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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.

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

This second edition cancels and replaces the first edition (ISO 16592:2006), of which it constitutes a minor revision involving the following changes:

- instructions concerning the establishment of a conductive path from the specimen to ground to prevent charging and instructions concerning the minimization of outgassing of the specimen-mounting medium have been added to Subclause 2.3.2;
- in Subclause 2.3.3, the meaning of carbon-free ultrasonic cleaning has been clarified;
- the second sentence in Subclause 2.4.2 has been reworded to make it clear that the requirements apply to both the reference material and the unknown specimen.

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 and copper-filled or aluminium-filled (or even graphite-filled) resins, and it is recommended that the user evaluate the different types.

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

A conductive path must be established from the specimen or reference material to ground to prevent charging.

Outgassing of the specimen-mounting medium should be minimized. Virtual leaks from porosity in the specimen and gaps in the mounting medium/specimen interface will degrade the vacuum, resulting in higher contamination levels.

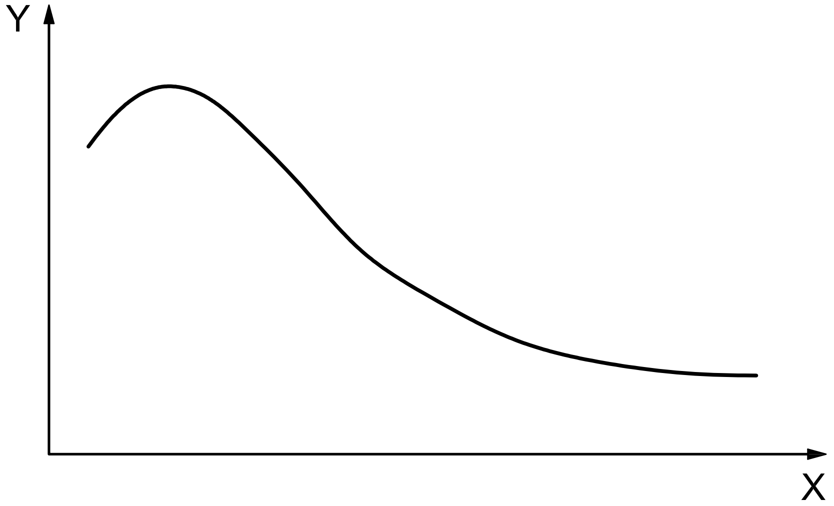
2.3.3 Specimen polishing and cleaning

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 a carbon-free liquid, such as ultrapure water, for 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 for both the reference material and the unknown specimen.

NOTE 1 For an instrument with high contamination rates, a better strategy might 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 might 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.). As mentioned above, the contamination which arises from the electron irradiation can be reduced by a liquid-nitrogen cooling plate and/or 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.

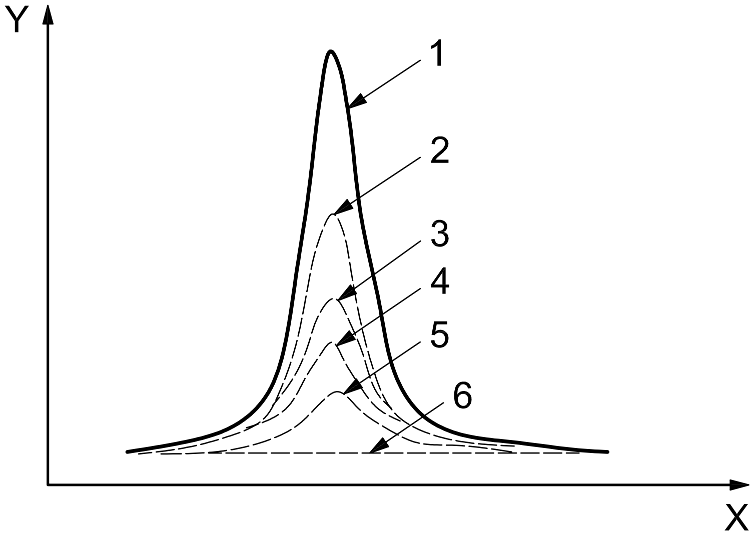
NOTE It is easier to adjust the PHA settings when using a specimen with a high carbon content such as Fe_3C.

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 might 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 (curve 4 in Figure 2), the intensity from the carbon contamination due to electron irradiation during measurement (curve 3), the intensity of continuous X-rays (curve 6) and the intensity of any overlapped peak (curve 5). 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 from contamination due to electron irradiation during measurement

4 intensity from contamination due to specimen preparation

5 intensity of overlapped peak

6 continuous X-ray intensity

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 (curve 6). However, the resultant peak height and/or area does not give the net intensity in the specimen because the intensities resulting from contamination (curves 3 and 4) are still included. To estimate the net intensity generated in the specimen without the contributions due to contamination (curves 3 and 4), it is very useful to measure C Kα intensity on a pure iron reference specimen under conditions identical to those used for 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 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;

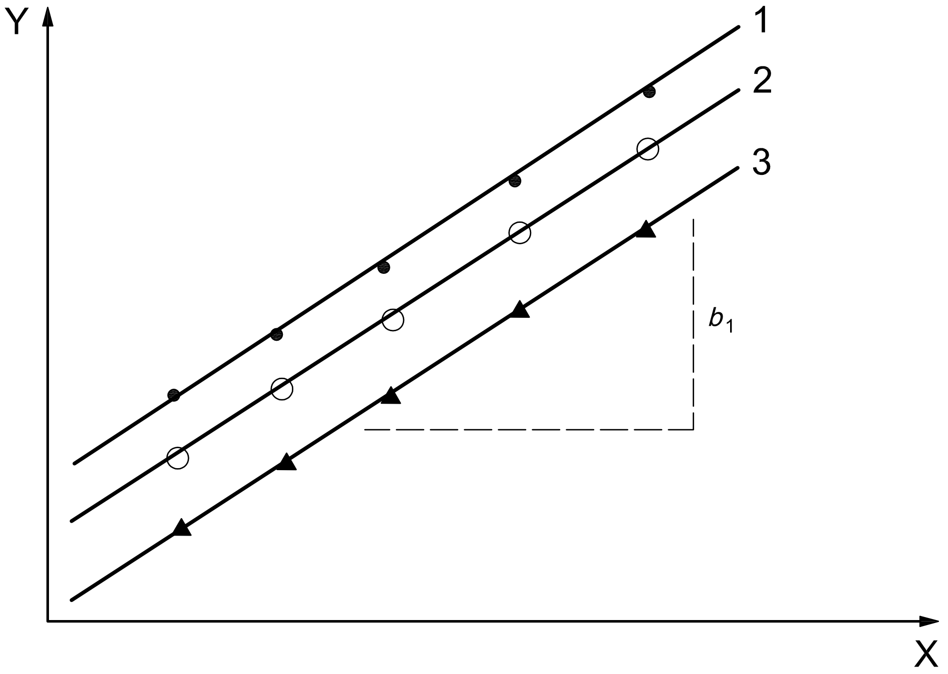
C_i is the mass fraction of carbon in the reference material;

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 to 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

3 Evaluation of uncertainty

Validation of the method should be carried out prior to any analyses. This may be accomplished using certified reference materials. The analyst should establish the repeatability, reproducibility and uncertainty of measurement for typical samples analysed in the laboratory. The analyst should also validate the method to ensure that it is fit for the intended purpose.

Factors that contribute to the uncertainty of measurement should be identified. Typical factors are associated with the instrument, changes in ambient conditions, the analytical procedure, the specimen and the operator. Large differences in the chemical composition of the sample over small areas can be a major source of uncertainty in the measurement. The repeatability of the measurement should be obtained from repeat readings obtained by the same operator using the same instrument operating under the same conditions and examining the same area of specimen during a relatively short time period.

The reproducibility of the measurement should be established by performing the repeatability tests at intervals. This can incorporate different operators and different specimen areas. Participation in proficiency testing schemes and round-robin specimen analyses will provide a useful measure of the reproducibility among laboratories.

A measure of the accuracy of the result may be obtained from the analysis of certified reference materials (CRMs) using identical operating conditions. This approach will also establish the traceability of the results to recognized standards and identify the occurrence of systematic errors. The alternative is for the laboratory to establish the accuracy using results obtained by an established analytical method or methods.

The uncertainty of values calculated from the calibration curve should be estimated using the methods given in Annex A[3],[4]. The measurements of repeatability/reproducibility provide some estimate of the combined uncertainty from random sources. A practical example of the determination of the carbon content in a steel and the evaluation of uncertainty is shown in Annex B.

4 Test report

Records of the instrument and individual investigations should be kept so that, if required, a test report conforming to ISO/IEC 17025:2005, 5.10, can be issued, including the following:

a) a reference to the test method used, i.e. ISO 16592:2012;

b) the name and address of the laboratory that performed the calibration(s) or test(s), and the address where the calibration(s) or test(s) were carried out if that address is different from the address of the laboratory;

c) the name and address of the client, where relevant;

d) the date of receipt of the calibration item or test item and the date(s) that the calibration(s) or test(s) were performed, where relevant;

e) the instrument type and reference number;

f) the take-off angle of the instrument;

g) a reference to the sampling procedure used, where relevant;

h) the reference materials used for the establishment of the calibration curve;

i) the specimen preparation method;

j) the beam energy;

k) the beam current;

l) the crystal used;

m) the PHA settings;

n) the counting time for the measurement of C Kα intensity,

o) the method used for the background measurement;

p) the results and a measure of their uncertainty;

q) any deviations from, additions to or exclusions from the calibration method or test method, and any other information relevant to a specific calibration or test, e.g. the environmental conditions;

r) the date of the test and the date the test report was issued;

s) the signature of the person taking responsibility.

Annex A
(informative)

Method of estimating the uncertainty of the calculated value using a calibration curve

The mass fraction of carbon in the steel sample may be calculated using a calibration curve based on suitable reference materials. The linear least-squares fitting procedure used assumes that the uncertainties in the values of the carbon content are considerably smaller than those of the values of the net C Kα intensity. Therefore the usual calculation procedure for the uncertainty reflects the uncertainty in the X-ray intensity measured by EPMA and not an uncertainty in the reference materials.

The calibration curve is given by

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

where

I_i is the X-ray intensity measured on the reference materials;

C_i is the mass fraction of carbon in the reference materials;

b_0 is the intercept on the intensity axis;

b_1 is the slope of the calibration curve.

The standard uncertainty $u_c(y)$ is given by the following equation, where y depends on the variables x_1, x_2, ... x_n (see References [3] and [4]):

$$u_c^2\left[y(x_1,x_2,\ldots)\right] = \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\partial y}{\partial x_i}\frac{\partial y}{\partial x_j}u(x_i,x_j) = \sum_{i=1}^{N}\left(\frac{\partial y}{\partial x_i}\right)^2 u^2(x_i) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial y}{\partial x_i}\frac{\partial y}{\partial x_j}u(x_i)u(x_j)r(x_i,x_j) \tag{A.2}$$

where $r(x_i, x_j)$ is the correlation coefficient.

Then the uncertainty $u(C_S)$ is calculated as follows:

$$C_S = (I_S - b_0)/b_1 \tag{A.3}$$

$$\begin{aligned} u^2(C_S) &= \left(\frac{1}{b_1}\right)^2 u^2(I_S) + \left(\frac{1}{b_1}\right)^2 u^2(b_0) + \left(\frac{I_S - b_0}{b_1^2}\right)^2 u^2(b_1) + 2u(b_0)u(b_1)r(b_0,b_1)\left(\frac{I_S - b_0}{b_1{}^2}\right) \\ &= \left(\frac{1}{b_1}\right)^2 u^2(I_S) + \left(\frac{1}{b_1}\right)^2 u^2(b_0) + \left(\frac{C_S}{b_1}\right)^2 u^2(b_1) + 2u(b_0)u(b_1)r(b_0,b_1)\left(\frac{C_S}{b_1^2}\right) \\ &= \left(\frac{1}{b_1}\right)^2\left[u^2(I_S) + u^2(b_0) + C_S^2 u^2(b_1) + 2C_S u(b_0)u(b_1)r(b_0,b_1)\right] \end{aligned} \tag{A.4}$$

Equations to be used in the calculation of b_0, b_1, $u^2(b_0)$, $u^2(b_1)$, $r(b_0,b_1)$ are as follows[5]:

$$b_0 = \frac{1}{D}\left(\sum_{i=1}^{n} \frac{I_i}{\sigma_i^2} \cdot \sum_{i=1}^{n} \frac{C_i^2}{\sigma_i^2} - \sum_{i=1}^{n} \frac{I_i C_i}{\sigma_i^2} \cdot \sum_{i=1}^{n} \frac{C_i}{\sigma_i^2} \right)$$

$$b_1 = \frac{1}{D}\left(\sum_{i=1}^{n} \frac{1}{\sigma_i^2} \cdot \sum_{i=1}^{n} \frac{I_i C_i}{\sigma_i^2} - \sum_{i=1}^{n} \frac{I_i}{\sigma_i^2} \cdot \sum_{i=1}^{n} \frac{C_i}{\sigma_i^2} \right)$$

$$D = \sum_{i=1}^{n} \frac{1}{\sigma_i^2} \cdot \sum_{i=1}^{n} \frac{C_i^2}{\sigma_i^2} - \left(\sum_{i=1}^{n} \frac{C_i}{\sigma_i^2} \right)^2$$

$$u^2(b_0) = \frac{1}{D} \sum_{i=1}^{n} \frac{C_i^2}{\sigma_i^2}$$

$$u^2(b_1) = \frac{1}{D} \sum_{i=1}^{n} \frac{1}{\sigma_i^2}$$

$$r(b_0, b_1) = -\frac{\displaystyle\sum_{i=1}^{n} \frac{C_i}{\sigma_i^2}}{\sqrt{\displaystyle\sum_{i=1}^{n} \frac{1}{\sigma_i^2} \cdot \sum_{i=1}^{n} \frac{C_i^2}{\sigma_i^2}}}$$

where

b_0 is the intercept of the calibration curve on the intensity axis;

b_1 is the slope of calibration curve;

n is the number of measurements for the calibration;

C_S is the mass fraction of carbon determined for a sample;

I_S is the X-ray intensity measured on a sample;

σ_i^2 is the standard variation of I_i;

I_i is the X-ray intensity measured on the reference materials;

C_i is the mass fraction of carbon in the reference materials.

Annex B
(informative)

A practical example of the determination of the mass fraction of carbon and the evaluation of uncertainty in a steel

The mass fraction of carbon was determined using a prepared calibration curve. For this purpose, five reference materials were used, whose mass fractions of carbon were 0,089 %, 0,188 %, 0,281 %, 0,460 % and 0,680 %. The measurements of C Kα intensity on the five reference materials were carried out five times each, giving the results in Table B 1.

Table B.1 — C Kα intensities measured on the reference and the unknown materials (unit: counts)

Mass fraction of carbon %	**1**	**2**	**3**	**4**	**5**	**Average**	**Standard deviation**
0,089	7 842	7 908	7 806	7 956	7 896	7 882	58,6
0,188	9 360	9 168	9 240	9 396	9 342	9 301	94,3
0,281	10 158	10 230	10 380	10 182	10 218	10 234	86,7
0,460	12 612	12 552	12 546	12 930	12 480	12 624	177,3
0,680	14 730	15 012	14 868	14 736	14 562	14 782	168,5
Unknown	12 372	12 006	12 180	—	—	12 186	183,1

Applying the equations given in Annex A, the following results were obtained:

$$b_0 = 6\ 882$$

$$b_1 = 11\ 948$$

$$u(b_0) = 66{,}87$$

$$u(b_1) = 260{,}46$$

$$r(b_0, b_1) = -0{,}794$$

When the X-ray intensity (I_S) measured on the unknown sample was equal to 12 186, the mass fraction of carbon in the unknown sample calculated by the calibration curve was as follows:

$$C_S = (12\ 186 - 6\ 882)/11\ 948 = 0{,}44\ \%$$

Then the uncertainty $u(C_\mathrm{S})$ was calculated as follows:

$$\begin{aligned} u^2(C_\mathrm{S}) &= \left(\frac{1}{b_1}\right)^2 \left[u^2(I_\mathrm{S}) + u^2(b_0) + C_\mathrm{S}^2 u^2(b_1) + 2C_\mathrm{S} u(b_0) u(b_1) r(b_0, b_1)\right] \\ &= \left(\frac{1}{11\,948}\right)^2 \left[183{,}1^2 + 66{,}87^2 + 0{,}44^2 \times 260{,}46^2 + 2 \times 0{,}44 \times 66{,}87 \times 260{,}46 \times (-0{,}794)\right] \\ &= 0{,}000\,273 \end{aligned}$$

where $u^2(I_\mathrm{S}) = 183{,}1^2$ calculated as based on the X-ray intensity measured on the unknown sample.

Thus $u(C_\mathrm{S}) = 0{,}017$ %.

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