

Challenges and opportunities in assessing the effectiveness and harmfulness of storage conditions for three dimensional cellulose nitrate museum objects

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Cellulose nitrate (CN) was one of the first plastics used for the mass production of daily common objects and cinema films. Museums face various challenges in preserving this kind of objects, connected with their flammability and their emission of nitrous gases. In order to slow down their chemical degradation, some authors recommend reducing their storage temperature. Even though several procedures suggest how to store CN films below room temperature, only a few published studies focus on 3D-CN objects, in which harmful effects like condensation phenomena and mechanical changes have been detected.

On a long-term perspective, our research project aims to assess the effectiveness and harmfulness of various storage conditions below room temperature of specific 3D-CN specimens by imaging methods, chemical analyses and mechanical testing methods.

In this preliminary study, for the definition of the experimental design we followed two strategies:

1. Development of a questionnaire, which was sent in December 2018 to several museums and research institutions to narrow down the following testing variables:
 - Storage temperatures;
 - Cooling and warming rates;
 - Specimen's condition state (good, moderate, poor);
 - Specimens with complex geometries (thick/thin, sharp/round);
 - Specimens containing mixed materials (i.e. CN-metal);
 - Relative humidity.
2. For characterizing the loss of the main CN-plasticizer, camphor, we tested four chemical analytical methods to choose one with good sensitivity and feasibility. GPC, EGA-MS, TGA-FTIR and TD-Py/GCMS were tested on CN specimens in fresh (**i**) and in moderate (**ii**) and severe (**iii**) artificially aged conditions.
 - GPC was used for quantifying the decrease of camphor, which progressed with chemical degradation: **i**) 26%; **ii**) 23% and **iii**) 18%.
 - EGA-MS and TGA-FTIR were used for the qualitative monitoring of the evolved gas production of camphor during specimens' heating. The latter gave us further quantitative information of the samples' weight loss related to characteristic temperatures, however in combination with all the other emitted gases (e.g. NO_x and CO₂). For **i**) and **ii**) specimens the main decomposition steps happened at around 178

°C, 188 °C, 191 °C and 214 °C, while for **iii**) specimens they happened at 122 °C, 151 °C and 191 °C.

- TD-Py/GCMS was applied with a semi-quantitative approach for monitoring of camphor. Its presence was detected in both TD and Py analyses and the comparison of its peak areas suggested a decreasing trend of the ratio from **i**) specimens to **iii**) specimens.

Based on our results, the most suitable analytical techniques for assessing the loss of camphor in future tests seem to be GPC and TGA-FTIR. The authors intend to enhance the differentiation of this plasticizer from other volatiles with TGA-FTIR by improving the method and the sample preparation.

The Summer School is an excellent opportunity for discussing our strategy, narrowing down the testing variables, receiving further input and judging which analytical methods shall be used for further tests. Moreover, our research approach can be useful for researchers performing similar studies.

Keywords: cellulose nitrate, experimental design, GPC, TGA-IR, EGA-MS, TD-Py/GCMS