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EVALUATION OF CORRECTION PROCEDURES FOR QUANTITATIVE LIGHT ELEMENT EPMA

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Résumé - On évalue les modèles de correction utilisés en microanalyse des éléments légers. On examine particulièrement la variation du facteur de correction d'absorption en fonction de l'énergie des électrons.

Abstract - The performance of correction models used in light element EPMA is assessed, with a special emphasis on the energy dependence of the absorption correction factor.

Recently Love and Scott /1/ have assessed the performance of the established correction procedures and some new models used in electron probe microanalysis (EPMA). They concluded that all methods are approximately equivalent in accuracy when applied to a wide range of medium to high Z microanalysis data (430 measurements), giving the root mean square (RMS) error in the calculated concentration of the order of 5.4-7.3%. Serious improvements are required, however, in light element studies. The conventional ZAP procedures give for light element systems unacceptably large RMS errors (9-14%) in contrast with the correction model proposed recently by Love and Scott /2/ which appears to give reasonable results, with an RMS error of 5.6%. It should be noted, however, that so far 1) only a limited set of experimental data, say for oxides /3/, has been used to estimate the efficiencies of some particular correction methods, 2) the "optimised" mass absorption coefficients have been used to minimise errors in the concentration obtained by a given method, 3) microanalysis data for a wide range of electron energies E have been included into the estimated RMS errors whereas the performance of different models used in light element EPMA is known to be sensitive to E_0 (or X/6) values.

In the present work microprobe data available for light element systems containing O, C and B are considered in order to estimate the efficiency of different correction procedures. Since for light element systems the absorption correction factor F_a (and its dependence upon E_a) is dominant over atomic number effects, we shall compare here the performance of different absorption corrections, using in all cases Love-Cox-Scott (LCS) expression /4/ for the stopping power factor F_s and the tables of R values /5/ to compute the backscatter factor F_b. The mean ionisation potential J and the surface ionisation parameter α(0) are obtained with the use of Berger-Seltzer's and LCS's formula respectively. Adopted values of mass absorption coefficients are those of Henke and Ebisu /6/, the backscattering coefficients α are taken from tables /7/. The LCS approach to the calculation of the stopping power factor based upon a modified form of the Bethe-Ashkin equation for electron energy loss permits to avoid dE/dx becoming zero when E=J/1.166. This would be the case, for example, in analysis for light element 1 from the binary system 1-2 if €E_1=J_1 (J_2 /J_1) ^1/1.166,
where $J_1$, $J_2$ are the ionisation potentials of the constituent elements, $C$ is the light element mass concentration, and $E_c$ the critical excitation energy. Such situation occurs, in particular, in analysis of Be in Cu-Be alloys ($C < 67\%$), in the Fe-B system ($C < 21\%$) etc.

In the present paper we estimate the performance of the following correction models: the simplified Philibert approximation ($\mathcal{F}(o)=0$ with 1) $c_1=4.5$ and $n=1.65$ (Heinrich), 2) $c_2=2.39$, $n=1.5$ (Duncumb-Shields); 3) the Philibert rigorous model with $c_3=2.54$, $n=1.5$ (Duncumb-Melford), 4) the Ruste-Zeller (RZ) absorption correction /8/ in which and $n$ are $Z$ dependent and $h$ is energy dependent; 5) the LCS approximation /9/ with $c_4=9.5$, $n=2$; 6) the Love-Scott (LS) absorption correction based upon Bishop's rectangle approximation to $\mathcal{F}(\rho^2)$; 7) the thin film (TF) model by Duncumb and Melford which combines atomic number and absorption corrections. The expressions for $h$ recommended for the above corrections are used in the calculations.

In addition to the microanalysis data for binary and ternary oxides /3/ we take into consideration the oxygen, carbon and boron analyses /10,11/ carried out on the ARL instrument with $\Phi=52.5^\circ$, the results of Ruste and Gantois /12/ obtained on the MS-46 microprobe with $\Phi=18^\circ$ and some other data. The whole collation comprises 272 measurements on 49 systems at 6 different voltages (5-30 kV). The measured intensity ratios, $k$, except those from /3/ were taken from the figures in the papers /10,11/; errors arising from reading the curves vary from 2-3\% to 8\%, while the statistical counting error will be ~1.5\%. Some of the measurements /10,11/ obtained at low (5 kV) voltage and the results for Pb /3/ were excluded from the assessment as unreliable due to large RMS errors (>15\%) in the estimated concentration. Typical overall correction factors, $F$, calculated by different methods for moderately ($\chi > 20000$, $\chi/\chi_0 > 3$) and heavily ($\chi < 20000$, $\chi/\chi_0 < 3$) absorbing systems are plotted in Fig.1,2 as a function of probe energy $E_c$. For comparison, the experimental $F(=c/k)$ values are also given in the figures.

The RMS errors in the estimated concentration (Table, next page) were evaluated a) for all the systems in the energy range 5-30 keV and, separately b) for low ($\chi < 20000$) and high absorbing systems ($\chi > 20000$). The RMS data are also subdivided into two groups according to the probe voltage (5-15 kV, 20-30 kV) and separately for low and high absorbers.

Fig.1,2. Probe energy dependence of the overall correction factors calculated for NiTiO, $\Phi=35^\circ$(1) and SiC, $\Phi=18^\circ$(2) by different methods: DS - Duncumb-Shields, H-Heinrich, DM- Duncumb-Melford; LCS - Love-Cox-Scott /9/, Love-Scott/2/, LS - Love-Scott/2/; TF - thin film model; - exp. $F$ values.
Table. RMS errors(%) obtained using different correction models

<table>
<thead>
<tr>
<th>Model</th>
<th>5-30 keV</th>
<th>5-15 keV</th>
<th>20-30 keV</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
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<td>Heinrich</td>
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<td>15.8</td>
</tr>
<tr>
<td>Duncumb-Shilds</td>
<td>12.9</td>
<td>10.7</td>
<td>16.8</td>
</tr>
<tr>
<td>Duncumb-Nelford</td>
<td>5.3</td>
<td>8.1</td>
<td>8.8</td>
</tr>
<tr>
<td>Ruste-Zeller</td>
<td>10.8</td>
<td>10.0</td>
<td>12.4</td>
</tr>
<tr>
<td>Love et al. /9/</td>
<td>8.6</td>
<td>7.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Love-Scott /2/</td>
<td>9.1</td>
<td>8.1</td>
<td>11.0</td>
</tr>
<tr>
<td>Thin film model</td>
<td>33.</td>
<td>29.</td>
<td>39.</td>
</tr>
</tbody>
</table>

N - number of analyses; a) all(272) measurements for all (49) systems; b) measurements for moderate (X<20000 cm/g) absorbers; c) measurements for high (X>20000 cm/g) absorbers. First two models are related to the simple Philibert absorption correction. See also Fig.3,4.

From an examination of the $F(E_0)$ curves and the RMS errors the following conclusions can be drawn:

1. For light element systems, the absorption correction factor $F$ and, as a consequence, the overall correction $F$ are strongly dependent upon the probe energy $E_0$. Discrepancies between $F$ values predicted by different correction models are greater for higher $X$ and $E_0$. Hence, it is not reasonable to incorporate into some kind of histogram or table illustrating the performance of a particular correction procedure microanalysis data for a wide range of $E_0$.

2. Each particular correction method has its own characteristic energy dependence of $F$. For the systems with $X> X_0$, for example, the $F(E_0)$ curves calculated using the simplified Philibert formula (DS or H in Fig.1,2) rise monotonically with $E_0$ and lie higher than the $F(E_0)$ curves obtained with the use of the full Philibert expression (DM, LCS, RZ; see also LS or TF, Fig.1,2) at high voltages. The Ruste-Zeller model predicts too rapid increase in $F$, and $F$ in the intermediate range of $E_0$, between 5 and 10-12 keV, and the limiting values of (in the 25-30 keV regime) lie higher than the values obtained by other methods based on the rigorous Philibert model but usually lower than those calculated using the simple Philibert method (DS or H). The LS values lie close to the $F(E_0)$ curve obtained by the RZ method at low voltages, while the limiting values at higher energies are close to the values predicted by the thin film model. The $F(E_0)$ curves calculated by the rigorous Philibert method with LCS's constants /9/ are close at low energies ($<15$ keV) to the values obtained using the simple Philibert formula with Heinrich's constants $\sigma_c$, n and $h$.

3. The minimum RMS error of 5% can be obtained at low energies ($<5$ keV) by using the LCS, RZ and LS methods or Philibert's simple model with Heinrich's constants if one takes into account only the oxygen analyses /3/ for the systems with $X<25000$.

4. The LCS and DM models are most "stable" within the energy range 10-30 keV, giving the RMS error of 9-11%. The RZ method gives similar results, but only at higher (>20 keV) voltages.

5. The RMS error predicted by the LS model based upon Bishop's approximation increases with $E_0$ and at high energies (>20 keV) is close to the value obtained with the use of the TF model.

6. The thin film model fails in the range of $E_0$ suitable for light element analysis. Inadequacy of the model is determined primarily by its breakdown for light element standards (such as Al$_2$O$_3$, MgO, C, B for which X/\sigma=3.5 at $E_0<25$ keV) rather than uncertainties in $\Phi(0)$ values.
Fig. 3. RMS errors(%) obtained using different correction procedures.

Fig. 4. RMS errors(%) obtained using the Love-Scott method [2] for low ($\chi < 20000$) and high ($\chi > 20000$) absorbers.

7. An additional information can be derived from an examination of the mean values of $\Delta C/C$, where $\Delta C$ is the difference between the true concentration of the light element and that predicted by a particular correction method. With the $\mu / \rho$ data of Henke and Ebisu [6] we find, for example, that the mean values of $\Delta C/C$ calculated by most of the existing methods are negative for $\text{SiO}_2$, $\text{MoO}_3$, $\text{ZrO}_2$, $\text{MgO}$, $\text{Cr}_2\text{O}_3$, $\text{NiO}$, $\text{BeO}$ and positive for $\text{TiO}_2$, $\text{PbO}$ and some other systems, at least in the range of 5-20 keV. This means that $\mu / \rho$ values of Henke and Ebisu for $\text{O K x-rays}$ in $\text{Si, Mo, Zr, Mg, Cr, Ni, Be, Ti, Pb and Al}$ may be in error. It should be emphasized, however, that any "optimisation" of mass absorption coefficients must be relied upon the close consideration of the $\mu / \rho$ curves or $\Delta C/C$ values obtained by different correction methods in the energy range where these methods are working well.

8. Situation for heavily absorbing systems ($\chi > 35000$) is rather uncertain because of the paucity of reliable experimental data. There may be some evidence, however, that for high X values the $\text{RZ}$ model works better than others, especially at $E_x \leq 20$ keV (Fig. 2). All other methods give for heavily absorbing systems ($\text{SiC}, \theta = 18^\circ$ and $52^\circ$; $\text{MoO}_3$, $\text{TiO}_2$, $\text{ZrO}_2$, $\text{PbMoO}_4$, $\theta = 20^\circ$ etc) extremely high RMS errors ($> 20\%$).

References
10. SHIRAIWA T., FUJINO N. and MURAYAMA J., X-ray Optics and Microanalysis, ed. Shinoda et al., Tokyo, Tokyo Univ.Press, 1972, p.213.