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Case study

Use of pyrolysis-gas chromatography/mass spectrometry to characterise binding media and protectives from a Coronelli's terrestrial globe

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Abstract

During one of Coronelli's terrestrial globes restoration, belonging to the Bologna University, we found some substances considered not to be original. Their presence was both on the globe surface and under one of the gores. In order to characterise the organic material (original or added in restoring procedures) we employed pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The analytical results reveal the presence of the original materials, such as natural gums and animal glues, together with industrial products, such as synthetic germicides.

Keywords: Gas chromatography-mass spectrometry; Pyrolysis; Coronelli; Terrestrial globe; Restoration products

1. Introduction

Vincenzo Coronelli (Venice 1650–1718), friar of Minoriti Conventuali, cosmographer of the Republic of Venice, left many geographical and historical engravings in addition to his production of great globes. Coronelli's fame lasts not only for the sizes of his globes, but also for the quantity of geographical and historical information he printed on them. The production of the three and a half feet globes started in 1688 and continued almost till his death with very few changes and always with the same year (1688). These globes were always built in pairs: the terrestrial and the celestial sphere, but in many cases only one of them has survived men's destruction (wars, fires etc.). Survived globes were subjected to various maintenance and conservation interventions which have changed their original aspect often presenting coats of the different materials used. All three and a half feet globes derived from the great globes built for Louis XIV and were made of 24 engraved gores, 12 gores North and 12 South, plus two plates for the polar calottes. The engraved gores were glued onto the pre-made spheres, then coloured and finally coated with varnishes. Techniques and materials used were described by Coronelli himself in his "Epitome Cosmografica" [1].

In 1993 Enriques family presented the University of Bologna with a Coronelli's three and a half feet terrestrial globe previously belonging to Giovanni Enriques (1905–1990). The globe, shown in Fig. 1, underwent various maintenance interventions consisting in overcoating of different paints which altered the original appearance. For instance, the northern hemisphere was darker than the southern one because of a thicker coat of paint, dust and the action of light. The main features of this globe were not only due to the above listed damages, which are common to other globes, but also to peculiarities which distinguished and made it unique and for these reasons a restoration program started in 1993 [2,3].

During the restoration some gaps were observed and a large circular depression was noted between the southern part of India and the isle of Ceylon (Fig. 2). The last part of this gore was cut longitudinally thus obtaining a square which was later put back again. After removing that part of the gore, 78 mm of a wooden plastered stopper was discovered. Two kinds of adhesive and a reddish material were observed between the paper and the plaster which covered the whole paper mache sphere. Samples were taken in order to characterise organic materials occurring in this area which could provide information on the

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Fig. 1. The Coronelli's three and a half feet terrestrial globe. Museo di Astronomia of the University of Bologna.

past restorations performed on the globe as well as on the materials used by Coronelli.

Analytical pyrolysis is a powerful technique for the analysis of complex, heterogeneous organic materials which is based on the controlled thermal degradation of the sample in an inert atmosphere [4]. The identification of the evolved pyrolysis products is facilitated by means of their retention times and mass spectra which is accomplished by coupling pyrolysis with gas chromatography and mass spectrometry (Py-GC/MS). Since pyrolysis can be performed using minute amounts of sample (< 1 mg) and does not require chemical pre-treatments, Py-GC/MS has been largely applied in the field of art conservation for characterising binding media and protectives [5–19]. This study reports on the results of Py-GC/MS applied to the analysis of organic materials occurring in Coronelli's terrestrial globe.

2. Experimental

Samples were withdrawn from different areas of the globe during the restoration work as reported in Fig. 2. Fig. 3 shows a microscope observation of a paper fragment.

Pyrolysis experiments were performed with a Pyroprobe 1000 (Chemical Data System, Oxford, PA, USA) consisting of a platinum heated filament pyrolyser fitted with a quartz-tube sample holder. The pyrolyser was connected to a Varian 3400 gas chromatograph which, in turn, was coupled to a Varian Saturn II ion trap mass spectrometer. Gas chromatographic separations were performed with a J&W DB-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness), which was heated from 50 to 250 °C at 10 °C/min, holding the starting temperature for 5 min. Pyrolysis runs were performed at 800 °C for 10 s using minute amounts of sample (less than 10 μg). The injection port (split ratio 1/100) and the Py-GC interface were kept at 250 °C. Mass spectra were acquired under electron impact at 70 eV from *m*/*z* 40 to *m*/*z* 500 (1 scan/s).

Pyrolysis products were identified on the basis of the interpretation of their mass spectra and on comparison with retention data of chromatographic standards.

3. Results and discussion

Fig. 4 shows the pyrogram obtained from the thermal degradation of sample 1, the plastered stopper (see Fig. 2 for sample numbering). The most intense peak is associated to pyrrole, an indication of the presence of animal glue in this sample as confirmed by the quite high levels of diketodipyrrole. Both pyrrole and diketodipyrrole have been observed as predominant products in pyrolysates of animal glue, since they are thermal degradation products of proline and hydroxyproline, two amino acids abundant in collagen [6,11,15]. The identification of several nitrogen containing compounds (peak numbers 3, 4, 7, 8, 10, 11, 12, 17 of Fig. 4) is consistent with the presence of proteinaceous materials in sample 1.

Similarly to sample 1, the total ion chromatogram of sample 2 (not shown), exhibits pyrrole as the most abundant thermal degradation product, confirming the use of animal glue as binding medium. A detailed analysis of Py-GC/MS data reveals the presence of pyrolysis products arising from non-pro-

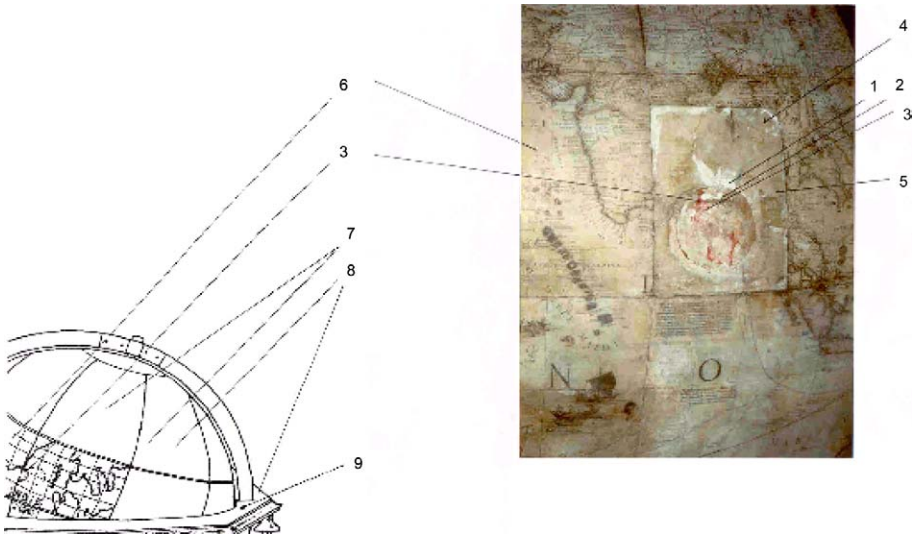

Fig. 2. Sampling area. Sample numbering: 1) plastered stopper; 2) plaster with red paint; 3) red paint; 4) and 5) adhesive; 6) original paint; 7) white paint; 8) external paint; 9) clot of white paint.