A New Method for Quantitative X-ray Analysis of Multiphase Mixtures

BY E. R. WÖLFEL

STOE Application Laboratory, D-6100 Darmstadt, Hilpertstrasse 10, Federal Republic of Germany

(Received 7 October 1980; accepted 23 February 1981)

Abstract

This new method for quantitative X-ray analysis of multiphase mixtures is based on transmission measurements of thin samples in combination with absorption measurements from defined circular parts of these samples. The method has the advantage that only a few (1–5) mg of substance are required. There is no limitation on the number of phases because no matrix problems exist. The automated method is safe in operation since the measured intensities (E_d) and absorption factors (S) can be checked for consistency. The measurements are made with monochromatic Cu Kα (or Co Kα) radiation on the STOE/CSS automatic focusing X-ray powder diffractometer. The optical principle of the diffractometer and the theoretical basis of the method are described. The practical use of the method and two examples of analyses are given.

I. The STOE/CSS automatic focusing X-ray diffractometer

The optical principle of the focusing X-ray diffractometer is shown in Fig. 1. A convergent monochromatic X-ray beam from a curved graphite monochromator is focused at the receiving slit in front of the detector. Thin samples in the centre of the ω circle of the diffractometer do not disturb the focusing condition, so that its advantages can be utilized over the whole ±20 range. The distances X-ray tube to monochromator and monochromator to detector are chosen to be 260 mm in order to provide sufficient angular resolution. The diffractometer can be pivoted around the vertical axis of the curved monochromator allowing easy adjustment of the primary X-ray beam towards the centre of the diffractometer. Two Soller slits in the primary beam and in front of the detector limit the vertical divergence. The cross section of the primary beam is defined by slit 3 between the monochromator and the specimen. In front of the detector the width of the beam can be set by a precision slit to 0.001 mm.

An automatic sample changer with two storage tubes is mounted on the diffractometer. The capacity of each tube is 30 samples. The samples, which are held in circular disks, are brought automatically from one tube to the rotating sample holder in the centre of the diffractometer for transmission or absorption measurements and are stored after measurement in the other tube.

In the case of severe preferred orientation, the diffractometer can be used for combined transmission–reflection scans of the sample. For combination scans the width of the primary beam has to be limited to 0.2–0.3 mm by slit 3.

II. Theoretical background of the method

Since the new method for quantitative X-ray analysis differs from the ones known from the literature, the theoretical basis will be provided in this paragraph.

The symmetrical transmission (Laue) case is shown in Fig. 2. A reflection from a thin powder plate is measured in such a way that the reflecting plane is in its symmetrical position at θ° between the primary X-ray beam and the reflected beam. The number of reflecting lattice planes N_r within the irradiated volume of the sample is known to be (James, 1965, p. 47)

\[ N_r = \frac{1}{2}NH \cos \theta \Delta \theta , \]

where \( N \) is the number of particles (crystallites) within the irradiated volume, \( H \) is the multiplicity factor, and \( \Delta \theta \) is the angular range of the Bragg reflection.

Each crystallite contributes with its integrated intensity to the reflection within the Debye–Scherrer cone. The integrated intensity of a crystallite is known to be (James, 1965, p. 41)

\[ \frac{E_\omega}{I_0} = Q V_1 , \]

where \( I_0 \) is the flux (power m\(^{-2}\)) of the monochromatic primary X-ray beam, \( E \) is the total energy of the reflected beam which is proportional to the area under the rocking curve (Fig. 3), \( \omega \) is the angular velocity of the crystallite rotating through the reflection range, \( V_1 \) is the volume of the crystallite, and \( Q \) is the 'reflection coefficient' [mm\(^{-1}\)].

\[ Q = \left( \frac{e^2}{mc^2} \right)^2 \left( 1 + \frac{\cos^2 2\theta}{2 \sin 2\theta} \right) \frac{\lambda^3}{v^2} |F_{hk0}|^2 , \]

where \( e, m \) are the charge and mass of an electron, \( c \) is the velocity of light, \( \theta \) is the Bragg angle, \( \lambda \) is the wavelength of the X-ray beam, and \( v \) is the volume of the unit cell.

© 1981 International Union of Crystallography
\[ F_{hkl} = \sum_i f_i \exp \left[ 2\pi i (h x_i + k y_i + l z_i) \right] \]

is the well-known structure amplitude, \( f_i \) being the atomic scattering factors of the \( i \) atoms within the unit cell and \( x_i y_i z_i \) being the coordinates of the \( i \) atoms.

Fig. 3 shows the rocking curve of one crystallite, the integral of which is proportional to the total reflected energy \( E \). In each angular position \( \theta \) of the crystallite the power \( P(\theta) I_0 \) is measured, \( I_0 \) being the flux of the primary beam as defined above. Since the total reflected energy \( E \) is proportional to \( 1/\omega \),

\[ E = \frac{I_0}{\omega} \int P(\theta) d\theta, \quad (4) \]

from which the 'integrated intensity' \( P \theta d\theta \) follows:

\[ \int P(\theta) d\theta = \frac{E \omega}{I_0} = QV_1. \quad (5) \]

If we apply the above formulae to our powder slab of Fig. 2, the fraction \( P_1 \) of the power of the reflected beam within the length of the receiving slit \( l \) in front of the detector is known to be (James, 1965, p. 49)

\[ P_1 = \frac{HQlt}{4R\sin 2\theta} \frac{Q^1}{Q} I. \quad (6) \]

where \( I \) is the power of the primary beam after passing the powder slab in its symmetrical position of Fig. 2, \( Q^1/Q \) defines the packing density of the slab, \( R \) is the specimen-to-detector distance, and \( Q \) is the reflection coefficient as defined by (3).

The combination of (6) with (3) gives us the fraction of the two powers \( P_1 \) and \( I \):

\[ \frac{P_1}{I} = \frac{\left( \frac{e^2}{mc^2} \right)^2 \left( \frac{\lambda^2}{\beta_0^2} \right) \left( \frac{1}{4R\pi} \right) H|F_{hkl}|^2}{1 + \cos^2 2\theta} \frac{1}{2\sin^2 2\theta} \frac{tQ^1}{q}. \]

Factor 1 is a constant for all reflections of a particular compound (phase) within a mixture. Factor 2 can be considered as being constant for a particular reflection of one phase. Factor 3 refers to the thickness (\( t \)) and the packing density (\( Q^1/Q \)) of the powder slab.

For quantitative analyses one is usually interested in one reflection per phase. In this case the factors 1 and 2 can be written as a constant \( C'' \), thus

---

**Fig. 1.** The principle of the STOE/CSS focusing powder diffractometer. The transmission specimen and the counter are shown in three different angular positions.

**Fig. 2.** The symmetrical transmission case.
From practical considerations, however, some modifications of (7) are made. Usually only a few mg of a mixture are available for analysis and it is not possible to prepare from that amount of material a slab of uniform thickness. The best way to prepare the specimen is to distribute the material as uniformly as possible within a circular area of diameter $d$ onto a supporting foil (Fig. 4), where $d < L$, $L$ being the length of the primary beam. It is assumed that the sample is rotating and that the intensity of the monochromatic primary beam is uniform over $L$, which is achieved by carefully selected monochromators in combination with Soller slits.

Under these conditions the total mass $m$ is caught by the primary beam and it is advisable to modify (7) as follows. Since the mass $m$ of the specimen is given by

$$m = \frac{d^2}{2} \pi t \rho' ,$$

$d, t, \rho'$ being mean values for the diameter, the thickness and the density of the rotating specimen, (7) can be written as

$$\frac{P_d}{I_d} = \frac{C'''}{\left(\frac{d}{2}\right)^2 \pi t \rho'} \frac{d^2}{2} \pi t \rho' = C'''m ,$$

$C'''$ being a new constant.

Note that the power of the reflected beam $P_d$ is now determined by the specimen of mean diameter $d$ as well as by the receiving slit of length $l$ in front of the detector.

Since in our present conception of Fig. 4 only a certain fraction $I_d$ of the power $I$ of the primary beam is actually used, which cannot be measured, we include $I_d$ into the constant, giving

$$P_d = C'm .$$

But we have now to consider that $P_d$ depends on the thickness $t$ of the specimen. Therefore, the above formula has to be corrected for absorption. From Fig. 2, it is known that the path of the reflected beam within the rotating specimen in its symmetrical position is $t/cos \theta$, $t$ being its mean thickness. The power of the reflected beam passing through the specimen is therefore reduced by the factor $\exp \left[ -\frac{\mu t}{cos \theta} \right] = S^{-1}$. $S$, the absorption factor, is defined as

$$S = \frac{\text{intensity of the primary beam before specimen}}{\text{intensity after the specimen in symmetrical position}} = \exp \left[ \frac{\mu t}{cos \theta} \right] ,$$

whereby in most of the practical cases $cos \theta$ can be considered as a constant over the limited angular $\theta$ range ($\Delta \theta \sim \pm 5^\circ$) of the reflection from different phases to be analysed.

The absorption-corrected formula for $P_d$ reads

$$P_d = C'S^{-1}m .$$

In order to measure $P_d$ and $S$ conveniently, only a small circular fraction of the specimen is used, which is defined by a circular hole in a thin brass mask which covers the specimen towards the detector. The diameter of the mask is chosen to be smaller than the mean diameter of the specimen.

In order to determine $S$, two measurements have to be made in the position $2\theta = 0^\circ$ of the detector: (a) the intensity of a fraction of the primary beam is measured as determined by a circular mask in the symmetrical position of Fig. 2 without the specimen; (b) the same, but with the specimen in place.

The last modification of our formula concerns the background under the reflection. Formula (9) would require the measurement of the reflection over the whole angular range $\Delta \theta$ with a wide slit in front of the detector, and the correction of the background would be difficult to apply for closely spaced reflections.

With automatic diffractometers it is more convenient to scan through the reflection, having a narrow slit in front of the detector. Then the background can be easily corrected as indicated in Fig. 3. This method means that instead of the power $P_d$ one measures the total intensity $E_d$ of the reflected beam. Since from (4) it follows that $E_d = (1/\omega)P(d)$, we can write for $(E_d)$:

$$(E_d) = CS^{-1}m ,$$

where the new constant $C$ includes the factor $1/\omega$. 

![Fig. 3](image-url) The integrated intensity of a single crystal. $P(\theta)I_0$ is the power of the reflected beam as measured in each angular position $\theta$ of the crystal, $I_0$ is the flux of the primary beam.

![Fig. 4](image-url) The shaded area shows the specimen of mean diameter $d$ fixed on a supporting foil, $L$ is the length of the rectangular primary beam.
From (10) we expect $E_aS$ to be proportional to the total mass $m$ of the specimen, thus

$$E_aS = Cm.$$ \hspace{1cm} (11)

Formula (11) can be applied both for pure phases used as standards and also for the different phases in mixtures to be analysed.

The new method for quantitative analysis is therefore based on two experimental values, $E_a$ and $S$. Usually one strong reflection is measured for each compound within a mixture as will be shown in the examples in §IV.

For checking the uniformity of the thickness of the specimen, it is advisable to measure two values of $S$ for two masks of different diameters ($S$ criterion). If they differ by more than 5%o, the specimen should not be considered for further measurement.

From (11) it follows that $E_aS$ versus $m$ plots should be straight lines through the origin $[(E_aS)_i/m_i$ criterion]. Because of this simple relation it is advisable to prepare a number of samples from each compound or mixture with different weights, determine $E_a$ and $S$ for each sample and check the linearity of the plots.

If for one pure substance used as a standard the different experimental values $(E_aS)_i$ as obtained from samples of different weights $m_i$ scatter appreciably around the straight line $(E_aS)_i = Cm_i$, this indicates that the grain size of the standard is not fine enough. If, however, the same effect is observed for a certain compound within a mixture, variations in composition might be the reason, especially if the different compounds within the mixture have different grain sizes. In such cases great care has to be taken to prepare samples of different weights with identical compositions. For checking purposes, the $(E_aS)_i/m_i$ criterion has been found very valuable.

The conditions for obtaining proper results for quantitative analyses as discussed in this paragraph can be summarized as follows:

1. Preferred orientation has to be carefully excluded. For most cases the usual method of preparation and the rotation of samples measured in transmission will be sufficient. In serious cases of preferred orientation, combined transmission–reflection scans clearly indicate the absence of preferred orientation. No general rule can be given to avoid preferred orientation, but occasionally some changes in preparation as the amount of glue or changes of supporting materials improve the situation.

2. The thickness $t$ of specimen should be nearly constant, being perhaps somewhat larger in the middle. The corresponding $S$ values as measured with 5 mm $\phi$ and 4 mm $\phi$ masks should be equal within about 5%o. Bad samples should be rejected ($S$ criterion).

3. Substances used as standards should have grain sizes of about 5–10 $\mu$m. Sieves should be used to obtain standards of uniform grain size. Several specimens should be measured to take advantage of the $E_aS/m$ criterion (11).

4. Only a high quality monochromatic beam will guarantee good results. Therefore (a) the focusing monochromator has to be carefully selected to provide a rectangular uniform cross section; (b) Soller slits have to be used to limit the vertical divergence of the beam; (c) the primary beam has to be carefully adjusted over the $\omega$ axis of the diffractometer and the zero mark of the 20 scale has to be carefully determined.

5. In order to minimize the time for analysis, the conditions for measurements should be kept constant (collimators, slits, operating conditions for the X-ray tube, etc.). Only for $S$ measurements do the operational conditions for the X-ray tube have to be changed (e.g. 2 mA, 20 kV) and attenuation filters have to be used in front of the receiving slit of the detector.

### III. Experimental details

1. **Preparation of the specimens**

   The specimens are usually supported on polyacetate foils of ~ 20 mm $\phi$ and water-soluble ‘Elmers white glue’ is used. In cases of multiphase mixtures with different particle sizes, care has to be taken that samples of various weights have the same composition. It has been found, in practice, that in such cases the amount of glue is critical and should be as low as possible.

   The foils with specimen are placed into circular inserts and are held in position by brass masks. 8 mm $\phi$ masks are used for preparation and for $E_a$ measurement, and 5 mm $\phi$ or 4 mm $\phi$ masks for $S$ measurement.

2. **$S$ measurements**

   As already indicated, two $S$ values should be measured from one specimen for checking purposes. $S$ requires two measurements. For one of these measurements the mask is mounted on the specimen within the circular insert. For the other an identical mask of the same diameter is used with a plain foil only. Both circular inserts are loaded into the sample changer. In practical use a sequence of five specimens with masks is supplied to the sample changer followed by one circular insert with the mask and the plain foil only. The positioning of the samples and the output of the $S$ values is computer controlled.

3. **$E_a$ measurements of standards**

   For each substance within a mixture an $(E_aS)_i = Cm_i$ calibration plot is required. In order to obtain this calibration plot a number of $i$ samples with different weights have to be prepared according to the instructions given above.

   For each specimen the following four measurements have to be made: (a) determination of weights in mg (accuracy $\pm 0.05$ mg); (b) $S$ from a 5 mm mask; (c) $S$ from a 4 mm mask; and (d) $E_a$ for one selected reflection (e.g. for SiO$_2$, the reflection at $2\theta = 26.65^\circ$ for Cu K$\alpha$ radiation is used).
$E_d$ measurement is usually made in angular increments of 0.04° (in 2θ), the number of steps being about 50 for single reflections and 60–70 for doublets. The measuring time per step is usually 15 s for $E_d$ and 5 s for $S$.

$E_dS/m$ plots are obtained on a graphical display and numerical $E_dS/m$ values can be calculated automatically, which give the reflecting power per mg of standard under the chosen experimental conditions (slits, collimators, operational conditions of the X-ray tube, etc.).

4. $E_d$ measurements from mixtures

The samples are prepared in the same way as described above. For each mixture 3–5 samples with weights between 1–5 mg are prepared. Up to 30 samples from different mixtures are loaded into the sample changer after the weights have been determined. Two $S$ values for each sample and one $E_d$ value per phase have to be measured as described above. From $E_dS/m$ plots it can be observed whether the straight lines lead through the origin ($E_dS/m$ criterion) and whether or not the deviations of the points from the straight line are acceptable or not.

Even if the conditions for measurement are kept carefully constant, it is advisable to include a small number of known standard samples for checking purposes in the sample changer.

The composition of the multiphase mixture is calculated from comparisons between the numerical $E_dS/m$ values of standards and the corresponding phases within the mixture.

An important prerequisite for reliable results is the proper choice of standard materials. The chosen standards should not only be chemically identical with the corresponding phases within the mixture, but their grain sizes and their degree of lattice perfection should also be as similar as possible. For analyses of coal dusts for example, standard SiO$_2$ and standard silicates of illite type have to be chosen with great care. Some experimental details will be given in the next section.

It should be mentioned that a re-evaluation of experimental results obtained for a mixture is always possible at any time, should one decide later to change standard materials. Therefore the experimental material should always be kept.

If all the requirements mentioned above are carefully observed, the described method for quantitative analysis has the following advantages: (a) There is no limitation to two or three phases in mixtures and there are no difficulties connected with matrix problems. (b) Only a few mg are required for analysis. (c) The $E_dS/m$ criterion and the $S$ criterion provide a reliable self-checking system for the method. (d) The method is automated except for preparing the specimen and loading the samples into the sample changer.

IV. Examples of quantitative analyses

1. The $E_dS/m$ plot for SiO$_2$ as a standard

For SiO$_2$, the reflection at 2θ = 26.65° (Cu Kα) was used as the characteristic reflection.

It should be mentioned here that a correction has to be applied if mixtures between illite-type silicates and SiO$_2$ are to be analysed, because in these cases some weak illite reflections are found within the region of the SiO$_2$ peak. For further details see § 2 below.

Natural SiO$_2$ was chosen as the standard substance and was ground under soft conditions and sieved through a 0.05 mm mash sieve. Eight specimens of different weights have been carefully prepared.

Table 1 shows the following results: Column 1 number of specimen; column 2 weights of specimens in mg; column 3 $S$ as measured with 4 mm masks; column

<table>
<thead>
<tr>
<th>$m$</th>
<th>$S$ (4 mm)</th>
<th>$E_d$</th>
<th>$E_dS$</th>
<th>$E_dSm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.85</td>
<td>1.172</td>
<td>1.767</td>
<td>2071</td>
</tr>
<tr>
<td>2</td>
<td>1.20</td>
<td>1.215</td>
<td>2.881</td>
<td>3500</td>
</tr>
<tr>
<td>3</td>
<td>1.65</td>
<td>1.317</td>
<td>3.198</td>
<td>4212</td>
</tr>
<tr>
<td>4</td>
<td>2.20</td>
<td>1.483</td>
<td>3.857</td>
<td>5720</td>
</tr>
<tr>
<td>5</td>
<td>2.44</td>
<td>1.589</td>
<td>4.629</td>
<td>7355</td>
</tr>
<tr>
<td>6</td>
<td>3.30</td>
<td>1.628</td>
<td>5.480</td>
<td>8921</td>
</tr>
<tr>
<td>7</td>
<td>4.10</td>
<td>1.814</td>
<td>5.998</td>
<td>10880</td>
</tr>
<tr>
<td>8</td>
<td>4.65</td>
<td>2.108</td>
<td>6.272</td>
<td>13221</td>
</tr>
</tbody>
</table>

Fig. 5. $E_dS$ versus $m$ plots of the 2θ = 26.6° SiO$_2$ peak. I for selected natural SiO$_2$ standard; II for a mixture of 68% SiO$_2$ and 32% of illite-type silicates.
296

QUANTITATIVE X-RAY ANALYSIS OF MULTIPHASE MIXTURES

Table 2. Results of analyses for SiO\textsubscript{2} and silicates

<table>
<thead>
<tr>
<th>No.</th>
<th>(m)</th>
<th>(S)</th>
<th>(E_d)</th>
<th>(E_{d,\text{corr}})</th>
<th>(E_{d,\text{corr}}S)</th>
<th>(E_{d,\text{Sm}^{-1}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal dust</td>
<td>1</td>
<td>1.60</td>
<td>1.290</td>
<td>588</td>
<td>566</td>
<td>730</td>
</tr>
<tr>
<td>30 s step (^{-1}) 2</td>
<td>2.25</td>
<td>1.380</td>
<td>768</td>
<td>740</td>
<td>1021</td>
<td>454</td>
</tr>
<tr>
<td>Coal dust</td>
<td>3</td>
<td>1.60</td>
<td>1.146</td>
<td>503</td>
<td>485</td>
<td>556</td>
</tr>
<tr>
<td>30 s step (^{-1}) 4</td>
<td>2.46</td>
<td>1.380</td>
<td>768</td>
<td>740</td>
<td>1021</td>
<td>454</td>
</tr>
<tr>
<td>30 s step (^{-1}) 5</td>
<td>2.94</td>
<td>1.277</td>
<td>826</td>
<td>795</td>
<td>1015</td>
<td>454</td>
</tr>
<tr>
<td>30 s step (^{-1}) 6</td>
<td>3.45</td>
<td>1.460</td>
<td>603</td>
<td>578</td>
<td>844</td>
<td>245</td>
</tr>
<tr>
<td>30 s step (^{-1}) 7</td>
<td>4.25</td>
<td>1.543</td>
<td>827</td>
<td>785</td>
<td>1211</td>
<td>381</td>
</tr>
<tr>
<td>30 s step (^{-1}) 8</td>
<td>5.45</td>
<td>1.645</td>
<td>615</td>
<td>590</td>
<td>971</td>
<td>272</td>
</tr>
<tr>
<td>15 s step (^{-1}) 9</td>
<td>3.18</td>
<td>1.543</td>
<td>827</td>
<td>785</td>
<td>1211</td>
<td>381</td>
</tr>
<tr>
<td>15 s step (^{-1}) 10</td>
<td>4.55</td>
<td>1.645</td>
<td>615</td>
<td>590</td>
<td>971</td>
<td>272</td>
</tr>
<tr>
<td>15 s step (^{-1}) 11</td>
<td>4.55</td>
<td>1.645</td>
<td>615</td>
<td>590</td>
<td>971</td>
<td>272</td>
</tr>
<tr>
<td>15 s step (^{-1}) 12</td>
<td>4.55</td>
<td>1.645</td>
<td>615</td>
<td>590</td>
<td>971</td>
<td>272</td>
</tr>
</tbody>
</table>

For the silicates of illite type, the \(2\theta = 35^\circ\) doublet has been chosen as the characteristic reflection. A \(5\%\) correction of the intensity of that doublet has to be made for the \(E_d\) values of SiO\textsubscript{2}, because of the superposition of a small illite reflection within the SiO\textsubscript{2} peak. This correction was determined earlier from SiO\textsubscript{2}-free silicates of the illite type. As the silicate standard a mine mineral with 39\% SiO\textsubscript{2} and 61\% silicates of illite type has been used.

In Table 2 the results of the analyses are shown for SiO\textsubscript{2} and the silicates. In column 5 the \((E_{d,\text{corr}}S)\) are listed for which the illite contributions under the SiO\textsubscript{2} reflections were subtracted.

Plot II of Fig. 5 shows a better fit of measured values around a straight line. In this case a SiO\textsubscript{2}(68\%)--silicate(32\%) mixture was analysed, but only those samples for which \(S\) values as measured with 5 mm and 4 mm masks agreed within 5\% were considered for \(E_d\) measurements.

2. Quantitative analyses of SiO\textsubscript{2} and silicates of six dusts from different coal mines

The following example concerns six dusts from different coal mines of a region. From each mixture 2–3 samples were prepared. Two \(S\) values have been determined for each specimen and only these samples have been considered for \(E_d\) measurements, which agreed in \(S\) within \(\pm 5\%\). For the first two mixtures, the measuring time per step was chosen to be 30 s. For the others the normal conditions were chosen as reported in the last paragraph.

The mean \(E_{d,\text{Sm}^{-1}}\) values for the standards were measured as follows: \(E_{d,\text{Sm}^{-1}} = 2715 \text{ mg}^{-1}\) for SiO\textsubscript{2} (see § 1); and \(E_{d,\text{Sm}^{-1}} = 800 \text{ mg}^{-1}\) for silicates of illite type.

4 \(E_d\) for the \(2\theta = 26-65^\circ\) SiO\textsubscript{2} reflection in 'total number of pulses over the whole range of the rocking curve', the width of the receiving slit was 0.3 mm; column 5 products of \(E_dS\); column 6 products of \(E_{d,\text{Sm}^{-1}}\) (reflected energy mg\(^{-1}\) standard). From the eight measurements a mean value of \(E_{d,\text{Sm}^{-1}} = 2715 \text{ counts mg}^{-1}\) was obtained.

From plot I of Fig. 5 it follows that the measured points scatter around a straight line through the origin. Thus the origin criterion seems to be fulfilled for this standard material; however, the deviations of some points are appreciable, amounting to 0.1 mg in weight and 500 units in energy. These deviations can be explained with errors in weight (± 0.05 mg) and errors in \(S\). It should be noted that for this set of measurements only one \(S\) value was measured for each specimen. Therefore, inhomogeneities in \(t\) could not be excluded.

Plot II of Fig. 5 shows a better fit of measured values around a straight line. In this case a SiO\textsubscript{2}(68\%)--silicate(32\%) mixture was analysed, but only those samples for which \(S\) values as measured with 5 mm and 4 mm masks agreed within 5\% were considered for \(E_d\) measurements.

For the silicates of illite type, the \(2\theta = 35^\circ\) doublet has been chosen as the characteristic reflection. A \(5\%\) correction of the intensity of that doublet has to be made for the \(E_d\) values of SiO\textsubscript{2}, because of the superposition of a small illite reflection within the SiO\textsubscript{2} peak. This correction was determined earlier from SiO\textsubscript{2}-free silicates of the illite type. As the silicate standard a mine mineral with 39\% SiO\textsubscript{2} and 61\% silicates of illite type has been used.

In Table 2 the results of the analyses are shown for SiO\textsubscript{2} and the silicates. In column 5 the \((E_{d,\text{corr}}S)\) are listed for which the illite contributions under the SiO\textsubscript{2} reflections were subtracted.

It should be noted that in specimen 1 CaSO\textsubscript{4} \_2H\textsubscript{2}O was also present which has already been analysed. From the mean \(E_dS/m\) values of standards and mixtures, the amounts of SiO\textsubscript{2} and silicates have been calculated. The results are given in Table 3. There is quite a large percentage range of SiO\textsubscript{2} of between 5 and 25\%. The percentage range of illite was found to be between about 15 and 52\%. The above analyses of six mixtures were made within about 6 h.

Table 3. Amount of SiO\textsubscript{2} and silicates in the samples calculated from mean \(E_dS/m\) values

<table>
<thead>
<tr>
<th>No.</th>
<th>(m)</th>
<th>(S)</th>
<th>(E_d)</th>
<th>(E_{d,\text{corr}})</th>
<th>(E_{d,\text{corr}}S)</th>
<th>(E_{d,\text{Sm}^{-1}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal dust</td>
<td>1</td>
<td>1.60</td>
<td>1.290</td>
<td>588</td>
<td>566</td>
<td>730</td>
</tr>
<tr>
<td>30 s step (^{-1}) 2</td>
<td>2.25</td>
<td>1.380</td>
<td>768</td>
<td>740</td>
<td>1021</td>
<td>454</td>
</tr>
<tr>
<td>Coal dust</td>
<td>3</td>
<td>1.60</td>
<td>1.146</td>
<td>503</td>
<td>485</td>
<td>556</td>
</tr>
<tr>
<td>30 s step (^{-1}) 4</td>
<td>2.46</td>
<td>1.380</td>
<td>768</td>
<td>740</td>
<td>1021</td>
<td>454</td>
</tr>
<tr>
<td>30 s step (^{-1}) 5</td>
<td>2.94</td>
<td>1.277</td>
<td>826</td>
<td>795</td>
<td>1015</td>
<td>454</td>
</tr>
<tr>
<td>30 s step (^{-1}) 6</td>
<td>3.45</td>
<td>1.460</td>
<td>603</td>
<td>578</td>
<td>844</td>
<td>245</td>
</tr>
<tr>
<td>30 s step (^{-1}) 7</td>
<td>4.25</td>
<td>1.543</td>
<td>827</td>
<td>785</td>
<td>1211</td>
<td>381</td>
</tr>
<tr>
<td>15 s step (^{-1}) 9</td>
<td>3.18</td>
<td>1.543</td>
<td>827</td>
<td>785</td>
<td>1211</td>
<td>381</td>
</tr>
<tr>
<td>15 s step (^{-1}) 10</td>
<td>4.55</td>
<td>1.645</td>
<td>615</td>
<td>590</td>
<td>971</td>
<td>272</td>
</tr>
<tr>
<td>15 s step (^{-1}) 11</td>
<td>4.55</td>
<td>1.645</td>
<td>615</td>
<td>590</td>
<td>971</td>
<td>272</td>
</tr>
<tr>
<td>15 s step (^{-1}) 12</td>
<td>4.55</td>
<td>1.645</td>
<td>615</td>
<td>590</td>
<td>971</td>
<td>272</td>
</tr>
</tbody>
</table>

Reference