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QUANTITATIVE ANALYSIS OF A MULTICOMPONENT SILICATE GLASS BY ELECTRON MICROPROBE

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Quantitative analysis of a multicomponent silicate glass by electron microprobe

Abstract - A standard glass sample denoted by the National Institute of Standards and Technology as K-412 was analyzed using electron microprobe by an international collaborative team. The results of quantitative determination of the oxide glass components are compared and the deviations from the standard values are calculated. Also methods of glass surface treatment, conditions of quantitative determination and procedures used for evaluation of results are summarized.

INTRODUCTION

Determination of the composition of glasses using electron microprobe appears to be one of the methods most used in both research and in the glass industry. Despite the common use of this method there are still some uncertainties in the reproducibility and accuracy of the measurements. Those are caused by:

i) relative complexity of glass surface preparation,
ii) influence of voltage, electron beam diameter, time of counting and other parameters of the analysis,
iii) standards and methods used to convert X-ray intensities into concentration values.

Therefore, it is of great interest to compare conditions of measurement, reproducibility and accuracy of measurements in some laboratories dealing with glass analysis (ref. 1, 2).

GLASS SAMPLE CHARACTERIZATION

A standard probe K-412 supplied by the National Institute of Standards and Technology, Washington D.C. (USA) was used (ref. 3). The certified composition of the glass was as follows (in wt %):

\[
45.35 \pm 0.2 \text{ SiO}_2 \\
19.33 \pm 0.2 \text{ MgO} \\
15.25 \pm 0.2 \text{ CaO} \\
9.27 \pm 0.2 \text{ Al}_2\text{O}_3 \\
9.96 \pm 0.2 \text{ Fe}_2\text{O}_3
\]

The uncertainty of \( \pm 0.2 \) wt % assigned to the certified values is the 2-sigma value. This composition made it possible to compare the results of analytical measurements on the relatively stable glass containing very common oxides.

The samples were sent to the participants on the project (see Appendix) in the form of a small stick. The participants were asked to make quantitative analysis of the glass sample using an electron microprobe and procedures and conditions chosen by themselves.

SURFACE TREATMENT OF GLASS SAMPLES

Procedures used by the participants to prepare the glass surface for analysis are briefly summarized in the Table 1. Most of the authors fixed the glass sample by embedding in epoxy resin. Only in one case was the sample stuck using a carbon paste on a carbon block. Various procedures were used for grinding. Grinding powders, papers and discs made it possible to prepare glass surfaces with a roughness 5 \( \mu \)m. Not all authors stated how the grinding procedure was performed and which roughness of the surface was obtained.

In one case the fracture surface of the glass sample was used without any grinding and polishing. Cerium oxide in the form of a disk or a paste was used preferably to polish glass surface. Also alumina powder and diamond pastes were used in some cases. After cleaning of the glass surface with alcohol or water a thin carbon layer was sputtered on the sample. The thickness of the layer was 20-50 nm.
TABLE 1. Glass sample preparation

<table>
<thead>
<tr>
<th>embedding</th>
<th>grinding</th>
<th>polishing</th>
<th>cleaning carbon coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. epoxy resin grinding machine</td>
<td>polishing diamond pastes</td>
<td>alcohol</td>
<td>C 20-30 nm</td>
</tr>
<tr>
<td>2. sticking by a carbon paste on a carbon block</td>
<td></td>
<td></td>
<td>C 40 nm</td>
</tr>
<tr>
<td>3. hot pressing using fenol resin</td>
<td>grinding diamond discs (30-5 μm)</td>
<td>polishing disc (CeO₂)</td>
<td>alcohol</td>
</tr>
<tr>
<td>4. epoxy resin</td>
<td>grinding discs (30-5 μm)</td>
<td>polishing disc (CeO₂)</td>
<td>alcohol</td>
</tr>
<tr>
<td>5. epoxy SiC on glass</td>
<td>polishing diamond pastes</td>
<td>warm water, soap</td>
<td>C 25 nm</td>
</tr>
<tr>
<td>6. resin and wax corundum powder (20-7 μm)</td>
<td>CeO₂-paste</td>
<td>water, alcohol</td>
<td>C 30 nm</td>
</tr>
<tr>
<td>7. epoxy resin SiC-papers-800</td>
<td>0.3 um alumina + MgO</td>
<td>-</td>
<td>C 25 nm</td>
</tr>
<tr>
<td>8. epoxy resin grinding paper 200-600</td>
<td>alumina powder 1 um-0.3 μm</td>
<td>distilled water, freon</td>
<td>C 20 nm</td>
</tr>
<tr>
<td>9. brass block, carbon paste SiC-1000</td>
<td>CeO₂-powder</td>
<td>?</td>
<td>C 30 nm</td>
</tr>
<tr>
<td>10. sticking by a Ag paste on a carbon block</td>
<td></td>
<td></td>
<td>C 30 nm</td>
</tr>
</tbody>
</table>

EQUIPMENT AND EXPERIMENTAL CONDITIONS OF ANALYSIS

Different types of electron microprobe equipment were used for quantitative analysis of the K-412 glass samples (see Table 2). All equipment used was essentially based on the wavelength dispersive system (WDS) although an energy dispersive system (EDS) was alternatively used in some cases.

TABLE 2. Equipments and experimental conditions

<table>
<thead>
<tr>
<th>type of equipment</th>
<th>principle of operation</th>
<th>voltage (kV</th>
<th>intensity (nA)</th>
<th>electron beam diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. JCXA-733</td>
<td>WDS-aut.</td>
<td>15</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>2. JXA-50A</td>
<td>EDS, Kevex 7000</td>
<td>15</td>
<td>0.3</td>
<td>area of 13 x 13</td>
</tr>
<tr>
<td>3. JXA-5</td>
<td>WDS</td>
<td>10,15,20</td>
<td>13-18</td>
<td>5</td>
</tr>
<tr>
<td>4. JCXA-733</td>
<td>WDS</td>
<td>10,20</td>
<td>7-70</td>
<td>10</td>
</tr>
<tr>
<td>5. Camebac Micro</td>
<td>WDS-aut.</td>
<td>15</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>6. JCXA-733</td>
<td>WDS-aut.</td>
<td>15</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>7. JCXA-733</td>
<td>WDS-aut.</td>
<td>15,20</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>8. JCXA-733</td>
<td>WDS-aut.</td>
<td>15</td>
<td>17.1</td>
<td>10</td>
</tr>
<tr>
<td>9. SHIMADZU SM-7</td>
<td>WDS</td>
<td>15</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>10. ARL SEMQ</td>
<td>WDS-aut. EDS-Kevex 7000</td>
<td>20</td>
<td>9-WDS 3-EDS</td>
<td>0.5</td>
</tr>
</tbody>
</table>

WDS... wavelength dispersive system
EDS... energy dispersive system
The accelerating voltage applied varied between 10 and 20 kV but the value of 15 kV was used preferably. The corresponding absorbed current values differed significantly from about 10 to 70 nA. Extremely low values (0.3 and 3 nA respectively) were used with EDS method.

The electron beam diameter varied from 0.5 μm to 50 μm. In one case a scanning procedure was used and the scanned area was 13 x 15 μm.

In addition to the parameters summarized in the previous table the time and number of measurements together with correction methods and types of correction programmes were also compared (see Table 3).

Counting times varied between 5 and 300 seconds with the highest values pertaining to the EDS measurements. The maximum value observed in WDS measurements amounted to 100 s. The number of the measurements reported by participants differed significantly from 3 to 200. The value of this parameter clearly depends on the availability of an automation system.

All results of the measurements were evaluated by a correction programme. Different types of correction programmes were used but the ZAF correction method clearly predominated.

**STANDARDS AND MONOCHROMATORS**

Simple oxides were used as standard materials for quantitative determination of MgO, SiO₂, Al₂O₃ and Fe₂O₃. Also some multicomponent standards were applied (chromite, Zafirite, Pyrope, Albite, jadeite, Olivine, Wollastonite and Silicate glass) in some cases.

Three main crystals were used in the measurements: TAP (thallium acid phthalate) for Mg, Si, Al, PET (pentaerythrite) for Ca and Fe and LiF for Fe predominantly. The K lines were employed for Mg, Al, Si, Ca and Fe determination.

**RESULTS**

The results of the K-412 glass sample analyses are summarized in Table 4 which includes values of the oxide content in wt.% together with standard deviations as they were measured and calculated by the participants. Also the certified composition according to the NIST certificate is shown in that table. The deviations between values determined by the participants and corresponding NIST values are shown in Table 5.
Quantitative analysis of glass by electron microprobe

The results can be summarized as follows:

**MgO determination**
Most of the results are within the limits defined by NIST value and corresponding standard deviation (see Table 4). The highest deviation from the standard value amounts to 1.63 rel.%. Deviations from the standard value decreased if the voltage was raised from 10 to 20 kV. The accuracy of the determination does not depend significantly on the principle of the measurements (WDS, EDS) or on the type of correction programme (ZAF, BA). A more systematic study has to be done to verify this conclusion.

### TABLE 4. Results of quantitative analysis of the K-412 sample

<table>
<thead>
<tr>
<th></th>
<th>MgO±</th>
<th>Al₂O₃±</th>
<th>SiO₂±</th>
<th>CaO±</th>
<th>FeO±</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt %</td>
<td>rel. wt %</td>
<td>rel. wt %</td>
<td>rel. wt %</td>
<td>rel. wt %</td>
<td>rel. wt %</td>
</tr>
<tr>
<td>1.</td>
<td>19.44</td>
<td>0.8</td>
<td>9.42</td>
<td>1.5</td>
<td>45.54</td>
</tr>
<tr>
<td>2.</td>
<td>17.7</td>
<td>5.0</td>
<td>8.8</td>
<td>3.4</td>
<td>46.1</td>
</tr>
<tr>
<td>3.</td>
<td>19.44</td>
<td>2.8</td>
<td>8.94</td>
<td>2.1</td>
<td>44.84</td>
</tr>
<tr>
<td>4.</td>
<td>19.83</td>
<td>0.8</td>
<td>9.38</td>
<td>1.0</td>
<td>46.76</td>
</tr>
<tr>
<td>5.</td>
<td>19.8</td>
<td>1.0</td>
<td>9.70</td>
<td>0.8</td>
<td>45.20</td>
</tr>
<tr>
<td>6.</td>
<td>19.11</td>
<td>0.3</td>
<td>9.87</td>
<td>0.7</td>
<td>45.92</td>
</tr>
<tr>
<td>7.</td>
<td>19.23</td>
<td>0.3</td>
<td>9.41</td>
<td>0.7</td>
<td>45.80</td>
</tr>
<tr>
<td>8.</td>
<td>19.11</td>
<td>0.7</td>
<td>8.7</td>
<td>0.6</td>
<td>45.52</td>
</tr>
<tr>
<td>9.</td>
<td>19.97</td>
<td>0.1</td>
<td>9.2</td>
<td>0.2</td>
<td>45.19</td>
</tr>
<tr>
<td>10.</td>
<td>19.54</td>
<td>1.2</td>
<td>9.67</td>
<td>2.0</td>
<td>46.3</td>
</tr>
</tbody>
</table>

**K-412 (NIST certificate value)** 19.33 0.5 9.27 1.0 45.35 0.2 15.25 0.6 9.96 1.0 99.16

### TABLE 5. Absolute value of deviations from NIST certificate values in wt %

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>+0.11</td>
<td>+0.15</td>
<td>+0.16</td>
<td>+0.01</td>
<td>+0.33</td>
</tr>
<tr>
<td>2.</td>
<td>-1.63</td>
<td>-0.47</td>
<td>+0.75</td>
<td>+1.75</td>
<td>+0.44</td>
</tr>
<tr>
<td>3.</td>
<td>+0.14</td>
<td>-0.17</td>
<td>+0.52</td>
<td>-0.39</td>
<td>-0.32</td>
</tr>
<tr>
<td>4.</td>
<td>+0.5</td>
<td>+0.11</td>
<td>+1.41</td>
<td>-0.38</td>
<td>-0.46</td>
</tr>
<tr>
<td>5.</td>
<td>+0.47</td>
<td>+0.43</td>
<td>-0.15</td>
<td>-0.35</td>
<td>+0.54</td>
</tr>
<tr>
<td>6.</td>
<td>+0.77</td>
<td>-0.05</td>
<td>+0.49</td>
<td>-0.5</td>
<td>+0.46</td>
</tr>
<tr>
<td>7.</td>
<td>-0.22</td>
<td>+0.6</td>
<td>+0.57</td>
<td>-0.31</td>
<td>+0.31</td>
</tr>
<tr>
<td>8.</td>
<td>-0.32</td>
<td>-0.57</td>
<td>+0.17</td>
<td>+0.17</td>
<td>-0.82</td>
</tr>
<tr>
<td>9.</td>
<td>+0.64</td>
<td>-0.07</td>
<td>-0.16</td>
<td>+0.15</td>
<td>-0.71</td>
</tr>
<tr>
<td>10.</td>
<td>+0.77</td>
<td>-0.37</td>
<td>+1.05</td>
<td>-0.45</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

The results can be summarized as follows:

MgO determination
Most of the results are within the limits defined by NIST value and corresponding standard deviation (see Table 4). The highest deviation from the standard value amounts to 1.63 rel.%. Deviations from the standard value decreased if the voltage was raised from 10 to 20 kV. The accuracy of the determination does not depend significantly on the principle of the measurements (WDS, EDS) or on the type of correction programme (ZAF, BA). A more systematic study has to be done to verify this conclusion.
Al₂O₃ and SiO₂ determination
Deviations from the certified standard value are in all cases comparable with
the standard NIST deviation value. The analytical results show that the accu-

racy of the measurements is comparable with the results of other oxides. The
deviations from the certified value are probably also caused by the drift of
monochromator caused by its mechanical and thermal instability. Charging
effects can also contribute to a certain lateral defocussation of the spectro-

meter.

CaO determination
The results are in satisfactory agreement with the standard NIST value (see
Table 4) although in some cases the difference between determined value and
NIST standard exceeds the certified standard deviation.

FeO determination
The analytical results are in a good agreement with the standard value (see
Table 4). Deviations exceed in some cases slightly the certified NIST stan-
dard deviation. Quantitative determination of FeO in the multicomponent si-
licate glass thus seems to be quite reliable.

The reasonable agreement of the analytical results of all glass components
indicates that the different procedures and conditions used by the parti-
cipants do not have a pronounced effect on the accuracy and reproducibility
of the measurements. As had to be expected the error of the measurements on a
fracture surface are much larger than on polished surfaces.

CONCLUSION
Quantitative analysis of the K-412 glass standard glass using the electron
microprobe was carried out by an international collaborative team. The analy-
tical results are in good agreement with the certified values confirming the
reliability and accuracy of the work in laboratories participating on the
project.

The results show that comparable results can be achieved using different
types of equipment with good standards even when procedures and conditions
applied are not quite identical.

Values of oxide content obtained in different laboratories were usually
within the relative standard deviations certified for the standard K-412
glass. The accuracy of the measurements is affected by the quality of the
glass surface, a good polishing procedure is essential.

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REFERENCES
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WILDE P.M. Central Institute of Inorganic Chemistry, Berlin, (DDR)