# INTERNATIONAL STANDARD

# ISO 17470

First edition
2004-09-01

# Microbeam analysis — Electron probe microanalysis — Guidelines for qualitative point analysis by wavelength dispersive X-ray spectrometry

*Analyse par microfaisceaux — Analyse par microsonde électronique (Microsonde de Castaing) — Lignes directrices pour l'analyse qualitative ponctuelle par spectroscopie de rayons X à dispersion de longueur d'onde*

Reference number
ISO 17470:2004(E)

**PDF disclaimer**

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO 17470:2004

© ISO 2004

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

# Contents

# 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 17470 was prepared by Technical Committee ISO/TC 202, *Microbeam analysis*, Subcommittee SC 2, *Electron probe microanalysis*.

## Introduction

Electron probe microanalysis is used to qualitatively identify the elements present in a specimen on a micrometric scale. It is necessary to specify the measurement conditions and identification method in order to avoid reporting erroneous or inconsistent results.

# Microbeam analysis — Electron probe microanalysis — Guidelines for qualitative point analysis by wavelength dispersive X-ray spectrometry

## 1 Scope

This International Standard gives guidance for the identification of elements and the investigation of the presence of specific elements within a specific volume (on a $\mu m^3$ scale) contained in a specimen, by analysing X-ray spectra obtained using wavelength dispersive X-ray spectrometers on an electron probe microanalyser or on a scanning electron microscope.

## 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 14594:2003, *Microbeam analysis — Electron probe microanalysis — Guidelines for the determination of experimental parameters for wavelength dispersive spectroscopy*

## 3 Terms and definitions

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

**3.1**
**higher order reflections**
peaks appearing at the diffracted angles corresponding to $n = 2, 3, 4\ldots$

NOTE In WDS, X-rays are dispersed according to Bragg's law, $n\lambda = 2d \sin\theta$, where $\lambda$ is the X-ray wavelength, $d$ is the interplanar spacing of the diffraction crystal, $\theta$ is the diffraction angle, and $n$ is an integer. The higher order reflections are the peaks appearing at the diffracted angles corresponding to $n = 2, 3, 4\ldots$

**3.2**
**point analysis**
analysis in which the primary beam is fixed, thus irradiating a selected region of a sample surface

NOTE The method where the primary beam rapidly scans over a very small region on the sample surface is also included. The maximum size of a static beam or a raster area should be chosen such that relative X-ray intensities do not change when enlarging the analysis area.

**3.3**
**Rowland circle**
⟨in a wavelength dispersive X-ray spectrometer⟩ the circle of focus along which the X-ray source, diffractor and detector must all lie in order to satisfy the Bragg condition and obtain constructive interference

### 3.4
### X-ray line table

table of X-ray lines used for qualitative analysis by EPMA

NOTE The X-ray line table for qualitative analysis by EPMA lists the wavelengths of K-, L-, and, M-lines for the elements observed on each diffraction crystal. It may also list their relative intensities, the full width at half maximum (FWHM) of each peak, the interplanar spacings of the diffraction crystals, and the wavelengths of satellite peaks.

## 4 Abbreviated terms

| | |
|---|---|
| EPMA | electron probe microanalysis |
| WDS | wavelength dispersive X-ray spectroscopy or spectrometry |

## 5 Apparatus

Care should be taken to ensure that the instrument is properly adjusted. In particular, it should be ensured that the electron beam is stable and passes properly along the optical axes of each involved lens and each forming and/or limiting aperture, that beam current and accelerating voltage values are suitable for the sample, that the sample surface has been suitably prepared for qualitative analysis, the working distance is correct and that the spectrometer X-ray crystals and counters are aligned, calibrated and showing the signals which have proper intensities and spectral shapes.

NOTE 1 Operators should be aware that parameters such as peak position, relative peak heights, peak resolutions, FWHM values etc., may vary slightly from instrument to instrument, and also from sample to sample. This can be largely corrected for by periodically comparing values with an appropriate X-ray line table and data from appropriate laboratory reference materials.

NOTE 2 If the sample surface is not planar or polished or perpendicular to the beam, care should be taken in determining the actual value of the local take-off angle, and the ability of the spectrometer to properly analyse this kind of sample.

## 6 Procedure for identification

### 6.1 General

X-ray spectra are obtained by directing the incident electron beam at the point to be analysed on the sample surface and scanning the X-ray spectrometers over a specified wavelength range. Qualitative analysis is performed by identifying each peak in the resulting X-ray spectra.

It is necessary to verify whether the peak identified interferes with a peak resulting from another element. Particular care is needed for possible higher order reflections originating from other elements in the sample, usually – but not always – at higher concentrations.

### 6.2 Setting of analysis conditions

#### 6.2.1 Primary beam

The primary beam energy should be higher than the X-ray excitation energies of analysed elements, but low enough to minimize sample damage, contamination of the sample and saturation of the X-ray detectors.

NOTE 1 The Bethe inner shell ionization cross section has a maximum for an overvoltage ratio equal to Napier's number (about 2,7). Taking into account the energy loss of the primary electrons, optimum excitation occurs at overvoltage ratios slightly greater than Napier's number. However, in the case of ultra-light elements and low energy X-rays from other elements (i.e., low energy L- and M-lines), absorption from surface layers can significantly affect the optimum overvoltage causing it to be substantially higher than 2,7.

NOTE 2 The intensity of a generated characteristic X-ray, $I$, is given approximately by Equation (1):

$$I = C \times i\left[\left(E_0 - E_\mathrm{c}\right)/E_\mathrm{c}\right]^{1,7} = C \times i\left(U - 1\right)^{1,7} \qquad (1)$$

where

$C$ is a constant;

$i$ is a primary beam current, in amperes (A);

$E_0$ is a primary beam energy, in kilo-electron volts (keV);

$E_\mathrm{c}$ is a critical excitation energy, in kilo-electron volts (keV);

$U$ is an overvoltage ratio $E_0/E_\mathrm{c}$.

Note that as the primary beam energy increases, the intensity of generated X-rays become larger. Since the depth of the generation also increases, absorption of X-rays leaving the sample occurs, so the intensities of the detected X-rays do not necessarily become proportionally larger. In samples where absorption is particularly high, such as with light elements Be to F, it is recommended that a primary beam energy of 15 keV or less be used to reduce the depth of X-ray generation and hence the absorption effect. In the case of a thin film sample or a powder sample, primary beam energy should be determined by referring to 5.2 of ISO 14594:2003.

The primary beam current should be also set in the range in which sample damage, sample contamination and saturation of the X-ray detectors are minimized.

### 6.2.2 X-ray spectrometer

#### 6.2.2.1 Selection of diffraction crystals

The diffraction crystals selected should be capable of detecting the intended elements, with a maximum peak-to-background ratio and peak resolution, but with minimum interference from peaks of other elements in the sample. Since it is not always possible to optimize all of these parameters simultaneously, the analyst should select the diffraction crystal that will provide the best compromise for the specific analysis requirements.

#### 6.2.2.2 Scanning speed

A scanning speed should be selected that will enable the detection of the anticipated elements at their anticipated concentrations.

NOTE 1 The scanning speed of a digitally scanned spectrometer is defined by the number of steps, the length of a step and the sampling time per step. The number of steps should be high enough and the length of a step should be short enough to sufficiently resolve the shape and height of the detected peaks. In practice a measured peak should contain a minimum of five data points.

NOTE 2 When the signal from the analysed element is low relative to the background, a slower scanning speed should be used.

#### 6.2.2.3 Pulse height analyser

As peaks of higher order reflections, originating from other constituents, appear in WDS spectra, some uncertainty may arise about the presence of elements having a peak in the same position as one of these higher order reflections. In this case, the higher order reflection may be suppressed by using the discrimination of a pulse height analyser. Care should be taken in selecting a proper discrimination window size and baseline level to avoid unnecessary loss of peak intensity from the element of interest. The analyst should confirm proper transmission of signal by analysing an appropriate reference material and comparing the peak height and shape both with and without pulse height discrimination.

## 6.3 Method for analysing an X-ray spectrum

### 6.3.1 Recognition of a peak

Recognition of a peak is done by reference to both its width and its height. In spectra the FWHM of the peak should be nearly equal to the FWHM of the same peak in the X-ray line table or equal to the same peak measured from a laboratory standard. Narrower peaks may be noise spikes and can usually be disregarded. The peak height should be determined by the difference between the peak intensity and the background intensity. The background intensity should be determined in accordance with 6.3.3 of ISO 14594:2003.

NOTE In the case where the peak intensity approaches the background level, if a peak is found by visual examination, the probability of the presence of the peak is given as follows:

If $N_{\mathrm{P}} - \bar{N}_{\mathrm{B}} > 2\sqrt{\bar{N}_{\mathrm{B}}}$, then the confidence level is 97,7 %

$N_{\mathrm{P}} - \bar{N}_{\mathrm{B}} > 3\sqrt{\bar{N}_{\mathrm{B}}}$, then the confidence level is 99,9 %

where

$N_{\mathrm{P}}$ is the peak intensity, expressed in X-ray counts;

$\bar{N}_{\mathrm{B}}$ is the mean background intensity in the vicinity of the peak expressed in X-ray counts;

$\sqrt{\bar{N}_{\mathrm{B}}}$ is the standard deviation of the background intensity in the vicinity of the peak.

The above expressions are explained as follows.

As the distribution of the X-ray counts can be approximated by Gaussian distribution, the standard deviation of the background X-ray counts is given by $\sqrt{\bar{N}_{\mathrm{B}}}$. Therefore, if the height of a suspected peak (in counts) exceeds $\bar{N}_{\mathrm{B}} + 2\sqrt{\bar{N}_{\mathrm{B}}}$ or $\bar{N}_{\mathrm{B}} + 3\sqrt{\bar{N}_{\mathrm{B}}}$ there is a 97,7 % or 99,9 % probability respectively, that they do not originate from the background.

### 6.3.2 Identification of detected peaks

In analysing the X-ray spectra obtained, reliable or traceable X-ray wavelength tables or spectra from laboratory standards should be used. An example X-ray line table is given in reference [2].

NOTE 1 The wavelengths can be either in nanometers (nm) or in kilo-electron volts (keV). The use of ångström (Å) should be avoided.

Identification of the most intense peaks should be carried out first. These should be the first order peaks of the major constituents of the sample. Use the X-ray line tables to match smaller peaks in the spectra with other characteristic lines of these major elements. If possible, it should be confirmed that the positions, relative intensities and the FWHMs of all peaks obtained from other diffraction crystals used agree with those of the X-ray line table. Where the measured peaks do not agree with the X-ray line table values, evidence for underlying peaks from other elements should be looked for.

NOTE 2 Absorption and fluorescence effects, and chemical bonding effects within the sample can modify peak heights and ratios, producing deviations from the values expected from the X-ray line tables in the low energy range.

Repeat this identification procedure for the next largest unidentified peaks until all the peaks present in the spectra have been identified. Confirmation by multiple peaks will become progressively more difficult until, with the minor and trace components, only one peak may be present for some elements.

All unidentified peaks should be marked.

NOTE 3 When the wavelength of a measured peak originates from the transition of an outer shell electron, it may not coincide exactly with the value in the X-ray line table. This discrepancy of wavelength and spectral shape may give some information on the element's chemical state in certain cases.

NOTE 4 In some instances, sample preparation processes may introduce “contaminant” elements into the sample, e.g. polishing or grinding media can become trapped in the surfaces of soft or porous materials. Also, it may be necessary to vacuum evaporate a conducting film on to the sample surface. Care should be taken to distinguish between these artefact elements and those inherently present in the sample.

## 6.4 Detection limit

Even though a given element is not detected in qualitative analysis of a sample, one cannot conclude that the element is not present in the sample. This means only that the concentration of the element is below the detection limit in EPMA. The detection limit can be calculated, if required.

Detection limit is derived from the following equation:

$$\mathrm{DL} = \frac{\alpha\sqrt{\left(2 \times I'_{\mathrm{B}}\right)}}{\left(I_{\mathrm{P}} - I_{\mathrm{B}}\right)\sqrt{t}} \times c \tag{2}$$

where

DL is a detection limit, in mass percent;

$\alpha$ is a constant depending on the confidence level;

$c$ is the concentration of a reference material, in mass percent;

$I_{\mathrm{P}}$ is the peak intensity on the reference material, in counts per second (cps);

$I_{\mathrm{B}}$ is the background intensity on the reference material, in counts per second (cps);

$I'_{\mathrm{B}}$ is the background intensity on the sample, in counts per second (cps);

$t$ is the sampling time in seconds (s) equal for both the peak and the background.

When the concentration of an element approaches the detection limit, the peak intensity from the sample, $I'_{\mathrm{P}}$, and the background intensity, $I'_{\mathrm{B}}$, are close together. As the standard deviation of the net intensity, $\left(I'_{\mathrm{P}} - I'_{\mathrm{B}}\right)$, is given by $\sqrt{\left(I'_{\mathrm{P}} + I'_{\mathrm{B}}\right)}$, it can be approximated by $\sqrt{2I'_{\mathrm{B}}}$. Also, a linear relationship is assumed to hold between X-ray intensity and concentration in a trace analysis. An approximate expression for DL can be derived from these viewpoints.

NOTE 1 In practical use, the analyst may use an approximate equation as follows.

$$\mathrm{DL} = \frac{\alpha\sqrt{\left(2 \times I_{\mathrm{B}}\right)}}{\left(I_{\mathrm{P}} - I_{\mathrm{B}}\right)\sqrt{t}} \times c \tag{3}$$

NOTE 2 This equation does not include matrix effect correction.

NOTE 3 As the concentrations of elements are measured to be less than DL, in certain probability even if the concentrations of the elements are greater than DL, this formula may confirm the absence of elements.

NOTE 4 The probability of taking a wrong decision about the presence/absence of an element is given by 1-$\beta$. $\beta$ is a confidence level and is given as 0,954 or 0,997 if $\alpha$ is equal to 2 or 3, respectively.

## 7 Test report

The test report should include the following information: (see Annex A)

a) the name and address of the laboratory

b) the name and address of the client;

c) the date(s) of performance of the test;

d) the name(s), function(s) and signature(s) of person(s) authorizing the test report;

e) the test results, where relevant;

f) the type of instrument used;

g) take-off angle of the instrument used;

h) primary beam energy;

i) primary beam current;

j) area irradiated by primary beam.

In addition to above details, the test report should include following details, if required:

k) use of pulse height analyser, its threshold and window level;

l) scanning speed of X-ray spectrometer;

m) names of detected elements with identified X-ray lines and diffraction crystals used;

n) peak positions and peak intensities of detected elements and diffraction crystal (if more than one line for the same element is detected, report the stronger line);

o) background intensities corresponding to the peaks of detected elements;

p) X-ray spectral plots (with fully labelled axes);

q) configuration of spectrometer (vertical or inclined), type of counter (flow or sealed and gas type), and pressure of counter (high or low);

r) recent laboratory calibration spectra when appropriate;

s) unidentified peaks;

t) any eventual warning, e.g. if the line $\beta$ was in a scan range but not found or if its intensity is too low.

# Annex A
(informative)

## Example of the test report on qualitative analysis of a stainless steel sample by EPMA

Required items:

| Item | Example |
|---|---|
| a) the name and address of the laboratory: | |
| b) the name and address of the client: | |
| c) the date(s) of performance of the test: | |
| d) the name(s), function(s) and signature(s) of person(s) authorizing the test report: | |
| e) test results, where relevant: | identified elements; Fe, Mn, Cr, Ni, Mo, Ti, Si |
| f) the type of instrument used: | |
| g) take-off angle of the instrument used: | 52,5 degrees |
| h) primary beam energy: | 15,0 keV |
| i) primary beam current: | 0,25 µA |
| j) area irradiated by primary beam: | 100 µm$^2$ |

<table>
<tr><td colspan="5">Additional items:</td></tr>
<tr><th>Item</th><th colspan="4">Example</th></tr>
<tr><td>k) use of pulse height analyser, its threshold and window level</td><td colspan="4">integrated mode, base level: 0,5 V</td></tr>
<tr><td>l) scanning speed of X-ray spectrometer</td><td colspan="4"></td></tr>
<tr><td>m) names of elements detected, their all X-ray lines and diffraction crystals</td><td colspan="4">Fe: Kα(LiF), Kβ(LiF), Lα(TAP), Lβ(TAP), Mn: Kα(LiF), Cr: Kα(LiF), Kβ(LiF), Ni: Kα(LiF), Kβ(LiF), Lα(TAP), Mo: Lα(PET), Lβ(PET), Ti: Kα(PET), Si: Kα(PET)</td></tr>
<tr><td rowspan="9">n) peak positions and intensities of detected elements<br>o) background intensities corresponding to the peaks of detected elements</td><th>Element</th><th>Peak position nm</th><th>Peak intensity counts</th><th>Background intensity counts</th></tr>
<tr><td>Fe (FeKα)</td><td>0,193 402</td><td>4 829</td><td>41</td></tr>
<tr><td>Mn (MnKα)</td><td>0,210 206</td><td>131</td><td>26</td></tr>
<tr><td>Cr (CrKα)</td><td>0,228 931</td><td>1 775</td><td>31,3</td></tr>
<tr><td>Ni (NiKα)</td><td>0,165 562</td><td>621</td><td>35,6</td></tr>
<tr><td>Mo (MoLα)</td><td>0,540 602</td><td>95</td><td>11</td></tr>
<tr><td>Ti (TiKα)</td><td>0,274 321</td><td>87</td><td>66</td></tr>
<tr><td>Si (SiKα)</td><td>0,712 904</td><td>76</td><td>4</td></tr>
<tr><td>Unidentified peak</td><td></td><td></td><td></td></tr>
<tr><td>p) X-ray spectral plots (with fully labelled axes)</td><td colspan="4">See Figure A.1</td></tr>
<tr><td>q) configuration of spectrometer (vertical or inclined), and pressure of counter (high or low)</td><td colspan="4"></td></tr>
<tr><td>r) recent laboratory calibration spectra when appropriate</td><td colspan="4"></td></tr>
<tr><td>s) wavelength of unidentified peaks (nm)</td><td colspan="4"></td></tr>
<tr><td>t) any eventual warning, e.g. if the line $\beta$ was in a scan range but not found or if its intensity is too low</td><td colspan="4"></td></tr>
</table>