Application of TD/CGC/MS and FT-IR in chemical characterization of Romanian amber

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INTRODUCTION

Research on the chemical composition of fossil resins has been developing during the last decades as a multidisciplinary field strongly related with their geological and botanical origin. Various extraction procedures and chromatographic techniques have been used to identify the volatile compounds (VCs) trapped in fossil resin matrix. Thermal desorbtion coupled with capillary GC/MS was chosen to investigate the volatile compounds from ambers with a focus on Rumanite (Romanian amber) and Baltic amber. A special data analysis procedure was developed for the purpose of fingerprinting ambers based on their highly characteristic semi-quantitative pattern of volatile compounds. Chromatographic data analysis was based entirely on AMDIS software to produce clean deconvoluted mass spectra which were used to build-up an in-house mass spectra and retention index library. Multivariate data analysis was further applied on AMDIS results with successful discrimination between Rumanite and Baltic amber. Preliminary results are promising and suggest that TD/CGC/MS has good potential for fossil resins fingerprinting especially used in conjunction with multivariate data analysis for classification and FT-IR spectroscopy for confirmation.

EXPERIMENTAL

Standards (Rumanite and Baltic amber)

Sample selection for method development was made under the supervision of Romanian National History Museum: 12 Romanian ambers (Rumanite, R1 - R12) and 9 Baltic ambers (Succinite, B1 - B9). Rumanite samples originated from Buzău county, Sibiciul de Jos village part of Pănătău (R1, R12) and Colţi - Pătârlagele hollow (R2 - R11). Baltic ambers originated from Bitterfeld - Germany (B1), Konigsberg - Kaliningrag - Russian Federation (B2, B5), Palanga - Lithuania (B3), Poland (B4, B7, B8) at the Baltic Sea and Earth's Museum from Warshaw, Denmark (B6) and Riga - Latvia Republic (B9). Other 5 "unknown" samples (U1 - U5) were used to test the method's efficiency to discriminate between Rumanite and Baltic amber. First two were presumed of Baltic origin (U1 coming from Bitterfeld museum of amber and U2 from Baltic sea) and the remaining three presumed to be Rumanite, burnt (U3) and red (U4) amber from Colţi Amber Museum, and one called "Muntenite" from Olanesti (U5)

Sample preparation

Samples were ground to powder.
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 analysed in transmission.

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 with a temperature programme of 2 K/min ramp from 40 to 250 ºC. MS detection was made with Agilent 5975 inert MSD in fragmentation mode by electron ionisation at 70 eV, data acquisition in SCAN mode 35 - 700 amu. All FT-IR spectra were collected on a Bruker Tensor 27 and analysed at a 4 cm-1 spectral resolution.

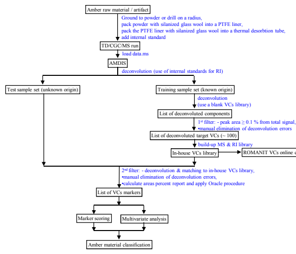

Figure 1. TD/CGC/MS data analysis workflow

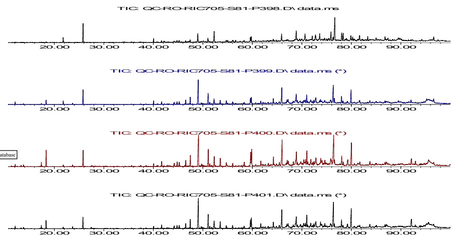

Figure 2 . TD/CGC/MS VCs fingerprint of a Rumanite piece drilled at different depths (P398 corresponds to the surface and P401 to the centre of the amber piece)

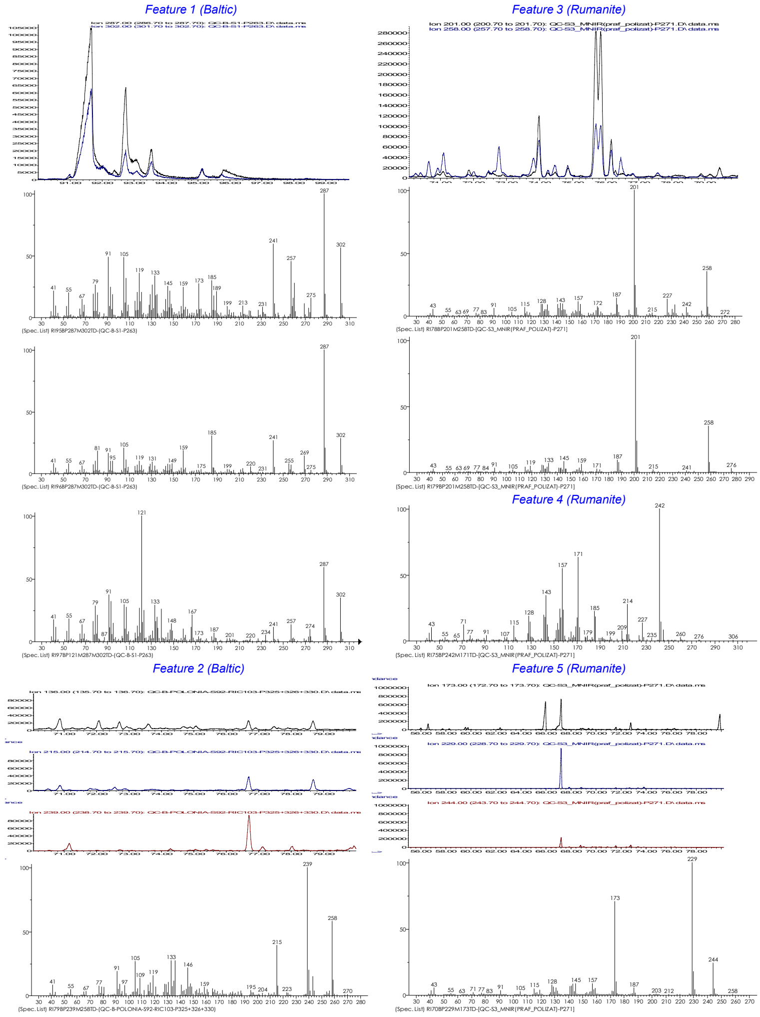

Figure 3. Rumanite and Baltic amber markers: Feature 1 and 2 (Baltic), Feature 3, 4 and 5 (Rumanite)

RESULTS

TD/CGC/MS data analysis (figure 1) is based almost entirely on AMDIS to generate semi-quantitative results. Figure 2 shows how characteristic and reproducible is the VCs pattern for an amber specimen sampled on a radius.
Extracted Ion Chromatograms (EIC) of specific fragment ions for the most characteristic VCs were first taken into consideration for discrimination between Rumanite and Baltic amber. EIC fingerprints were named features (figure 3, features 1-5). Features 1 and 2 were found characteristic for Baltic amber, while features 3, 4 and 5 were found characteristic for Rumanite .
Because Rumanite was recently identified a thermally degraded specimen of Baltic amber [Stout 2000], multivariate analysis was selected as an advanced tool for pattern fingerprinting recognition and classification. Principal Component Analysis (PCA) and Cluster Analysis were used considering the VCs as variables.
The PCA was selected for data analysis because is designed to solve large-sized problems, in our case over 70 VCs designated as variables, while providing visual aid for the classification of variables and cases. The PCA was carried out via the correlation matrix with successful discrimination between Rumanite and Baltic amber (figure 4).
Cluster Analysis results were also successful in dividing the training and test sample sets into two groups related with geological origin (figure 5). Only U2 sample was considered apart from the two groups but this exception is accepted based on the experimental observation that only 20 % of its VCs were identified using the in-house MS & RI library. By cross-referencing the EI fragmentation mass spectra with other online available databases some unidentified VCs were found to be characteristic to a subgroup of Baltic amber specimens brought by sea currents on the Polish coast line.
FT-IR was used as a complementary confirmation technique, with a high rate of success for all investigated samples. The characteristic features used as differentiation criteria between Rumanite and Baltic amber are presented in figure 6.

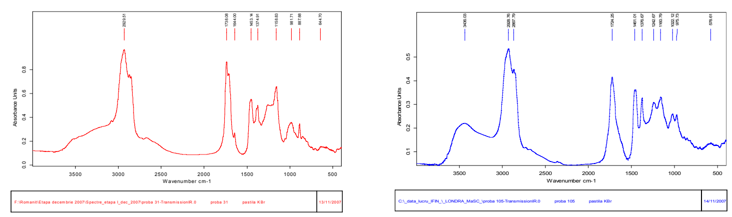

Figure 6. FT-IR spectra of Baltic amber (left) and Rumanite (right). Note: According to Beck, Baltic amber presents a horizontal shoulder at 1250-1160cm-1 followed by a strong signal at 1157 cm-1 [Beck 1986]. Rumanite is characterised by a strong signal at 1241 cm-1 [Angelini 2005]

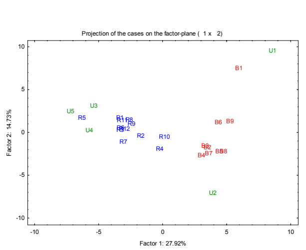

Figure 4. PCA Projection of the cases on the factor - plane (1 x 2) for Rumanite (R1 ÷ R12), Baltic amber (B1 ÷ B9) and test (U1 ÷ U5) sample sets.

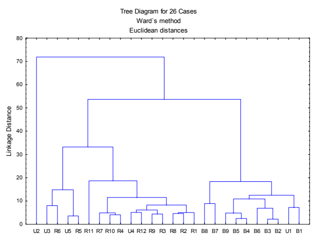

Figure 5. Cluster analysis for Rumanite (R1 ÷ R12), Baltic amber (B1 ÷ B9) and test (U1 ÷ U5) sample sets.

CONCLUSIONS

The present work confirms that TD/CGC/MS and FTIR could be successfully used for characterization and classification of fossil resins. Complementary techniques are useful especially in the case of archaeological amber artifacts, where due to chemical oxidative degradation and other interactions with the surrounding environment in the archaeological site, a strong interfering matrix may affect the targeted features for geological classification or even make them unrecognizable. 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 geological origin for archaeological amber artifacts. In order to improve amber specimen recognition, a more elaborate characterization is required. Multivariate data analysis may be the perfect tool to consolidate marker approach results.

REFERENCES

[1] Stout, E.C., Beck C. W., Anderson K. B.: Identification of Rumanite (Romanian Amber) as thermally altered succinite, *Phys. Chem. Minerals*, 27 (2000) 665-678.
[2] Thickett D. & al The Conservation of Amber, *Studies in Conservation* 40 (1995) 217-226.
[3] Angelini, I., Bellintani P., Archaeological ambers from Northern Italy: an FTIR-DRIFT study of provenance by comparison with the geological amber database, *Archaeometry* 47 (2005) 441-454.
[4] Beck C. W., Spectroscopic Investigations of Amber, *Applied Spectroscopy Reviews*, 22:1 (1986) 57-110.
[5] Guiliano M. et all., Applications of diamond crystal ATR FTIR spectroscopy to the characterization of ambers, *Spectrochemica Acta A Mol. Biomol. Spectrosc. 67* (2006) 1407-1411

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