The validation and application of a reproducible analytical protocol for the study of unstable glass

van Bommel, M.R.; Verhaar, G.; Tennent, N.H.

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The validation and application of a reproducible analytical protocol for the study of unstable glass

Guus Verhaar1,2, Maarten R. van Bommel1,3 and Norman H. Tennent1

1) University of Amsterdam, Faculty of Humanities, Conservation and Restoration department; 2) Rijksmuseum, Conservation and Research Department; 3) University of Amsterdam, Faculty of Science, Van ’t Hoff Institute for Molecular Sciences (HIMS); *g.verhaar@uva.nl

Introduction

Glass of unstable composition can develop very dramatic changes in appearance (Figure 1) and visual examination of glass collections around the world indicate that up to 30% of vessel glasses in museum collections may be of unstable composition. Objects at risk could benefit from measurements delaying the degradation process to prevent, but up to now it has not been possible to identify unstable glasses with certainty before changes in appearance occur.

Glass deterioration is generally associated with the leaching of cationic compounds from the surface layer of the glass and subsequent formation of (hygroscopic) salts on the surface. The present research focusses on the development and application of an analytical protocol for the reproducible and quantitative identification of those ionic compounds in low concentrations for the identification of unstable glass. Results of protocol validation, artificial aging, and museum object studies will be presented.

Protocol validation

A protocol was developed for the sampling and analysis of standard solutions containing those ions indicative of glass deterioration. The protocol consists of the following steps (please contact the authors for more detailed information):

1. Swabbing the surface (Figure 2)
2. Extraction of ions from deionized water
3. Centrifugation of the sample
4. Analysis using Dionex IC systems

The analytical results for validation of the protocol are generally good for sampling standard solutions from Melinex surfaces (Table 1).

Table 1. Results of sampling protocol validation. Listed are coefficient of determination (R²), relative recovery of analyte, relative standard deviation (RSD) as a measure for repeatability, limits of detection (LOD) and limits of quantification (LOQ).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R²</th>
<th>Recovery (%)</th>
<th>Repeatability (RSD %)</th>
<th>LOD (mg/L)</th>
<th>LOQ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>0.9991</td>
<td>94.75 ± 4.97</td>
<td>4.20</td>
<td>0.140</td>
<td>0.423</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.9973</td>
<td>99.16 ± 2.93</td>
<td>2.93</td>
<td>0.648</td>
<td>1.964</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.9992</td>
<td>91.96 ± 5.68</td>
<td>4.09</td>
<td>0.258</td>
<td>0.781</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.9986</td>
<td>89.45 ± 4.61</td>
<td>4.39</td>
<td>0.067</td>
<td>0.203</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.9997</td>
<td>91.77 ± 4.83</td>
<td>4.42</td>
<td>0.404</td>
<td>1.223</td>
</tr>
<tr>
<td>Acetate</td>
<td>0.9997</td>
<td>101.37 ± 3.12</td>
<td>2.96</td>
<td>0.038</td>
<td>0.116</td>
</tr>
<tr>
<td>Formate</td>
<td>0.9994</td>
<td>94.25 ± 2.19</td>
<td>2.21</td>
<td>0.046</td>
<td>0.141</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.9337</td>
<td>71.37 ± 25.68</td>
<td>13.57</td>
<td>0.164</td>
<td>0.496</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.9990</td>
<td>91.93 ± 2.92</td>
<td>2.87</td>
<td>0.063</td>
<td>0.192</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.9926</td>
<td>n.d.</td>
<td>43.24</td>
<td>0.185</td>
<td>0.561</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.9966</td>
<td>78.18 ± 4.28</td>
<td>4.32</td>
<td>0.179</td>
<td>0.542</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.9960</td>
<td>95.81 ± 3.08</td>
<td>3.05</td>
<td>0.194</td>
<td>0.588</td>
</tr>
</tbody>
</table>

Application 1: artificially aged unstable glass

Artificial aging caused the unstable glass to deteriorate notably within 2 weeks. The clear circles represent the sampled area, indicating the removal of surface deposits (figure 3).

Figure 3. Unstable glass after aging and sampling. Aging was carried out at 70% RH and at 70 °C for 2 weeks.

Figure 4. Average ion concentrations in mg/L of 6 samples taken from the unstable glass in figure 3 before and after sampling. Error bars indicate the standard deviation of ion concentrations (n=6).

Application 2: museum objects

Two groups were sampled using the validated protocol:

1. Glasses showing no visual signs of deterioration prior to cleaning (stable)
2. Glasses showing clear signs of deterioration prior to cleaning (unstable)

Striking results are (figure 5):

- Sodium, potassium, formate and acetate are the ions found in high concentrations on unstable glass.

Figure 5. Ion concentrations of samples obtained from objects from museum Boijmans van Beuningen with ions in major concentrations (L) and ions in minor concentration (R) separated. Each bar represents the average ion concentration for one object (3-5 samples for each object), error bars indicate the standard deviation. Between 2011 and 2013 all glasses were investigated for signs of deterioration, cleaned and stored in a stable climate of 50% RH and 20 °C.

Table 1. Results of sampling protocol validation. Listed are coefficient of determination (R²), relative recovery of analyte, relative standard deviation (RSD) as a measure for repeatability, limits of detection (LOD) and limits of quantification (LOQ).

Conclusions

- An analytical protocol with high repeatability (RSD < 5%) and high recovery (> 90%) was validated for ions related to glass deterioration. Chloride and carbonate showed a repeatability of > 5%. Sulfate has good repeatability, but the recovery is lower: 78.15%.
- The results of artificially aged unstable glass and museum glass samples indicate that sodium, potassium, acetate and formate are the main ions present on unstable glass surfaces. The presence of sodium and potassium can be attributed to the glass, acetate and formate must originate from the environment, but the high concentrations are peculiar.
- Analysis of the museum samples demonstrate that high ion concentrations indicate glass instability, but results from visual categorisation of glasses as stable and unstable. Further work will scrutinise this issue more closely.

Acknowledgements

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Figure 1. Object in extremely advanced stage of deterioration. Flagon, Rijksmuseum, reg. no. BK-NM-809.