \left(T \left[\frac{E_2 - E_1}{1\,000} \right] \right)^2} \quad (18)$$

where

- σ_T is the mean standard uncertainty of T across the energy range E_1 to E_2 ;
- σ_q is the mean standard uncertainty of Q ;
- h is the magnitude of the slope of the ratio between the initial and final survey spectra;
- T is the relative response at $(E_1 + E_2)/2$;
- E_1 is the lowest kinetic energy in the range of intensity comparison;
- E_2 is the highest kinetic energy in the range of intensity comparison;
- X is the minimised root mean square error of the fit.

NOTE The local error in T , for regions which are separated by less than 100 eV, is characterised by either σ_q (see 6.3.2.6) for linear interpolation (7.2.3.2), or by X for fitting (7.2.3.3). For regions which are widely separated in kinetic energy, the error of the reference data becomes important and the ~2 % uncertainty^[5] is characterised as a slope error of 4 % across the full range from 180 eV to 1 428 eV which is 3,2 % per 1 000 eV.

7.3 Use of relative response, T

7.3.1 Correction of survey spectra

XPS survey spectra acquired using the same operating mode, pass energy or retardation ratio, slit widths and aperture settings for which the relative response T is relevant can be corrected to provide spectra consistent with other users of this standard. If this is required, the signal rates from the sample being analysed $Y(E)$ at each kinetic energy, E , shall be converted into calibrated intensities $Z(E)$ in units of I_A using [Formula \(19\)](#). After relative response correction, the relative intensities of peaks in the spectrum and the shape of backgrounds can be directly compared to theory.

$$Z(E) = \frac{Y(E)W_r}{T(E)W} \quad (19)$$

where

$Z(E)$ is the calibrated intensity at E ;

$Y(E)$ is the measured signal rate at E ;

$T(E)$ is the relative response at E ;

W is the X-ray anode power during the measurement of $Y(E)$;

W_r is the X-ray anode power during the calibration.

7.3.2 Use in quantification

If quantification is performed on raw data which has not previously had a relative response correction, the peak areas can be converted into equivalent-homogeneous atomic fractions in at. % using [Formula \(20\)](#) using XPS peak areas in eV s^{-1} measured from the data.

$$x_i = \frac{A_i / s_i T(E_i)}{\sum_j [A_j / s_j T(E_j)]} \cdot 100 \% \quad (20)$$

where

x_i is the equivalent-homogeneous atomic fraction of element i ;

A_i is the XPS peak area of the selected peak of element i ;

s_i is the average-matrix relative sensitivity factor of the selected peak of element i ;

$T(E)$ is the relative response at E ;

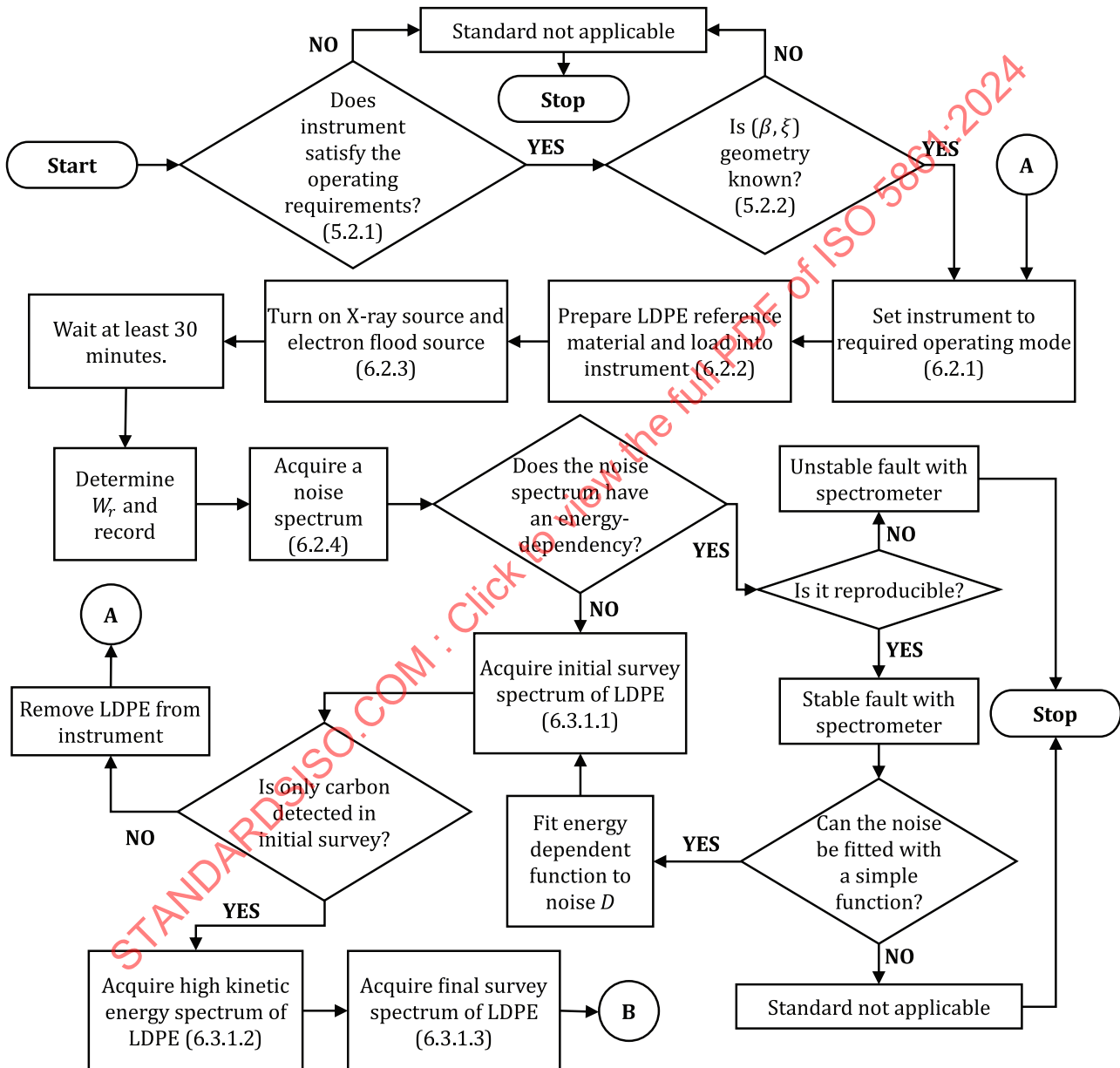
E_i is the kinetic energy of the selected peak of element i ;

j is the set of all elements detected in the sample.

Annex A (informative)

Flow charts

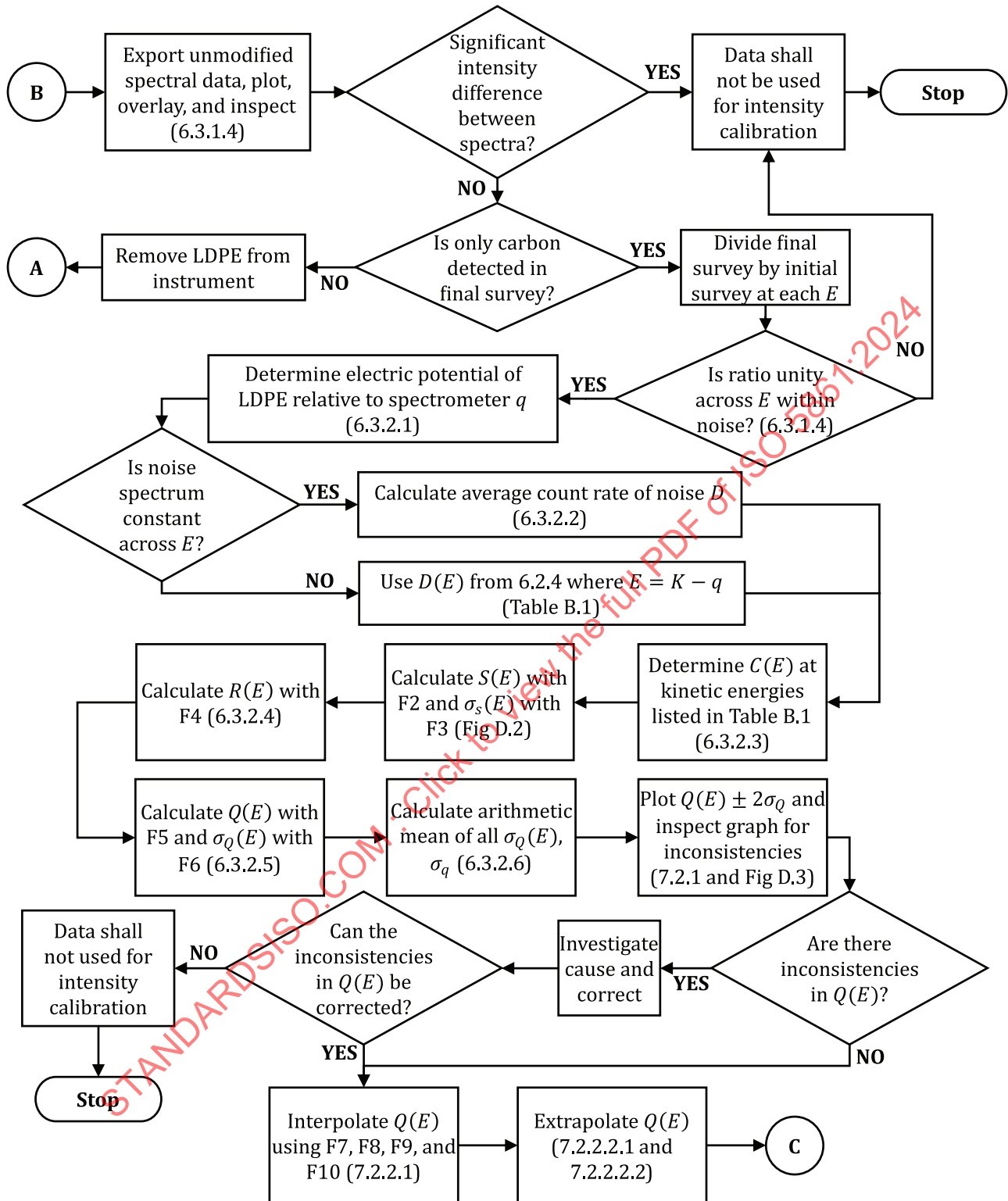
A.1 Flow chart for instrument set-up and acquisition of data



NOTE 1 Point "A" connects to the earlier point "A".

NOTE 2 Point "B" connects to the flow chart in [Figure A.2](#)

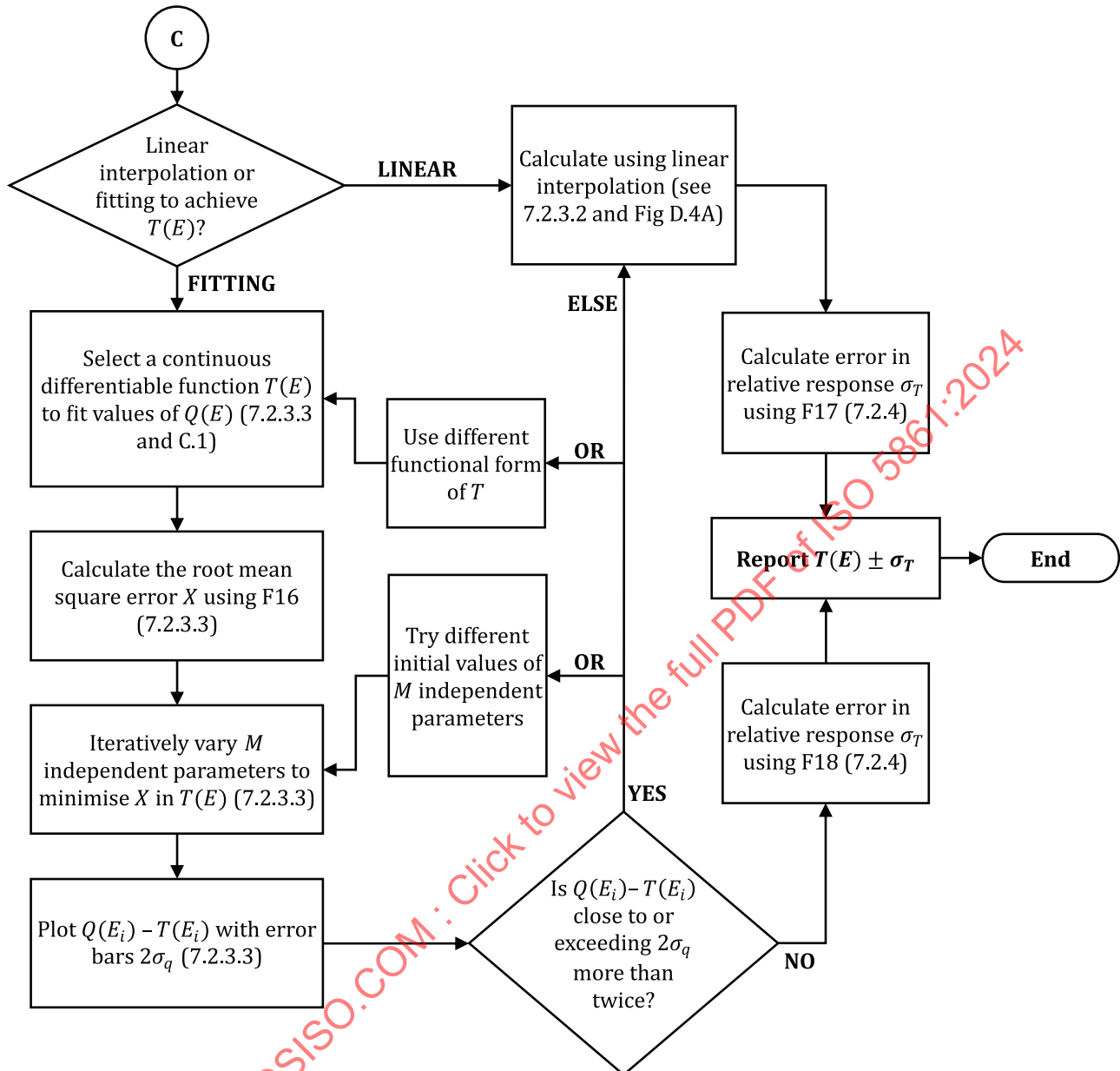
Figure A.1 — Flow chart of the instrument set-up and acquisition of the LDPE spectra.

A.2 Flow chart for inspection of data and determining $Q(E)$ 

NOTE 1 Point "A" connects to the flow chart in [Figure A.1](#)

NOTE 2 Point "C" connects to the flow chart in [Figure A.3](#)

Figure A.2 — Flow chart for the inspection of LDPE spectra and the process of determining $Q(E)$

A.3 Flow chart for fitting $Q(E)$ to obtain $T(E)$ Figure A.3 — Flow chart for the process of fitting $Q(E)$ to obtain $T(E)$

Annex B

(normative)

Table of reference kinetic energies and intensities for LDPE

B.1 Reference values and geometry corrections

[Table B.1](#) provides a list of kinetic energies and intensity parameters, I and F , for LDPE for use in [Formula \(4\)](#). It also lists values of LDPE reference intensities, R , for commonly used detection angles with $\xi = 180^\circ$. Reference intensity values are internally consistent, with a relative error in their ratios of approximately 2 %.^[5] The absolute values, which are not important for practical purposes, have a relative error of approximately 10 %.

Table B.1 — List of reference intensity parameters and values

K (eV)	I (I_X)	F	R (I_X) for detection angle β		
			$\beta = 45^\circ$	$\beta = 54,7^\circ$	$\beta = 60^\circ$
180	6,062	-0,247	6,711	6,387	6,210
212	6,670	-0,199	7,247	6,960	6,802
244	7,976	-0,155	8,513	8,245	8,099
308	3,408	-0,077	3,522	3,465	3,434
340	3,598	-0,043	3,665	3,632	3,613
372	3,806	-0,012	3,826	3,816	3,811
404	4,031	0,015	4,004	4,017	4,025
436	4,271	0,041	4,196	4,233	4,254
468	4,524	0,064	4,398	4,461	4,495
500	4,787	0,086	4,609	4,698	4,746
532	5,056	0,106	4,823	4,939	5,002
564	5,327	0,126	5,037	5,182	5,261
596	5,599	0,145	5,247	5,422	5,518
628	5,868	0,164	5,450	5,658	5,772
660	6,133	0,183	5,644	5,888	6,021
692	6,394	0,204	5,829	6,110	6,264
724	6,652	0,225	6,003	6,327	6,504
756	6,911	0,247	6,170	6,540	6,742
788	7,175	0,271	6,331	6,752	6,982
820	7,449	0,297	6,489	6,967	7,229
852	7,738	0,325	6,647	7,191	7,489
884	8,051	0,355	6,810	7,428	7,767
916	8,393	0,388	6,979	7,684	8,070
948	8,771	0,424	7,156	7,961	8,402
980	9,192	0,463	7,343	8,265	8,769
1 012	9,661	0,506	7,538	8,596	9,175
1 044	10,182	0,553	7,739	8,957	9,623
1 076	10,762	0,604	7,941	9,347	10,116
1 108	11,403	0,659	8,138	9,766	10,656

Table B.1 (continued)

K (eV)	I (I _X)	F	R (I _X) for detection angle β		
			$\beta = 45^\circ$	$\beta = 54,7^\circ$	$\beta = 60^\circ$
1 140	12,109	0,720	8,323	10,211	11,243
1 268	0,384	0,512	0,298	0,341	0,364
1 300	0,399	0,559	0,302	0,350	0,376
1 332	0,420	0,610	0,308	0,364	0,394
1 364	0,446	0,667	0,317	0,381	0,417
1 396	0,478	0,728	0,327	0,402	0,443
1 428	0,513	0,795	0,336	0,425	0,473

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Annex C

(informative)

A fitting curve for relative response

C.1 A rational function

A rational function which has been used to describe electron spectrometer response functions is provided in [Formula \(C.1\)](#). This function can usefully describe most, but not all, response functions and can be used in conjunction with [7.2.3.3](#) noting that $M = 9$. If this formula is employed, the fitting algorithm must ensure that the divisor is positive throughout the full range of E . It is also worth noting that this functional form, after fitting, tends to diverge rapidly outside the extended range of $Q(E)$.

$$T = \frac{\sum_{i=0}^4 c_i \left(\frac{E}{1\ 000} - 1 \right)^i}{1 + \sum_{j=1}^4 d_j \left(\frac{E}{1\ 000} - 1 \right)^j} \quad (\text{C.1})$$

where

T is the relative response function;

E is the analyser kinetic energy in eV;

c_i are a set of five polynomial coefficients used as variable fitting parameters, $i = 0$ to 4;

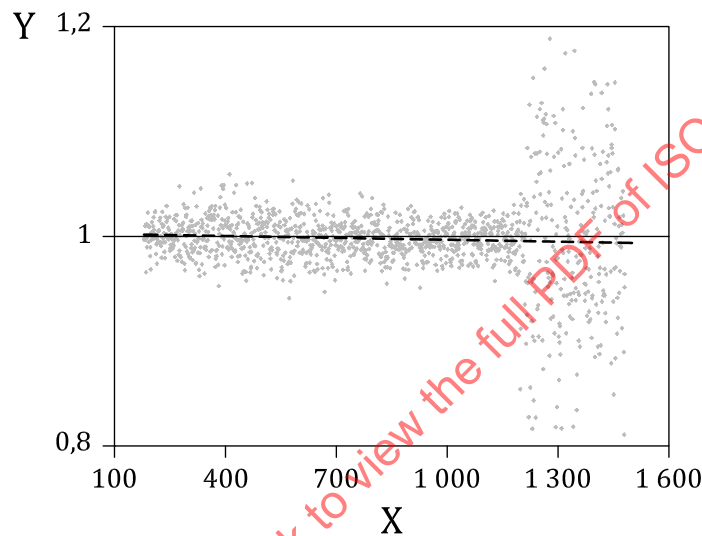
d_j are a set of four polynomial coefficients used as variable fitting parameters, $j = 1$ to 4;

Annex D (informative)

Examples

D.1 Example of an intensity calibration

Data was acquired from an XPS instrument which has $\beta = 60^\circ$ and $\xi = 180^\circ$ in accordance with 6.2 and 6.3. The geometry factor from Formula (1) is $g = -0,099\ 3$, see 5.2.2. The ratio between the final and the initial survey spectra are shown to have no significant difference in Figure D.1, see 6.3.1.4.



Key

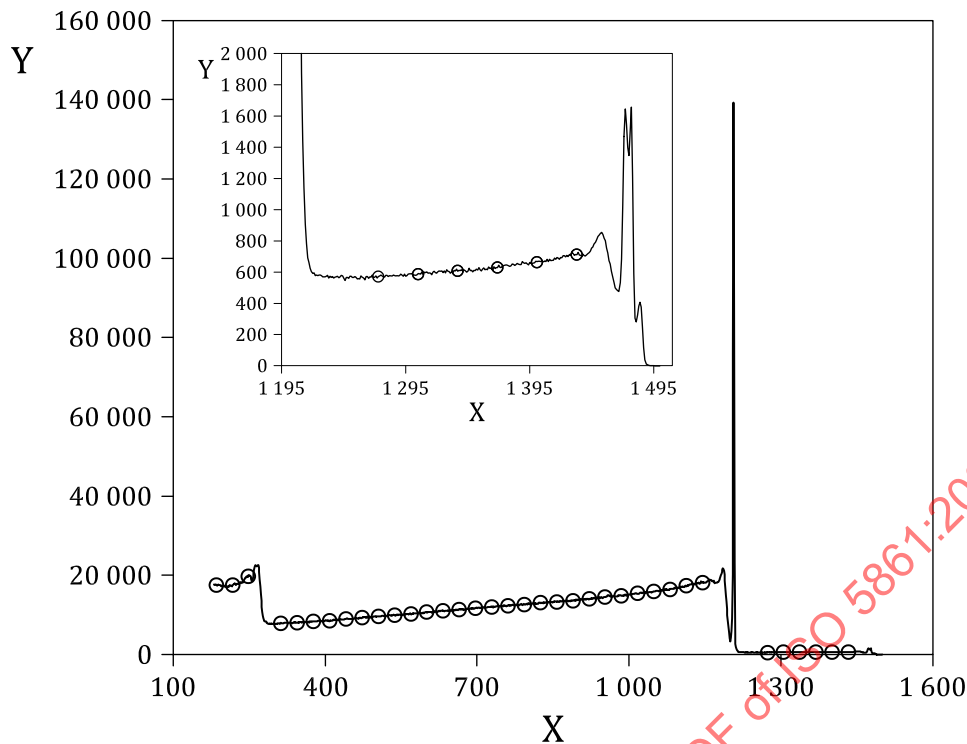
X analyser kinetic energy, E (eV)

Y ratio of final to initial counts in spectrum

Figure D.1 — Ratio of first and last survey spectra

In Figure D.1 the data are shown as points and the dashed line is a linear fit which demonstrates negligible difference from unity. The mean ratio is 0,997 and the slope of the ratio is $-6,2 \times 10^{-6} \text{ eV}^{-1}$ which are both within the acceptable limits defined in 6.3.1.4.

A complete survey scan, compiled as the average of all data and indicating the regions selected to obtain the set of signal rates, S , is shown in Figure D.2. From the peak position of the C 1s peak at $E = 1\ 206 \text{ eV}$, the value of the LDPE potential is determined the be $q = -5 \text{ eV}$, see 6.3.2.1. The noise rate was found to be $D = 4,0 \text{ s}^{-1}$ and this has been subtracted from the raw data, C , see 6.3.2.3.

**Key**X analyser kinetic energy, E (eV)Y signal rate, S (s^{-1})**Figure D.2 — The spectrum of clean LDPE**

In [Figure D.2](#) the data are shown as a solid line. Positions used for intensity calibration are indicated by circles. The inset is an expansion to show the high kinetic energy region which has low intensity. The inset shows the double-peak structure of the C 2s peak shape which is characteristic of poly(ethylene).

The regions shown in [Figure D.2](#) are used to obtain values of S . The reference intensities, R , are calculated using [Formula \(4\)](#), see [6.3.2.4](#). The values of the throughput, Q , are calculated from S and R using [Formula \(5\)](#), see [6.3.2.5](#), and [Formula \(6\)](#) is used to obtain the standard uncertainty of the relative throughput, σ_Q . The mean value of σ_Q was determined to be $16,6 I_X^{-1} s^{-1}$, see [6.3.2.6](#). The values of Q are plotted, in accordance with [7.2.1](#) in [Figure D.3](#) b) along with the final, fitted function of T for comparison. There are no values of Q that appear inconsistent. For information and to show the effect of using an incorrect value of g , [Figure D.3](#) a) shows the result if $\beta = 50^\circ$ is erroneously used and [Figure D.3](#) c) shows the result if $\beta = 70^\circ$ is used. The discontinuity, which manifests as a step in Q at $E \approx 1\,200$ eV, is annotated in [Figure D.3](#) a) and c).