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Microbeam analysis — Quantitative analysis using energy-dispersive spectrometry (EDS) for elements with an atomic number of 11 (Na) or above

Analyse par microfaisceaux — Analyse élémentaire quantitative par spectrométrie à sélection d'énergie (EDS) des éléments ayant un numéro atomique de 11 (Na) ou plus

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 22309 was prepared by Technical Committee ISO/TC 202, *Microbeam analysis*.

This second edition cancels and replaces the first edition (ISO 22309:2006), of which it constitutes a minor revision. The main changes are as follows:

— the title has been modified to make it quite clear that the method is not suitable for light elements with an atomic number of less than 11;

— Subclause 6.2 has been modified to take into account the use of silicon drift detectors.

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Introduction

X-rays generated when a high-energy electron beam interacts with a specimen have energies (wavelengths) which are characteristic of the chemical elements (atom types) present in the specimen. The intensity of these X-rays from each element is related to the concentration of that element in the specimen. If these intensities are measured, compared with those from a suitable reference material or set of reference materials, and corrected in an appropriate manner, the concentration of each element can be determined. “Standardless” procedures also provide quantitative information, but involve a comparison with previously measured reference intensities that are stored within the software package or are calculated theoretically; such procedures may, depending on any assumptions made, be inherently less accurate than the method employing reference materials (see References [1] to [8] in the Bibliography). There are two common methods of detecting the characteristic X-rays that are produced, one which relies on wavelength dispersive spectrometry (WDS) and the other which uses energy-dispersive spectrometry (EDS). This International Standard relates to the latter, EDS.

Using EDS, the quantitative analysis of light elements (i.e. atomic number $Z < 11$, below Na) is more complex and some of the problems are discussed in this International Standard.

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Microbeam analysis — Quantitative analysis using energy-dispersive spectrometry (EDS) for elements with an atomic number of 11 (Na) or above

1 Scope

This International Standard gives guidance on the quantitative analysis at specific points or areas of a specimen using energy-dispersive spectrometry (EDS) fitted to a scanning electron microscope (SEM) or an electron probe microanalyser (EPMA); any expression of amount, i.e. in terms of percent (mass fraction), as large/small or major/minor amounts is deemed to be quantitative. The correct identification of all elements present in the specimen is a necessary part of quantitative analysis and is therefore considered in this International Standard. This International Standard provides guidance on the various approaches and is applicable to routine quantitative analysis of mass fractions down to 1 %, utilizing either reference materials or "standardless" procedures. It can be used with confidence for elements with atomic number $Z > 10$.

Guidance on the analysis of light elements with $Z < 11$ is also given.

NOTE With care, mass fractions as low as 0,1 % are measurable when there is no peak overlap and the relevant characteristic line is strongly excited. This International Standard applies principally to quantitative analyses on a flat polished specimen surface. The basic procedures are also applicable to the analysis of specimens that do not have a polished surface but additional uncertainty components will be introduced.

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There is no accepted method for accurate quantitative EDS analysis of light elements. However, several EDS methods do exist. These are the following:

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a) Measuring peak areas and comparing intensities in the same way as for heavier elements. For the reasons explained in Annex D, the uncertainty and inaccuracy associated with the results for light elements will be greater than for the heavier elements.

b) Where the light element is known to be combined stoichiometrically with heavier elements ($Z > 10$) in the specimen, its concentration can be determined by summing the appropriate proportions of concentrations of the other elements. This is often used for the analysis of oxygen in silicate mineral specimens.

c) Calculation of concentration by difference where the light element percentage is 100 % minus the percentage sum of the analysed elements. This method is only possible with good beam-current stability and a separate measurement of at least one reference specimen and it requires very accurate analysis of the other elements in the specimen.

Annex D summarizes the problems of light element analysis, additional to those that exist for quantitative analysis of the heavier elements. If both EDS and wavelength spectrometry (WDS) are available, then WDS can be used to overcome the problems of peak overlap that occur with EDS at low energies. However, many of the other issues are common to both techniques.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 14594, *Microbeam analysis — Electron probe microanalysis — Guidelines for the determination of experimental parameters for wavelength dispersive spectroscopy*

ISO 15632:2002, *Microbeam analysis — Instrumental specification for energy dispersive X-ray spectrometers with semiconductor detectors*

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ISO 16700, *Microbeam analysis — Scanning electron microscopy — Guidelines for calibrating image magnification*

ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
absorption correction
matrix correction arising from the loss of X-ray intensity from an element due to photoelectric absorption by all elements within the specimen while passing through it to the detector

3.2
accuracy
closeness of agreement between the "true" value and the measured value

3.3
accelerating voltage
potential difference applied between the filament and anode in order to accelerate the electrons emitted from the source

NOTE Accelerating voltage is expressed in kilovolts.

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3.4
atomic number correction
matrix correction which modifies intensity from each element in the specimen and standards to take account of electron backscattering and stopping power, the magnitudes of which are influenced by all the elements in the analysed volume

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3.5
beam current
electron current contained within the beam

NOTE Beam current is expressed in nanoamperes.

3.6
beam stability
extent to which beam current varies during the course of an analysis

NOTE Beam stability is expressed in percent per hour.

3.7
bremsstrahlung
background continuum of X-rays generated by the deceleration of electrons within the specimen

3.8
certified reference material
CRM
reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body

3.9
characteristic X-ray
photon of electromagnetic radiation created by the relaxation of an excited atomic state caused by inner shell ionization following inelastic scattering of an energetic electron, or by absorption of an X-ray photon

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3.10
dead time
time that the system is unavailable to record a photon measurement because it is busy processing a previous event

NOTE This is frequently expressed as a percentage of the total time (see also live time).

3.11
energy-dispersive spectrometry
EDS
form of X-ray spectrometry in which the energy of individual photons are measured and used to build up a digital histogram representing the distribution of X-rays with energy

3.12
electron probe microanalysis
a technique of spatially resolved elemental analysis based on electron-excited X-ray spectrometry with a focused electron probe and an interaction/excitation volume with micrometre to sub-micrometre dimensions

3.13
escape peaks
peaks that occur as a result of loss of incident photon energy by fluorescence of the material of the detector

NOTE 1 These occur at an energy equal to that of the incident characteristic peak minus the energy of the X-ray line(s) emitted by the element(s) in the detector (1,734 keV for silicon).

NOTE 2 They cannot occur below the critical excitation potential of the detector material, e.g. Si K escape does not occur for energies below 1,838 keV.

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3.14
fluorescence
photoelectric absorption of any X-ray radiation (characteristic or bremsstrahlung) by an atom which results in an excited atomic state which will de-excite with electron shell transitions and subsequent emission of an Auger electron or the characteristic X-ray of the absorbing atom

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3.15
fluorescence correction
matrix correction which modifies the intensity from each element in the specimen and standards to take account of excess X-rays generated from element “A” due to the absorption of characteristic X-rays from element “B” whose energy exceeds the critical (ionization) energy of “A”

3.16
full width at half maximum
FWHM
measure of the width of an X-ray peak in which the background is first removed to reveal the complete peak profile

NOTE FWHM is determined by measuring the width at half the maximum height.

3.17
incident beam energy
energy gained by the beam as a result of the potential applied between the filament and anode

3.18
k-ratio
net peak intensity (after background subtraction) for an element found in the specimen, divided by the intensity, recorded or calculated, of the corresponding peak in the spectra of a reference material

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3.19
live time
time the pulse measurement circuitry is available for the detection of X-ray photons

See also **dead time** (3.10).

NOTE 1 Live time is expressed in seconds (s).

NOTE 2 Live time = real time for analysis − dead time. Real time is the time that would be measured with a conventional clock. For an X-ray acquisition, the real time always exceeds the live time.

3.20
overvoltage ratio
ratio of the incident beam energy to the critical excitation energy for a particular shell and sub-shell (K, LI, LII, etc.) from which the characteristic X-ray is emitted

3.21
peak intensity
total number of X-rays (counts) under the profile of a characteristic X-ray peak after background subtraction

NOTE This is sometimes referred to as the peak integral.

3.22
peak profile
detailed shape of a characteristic peak which depends on the relative intensities and energies of the individual X-ray emissions that are unresolved by the energy-dispersive spectrometer

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3.23
precision
closeness of agreement between the results obtained by applying the experimental procedure several times under prescribed conditions

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3.24
quantitative EDS
procedure leading to the assignment of numerical values or expressions to represent the concentrations of elements measured within the analysis volume

3.25
reference material
RM
material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a method, or for assigning values to materials

NOTE A reference material is said to be homogeneous with respect to a specified property if the property value, as determined by tests on specimens of specified size, is found to lie within the specified uncertainty limits, the specimens being taken either from a single or different supply unit.

3.26
repeatability
closeness of agreement between results of successive measurements of the same quantity carried out by the same method, by the same observer, with the same measuring instruments, in the same laboratory, at quite short intervals of time

3.27
reproducibility
closeness of agreement between the result of measurements of the same quantity, where the individual measurements are made by different methods, with different measuring instruments, by different observers, in different laboratories, after intervals of time that are quite long compared with the duration of a single measurement, under different normal conditions of use of the instruments employed

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3.28
resolution
⟨energy⟩ width of a peak measured by an energy-dispersive spectrometer and expressed as the peak width at half the maximum peak intensity

NOTE This is usually expressed as the value for Mn Kα (5,894 keV), although peaks from other suitable elements can be used.

3.29
resolution
⟨spatial⟩ spatial specificity of microanalysis

NOTE This is usually expressed in terms of a linear or volumetric measure of the region of the specimen that is sampled by the measured characteristic radiation.

3.30
standardless analysis
procedure for quantitative X-ray microanalysis in which the reference peak intensity in the k-value expression (unknown/reference) is supplied from purely physical calculations or from stored data from a suite of reference materials, adjustments being made to match analysis conditions and augment incomplete reference data

3.31
sum peaks
artefact peaks that occur as a result of pulse co-incidence effects that occur within the pulse pair resolution of the pile-up inspection circuitry

NOTE These peaks appear at energies corresponding to the sum of those energies of the two photons that arrive simultaneously at the detector.

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3.32
traceability
ability to trace the history, application or location of an entity by means of recorded identifications

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3.33
uncertainty
that part of the expression of the result of a measurement that states the range of values within which the "true" value is estimated to lie for a stated probability

3.34
validation
confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled

3.35
X-ray absorption
attenuation of X-rays passing through matter, arising primarily from photoelectric absorption for X-ray energies and ranges appropriate to EPMA/EDS and SEM/EDS

4 Specimen preparation

4.1 Material for analysis shall be stable under variable pressure conditions and the electron beam. As-received specimens can be examined after simple cleaning, but surface inhomogeneity or topography will adversely affect the quality of the quantitative analysis.

4.2 For reliable quantitative analysis, the specimen shall present a flat, smooth surface normal to the electron beam. This requirement is usually met by the application of conventional metallographic or petrographic techniques. The area for analysis should be homogeneous over a region, typically a few micrometres in diameter, around the electron beam.

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4.3 Solid specimens can be reduced to an appropriate size, making sure they undergo no transformation during the process. Prior to examination in the as-received condition, all surface debris should be removed using appropriate techniques, such as ultrasonic cleaning.

4.4 Specimens for sectioning should be embedded, where possible, in a conducting medium prior to metallographic or petrographic polishing using standard procedures. The medium shall be chosen with care, to avoid the possibility of the conducting component becoming smeared onto the specimen surface and being mistaken for a component of the specimen by effectively altering the composition of the analysed volume.

NOTE 1 Polishing may be carried through to 1/4 µm grade diamond, provided this can be done without introducing relief effects. Complete removal of all scratches is not essential, provided areas for analysis are clean and relief-free.

Damage to the specimen during preparation should be avoided. Potential damage mechanisms include:

a) the effects of lubricant;

b) the removal of second phases (precipitates);

c) differential polishing of phases with different hardness, thus introducing relief to the surface;

d) strain introduced into the surface;

e) edge curvature.

With cross-sections, the specimen can be coated with a harder material to improve edge retention.

NOTE 2 See ASTM E3[9] for further guidance.

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4.5 If optical examination is to be used for the location of areas for analysis, either prior to or while in the instrument, etching of the specimen may be necessary. The depth of etching should be kept to a minimum, being aware of the possibility of surface compositional changes or the development of undesirable topographic effects. Polishing away the etching may be needed after locating and marking the regions for analysis by reference to existing or added features, such as a scratch or hardness indent.

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4.6 The specimen should have a good conductivity to avoid charge-up generated by electron beam irradiation. The specimen shall be connected to the instrument ground either through a conducting mount, or by a stripe of silver or carbon paint. Any exposed non-conducting mounting material may be covered with a conducting medium to avoid disturbance of the electron beam during analysis.

Carbon to a thickness of about 20 nm can be used as a conductive coating, although a metallic (e.g. aluminium) coating of lesser thickness may be used if carbon is unacceptable.

NOTE Coating with an element already present in the specimen changes the apparent composition of that element in the specimen, the magnitude of the effect being dependent on accelerating voltage and the thickness of the coating.

4.7 The prepared specimens shall be positioned in the instrument stage in such a way that, for the majority of work, the surface can be reliably held normal to the incident electron beam.

4.8 Reference materials should conform to ISO 14595[18] and shall be prepared in a similar way to the unknown specimens, e.g. polished, carbon coated, and positioned in the same orientation relative to the electron beam.

5 Preliminary precautions

5.1 With a suitable vacuum level and the electron beam on, preliminary checks to ensure beam stability (better than 1 % per hour variation in counts from a standard specimen or in beam current as measured with a Faraday cup) and stable detector performance should be made prior to commencing calibration and analysis procedures. Detector stability shall be monitored by measuring the detector resolution and energy calibration (see ISO 15632).

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