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Microbeam analysis — Analytical electron microscopy — Calibration procedure of energy scale for elemental analysis by electron energy loss spectroscopy

Analyse par microfaisceaux — Microscope électronique analytique — Procédure d'étalonnage de l'échelle d'énergie pour l'analyse élémentaire par spectroscopie de perte d'énergie des électrons

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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.

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This document was prepared by Technical Committee ISO/TC 202, *Microbeam analysis*, Subcommittee SC 3, *Analytical electron microscopy*.

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

The electron energy loss spectroscopy (EELS) is an effective method for elemental analysis with high spatial resolution. In a transmission electron microscope (TEM) or a scanning TEM (STEM), incident electrons irradiating a sufficiently electron transparent sample, such as thin foil samples, are scattered by the atoms in the sample. Inelastically scattered electrons are analysed to identify elements in the sample by a spectrometer. All elements from hydrogen to uranium are identified based upon comparisons of the peak energies and shapes of the core-loss edges, with table of peak energies and spectra in handbooks for the different elements. To identify specific element core-loss peaks, calibration of the EEL spectrometer to an uncertainty of ±3 % is generally adequate for energy range 0 eV to 3 000 eV. This document details the procedure for the energy calibration intended for work at that level of accuracy.

Determination of a sample to be suitably electron transparent can be established by the EELS log ratio technique (t/λ) for specimen thickness. For further details on the determination of relative specimen thickness using the EELS log ratio technique (t/λ), see Reference [1].

Microbeam analysis — Analytical electron microscopy — Calibration procedure of energy scale for elemental analysis by electron energy loss spectroscopy

1 Scope

This document specifies a calibration procedure of the energy step and the energy scale for electron energy loss spectroscopy in (scanning) transmission electron microscopes to an uncertainty of ±3 % for the energy range 0 eV to 3 000 eV.

This document is intended for electron energy loss spectroscopy with transmitted electrons through sufficiently electron transparent samples, such as a thin foil sample, and is not designed for backscattered electrons from a bulk sample.

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 15932, *Microbeam analysis — Analytical electron microscopy — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 15932 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
acceptance angle
γ
half of the angle formed by an entrance aperture to the EEL spectrometer

Note 1 to entry: See Figure 1.

3.2
channel
range of one pixel in the *parallel detector* (3.13)

3.3
collection angle
β
half of the angle formed by an objective aperture in a transmission electron microscope

Note 1 to entry: See Figure 1.

3.4
convergence angle
α
half of the angle of an electron beam focused by a condenser lens in a transmission electron microscope

Note 1 to entry: See Figure 1.

3.5
core-loss
energy loss of an electron in the beam caused by excitation of an inner shell electron

[SOURCE: ISO 15932:2013, 2.2.2.4]

3.6
core-loss edge onset
beginning position of a core-loss edge

Note 1 to entry: See Figure 3.

3.7
core-loss peak
peak maximum position of a core-loss edge

Note 1 to entry: See Figure 3.

3.8
EEL spectrometer
equipment of electrons energetically dispersed by electrostatic/electromagnetic elements and detected by:

- direct electron detectors in *serial detection* (3.17),
- scintillator and a photomultiplier in *serial detection* (3.17),
- a scintillator and a *photodiode array* (3.14) in parallel detection, and
- optical lens coupled with scintillator and CCD/CMOS in parallel detection

3.9
elastically scattered electron
electron scattering in which energy and momentum are conserved in the collision system

[SOURCE: ISO 15932:2013, 2.2.1]

3.10
energy step
energy (eV) per one *channel* (3.2) in a spectrometer

3.11
in-column EEL spectrometer
EEL spectrometer (3.8) located in the imaging system of the TEM

3.12
inelastically scattered electron
electron scattering in which energy and/or momentum are not conserved in the collision system

Note 1 to entry: For inelastic scattering, the electron trajectory is modified by plasmon loss, core loss and other multiple inelastic scatterings.

[SOURCE: ISO 15932:2013, 2.2.2]

3.13

parallel detector

simultaneous detector for energy-dispersed electrons using a *photodiode array* (3.14) or CCD or CMOS

Note 1 to entry: See Figure 1.

3.14

photodiode array

group connected by light tubes to the scintillator positioned at the energy dispersion plane, which detects the energy of electrons simultaneously

3.15

plasmon-loss

type of energy loss in EEL in which the incident electron is affected by the collective oscillations of free electrons in the specimen and loses kinetic energy as a result

[SOURCE: ISO 15932:2013, 2.2.2.2]

3.16

post-column EEL spectrometer

EEL spectrometer (3.8) located behind the imaging/detecting system of the TEM

3.17

serial detection

single channel detection in serial times along the energy axis

3.18

zero-loss

unscattered and *elastically scattered electrons* (3.9) (with only minimal loss of energy due to phonon excitation), giving rise to an intensity peak or the position of which defines zero in the EEL spectrum

[SOURCE: ISO 15932:2013, 2.2.1.1]

4 Symbols and abbreviated terms

CCD	charge coupled device
D	measured energy step of the spectrometer, in eV / channel
dV	change of voltage applied to the drift tube in the magnetic prism
EEL	electron energy loss
EELS	electron energy loss spectroscope/spectroscopy
Ei	measured core-loss edges of the elements to be analysed, i, in eV
STEM	scanning transmission electron microscope/spectroscopy
TEM	transmission electron microscope/spectroscopy
Xi	measured positions of zero-loss peak and core-loss edges, i, in channel

5 Energy calibration and its determination methods

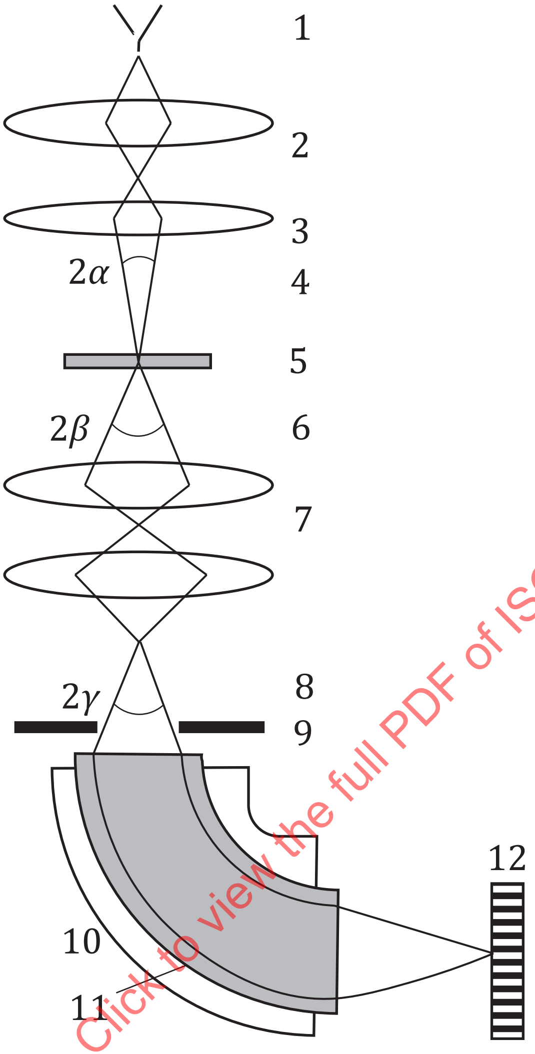
5.1 Equipment

This document is intended for in-column EEL spectrometer, post-column EEL spectrometer and alternative EEL spectrometer. EEL spectrometers basically work under the same principle as the post-column EEL spectrometer. Since the post-column EEL spectrometer is widely used, it is adopted as the typical EEL spectrometer. A serial detection system in the EEL spectrometer acquires a spectrum by changing the energy in serial times, where the energy loss spectra are recorded sequentially. Since serial times along the energy axis of serial detection can be replaced with multiple channels of parallel detection, parallel detection is adopted as the model detection in this document.

For the electron energy loss spectroscopy, the apparatus should consist of a spectrometer dispersing the electron energy and a TEM or a STEM with an electron gun and electromagnetic lens system for focusing the electron beam and imaging (see Figure 1).

The spectrometer consists of the following (see Figure 1):

- the entrance aperture which allows transmitted electrons within the acceptance angle to enter the magnetic prism;
- the magnetic prism which disperses transmitted probe electrons into a spectrum based on their energy;
- the parallel detector which is a simultaneous detection system of electron energies using a photodiode array or CCD or CMOS;
- the drift tube which accelerates velocities of electrons within a magnetic prism.



Key

1	electron source	7	lenses
2	condenser lens	8	acceptance angle
3	probe-forming lens	9	entrance aperture
4	convergence angle	10	magnetic prism
5	specimen	11	drift tube
6	collection angle	12	parallel detector

Figure 1 — Schematic diagram of incident beam, sample, scattered electrons and spectrometer, which consists of an entrance aperture, a magnetic prism, a drift tube and a parallel detector

5.2 Calibration procedure for energy step and energy scale

5.2.1 General

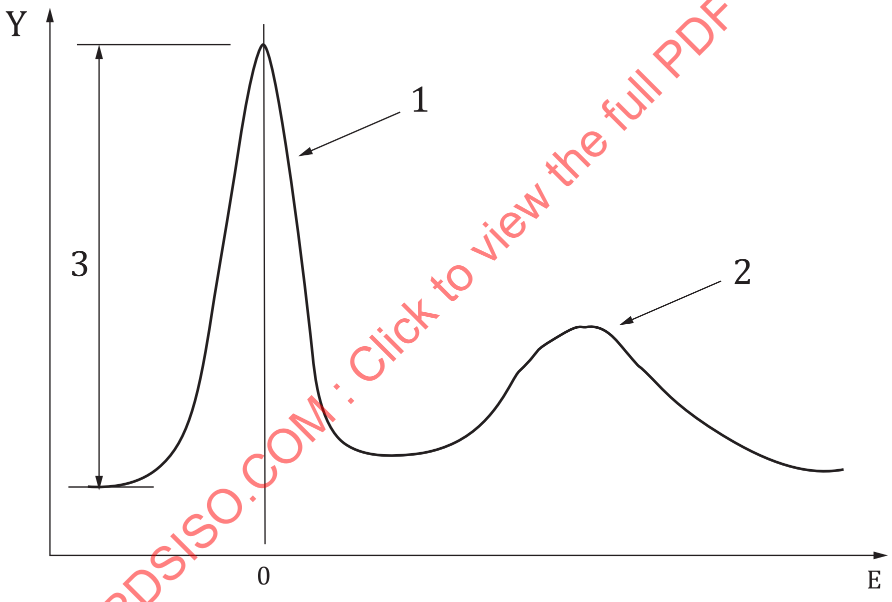
When detecting electron energy loss spectra by a parallel detector, both the energy step and the energy scale should be calibrated. The energy step should be calibrated before the energy scale calibration. The energy scale needs to be calibrated for every run of EELS analysis, but the energy step calibration does not need for every run. The absolute energy scale needs an accuracy of ±3 % to identify elements of core-loss edges.

In the parallel-type spectrometer, the energy range of a parallel detector is not wide (one or two hundreds eV) when high energy resolution is necessary for measurement. The energy width of 100 eV to 200 eV on the parallel detector such as 0 eV to 100 eV or 300 eV to 500 eV is not so wide to measure two or more kinds of core-loss edge. Energy shift is required to measure them separately. Because the energy shift (jump) is adjusted by ramping the drift tube voltage in a magnetic prism, the shift of the voltage should be calibrated to correspond to the well-calibrated energy axis on the monitor screen before energy scale calibration. If the ramping voltages of the magnetic prism are not correct, the drift tube voltage in the magnetic prism should be calibrated as described in Annex A.

5.2.2 Definition of peak positions

5.2.2.1 Zero-loss position

Unscattered and elastically scattered electrons almost without energy loss create a large and sharp peak in a spectrum. The speed of acquisition should be selected as the signal is not saturated. In accordance with the instruction manual, the energy resolution and the energy scale, respectively, should be adjusted to the minimum width of the zero-loss spectrum and zero-loss peak to the position of energy zero on the energy-loss scale. The peak position is defined as the position showing maximum intensity. The zero-loss position defines the zero of energy axis of the EEL spectrum as shown in Figure 2.



Key

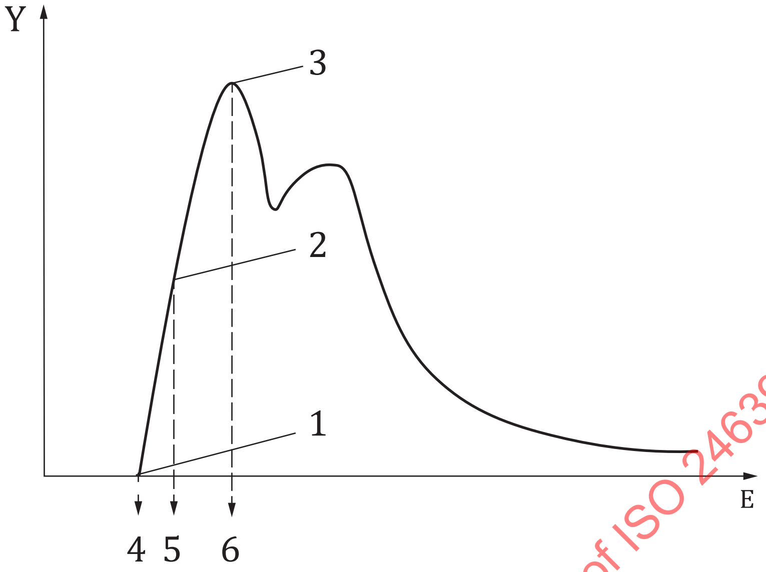
Y	signal intensity	1	zero-loss peak
E	energy loss	2	plasmon-loss peak
		3	maximum intensity

Figure 2 — Example of the zero-loss peak

5.2.2.2 Core-loss position

Core-losses occur mostly at energy losses above 100 eV. The location of core-loss is an important parameter, which can be used as elemental labelling and chemical state analysis. The edge of core-loss is not symmetric and superimposed upon a monotonically decreasing background. To measure an onset energy of core-loss edge, the background signals in the range of core-loss edge should be estimated with the power law equation by using the pre-edge signals of the core-loss edge and the raw signals should be subtracted with the estimated background signals of the core-loss edge range. Further the core-loss involves the plural scattering contribution by plasmon-loss. Thus, the location cannot be easily defined.

If the onset of the core-loss is clear, the location is defined as at the onset of the edge (core-loss edge onset). Otherwise, the location is defined as at the edge maximum as shown in Figure 3.



Key

Y	signal intensity	3	edge maximum
E	energy loss	4	energy of edge onset
1	edge onset	5	energy of midpoint of edge onset
2	midpoint of edge onset	6	energy of edge maximum

Figure 3 — Example of a core-loss peak and its position

5.2.3 Calibration for energy step

5.2.3.1 General

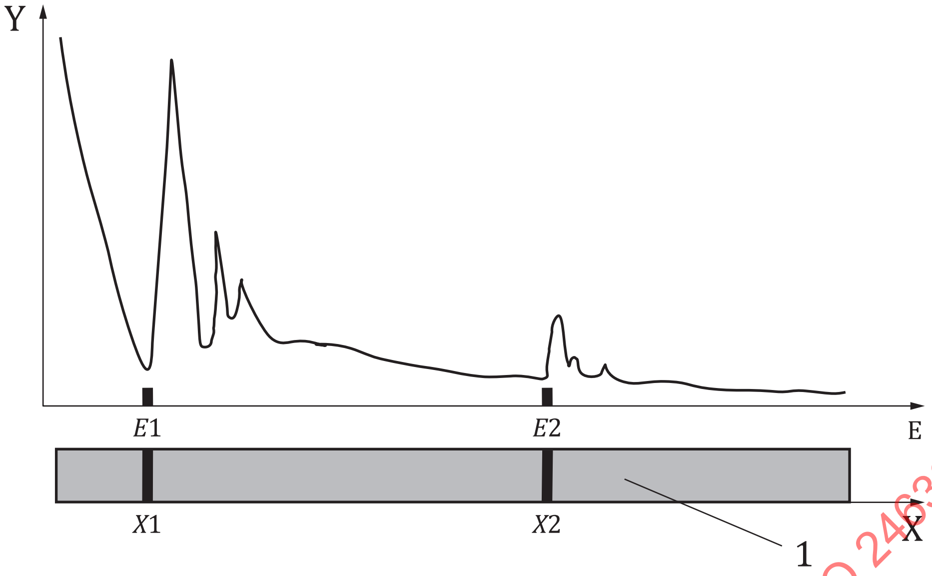
In any parallel-type spectrometer, there are two kinds of method for the energy step calibration. One is that two core-loss edges of the reference materials are detected (Method 1.1). The second method determines the energy step as a result of changes to the zero-loss peak after changing the drift tube voltage (Method 1.2).

Since the energy step depends on the distance from a crossover point for the spectrometer to the entrance point of the spectrometer, the energy step should be calibrated when the distance is changed. Linearity of the energy step should be estimated as described in Annex B.

5.2.3.2 Method 1.1-Two core-loss edges dispersion calibration method

Two core-loss edges, which are $E1$ and $E2$ (eV), of different reference materials should be observed on the parallel detector at $X1$ and $X2$ channels, respectively, Figure 4. The energy step (D) is given by dividing the energy difference of ($E2 - E1$) by the distance from $X2$ to $X1$ channel using Formula (1);

$$D = (E2\text{-}E1)/(X2\text{-}X1) \tag{1}$$



Key

X channel number

Y signal intensity

E energy loss

1 parallel detector

Figure 4 — Schematic diagram of EEL spectrum of two core-loss edges and a parallel detector

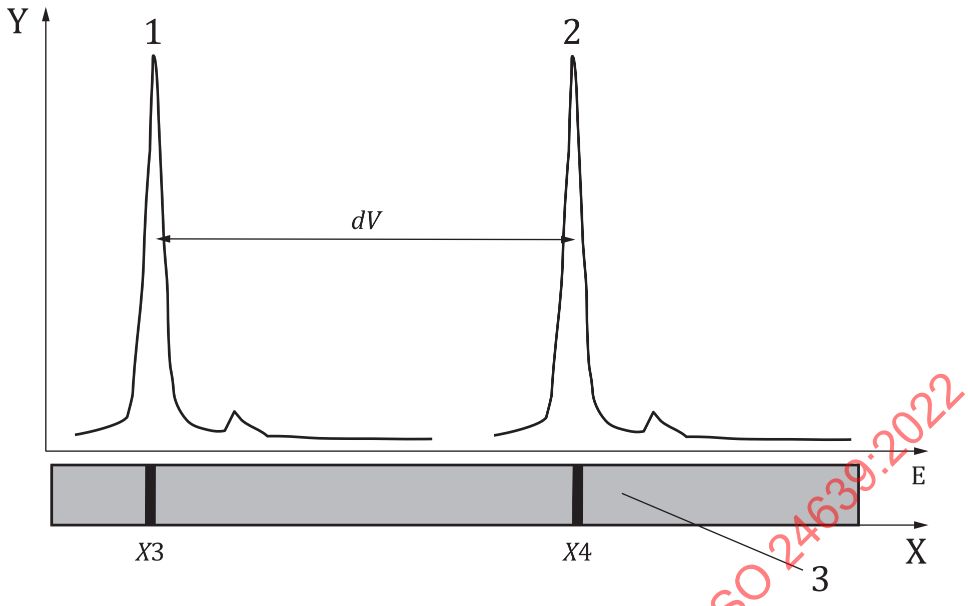
5.2.3.3 Method 1.2-Zero-loss peak dispersion calibration method

The energy step can also be calibrated by changing the position of the zero-loss peak as follows.

At first, the position of zero-loss peak (see Figure 5, key 1) should be recorded as channel $X3$ in a certain condition of the system. Next, by changing the voltages of the drift tube in the magnetic prism by dV (V), the zero-loss peak on the parallel detector should be shifted by more than 50 % of channels of the parallel detector span from $X3$ to $X4$ (channel) (see Figure 5, key 2).

The energy step (eV/channel) of the spectrometer is calibrated using Formula (2):

$$D = dV/(X4 - X3) \qquad (2)$$



Key

X	channel number	1	zero-loss peak
Y	signal intensity	2	shifted from 1 by *dV*
E	energy loss	3	parallel detector

Figure 5 — Schematic diagram of EEL spectrum of zero-loss peak and a parallel detector

5.2.4 Calibration for energy scale

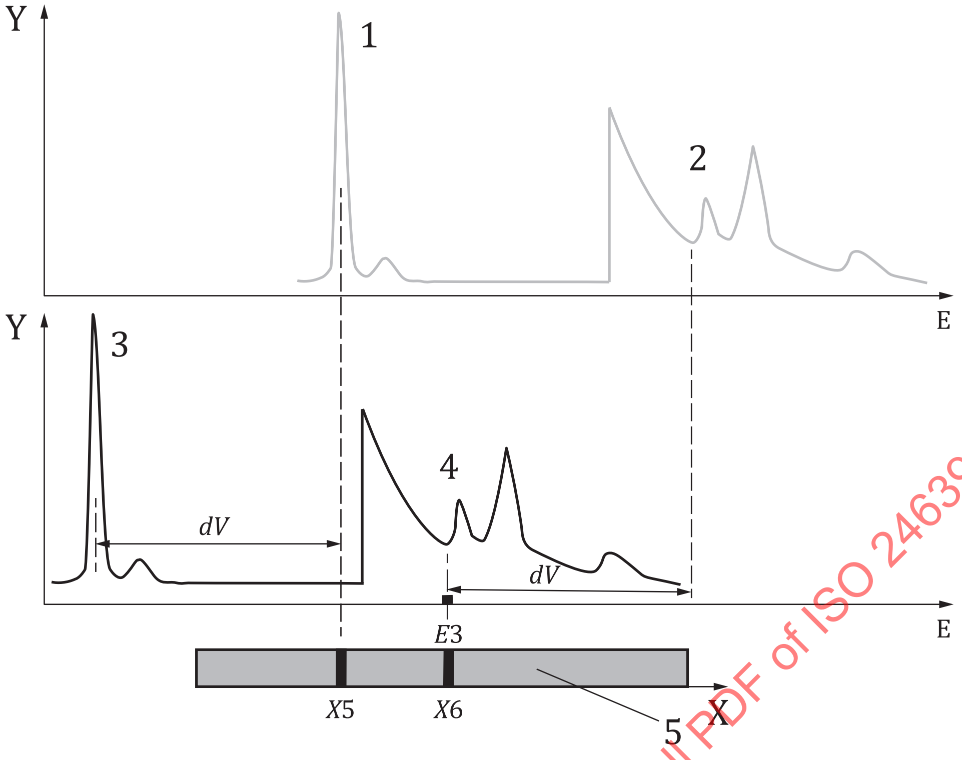
5.2.4.1 General

When the energy step has been already calibrated, in order to calibrate energy scale it is necessary to detect the zero-loss peak (Method 2.1) or a core-loss edge of the reference material (Method 2.2) on the parallel detector.

5.2.4.2 Method 2.1-Zero-loss peak energy scale calibration method

It should be noted that the position of a peak can be shifted when high speed acquisition is used for the zero-loss and longer acquisition are used for core-losses. At first, the position of zero-loss peak (see Figure 6, key 1) should be recorded as channel $X5$ in a certain condition of the system (see Figure 6, grey line). Next, by changing the voltages of the drift tube in the magnetic prism by dV (V), a core-loss edge (see Figure 6, key 4) of a sample should be on the parallel detector (see Figure 6, black line). The position of the core-loss edge should be recorded as channel $X6$. The energy of the core-loss edge, $E3$, is defined as Formula (3):

$$E3 = dV + D \cdot (X6 - X5) \tag{3}$$



Key

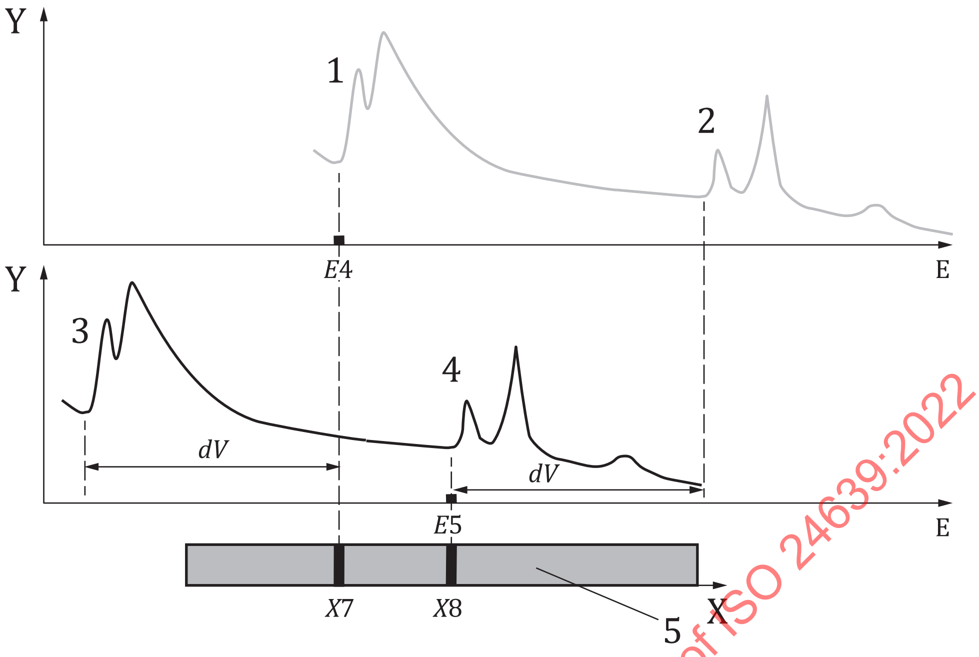
X	channel number
Y	signal intensity
E	energy loss
1	zero-loss peak
2	core-loss peak
3	zero-loss peak shifted by *dV*
4	core-loss peak shifted by *dV*
5	parallel detector

Figure 6 — Schematic diagram of EEL spectrum of zero-loss peak, core-loss edge and a parallel detector

5.2.4.3 Method 2.2-Core-loss edge energy scale calibration method

At first, the position of a core-loss edge (see Figure 7, key 1), which is $E4$, of the reference material should be recorded as channel $X7$ in a certain condition of the system, (see Figure 7, grey line). Next, by changing the voltages of the drift tube in the magnetic prism by dV (V), a core-loss edge of a sample (see Figure 7, key 4) should be on the parallel detector, (see Figure 7, black line). The position of the core-loss edge should be recorded as channel $X8$. The energy of the core-loss edge, $E5$, is defined as Formula (4);

$$E5 = E4+dV+D\cdot(X8-X7) \tag{4}$$



Key

X	channel number
Y	signal intensity
E	energy loss
1	core-loss edge of the reference material
2	core-loss edge of a sample
3	core-loss edge of the reference material shifted by *dV*
4	core-loss edge of a sample shifted by *dV*
5	parallel detector

Figure 7 — Schematic diagram of EEL spectrum of core-loss edges and a parallel detector

NOTE Calibration frequency for the energy scale is dependent on the energy drift of the instrument consisting of a (S)TEM and a spectrometer. Before or after measuring the core-loss edge to be analysed, the energy scale should be calibrated using zero-loss peak and/or a core-loss edge of the reference material. If the core-loss edge of the reference element is simultaneously observed in the electron energy loss spectrum of the element to be analysed, the energy scale can be calibrated using the core-loss edge of the reference element.

5.2.5 Reference materials

The reference material and its energy loss peak should be selected so that both the energy loss peaks of a sample and the reference material exist on the same chart of the spectrum. Materials, which are sufficiently homogeneous and stable in EELS analysis, are available as reference materials. The reference materials and their loss energy peaks for the energy calibration are recommended as follows:

— graphite (maximum of π* peak = 285,4 eV);

— amorphous carbon (edge onset = 284,0 eV);

— NiO (Ni L_3 maximum = 853,2 eV);

— silicon (K edge onset = 1 839 eV).

6 Test report

The report shall include at least the following:

a) the title of the ISO method used;