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Publication date
2017

Document Version
Final published version

Citation for published version (APA):

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

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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 50% 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 in 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 analytes, 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>0.991</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>0.997</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>0.992</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>0.998</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>0.997</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>0.999</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>0.994</td>
<td>94.25 ± 2.19</td>
<td>2.11</td>
<td>0.046</td>
<td>0.141</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.937</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>0.990</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>0.992</td>
<td>n.d.</td>
<td>43.24</td>
<td>0.185</td>
<td>0.561</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.966</td>
<td>78.15 ± 4.28</td>
<td>4.32</td>
<td>0.179</td>
<td>0.542</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.996</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).

Results of the IC analysis of the samples are (figure 4):
- Sodium, potassium, acetate and formate are the main ions detected, with a clear increase of after aging. Other ions showed less or no increase upon aging.
- The validated protocol works well for the quantitative analysis of ions on unstable glass surfaces.

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 glasses.
- Samples from objects categorized as stable do not show any high ion concentrations.
- Samples from objects categorized as unstable show both high and low ion concentrations.

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 and need further investigation.
• Analysis of the museum samples demonstrate that high ion concentrations indicate glass instability, even without visual signs of deterioration.
• Low ion concentrations are found on both stable and unstable objects, suggesting that low ion concentrations are not indicative of stable glasses.
• The interpretation of the analytical results is dependent on the veracity of the original visual categorisation of glasses as stable and unstable. Further work will scrutinise this issue more closely.

Acknowledgements

The authors would like to thank Robert van Langh (Rijksmuseum), Kate van Looikeren Campagne (University of Amsterdam), Suzan de Groot (Cultural Heritage Agency of the Netherlands), Cécilia Gauvin (Rijksmuseum), Christel van Hees (Museum Boijmans van Beuningen).