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TD/CGC/MS AND FT-IR CHARACTERIZATION OF ARCHAEOLOGICAL AMBER ARTEFACTS FROM ROUMANIAN COLLECTIONS (ROMAN AGE)

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Already documented trade routes since prehistoric times and fossil resins geological occurrence in the European region suggest that Roumanian amber (also known as Rumanite or Romanite) and Baltic amber (also known as Succinite) are the most probable raw materials used at the manufacture of archaeological amber artefacts found on Roumanian territory. In the present paper thermal desorbtion hyphenated with capillary GC/MS and FT-IR spectroscopy in transmission (TRANS) and variable angle reflectance (VAR) were used complementary for geological origin attribution of a set of samples belonging to archaeological amber objects dated as belonging to Roman age and excavated mainly from the Dobrogea region, Roumania. TD/CGC/MS data analysis was computerized with AMDIS software and interpreted by principal components analysis for sample classification. Geological attribution by FT-IR was based mainly on the 1125 – 1330 cm^{-1} wavenumber region.

INTRODUCTION

A significant number of archaeological amber collections, which are preserved in Roumanian museums, belong to the Roman age. From the historical point of view the most probable geological sources for these amber artefacts were Baltic and Roumanian. Baltic amber (also called Succinite) could have come on the Danube River, from the Roman trade well-established routes, while local origin amber (also called Rumanite or Romanite) may have been also used, if we consider that the exploitation region of Romanite (located in Buzău Mountains) is not more than 100 km far from the Roman frontier. Potential merchants of this raw material were the Goths, who populated at that time the region in front the limes and represented the majority in the Roman army in the Low Danube area.

Present paper focuses on the characterization of archaeological amber artefacts excavated in Dobrogea region (South Eastern part of Roumania, on the border of the Black Sea) and aims to determine if the geological origin of raw amber is Roumanian or Baltic. Because of the similarities between the chemical structure and composition of the two fossil resins,[1] a complementary approach with TD/CGC/MS (the hyphenation between thermal desorbtion, capillary gas chromatography and mass spectrometry detection) and the Fourier transform infrared spectroscopy in transmission (FTIR-TRANS)[2-5] and variable angle reflectance (FTIR-VAR)[6] analytical techniques have been chosen. Thermal desorbtion method was chosen

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due to several advantages compared to conventional extraction techniques: avoidance of tedious extraction steps and derivatization procedures, good automation capabilities which induces reproducibility of results. Operational parameters of the TD step were developed according to data resulting from thermal analysis studies applied on fossil resins.[7] Already a well established and practical technique for the structural characterisation and discrimination between amber specimens,[2-6] infrared spectroscopy have been used for the differentiation of Baltic amber from 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" has been described in the scientific literature as perfectly horizontal in well preserved Succinite, and with an increasingly negative slope in samples that have been subject to environmental conditions. This feature have not been found in any non-Baltic fossil resins, including those containing succinic acid.[2]

EXPERIMENTAL PART

Amber samples (controlled origin and archaeological)

A controlled geological origin set of 9 Baltic amber (Succinite, B1 - B9) and 12 Roumanian amber (Romanite, R1 – R12) samples were selected as reference materials. Romanite samples originated from Buzău County, Sibiciul de Jos village part of Pănătău (R2, R9) and Colţi - Pătârlagele hollow (R1, R3 – R8, R10 – R12). Baltic ambers originated from Bitterfeld - Germany (B5), Konigsberg - Kaliningrag - Russian Federation (B4, B6), Palanga - Lithuania (B2), Poland (B3, B8, B9) from the Baltic Sea and Earth's Museum of Warsaw, Denmark (B7) and Riga - Latvia Republic (B1). Roumanian National History Museum (MNIR) provided for the present study a set of samples which could be traced to archaeological amber objects excavated from Constanța/Tomis (U16), Mangalia/Callatis (U11 – U15, U17, U23 – U25), Piatra Frecăţei/Beroe (U8 – U10, U18 – U22), Hârşova-Carsium (U3), Isaccea-Noviodunum (U6, U7) and Tulcea/Aegyssus (U4, U5), all located in Dobrogea region, Roumania, in the Late Roman Empire territory (Scythia Minor region), and date from the 4th-5th century. Some other objects dated from Barbaricum (U1, U2) were also available.

Instrumentation

For TD/CGC/MS analysis, depending of archaeological sample availability, 3 - 10 mg of powder was packed with silanized glass wool plugs in PTFE liners (250 µL) and further into standard stainless steel thermal desorbtion tubes (O.D. = 6 mm, manufactured by Markes International) in reproducible geometry. 10 µL of methanol solution with 0.005% chrysene was used as internal standard and it was injected through the back of the tube. Markes "UNITY" Thermal Desorber was used for volatile compounds (VC) extraction at 200 ºC, focusing at -10 ºC on a general purpose hydrophobic trap and split injection at 300 ºC directly into the capillary GC column. Agilent GC 6890N equipped with a 25 m x 0.25 mm HP-5ms column was ramped with 2 ºC min^{-1} from 40 to 250 ºC and then held constant. MS detection was performed on an Agilent 5975 inert MSD used in fragmentation mode by electron ionization at 70 eV. MS data acquisition was made in SCAN mode from 35 to 700 amu.

FT-IR spectra were collected at the same spectral resolution of 4 cm^{-1} on two Bruker Optics Tensor 27 instruments configured with different accessories for FTIR-TRANS and FTIR-VAR with an aperture of 4 nm and a beam incidence angle of 45˚. Spectra were acquired with 32 scans/sample versus a background collected on a blank potassium bromide pellet for FTIR-TRANS and with 64 scans/sample versus a background collected on a clean gold foil for FTIR-VAR. For FTIR-TRANS samples about 1 mg were embedded in potassium bromide (spectroscopic purity) in a 1:10 w/w ratio, pressed in a 3 mm diameter pellet and analyzed in transmission. Samples analyzed by FTIR-VAR were fixed on a gold mirror without any pre-treatment.

RESULTS AND DISCUSSION

The geological origin was attributed based on the results obtained from at least two of the three analytical techniques involved, but whenever possible at least two complementary techniques should be used. In table 1 the confidence levels of classification into Baltic or Romanite amber are expressed on a scale that can be translated as good (*e.g.* R or B), poor (*e.g.* R - or B -), very poor (*e.g.* R - - or B - -) and unsatisfactory (event that did not happen for our samples).

Table 1

Comparative results of TD/CGC/MS with FT-IR spectroscopic techniques and archaeological material classification

Archaeological samples inventory ID			Geological origin attribution			
Object ID (MNIR inventory)	Sample ID (MNIR inventory)	PCA ID	TD/CGC/MS	FTIR-TRANS	FTIR-VAR	Overall classification
16	260	U1	B	N/A	B	B -
85	439	U2	B	N/A	B	B -
254	566-571	U3	B	B	B	B
254	566-571	U4	B	B	B	B
251	572-574	U5	B	B	B	B

251	572-574	U6	B	N/A	B	B -
255	576, 577	U7	B	R	B	B - -
260	583, 584	U8	R -	R	R	R
262	589	U9	B	N/A	B	B -
263	633-635	U10	R	R	R	R
263	633-635	U11	R	R	R	R
267	646-648	U12	B	R	B	B -
271	651, 652	U13	B	R -	B	B - -
277	696, 707, 708	U14	R	B	R	R - -
282	674-679, 712, 713	U15	R	N/A	R	R -
282	674-679, 712, 713	U16	B	N/A	B	B -
275	721	U17	R	N/A	R	R -
273	667, 668, 722,723,726	U18	R	R	R	R
72	434-437	U19	B	B	B	B
265	638, 642, 643, 644	U20	B	R	B	B - -
265	638, 642, 643, 644	U21	B	R	B	B - -
265	638, 642, 643, 644	U22	R	R	R	R
279	692, 709, 710	U23	R	R	R	R
283	670, 671, 715-717	U24	B	R	B	B - -
273	667, 668, 722,723,726	U25	B	N/A	B	B -

TD/CGC/MS

Automated **M**ass **S**pectral **D**econvolution & **I**dentification **S**ystem (AMDIS) software, version 2.65, (U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology (NIST), Standard Reference Data Program) was applied using a target compounds library of 312 volatile compounds (VC), developed on controlled origin geological ambers (Baltic and Romanite), for generation of deconvoluted area reports. 112 VC from the target compounds library were identified in the archaeological samples and for each sample (controlled origin and archaeological) a deconvoluted area percent report was generated. An example of TD/CGC/MS total ion chromatogram for volatile fraction targeted in amber is given in Figure 1.

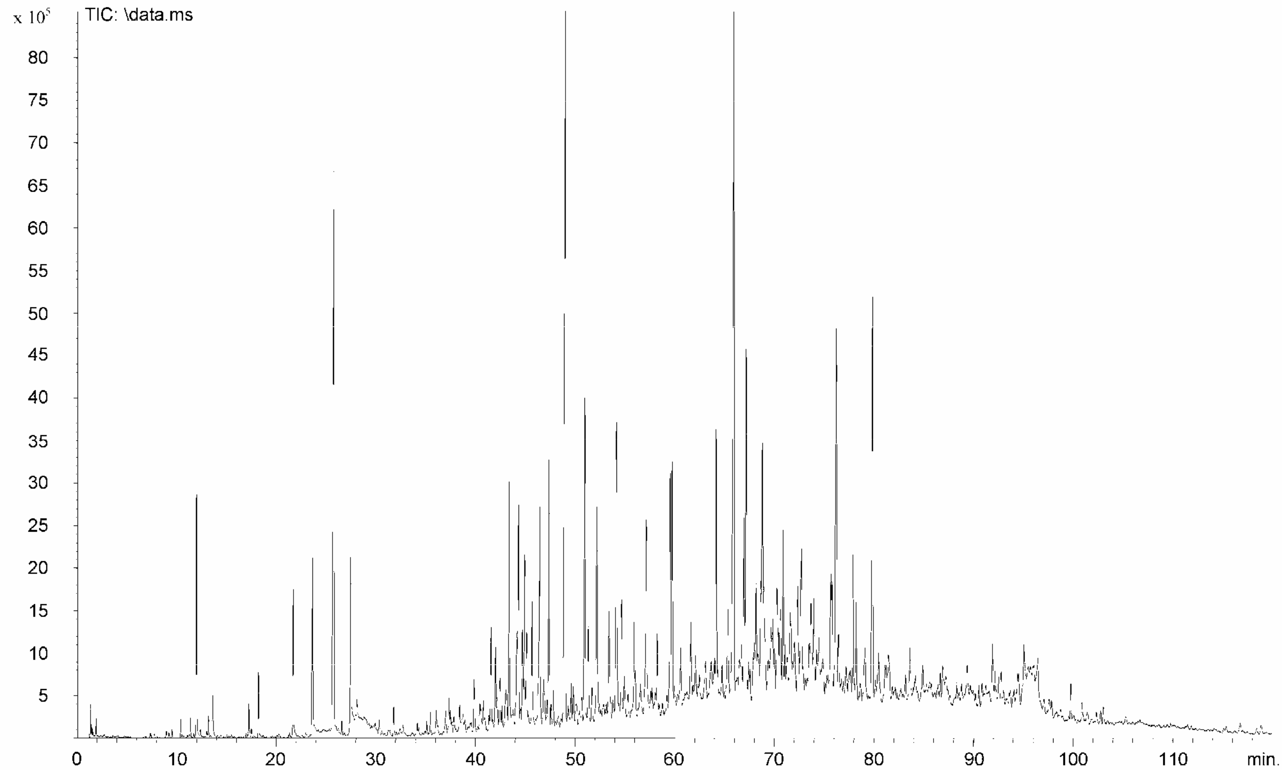

Fig. 1 – TD/CGC/MS Chromatogram of Roumanian amber from Colti, Buzau county.

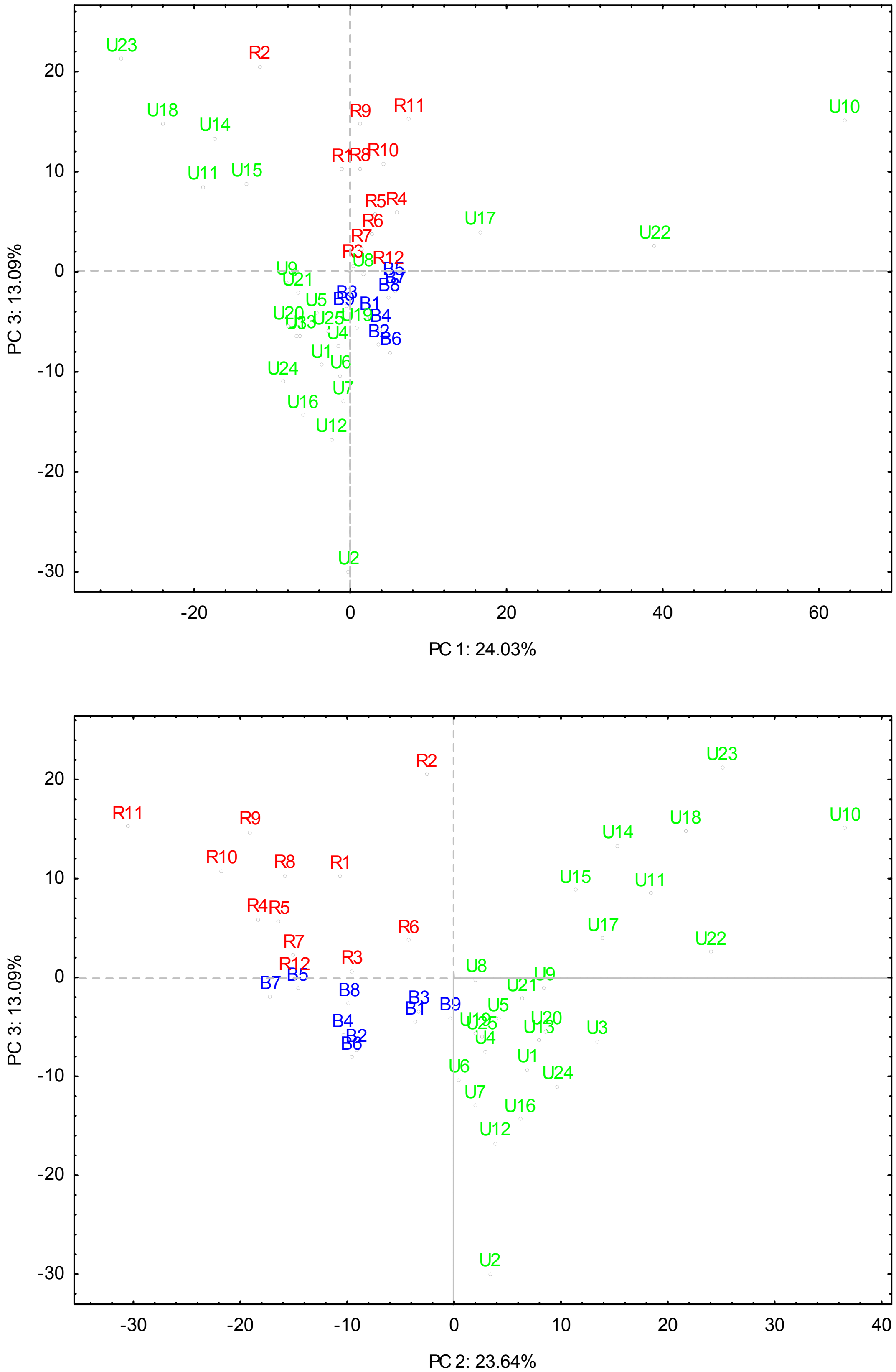

Fig. 2 – PCA projection of the cases in PC – planes (PC1 x PC3 and PC2 x PC3) for Baltic amber (B1 ÷ B9) Romanite (R1 ÷ R12), and archaeological (U1 ÷ U25) samples sets.

The resulted data set (ROMANIT_phase_2b_TD-CGC-MS_PCA_data_set.xls) was made available for free download together with updated versions of the "ROMANIT GC/MS database" in Microsoft Excel 97 - 2003 format from ROMANIT research project Internet site at URL http://www.romanit.ro/en/resources.html. The classification of archaeological samples as Romanite or Baltic ambers was made by applying the principal components analysis (PCA) with Statistica software, version 7.0 (StatSoft, Inc., Tulsa, Oklahoma, U.S.).[8-11] PCA was selected for data interpretation because is designed to solve large-sized problems, in our case 112 VC designated as variables, while providing visual aid for the classification of variables and cases. The PCA results obtained using covariance matrix with auto scaling of data showed that the first ten principal components account more than 89 % of the total variance. The 2D graphing scores onto the planes described by different combination of the first ten principal components were very useful as a display tool for examining the relationships between samples looking for trends, groupings or outliers. PCA 2D representations of PC-planes PC1 x PC3 and PC2 x PC3 (figure 2), both accounting for around 37 % of the total variance, were the only combinations that allowed reasonable discrimination between Romanite and Baltic ambers. This conclusion lead to a PCA 3D model with PC1, PC2 and PC3 explaining more than 60 % of the total variance. It was finally observed that the classification of cases by TD/CGC/MS (table 1) was made possible based on PC3 scores, which retain the discrimination information between the two fossil resins and explain only 13.09 % of the total variance.

FT-IR

FTIR-VAR spectra were analysed and explained on the three amber wavenumber domains of interest: 2000 - 3600 cm^{-1}, 1350 - 1820 cm^{-1} and 1045 - 1250 cm^{-1}, correlated with hydroxyl, carboxyl and carbonyl groups and with the C=C unsaturation. There are no notable differences between Romanite spectra and Baltic amber spectra in the 3000 - 3600 cm^{-1} region. The notable differences appear in "Baltic shoulder" region, 1045 - 1250 cm^{-1}. For the Baltic amber the shoulder appears in the region 1275 - 1142 cm^{-1}, while that of Romanite is shifted at about 1060 - 1020 cm^{-1}, as could be noticed from figure 3. The differences appearing in the 1642 - 1684 cm^{-1} region of Baltic amber with respect to 1546 - 1547 cm^{-1} region of Romanite are determined by the shift of asymmetric vibration frequencies for the carboxylic type groups, as a function of the length of hydrocarbon chains. A strengthening-ageing of polymeric chains leads to shifts toward smaller wavenumbers. This can be observed also in 1045 - 900 cm^{-1} region, where the shifts on the smaller wavenumbers are related to a better confirmation of the Baltic origin (data not shown).

FTIR-TRANS on geological amber showed that both resins present a single carbon-oxygen deformation band near 1150 cm^{-1}. For Baltic amber this is preceded by a broad shoulder between 1250 and 1175 cm^{-1} while for Romanite by a strong signal with a maximum at 1241 cm^{-1} (figure 4).

FTIR-TRANS spectra were baseline corrected on full spectral range with rubberband correction method (fitting in 200 baseline points), cut between 1125 – 1330 cm^{-1} (characteristic wavenumber region used for Baltic amber and Romanite identification) and normalized with "Min-Max" normalization method on the same spectral region for interpretation by PCA via the covariance matrix. The first five principal components account more than 95 % of the total variance. PCA 2D representations of PC-planes PC2 x PC3 (36.25 % of the total variance) and PC3 x PC4 (29.38 % of the total variance) were the only combinations which allowed reasonable discrimination between Romanite and Baltic ambers. The classification of cases by FTIR-TRANS (table 1) was made possible based on PC3 scores, corresponding to 10.49 % of the total variance of selected wavenumber region.

Both FTIR-VAR and FTIR-TRANS spectra revealed that archaeological amber is slightly different from geological raw amber and is characterized by a less intense signal in the 2000 - 3600 cm^{-1} zone, correlated with hydroxyl groups. FTIR-TRANS spectra of archaeological amber comparative with geological raw amber shows a decrease in intensity of the 975 cm^{-1} signal together with an increase of the signal around 1030 cm^{-1}, which may be correlated with the C-O stretching vibration.

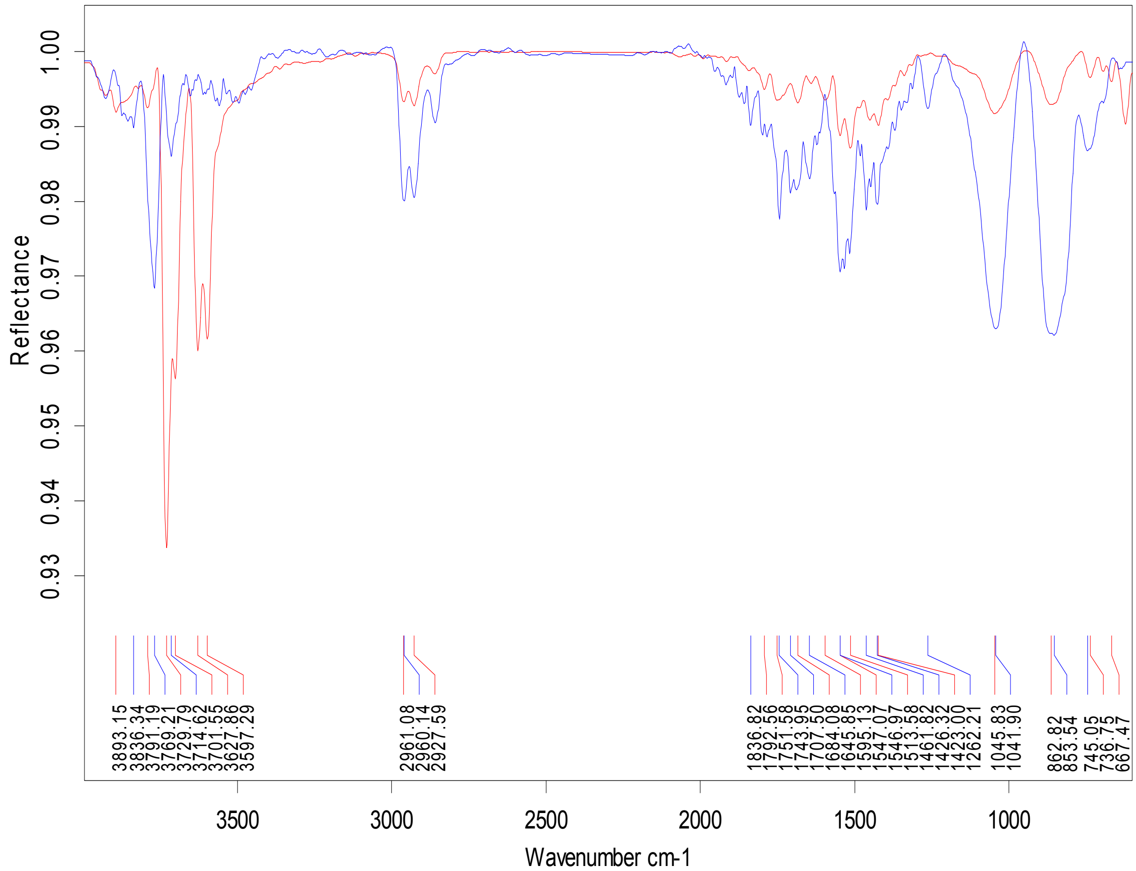

Fig. 3 – FTIR-VAR spectra of an archaeological amber from Piatra Frecaţei/Beroe (U18, buttom spectra) identified as Rumanite, overlaid with Colti, Buzau county - Rumanite (R1, upper spectra).

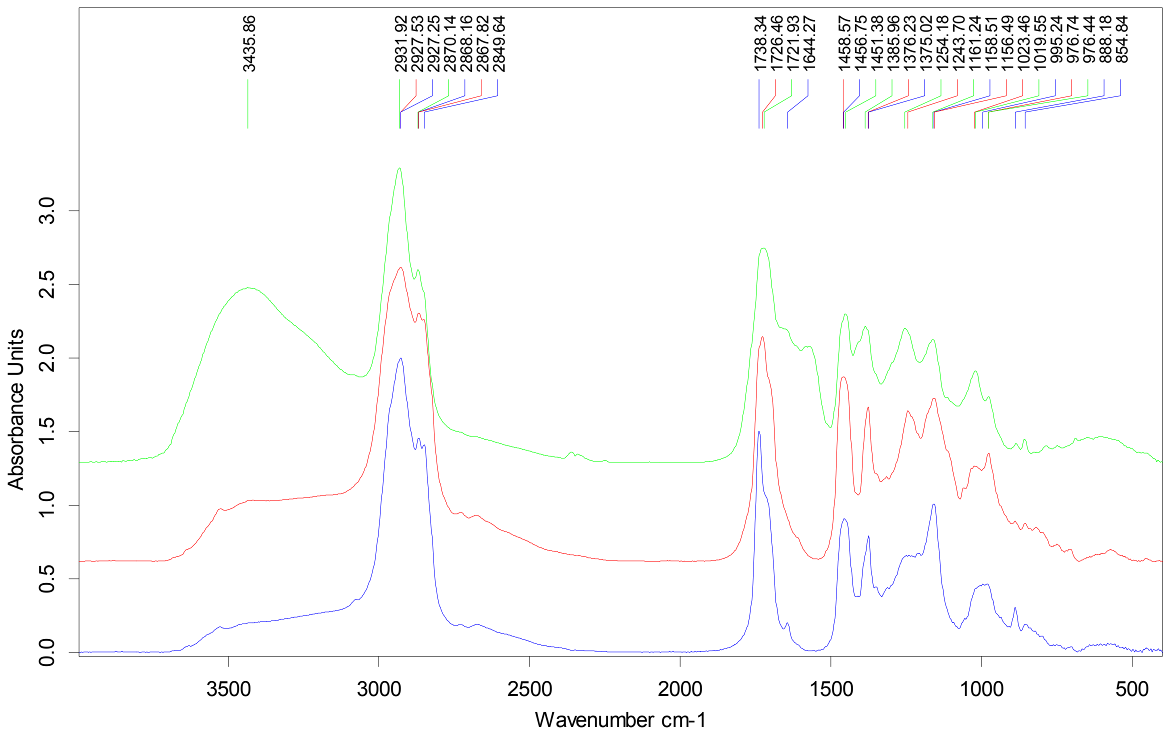

Fig. 4 – FTIR-TRANS spectra of an archaeological amber sample from Piatra Frecatei/Beroe (U22, top spectra) identified as Romanite, overlaid with Bitterfeld - Baltic amber (B5, bottom spectra) and Colti, Buzau county – Romanite (R1, middle spectra).

CONCLUSIONS

Present case study revealed the potential for tracking the archaeological amber geological origins by means of TD/CGC/MS, automated data analysis with AMDIS software and PCA data interpretation, even when geologically specific VC marker information was partially lost due to archaeological material degradation. FTIR spectra was used for discriminating between Baltic amber and Romanite, the classification results being in most cases in reasonable correlation with TD/CGC/MS results. Chemometric interpretation of characteristic Baltic shoulder wavenumber region was tested by PCA on FTIR-TRANS spectra. It was observed that archaeological amber samples are slight-different from geological raw amber samples and besides VC loss are characterized by a less intense signal in the 2000 - 3600 cm^{-1}, correlated with hydroxyl groups in the FTIR spectra.

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