AUTOMATED QUANTITATIVE ELECTRON MICROPROBE ANALYSIS OF PARTICULATE MATERIAL
P. Van Dyck, H. Storms, R. Van Grieken

To cite this version:

HAL Id: jpa-00223853
https://hal.archives-ouvertes.fr/jpa-00223853
Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
AUTOMATED QUANTITATIVE ELECTRON MICROPROBE ANALYSIS OF PARTICULATE MATERIAL

P. Van Dyck, H. Storms and R. Van Grieken

University of Antwerp, Belgium

Abstract - An automated electron microprobe, equipped with an energy-dispersive X-ray spectrometer and an additional backscattered electron signal digitalization system, can allow rapid sizing and major element analysis on numerous particles. A software package has been developed to exploit the particle size and shape information to achieve quantitative analysis of single particles, and to compare the performance of the different matrix correction procedures.

In the increasingly important field of particulate material analysis electron microprobe X-ray microanalysis (EPXMA) can offer a good precision, high speed and wide elemental range. New commercially available systems in combination with EPXMA can now automatically locate and size up individual particles by making use of the backscatter electron signal, and subsequently analyse them via energy-dispersive X-ray detection. However, the analysis results were hitherto qualitative only. In the present study, a computer algorithm has been developed that makes use of the sizing information to correct the measured X-ray intensities automatically for the particle matrix effects. This new software package was successfully tested. Its implementation leads to fully computer controlled sizing and quantitative elemental analysis of individual particles.

EQUIPMENT

Particles were sized and analysed with a JEOL JXA-733 electron probe X-ray microanalyzer, equipped with the TN-2000 energy-dispersive X-ray detection system of Tracor Northern and two MTII tape units. The resulting spectra, with the corresponding particle sizing data, were transferred via magnetic tapes to a VAX 11/780 mainframe computer, with software developed at this laboratory for processing.

AUTOMATED SIZING AND QUANTITATIVE ANALYSIS

In the particle detection and sizing routine the electron beam scans the target surface. A particle is "detected" when the digitalized backscattered electron signal exceeds a chosen threshold. The path length during which the signal exceeds the threshold is interpreted as one diameter of the particle. The mean diameter of the particle is the average result of 16 differently oriented cross-section measurements. The fingerprint or energy-dispersive X-ray spectrum of the particle is accumulated with the electron beam positioned in the centre of the particle.

To derive quantitative data the spectrum should first of all be deconvoluted. The importance of this step is very often overlooked in automated feature analysis algorithms. For example, differences between X-ray intensities outputted from the powerful AXIL-program (Analysis of X-ray spectra by Iterative Least-squares fitting) developed in this laboratory/1/, and the intensities calculated by the peak deconvolu-
tion routines already present on the system (which are based on the filtering principle) amounted to 21% for Na and 16% for Cl for a simple NaCl spectrum, where peak interference overlap is absent. It is obvious that those errors are reflected in the final results. Since, however the AXIL peak deconvolution routine implies a significant calculation time, it was decided not to use the LSI 11/23 computer available with the EPXMA instrument and the operating system. Instead, the X-ray spectrum of each localized and sized particle is transferred to a tape medium together with particle sizing information. After completion of the total sample field search with the microprobe, all the raw spectra are deconvoluted off-line on a VAX 11/780 computer, using the AXIL-program.

In the next step one has to convert peak intensities to weight fractions, while taking into account the well-known particle matrix effects: varying analysis volumes, particle dependent X-ray path lengths and X-ray absorption effects, electron side-scatter effects and secondary fluorescence by characteristic and continuum radiation. To correct for this matrix effects the modified ZAF-version of Armstrong and Buseck /2/ was preferred over the peak-to-background procedure/3,4/ because it is more amply developed and wide spread/5/ and can be combined better with the available EPXMA setup. In the particle ZAF-correction scheme of Armstrong and Buseck /2/ only the X-ray attenuation correction is considered in detail, while the other particle effects are supposed to be negligible or to be similar for different elements, hence cancelled out in the normalization of the results. The general form of the absorption correction factor \( f(\mu, D) \) is

\[
f(\mu, D) = \frac{1}{A_0} \int_{\rho z = 0}^{\rho a} \int_{\rho z = 0}^{\rho a} \phi(\rho z) \, d(\rho z) \\
\int_{\rho z = 0}^{\rho a} \phi(\rho z) \, d(\rho z)
\]

where \( A_0 = \) area of the portion of the electron beam passing through the top surface of the particle
\( a = \) vertical thickness of the particle
\( \phi(\rho z) = \) X-ray production function, depending on the density \( \rho \) and linear depth \( z \) (In our procedure the \( \phi(\rho z) \) equations of Bastin et al./6/are used)
\( y = \) linear absorption coefficient of the considered radiation
\( D = \) horizontal diameter of the particle
\( g(\rho x, \rho y, \rho z, D) = \) effective path length function

For the two inner integrations (over \( \rho x \) and \( \rho y \)) Armstrong and Buseck/2/ derived general expressions for different particle models, i.e. geometrical particle types. However, the total integral cannot be converted to a closed form solution. Hence a numerical integration has to be performed over \( \rho z \). This necessitates again the use of a fast computation system like the VAX 11/780. Inspection of eq.(1) reveals that this matrix correction depends on the particle diameter, density and thickness, and the model used. Therefore automatic procedures have to be developed and tested to account for these unknown factors. Since the average particle diameter is known from the sizing step, only three parameters remain to be treated. Firstly, the density of the particle can simply be obtained by weighting the densities of the pure elements (or corresponding oxides) according to their concentrations. A simple test for ten common randomly selected geological materials, such as albite, diopside, spinel, etc., revealed that the ratio between calculated and real density amounts to 0.998 \( \pm \) 0.084. This procedure is quite satisfactory; indeed the density influences the limit of the outer integration and the uncertainty on this limit, induced by the estimation of the linear particle thickness \( a \), will be much more significant.
Secondly the thickness of the particle should be derived on an automated basis. Since trials to use an independent automatic procedure (observation of the X-ray production yield as a function of particle thickness) did not give any successful results as yet, it was decided to adopt the arbitrary approach of Armstrong and Buseck/2/. They assumed that particles will eventually find a most stable position on their largest surface. Hence the vertical thickness will be smaller than the automatically measured diameter. Armstrong and Buseck supposed that a particle thickness-to-diameter ratio of 0.5 would be most useful in the particle analysis procedure/2/.

The third unknown factor is the particle model, which influences the effective path length function $g$ in eq. (1). Armstrong and Buseck/2/calcultated $g$-functions for the following models: flat-top group (right rectangular prism, tetragonal prism, cylinder), peak-top group (triangular prism, square pyramid), rounded top group (hemisphere, sphere). Up to now the only information that the automatic sizing step yields with respect to the particle model is defined as the projected particle area divided by $\pi/4$-times the square of the average horizontal diameter. Since this factor only reflects the two dimensional projected shape of the particle, it is not possible to automatically discriminate between the different particle models. The criterion to observe the characteristic X-ray variation, or the digitalized topographic backscatter signal, across a particle and select automatically a specific particle model based on this variation, is still under investigation.

RESULTS AND DISCUSSION

Table 1 shows the average results obtained from the automated EPXMA-analysis of 70 spherical glass particles (NBS standard # 610), with diameters ranging from 2.5 to 14 $\mu$m, when various conventional ZAF-correction algorithms are applied and for the modified particle ZAF correction with different assumed particle models.

When one compares the results obtained via the different ZAF-corrections to the real value, it appears hard to recommend one particular procedure, because there is nearly no difference between the results. All the procedures tested indeed represent a dramatic improvement compared to the use of uncorrected normalized X-ray intensities.

Of the particle models, the rounded top model does not yield the best results. The reason for this is probably in the fact that a spot mode was used during the particle analysis. The electron beam hits a small part of the surface and the assumptions of Armstrong and Buseck in the algorithm are not truly fulfilled.

Since the computer software for all the models has duly been implemented now, it will straightforwardly be possible in the near future to evaluate the various procedures for particle analysis by studying particles of much smaller size. A raster-scan or star-scan will be used during analysis to give more reliable information about the X-ray intensity for a certain particle shape.

Table 1: Average results (in %) for 70 NBS 610 glass standard spheres, obtained by using different conventional ZAF-correction models for bulk samples and considering the particle geometry

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified concentrations</th>
<th>Concentrations found via the algorithm of Duncumb-Reed/7/</th>
<th>Love et al/8/</th>
<th>Brown /9/</th>
<th>Bastin et al./6/</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>10.2</td>
<td>11.1 ± 0.1</td>
<td>11.3 ± 0.1</td>
<td>11.3 ± 0.1</td>
<td>11.3 ± 0.01</td>
</tr>
<tr>
<td>Al</td>
<td>1.70</td>
<td>1.68± 0.01</td>
<td>1.67± 0.01</td>
<td>1.67± 0.01</td>
<td>1.67± 0.01</td>
</tr>
<tr>
<td>Si</td>
<td>32.9</td>
<td>32.3 ± 0.1</td>
<td>32.3 ± 0.1</td>
<td>32.3 ± 0.1</td>
<td>32.3 ± 0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>7.6</td>
<td>6.87± 0.01</td>
<td>6.84± 0.01</td>
<td>6.85± 0.01</td>
<td>6.84 ± 0.01</td>
</tr>
</tbody>
</table>
B. Particle ZAF-correction procedures/2/: 

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentrations found assuming as a model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Right Rectangular prism</td>
</tr>
<tr>
<td>Na</td>
<td>10.0 ± 0.1</td>
</tr>
<tr>
<td>Al</td>
<td>1.54 ± 0.01</td>
</tr>
<tr>
<td>Si</td>
<td>32.9 ± 0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>7.37 ± 0.01</td>
</tr>
</tbody>
</table>

*The uncorrected normalized X-ray intensities (taking into account oxygen by stoicheometric considerations) lead to the following results:
1.29 % Na, 1.03 % Al, 39.7 % Si and 8.21 % Ca.

REFERENCES

6- G. BASTIN, F. VAN LOG and H. HEYLIGERS, submitted to X-ray Spectrometry