technart 2009

ROMANIT www.romanit.ro

Non-destructive and Microanalytical Techniques in Art and Cultural Heritage
Chromatography & Mass spectrometry (GC, HPLC) Section
Athens, 27 - 30 April

TD/CGC/MS and FT-IR characterization of archaeological amber artefacts from Romanian collections (Roman age)

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INTRODUCTION

Romanian museums preserve a large number of archaeological amber collections. Considering that Romanian amber (Rumanite) has been known for a long time it is of great interest to find out if the fossil resin used in these objects is of Romanian or Baltic origin. Despite the fact that Rumanite keeps the attention of Romanian geologists, it remained poorly characterized in what physical and chemical methods are concerned. Recently, within ROMANIT - a project developed at the national level and coordinated by Romanian National History Museum (MNIR), a multidisciplinary team was involved in the characterization of fossil resins with a particular focus on romanian amber (Rumanite). The project aims to establish certain methods to be used to characterize / differentiate Romanian from Baltic amber. The analytical techniques considered include TD/CGC/MS (thermal desorbtion / capillary gas chromatography / mass spectrometry) and Fourier Transform Infrared Spectroscopy, in transmission and variable angle reflectance (FTIR-VAR).

EXPERIMENTAL

Consideration on the methods used

Direct thermal desorbtion coupled with GC-MS was used to extract, concentrate and identify volatile compounds from amber in one single automated analysis. A chromatographic method together with a specific data analysis method based entirely on AMDIS software (figure 1) were developed for semi-quantitative and qualitative identification of biomarkers specific to amber specimens. Results showed some hundreds of volatile organic compounds, part of them previously found by other laboratories specialized in characterization of fossil resins and many without an assigned chemical structure. A mass spectra database, available on the project website, was created for all characterized volatiles. Full mass spectra of the developed database are currently being processed to be included in future versions of MaSC database (www.masc.org). Results evidenced marker compounds for both Baltic and Rumanite amber, which may be used to differentiate the two fossil resins from each other. A detailed description of the method was presented at the MASC Meeting in London. [Virgolici & al 2009].
Already a well established and practical technique for the structural characterisation and discrimination between amber types [Beck 1964/86, Thickett 1995, Angelini 2005, Guiliano 2006], infrared spectroscopy was used complementary to TD/CGC/MS. According to FTIR, Baltic amber (succinite) could be identified among other fossil resins by a single carbon-oxygen deformation band near 1150 cm^{-1}, which is preceded by a broad shoulder between 1250 and 1175 cm^{-1}. This characteristic „Baltic shoulder" is perfectly horizontal in well preserved succinite but assumes an increasly negative slope in samples that have been subject to atmospheric oxidation. It is not found in any non-Baltic fossil resins, including those containing succinic acid. [Beck 1986].
Considering that within FTIR/ trans sample withdrawal is compulsory, the method was used for controlled origin ambers and only occasionally for archaeological artifacts (when samples of ~ 1 mg were available). FTIR - VAR was suitable for small objects for which in situ analysis was possible, according to the instrument features.

Samples (controlled origin and archaeological amber)

Controlled origin amber samples (Baltic and Rumanite) were available from deposits, private and museum collections while the archaeological amber objects studied belong to several Romanian museum collections. According to art historians and archaeologists the objects belong to the Roman era.

Sample preparation

For TD/CGC/MS analysis, 10 mg of powder was packed with silanized glass wool plugs and 10 µl of methanolic solution with 0.005% chrysene were injected through the back of the tube as internal standard. FT-IR samples about 1 mg were embedded in potassium bromide (1:10 w/w), pressed in a 3 mm diameter pellet and analyzed in transmission. For FTIR-VAR samples were fixed on a gold mirror without any pre-treatment.

Instrumentation

Markes "UNITY" Thermal Desorber equipped with a General Purpose Hydrophobic Trap was used for direct TD at 200 ºC for extraction of volatile compounds (VCs) trapped in fossil resin matrix. An Agilent GC 6890N equipped with a 25 m x 0.25 mm HP-5ms column was used. The initial oven temperature of 40 ºC was ramped at rate of 2 ºC min^{-1} to 250 ºC and then held constant. MS detection was made with Agilent 5975 inert MSD in fragmentation mode by electron ionization at 70 eV, data acquisition in SCAN mode 35 - 700 amu. The optimal thermal desorbtion temperature was established by thermal analysis (figure 2).
All FT-IR spectra were collected on a Bruker Tensor 27 and analyzed at a 4 cm^{-1} spectral resolution.

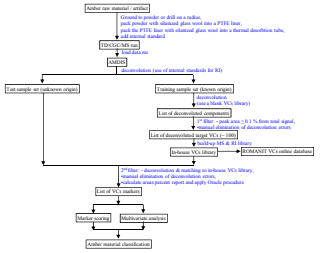

Figure 1. TD/CGC/MS data analysis workflow

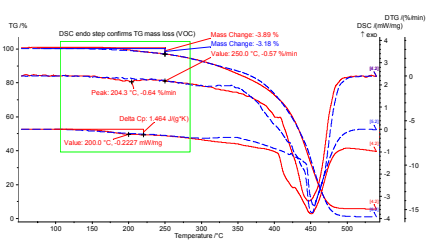

Figure 2. TG/DTG/DSC curves for Rumanite (red) and Baltic amber (blue) acquired at 10 ºC min^{-1} under inert atmosphere (nitrogen).

RESULTS

Using in-house databases of VCs detected in controlled geological origin ambers, archaeological samples were screened for the biological markers which could be correlated with geological origin. Extracted Ion Chromatograms (EIC) of specific fragment ions for the most characteristic VCs were taken into consideration for discrimination between Rumanite and Baltic ambers. EIC fingerprints were named features (figures 3 and 4). The occurrence of characteristic VCs was further correlated with the "Baltic shoulder" presence (1250-1175 cm^{-1}) in the FT-IR spectra (Figure 5).
These criteria, applied to archaeological amber from the Roman age, are summarized in Table 1. It should be mentioned that table one contains only the samples available for TD/GC/MS analysis, many others being tested only with spectroscopic techniques. From 17 available objects a clear result was obtained in about half of them while in about half of the rest attribution to Rumanite was not possible due to the lack of characteristic "features" according to TG/CGC/MS. It is hoped that multivariate exploratory data analysis (in progress now) will bring valuable information in this respect. It should be also mentioned that even in-situ analysis by FTIR/VAR was available, measurements on this technique was only possible for small objects (2–3 cm in diameter) due to the instrument configuration. We should also consider the difficulties of analysis when archaeological objects are concerned: previous treatment, storage conditions and even sample availability may also affect the quality of the obtained results.

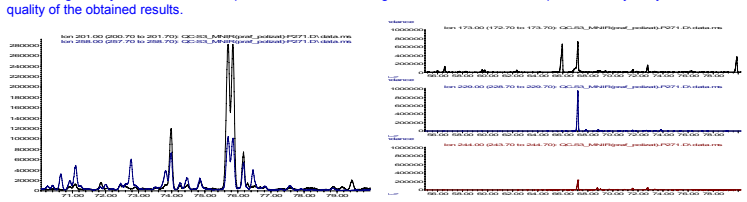

Figure 3. The most characteristic TD/GC/MS EIC features for Rumanite

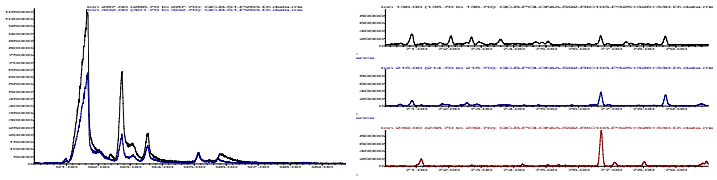

Figure 4. The most characteristic TD/GC/MS EIC Features for Baltic amber

Table 1. Comparative results of TD/GC/MS with FT-IR spectroscopic techniques and archaeological material classification

Object ID	Provenience	Sample ID	TD/CGC/MS	Characteristic features for B/R ambers according to FTIR		B/R
				trans	VAR	
72	Izoare NT	434-437	?	R	-	R
16	Izvoru GR	260	B	-	-	B
85	Harsova	439	?	R	-	R
83	Harsova	440-441	-	R	-	R
254	Tulcea	566-571	B	R?	-	?
251	Isaccea	572-574	B	?	-	B
255	Piatra Frecatei	576-577	B	?	-	B?
260	Piatra Frecatei	583-584	?	R	-	R
262	Piatra Frecatei	589	?	-	-	?
263	Archaeological Museum Mangalia	633-635	?	R	-	R
265	Mangalia	638,642	?	R	-	R
267	Archaeological Museum Constanta	646-648	?	R?	-	R?
271	Archaeological Museum Mangalia	651-652	?	?	-	?
279	Piatra Frecatei	709-710 692-693	?	R?	-	R?
282	Piatra Frecatei	712-713 674-679	B	B	B?	B
283	Piatra Frecatei	715-717	?	R	R	R
273	Mangalia	722,723,726	B	B	B	B

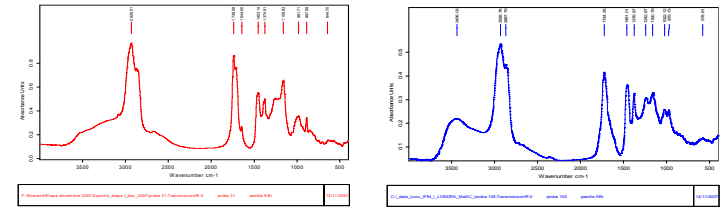

Figure 5. FT-IR spectra of Baltic amber (left) and Rumanite (right). Note: According to Beck, Baltic amber presents a horizontal shoulder at 1250-1160cm-1 followed by a strong signal at 1157 cm-1 [Beck 1986]. Rumanite is characterised by a strong signal at 1241 cm-1 [Angelini 2005]

CONCLUSIONS

TD/CGC/MS and FTIR techniques have good potential for identification of Rumanite and Baltic amber in archaeological artifacts. As in earlier publications, even if some analytical criteria to differentiate Romanian from Baltic amber were established, their use on archaeological amber artifacts may not be always successful. This may be due to chemical degradation in archaeological material and the restrictions imposed when historical objects are concerned (in situ analysis, amount of sample available, the measure the available sample is representative to the whole object).
Further studies to establish the limits of TD/CGC/MS and FTIR as well as development of new analytical techniques would be worthwhile for unambiguous attribution of archaeological amber artifacts geological origin.

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ACKNOWLEDGEMENTS

Authors are gratefully to CNMP Romania for financial support in the frame of grant no. 91-019/2007, ROMANIT research project entitled "Prestige and Power. Romanian Museums' Antique Items of Trade. Non-metallic adornments, with an archaeometrical study regarding the origin of amber beads." (http://www.romanit.ro). We would also like to thank the Romanian museums who provided us access to their collections.