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Microbeam analysis — Electron probe microanalysis — Guidelines for determining the carbon content of steels using a calibration curve method

Analyse par microfaisceaux — Analyse par microsonde électronique (microsonde de Castaing) — Lignes directrices pour le dosage du carbone dans les aciers par la droite d'étalonnage

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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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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.

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ISO 16592 was prepared by Technical Committee ISO/TC 202, *Microbeam analysis*, Subcommittee SC 2, *Electron probe microanalysis*.

Microbeam analysis — Electron probe microanalysis — Guidelines for determining the carbon content of steels using a calibration curve method

1 Scope

This International Standard gives guidance on a method for the determination of the carbon content in steels containing other alloying elements (less than 1 % to 2 % by mass) using the calibration curve method. It specifies the sample preparation, X-ray detection, establishment of the calibration curve and the procedure for the determination of the uncertainty of the measured carbon content. It is applicable to steels containing a mass fraction of carbon of less than 1,0 %. The method is not applicable to steels with higher carbon contents, which could significantly affect the accuracy of the analysis results.

This International Standard applies to analyses performed using normal beam incidence and wavelength-dispersive X-ray spectrometry; it is not designed to be used for energy-dispersive X-ray spectrometry.

2 Procedure

2.1 General

In order to determine the carbon content in steels using a calibration curve, suitable reference materials should be prepared. For accurate analysis, extreme care should be used to prevent carbon contamination which would otherwise increase the apparent carbon content of the specimen.

The measurement of C Kα intensity should be carried out using the same procedures for the specimen and the reference materials; that is, specimen preparation, beam energy, beam current, beam diameter, point counting mode, step between points in case of line analysis, and also the method of background subtraction.

2.2 Reference materials

To establish the calibration curve to determine the carbon content, a suitable reference material or set of reference materials should be used. Examples of reference materials are as follows:

— Fe-C solid solution reference materials which are manufactured by quenching from the austenite region at high temperature; these reference materials should be homogeneous and contain different carbon concentrations;

— Fe-C compound Fe_3C [1].

Reference materials with a different C Kα peak shape compared to the unknown materials should not be used because the use of these reference materials causes a lowering of the quantitative accuracy.

2.3 Specimen preparation

2.3.1 General

The presence of carbon and/or its compounds as contamination on the specimen surface as a result of specimen preparation significantly affects the accuracy of carbon analysis. Extreme care should be used to prevent this contamination. The specimen preparation (mounting, grinding and polishing) procedures should be the same for both the reference material and the unknown material.

2.3.2 Specimen mounting

Although it is often possible to analyse a specimen without the use of a mounting medium, for small or irregularly shaped specimens mounting will be necessary. It is important to realize that the mounting material can act as a source of carbon contamination. Various mounting media are available, such as Bakelite, copper-filled or aluminium-filled and even graphite-filled resins, and it is recommended that the user evaluates the different types.

Where a mounting medium is used, if possible, areas chosen for analysis should be close to the centre of the specimen to avoid smearing effects close to the mounting medium/specimen interface.

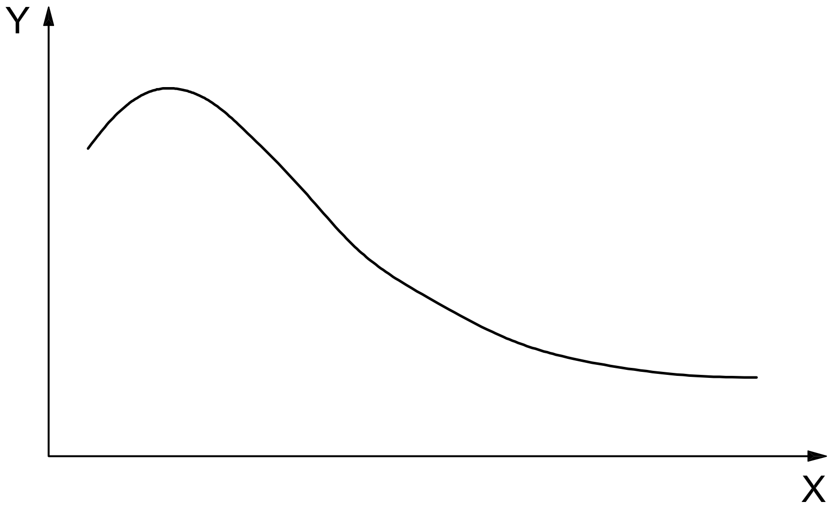
2.3.3 Specimen polishing and cleaning

The surface finish of the specimen to be examined should be flat, clean and dry. The specimen should be prepared in the standard metallographic manner, using silicon carbide papers for grinding and diamond-impregnated pads for polishing, etc. Final polishing should be with a carbon-free material such as alumina powder. After polishing, it is important to thoroughly clean the specimen so as to remove any residue resulting from the preparation using carbon-free ultrasonic cleaning.

2.4 Measurement of carbon Kα X-ray intensity

2.4.1 Beam energy and beam current

The X-ray emission level of carbon is low due to low ionization probability and also because the absorption of C Kα radiation is very strong in almost all matrix materials. Increasing the beam energy above the excitation potential of C Kα increases the depth of penetration of the electrons, which increases the number of X-rays generated. However, the emitted fraction of X-rays is strongly decreased compared to the generated intensity because of the high absorption of X-rays before reaching the surface (see Figure 1). The optimum beam energy, which produces the maximum emitted X-ray intensity, is specimen-dependent. Although the optimum beam energy for many types of carbide which commonly occur in steels is in the region of 6 keV [2], in practice a value of 10 keV to 15 keV is more usually used when measuring carbon composition from the viewpoint of intensity of C Kα and beam diameter. The use of a high beam current will increase the total number of X-rays but with an associated increase in beam diameter. Unless the beam diameter is an issue, the beam current for analysing carbon in steels should be set at a high value so as to be consistent with good counting statistics. The beam current should be kept constant when measuring the unknown and reference specimen. Normalization of the counts is acceptable if the current is measured at frequent intervals.



Key

X beam energy, keV

Y measured C Kα intensity, cps/nA

Figure 1 — Effect of the beam energy on the measured C Kα intensity (see Reference [2])

2.4.2 Counting time

For best results, the EPMA instrument should have an effective anti-contamination device with a liquid nitrogen cooling plate and/or a microleak of air or oxygen on the specimen to limit the contamination. In this case, the procedure should include a fixed time (depending on the instrument) on each point to stabilize the count rate before starting the measurement.

NOTE 1 For an instrument with high contamination rates, a better strategy may be to collect as many counts in as short a time as possible before the contribution of counts due to the contamination becomes unacceptably large. The preferred strategy will be different from instrument to instrument.

NOTE 2 The origins of the carbon that may contaminate the surface of the specimen by the electron irradiation are numerous (the specimen itself, residual gas inside the specimen chamber, oils associated with the vacuum pumps, lubrication of the spectrometer mechanics, etc.). The contamination which arises from the electron irradiation may be reduced by a liquid nitrogen cooling plate and a jet of air or oxygen on the specimen [2].

2.4.3 Pulse height analyser (PHA) setting

The PHA settings should be adjusted to remove all high-order diffraction lines at the wavelength used for the measurement of C Kα.

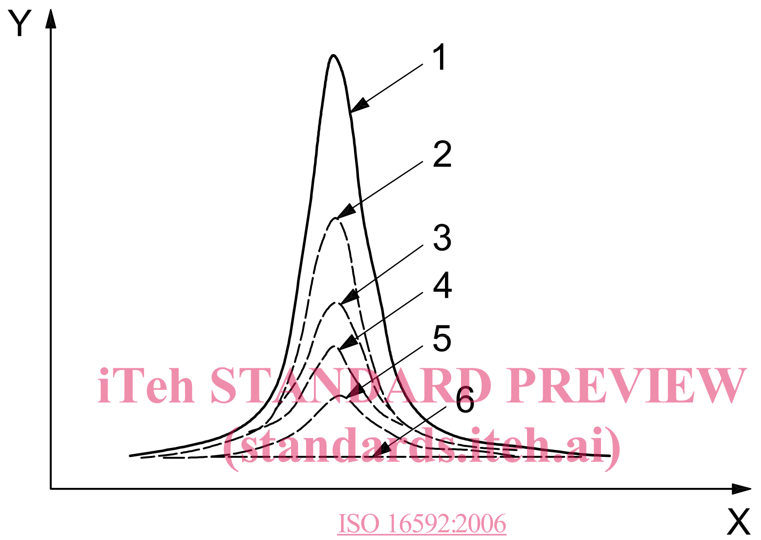
NOTE It is easier to adjust the PHA settings when using a specimen with a high carbon content such as Fe_3C.

2.4.4 Crystal choice

To obtain good counting statistics, the crystal used should provide a high count rate and a good peak-to-background ratio at the wavelength used for the measurement of C Kα. Older instruments use a lead stearate crystal, but synthetic multi-layer crystals with optimized d-spacing and much better intensity and peak-to-background values are available now.

2.5 Background subtraction

When performing quantitative analyses of heavier elements, care is taken in choosing suitable background positions either side of the peak to be measured. The choice of positions is determined by the avoidance of additional peaks from other elements that may be present within the specimen. In the case of carbon analysis, however, the measured C Kα intensity is the sum of five X-ray intensities, as shown in Figure 2. These five contributions to the total measured intensity are the intensity from the carbon atoms in the specimen, the intensity from the carbon contamination on the specimen surface due to specimen preparation (A), the intensity from the carbon contamination due to electron irradiation during measurement (B), the intensity of continuous X-rays (C) and the intensity of any overlapped peak (D). In order to determine the net C Kα intensity generated in the unknown and reference material, these additional intensities should be subtracted from the measured total intensity.



Key

X wavelength

Y measured C Kα intensity

1 total measured intensity

2 net intensity from carbon in specimen

3 intensity of contamination (B)

4 intensity of contamination (A)

5 intensity of overlapped peak (D)

6 continuous X-ray intensity (C)

Figure 2 — Contributions to the measured C Kα intensity

The peak profile method may be used to determine the level of continuous X-ray generation (C). However, the resultant peak height and/or area does not give the net intensity in the specimen because the intensities resulting from contamination (A) and contamination (B) are still included. To estimate the net intensity generated in the specimen without the contributions due to contamination (A and B), it is very useful to measure C Kα intensity on a pure iron reference specimen under identical conditions to the unknown. This method involves collecting counts on pure iron from the maximum peak intensity position for C Kα, without moving to background positions, to determine the X-ray intensity related to the zero carbon content. Where overlapping peaks are present, the contribution made by the element(s) must be estimated using appropriate reference materials.

2.6 Establishment of the calibration curve

The calibration curve for the determination of the carbon content of steels should be established from the relationship between the net C Kα intensity and a number of certified reference materials of differing carbon contents, as shown in Figure 3.

As there is a linear relationship between the carbon contents and the C Kα intensity in the range of 0 % to 1,0 % carbon (by mass), the calibration curve is given by Equation (1):

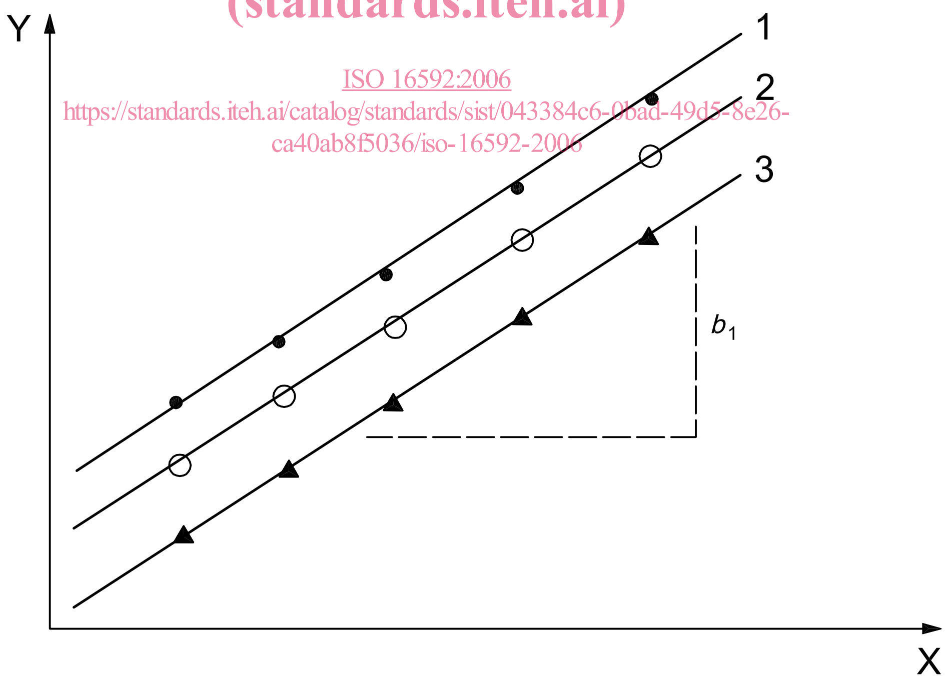
$$I_i = b_0 + b_1 C_i \tag{1}$$

where

- I_i is the X-ray intensity measured on the reference material;
- C_i is the mass fraction of carbon in the reference material;
- b_0 is the intercept on the intensity axis;
- b_1 is the slope of the calibration curve.

The coefficients b_0, b_1 may be calculated by the linear least-square fitting procedure (see Annex A).

When using pure iron for background subtraction, the net intensity when the carbon content is zero should theoretically correspond with zero, but will always have a finite value due to the effects of contamination. For this reason, care should be taken to reduce the carbon contamination.



Key

X mass fraction of carbon, %

Y C Kα intensity, cps/nA

1 total measured C Kα intensity

2 C Kα intensity after subtracting the contributions from overlapped peaks and continuous X-rays

3 net C Kα intensity after subtracting the background obtained on pure iron

b_1 slope

Figure 3 — Calibration curve for determining carbon content in steels