



Thermal desorption/gas chromatography/mass spectrometry approach for characterization of the volatile fraction from amber specimens: A possibility of tracking geological origins

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ABSTRACT

Research on the chemical composition of fossil resins has evolved during the last decades as a multidisciplinary field and is strongly oriented toward the correlation with their geological and botanical origin. Various extraction procedures and chromatographic techniques have been used together for identifying the volatile compounds contained in the fossil resin matrix. Hyphenation between thermal desorption (TD), gas chromatography (GC) and mass spectrometry detection (MS) has been chosen to investigate the volatile compounds fraction from ambers with a focus on Romanite (Romanian amber) and Baltic amber species. A data analysis procedure was developed for the main purpose of fingerprinting ambers based on the MS identity of the peaks generated by the volatile fraction, together with their relative percentual area within the chromatogram. Chromatographic data analysis was based entirely on Automated Mass Spectral Deconvolution & Identification System (AMDIS) software to produce deconvoluted mass spectra which were used to build-up a mixed mass spectra and relative retention scale library. Multivariate data analysis was further applied on AMDIS results with successful discrimination between Romanite and Baltic ambers. A special trial was conducted to generate pyrolysis “like” macromolecular structure breakdown to volatile compounds by gamma irradiation with a high absorbed dose of 500 kGy. Contrary to our expectations the volatile fraction fingerprints were not modified after irradiation experiments. A complementary non-destructive new approach by ESR spectroscopy was also proposed for discriminating between Romanite and Baltic ambers.

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1. Introduction

The demand for amber has been responsible for the first great impetus to trade which resulted in the spread of civilizations since prehistoric times [1]. The possibility of tracking geological origin of amber is of great importance by allowing more correlations with trade routes and prestige and power of amber artefacts owners. For biologists and geologists, fossil resins are a window into the distant earth's past, giving important clues about life on earth at the moment of resin formation. Occurrence around the globe cov-

ers wide areas and environments (e.g. coals, soil, shale, even the deep-sea sediments) [2,3]. Various analytical methods were developed with the purpose to correlate amber's chemical composition, spectral and physical properties with its botanical and geological origin [4–18]. Gas chromatography coupled with mass spectrometry (GC/MS) has been widely and successfully used for identification of volatile compounds (VCs) contained in the fossil resin matrix [2–4,6–15,17,19–27]. GC/MS analysis of amber solvent extractable fractions has evidenced cyclic mono-, bi-, tri- and sesquiterpenoids, and many other VCs [14]. Pyrolysis coupled with MS or GC/MS has been also widely used for characterization of macromolecular insoluble fraction of amber and even for unmasking amber forgeries [10]. Carlsen et al. have successfully applied multivariate analysis on pyrolysis data, obtaining interesting correlations between amber specimens based on their geographical occurrence [12]. In other studies, VCs have been used as markers for botanical sources or as markers for fossilization processes which could be correlated

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with amber's geological origin [21,23,24,27–31]. In the European region, Baltic amber has been the most studied fossil resin, because of its widest geographical spread and biggest abundance. Stout et al. has recently identified Romanite (Romanian amber) as thermally altered Baltic amber [14] based on systematic study of various samples originated especially from Buzău county. It has been shown that all derivatized VCs from the ether-soluble fraction of Romanite were identified either in the ether-soluble fraction or in the pyrolysis products of the Baltic amber. Feist et al. have studied the thermal behaviour of various fossil resins under inert atmosphere using thermo-gravimetry (TG) and differential thermal analysis (DTA). Resulting data suggest that a small mass loss occurs at temperatures higher than 200 °C and was attributed to the volatile fraction [18]. The thermal desorption temperature was studied for optimization and confirmation on our reference amber samples by simultaneous thermal analysis, thermo-gravimetry and differential scanning calorimetry (TG/DSC). The present study aimed to develop a GC/MS method for discriminating especially between Romanite and Baltic ambers. Thermal desorption (TD) method was chosen because of several inherent advantages compared to conventional extraction techniques: avoidance of tedious extraction steps and derivatization procedures, good automation capabilities enhancing on the precision of the results. Operational parameters of the TD step were developed according to data resulting from thermal analysis studies conducted on fossil resins [18]. Chromatographic data analysis of VCs was performed with Automated Mass Spectral Deconvolution & Identification System (AMDIS) software (U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology (NIST), Standard Reference Data Program) [32–36]. Deconvoluted mass spectra were used to build-up a library for future use on screening unknown geological amber samples.

Large-scale applications of nuclear techniques are a highly expanding multidisciplinary field which has a great potential for the characterization and preservation of Cultural Heritage artefacts [37]. In particular, interaction of gamma rays with any substance may change its chemical and physical properties. The effects are cumulative [38]. The change is proportional with the irradiation dose. The possibility to generate by gamma irradiation volatile and semi-volatile radiolysis products similar with pyrolysis products was investigated. Based on recent light microscopy studies which reported the appearance of an internal organization tendency for Romanite compared with Baltic amber [39], electron spin resonance spectroscopy (ESR) was proposed as a complementary non-destructive technique used to investigate if useful correlations between the free radicals concentration after irradiation and amber macromolecular structure can be made.

The contribution of the present work consists in chemical characterization of fossil resins by means of the combination between thermal desorption as a fast isolation technique for VCs, classic GC–MS analysis, GC–MS data interpretation through AMDIS software and advanced data computing with multivariate analysis techniques used to extract information related with the geological origin of the fossil resins.

2. Experimental

2.1. Sample and sample preparation

Selections of samples used for method development was made under the supervision of Romanian National History Museum: 12 Romanian ambers (Romanite, R1–R12) and 9 Baltic ambers (Succinite, B1–B9). Romanite samples originated from Buzău County, Sibiciul de Jos village part of Pânătau (R1 and R12) and Colți – Pătărlagele hollow (R2–R11). Baltic ambers originated from Bitterfeld – Germany (B1), Königsberg – Kaliningrad – Russian Federation

(B2 and B5), Palanga – Lithuania (B3), Poland (B4, B7 and B8) from the Baltic Sea and Earth's Museum of Warsaw, Denmark (B6) and Riga – Latvia Republic (B9). Other five unknown samples (U1–U5) were used to test the method's efficiency to discriminate between Romanite 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 Romanite, burnt (U3) and red (U4) amber from Colți Amber Museum, and one called "Muntenite" from Olanesti (U5).

For thermal desorption, the critical issue with solid samples is that they should have a high surface area as powders or granules with particle size usually smaller than 1 mm³. For this reason samples were ground to powder. 10 mg of powder was packed into a PTFE liner of 250 μL with silanized glass wool plugs. The PTFE liner was packed with silanized glass wool plugs into the central 60 mm section of the 89 mm standard stainless steel sample tube (O.D. = 6 mm) and protected with caps until sample run. Before each sample run on thermal desorber, 10 μL of methanol solution containing 0.005% chrysene was injected through the back of the tube as internal standard. For thermal analysis 10 mg of powder was transferred into 25 μL aluminium crucibles with pierced lid. Finally, 10 mg of solid amber fragments was transferred into ESR quartz tubes for non-destructive measurement before and after irradiation experiments.

2.2. Thermal desorption

Volatile compounds (VCs) were extracted by thermal desorption (TD) using Markes "Unity" Thermal Desorber (TDU) equipped with a General Purpose Hydrophobic Trap. The trap has been packed with 30 mm bed of Tenax TA, backed up by 30 mm Carbograph 1TDTM, separated and supported at each end by unsilanized glass wool plugs. TDU flow path and heated transfer line temperatures were set at 200 °C. Injection was achieved in three steps: 5 min pre-purge in split-less mode at 40 mL/min through the trap held at –10 °C, 10 min tube desorption in split-less mode at 200 °C and 40 mL/min through the trap held at –10 °C, and 3 min trap desorption in split mode (40.5:1) at 300 °C and 44.5 mL/min. Blank runs with internal standard solution were made between samples, until the trap memory produced no significant peaks in the chromatogram.

2.3. Chromatographic method

Agilent GC 6890N gas chromatograph was used with a HP-5ms column, 25 m × 0.25 mm and 0.25 μm film of (5%-phenyl)-methylpolysiloxane non-polar, bonded and cross linked stationary phase. GC 6890N auxiliary electronic pneumatic control module was used to regulate TDU carrier pressure in constant pressure mode with helium at 9.4 psi (1.1 mL/min at 40 °C, calculated with Hewlett-Packard FlowCalc version 2.0). Column temperature programming consisted in the following profile: isothermal for 5 min at 40 °C, ramp with 2 K/min to 250 °C and isothermal for at least 10 min at 250 °C.

2.4. MS detection

Agilent 5975 MSD equipped with electron ionisation (EI mode at 70 eV) source was used with following parameters: MSD transfer line temperature set at 280 °C, source temperature set at 230 °C, mass analyzer temperature set at 180 °C, data acquisition in SCAN mode from 35 to 700 a.m.u. with a threshold of 100 counts and a sampling rate of 2² samples/a.m.u. corresponding to 2.23 scans/s.

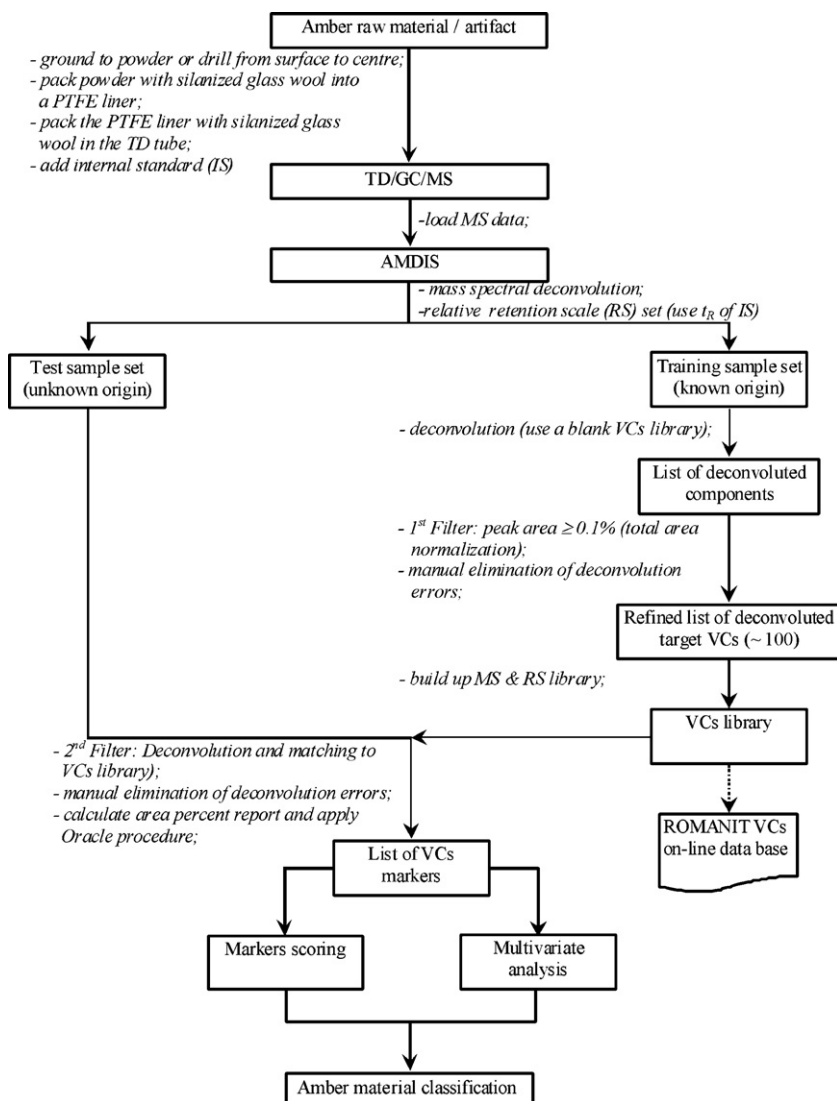


Fig. 1. Sample preparation and data analysis workflow.

2.5. Data analysis

Data analysis workflow is shown in Fig. 1. AMDIS software, version 2.65 (December 20, 2006, build 116.66) was used for deconvolution of VCs mass spectra. The training sample set (amber samples with known geological origin) “data.ms” files were deconvoluted using the following AMDIS analysis settings: “Use Internal Standards for Retention Index (RI)” type of analysis, identification by minimum match factor set at “80”, RI window set at “100”, maximum “match factor” penalties set at “20”; “default” instrument settings for “Agilent files”; deconvolution by 32 scans component width, “one” adjacent peak subtraction, “low” resolution, “low” sensitivity, “low” shape requirements; internal standards library with chrysene as internal standard and an blank target compounds library; QA/QC with 207 m/z selected for column bleed. AMDIS detected all deconvoluted VCs except internal standard as unidentified “components”.

A customized search through the NIST library converted into target VCs (1st filter) only deconvoluted peaks with an area above a pre-defined threshold. AMDIS selected options for Search NIST library – parameters were: maximum 1 hit reported per search; “use instrument m/z limits”; “build combined result”; “MainLib” NIST Library search; select from “only unidentified components”

with “consider all models” option checked; number of components searched with all above threshold of 0.1% of total signal (total ion current summed over all ions for the entire chromatogram) option checked; library search mode by “normal identity”. Deconvolution results were exported and a relative retention time (RRT) was calculated for each VC by normalization to the internal standard retention time. A relative retention scale (RS) associated with each deconvoluted mass spectra was calculated by multiplying the corresponding RRT with 10^4 . The deconvolution errors were manually identified in AMDIS (peak by peak) and excluded from exported results, the remaining VCs mass spectra and relative retention scale library (VCs library) in NIST Text *.MSP format. Updated versions of the library in Microsoft Excel 97 – 2003 format are available for free download from ROMANIT research project Internet site at URL <http://www.romanit.ro/en/resources.html>.

In order to study the possibility of tracking the geological origin of ambers based on VCs relative peak areas, both training sample set and test sample set (unknown geological origin) “data.ms” files were deconvoluted in AMDIS with the same analysis settings as previous except the amber VCs library was used as target compounds library. Deconvolution results were exported, deconvolution errors manually filtered, VCs area percent report calculated and VCs com-

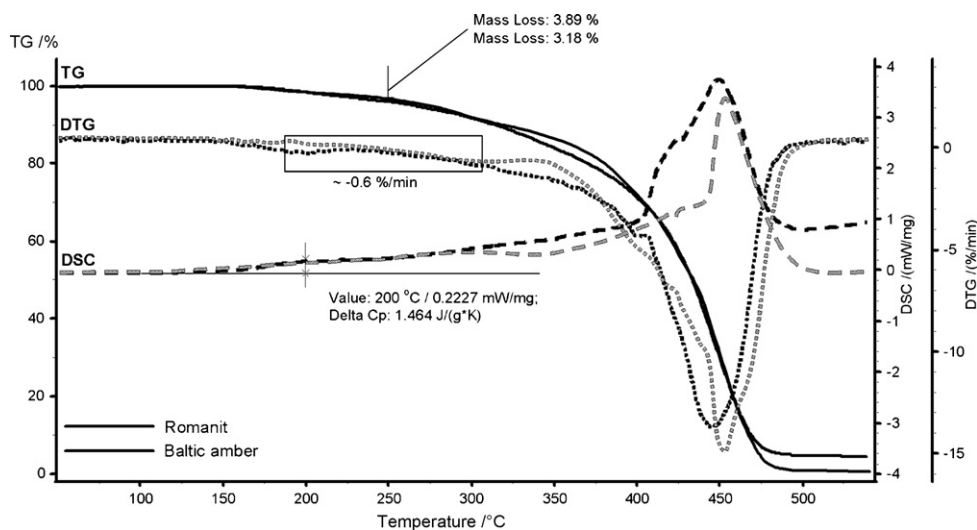


Fig. 2. TG/DTG/DSC curves for Romanite (dark line) and Baltic amber (grey line).

parative results generated by applying a procedure developed in Oracle 9i database (2nd filter). PL/SQL Developer software tool, version 7.0.0.1050, was used to generate the missing VCs in all amber specimens with NULL value for quantitative fields. Percent results from Table 1 were rounded to the nearest integer, traces ($0 \leq x \leq 0.5\%$) being displayed as zero value. Two approaches were used for amber material classification: multivariate data analysis and one empirical algorithm based on “VCs scoring”.

Multivariate data analysis was performed using principal components analysis (PCA) and cluster analysis (CA) incorporated in Statistica software, version 7.0 [40–43]. Many problems from chemistry and other technical fields are strongly related to PCA and CA [44–47]. PCA is a typical projection method, which allows one to find out the structure of data by depicting the objects (samples) in a reduced coordinate system with maximum possible information. Score plots, for example, are very useful as a display tool for examining the relationships between objects, looking for groups and trends, sorting out outliers. CA is a well-known and widely used unsupervised clustering procedure with its hierarchical and non-hierarchical approaches. There is a wide variability of ways how to measure the distances between objects and how to group objects based on various distance measures. However, the Euclidean distance and *Ward's method* as linkage procedure are strongly recommended [48–55].

2.6. Thermal analysis (TG/DSC)

Simultaneous Thermal Analyzer STA 409 PC Luxx (NETZSCH Geratebau GmbH, Germany) equipped with TG/DSC type K sample carrier was used to study the thermal stability of amber specimens in order to select the optimal thermal desorption temperature and avoid pyrolysis products formation. Dynamic atmospheric conditions with GC purity nitrogen in constant flow at 60 mL/min were used. Temperature programme consisted in the following profile: isothermal at 20 °C for 10 min, ramp with 10 K/min to 550 °C and isothermal at 550 °C for 5 min. Temperature and enthalpy calibration with In, Bi and Zn made in the same dynamic atmospheric conditions was used [56,57].

2.7. Gamma irradiation and ESR spectroscopy experiments

Trying to simulate pyrolysis “like” macromolecular structure breakdown, amber samples were irradiated in a SVST Co-60 gamma irradiator at IRASM Multipurpose Irradiation Facility (IFIN-HH),

under air with an absorbed dose of 500 kGy. It was expected that characteristic VCs obtained as radiolysis products will further contribute to distinguish Romanite from Baltic amber. The irradiation dose was established using the oscilloscopic method with ethanol–chlorobenzene (ECB) dosimeters (standard deviation of $\pm 2\%$) [58].

The natural free radicals and those induced by gamma irradiation in the amber samples were measured using a Magnetech Miniscan MS200 X band ESR spectrometer. The area of an ESR absorption spectrum is proportional to the quantity of free radicals contained within the sample. The ESR signal was recorded as the first derivative of the absorption spectrum, the calculation of the signal area being made according to Ref. [59].

3. Results and discussions

3.1. Thermal analysis results

Thermal stability of four Romanite (R1, R6, R8 and R11) and two Baltic (B5 and B9) ambers was investigated for a proper selection of desorption temperature. Under inert atmosphere all investigated ambers had similar thermal behaviour. A small VCs mass loss step was observed around 200 °C both into DTG and DSC curves (Fig. 2). For this reason 200 °C was selected as desorption temperature for TD/GC/MS analysis.

3.2. TD/GC/MS results

Amber is well known as a non-homogenous material. The main question is whether the VCs composition can be used for material fingerprinting in a minimum destructive sampling manner. Consequently, VCs composition variability was investigated in one piece of Romanite by drilling at different depths from surface to

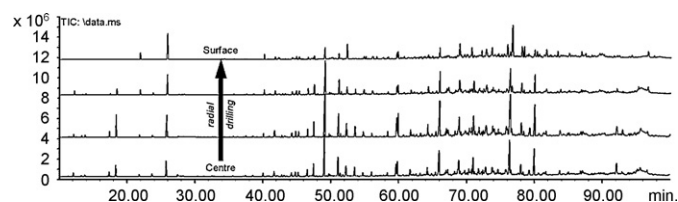


Fig. 3. VCs fingerprints by TD/GC/MS of a Romanite piece sampled at different depths (drilled from the surface to the centre of the amber piece).

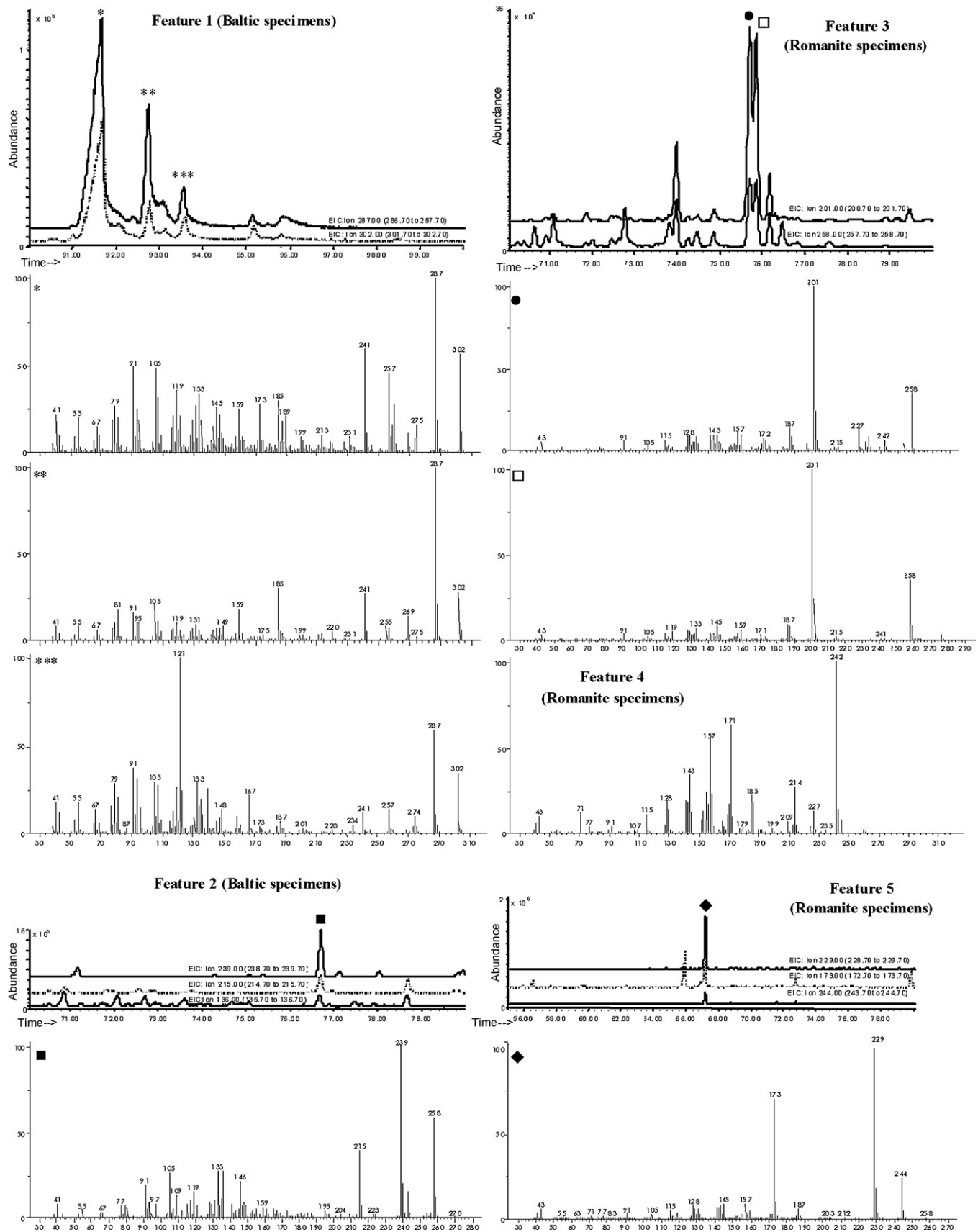


Fig. 4. Romanite and Baltic amber markers: Features 1 and 2 for Baltic amber specimens and features 3–5 for Romanite specimens.

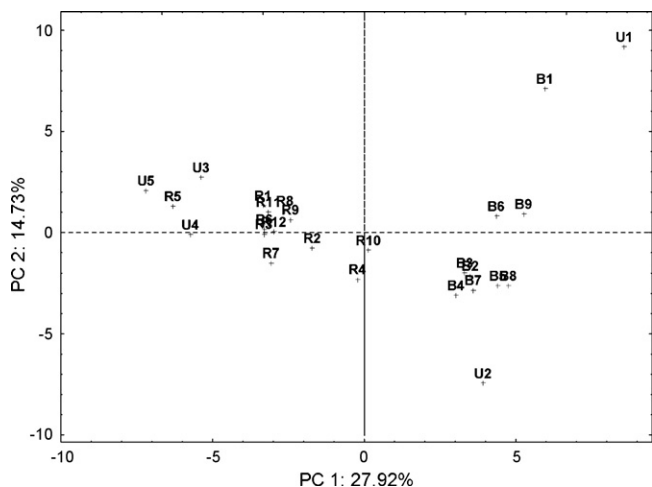


Fig. 5. PC1–PC2 score plot: Romanite (R1–R12), Baltic amber (B1–B9) and test (U1–U5) sample sets.

centre (chromatograms illustrated in Fig. 3). A difference in quantitative ratios of VCs was observed between the sample surface and the inner sampling places. VCs patterns still retain over 80% of the qualitative information, indifferently to the sampling depth. The representativity of the test specimen for an amber sample is conserved by sampling whenever possible from the surface to the depth.

Extracted Ion Chromatograms (EIC) according to specific fragment ions for the most characteristic VCs were also taken into consideration for discrimination between Romanite and Baltic amber. EIC fingerprints were named features (Fig. 4, features 1–5). Features 1 and 2 were found characteristic for Baltic amber, while features 3–5 were found characteristic for Romanite. Feature 1 is formed from three VCs which elute at RS 9500, 9600 and 9700 and is characterized by m/z values 287 and 302 a.m.u. Feature 2 is formed from a single VC which elute at RS 7900 and is characterized by m/z values 215, 239 and 258 a.m.u. Feature 3 is formed from a pair of VCs which elute at RS 7800 and 7900 and is characterized by m/z values 201 and 258 a.m.u. Feature 4 is formed from a single VC which elute at RS 7500 and is characterized by m/z values 242 and 271 a.m.u. Feature 5 is formed from a single VC which elutes at RS 7000 and is characterized by m/z values 173, 229 and 244 a.m.u.

A sample of TD/GC/MS results is shown in Table 1. The first column lists the relative retention scale (RS), the second lists the base peak (m/z) from the acquired mass spectrum, the third column lists the following nine signals as intensity from the mass spectrum and their relative abundance (between brackets). The next columns contain the peak area percent report of training (B1–B9 and R1–R12) and test (U1–U5) sample sets. A free space means that the peak was not identified in the chromatogram.

The PCA results obtained via the correlation matrix of peak area percent reports available in Table 1 showed that the first 10 principal components account more than 85% of the total variance. The first principal component explains 27.92% of the total variance and the second one 14.73%. These findings illustrate that the considered variables are more or less correlated. The graphical representation of scores onto the plane described by different combination of the first 10 principal components is very useful as a display tool for examining the similarities and differences between samples, looking for trends, groupings or outliers. A fair discrimination of samples was obtained for any combination between PC1 and PC2, PC1 and PC3, ..., PC1 and PC10. Any other combination was unsatisfactory. By a careful visual examination of the pattern obtained by PC1–PC2 score plot (Fig. 5), for example, it is possible to distinguish that the investigated Romanite and Baltic ambers form practically two dif-

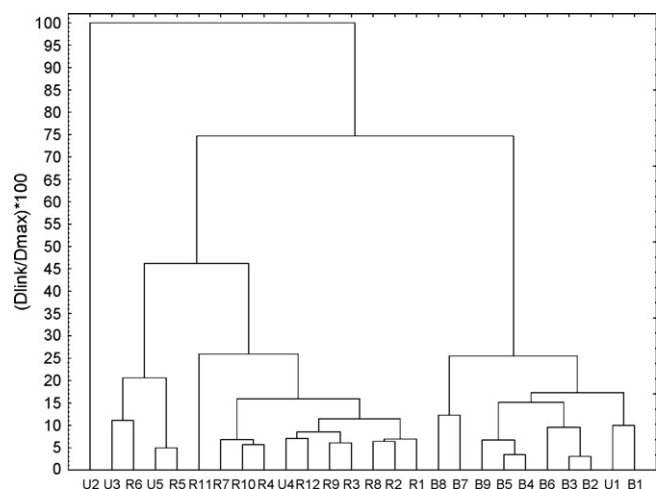


Fig. 6. Dendrogram using the Euclidean distance and Ward's-linkage method: Romanite (R1–R12), Baltic amber (B1–B9) and test (U1–U5) sample sets.

ferent groups, in a very good agreement with their geographical location. Concerning the test samples, we have to observe also a satisfactory assigning excepting U1 and U2 samples which appear more or less like outliers. These conclusions are also well supported by the hierarchical dendrogram (Fig. 6) obtained with CA.

Based on the hypothesis that on Romanian territory amber artefacts can have mainly Romanian or Baltic geological origin, a Romanite–Baltic VCs scoring empirical algorithm was developed to differentiate between the two types of fossil resins. VCs scoring was based on associating a geological origin attribute (R, R?, R??, B, B? or B??) with the peak area percent of the corresponding VCs (e.g. in Table 1 for the test sample set). The attribute association was made on VC occurrence in the training sample set, as follows: R (Romanite) or B (Baltic) attribute when VC occurred only in one type of fossil resin; R? or B? attribute when VC occurred in one type of fossil resin in higher concentrations than 0.5%, but was also found below the threshold in the other type of amber; R?? or B?? attributes when VC occurred in both types of fossil resin, but the maximum relative peak area was at least double in one type of amber. A mathematical weighing factor was assigned to each attribute class as follows: B (1), B? (0.5), B?? (0.1), R (–1), R? (–0.5) and R?? (–0.1). By summing the results of the multiplication between the VCs percents with the corresponding mathematical weighing factor positive, negative or null results may be obtained. If the result was positive the material was classified as Baltic amber (B), if negative as Romanite (R) and if null ($-0.5 \leq x \leq 0.5$) unknown or unrecognizable (UN). Last two rows from Table 1 contain the VCs scoring geological classification results for the test sample set, as follows: Baltic origin was attributed to U1 and U2 samples and Romanite origin to U3–U5 samples.

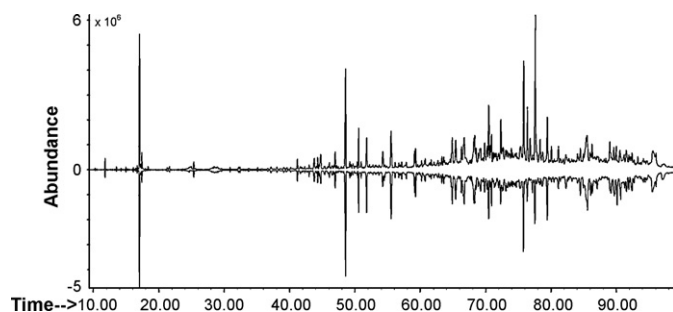


Fig. 7. TD/GC/MS chromatograms for U1 test sample under irradiated (top) and un-irradiated (bottom) conditions.

Table 2
ESR signal area ratios for test samples set.

Sample	U1	U1 ^a	U1 ^a /U1	U2	U2 ^a	U2 ^a /U2	U3	U3 ^a	U3 ^a /U3	U4	U4 ^a	U4 ^a /U4	U5	U5 ^a	U5 ^a /U5
ESR signal area	21315	906632	42.5	17556	1014805	57.8	84285	99460	1.2	18269	85255	4.7	31165	81204	2.6

^a Gamma irradiated amber with an absorbed dose of 500 kGy.

EIC, VCs scoring and multivariate analysis performed on TD/GC/MS results were not significantly modified after irradiation experiments and no volatile radiolysis products have been detected with our data analysis procedure (chromatogram illustrated in Fig. 7). VCs variation was within amber material variability based on repeatability tests which concluded that gamma irradiation process had no significant influence on the VCs chromatographic fingerprints.

3.3. ESR spectroscopy results

The ESR spectra of irradiated and un-irradiated amber samples show single signals, centred at 335 mT, having different widths and intensities. The signal areas for un-irradiated ambers were quite similar for all samples, except U3 amber which is a “burnt” amber and so even un-irradiated contains several times more free radicals. After irradiation, signal areas of Baltic ambers were 10 times greater compared with Romanite ambers, again except U3 amber which exhibited almost no variation after irradiation (see Table 2). ESR experiments were performed with similar results on a larger number of irradiated ambers (10 Romanite and 10 Baltic ambers), but only samples submitted to the chromatographic analysis are reported and discussed here.

4. Conclusions

Characteristic patterns in the TD/GC/MS chromatograms of Romanite and Baltic amber specimens have been confirmed by EIC and multivariate data analysis classification and discrimination results. The present work uses the combination between TD/GC/MS, AMDIS software and multivariate data analysis as a powerful tool for characterization and classification of fossil resins, even for strongly related specimens as Romanite and Baltic ambers.

Unexpected, the TD/GC/MS VCs fingerprint was not significantly modified by gamma irradiation experiments. This is a positive finding because allows TD/GC/MS analysis to be performed after non-destructive analysis of gamma irradiated samples by ESR spectroscopy, as a complementary technique for the differentiation between Romanite and Baltic ambers.

Further studies to establish the limits of TD/GC/MS method, as well as development of new analytical techniques would be worthwhile for unambiguous attribution of geological origin for amber artefacts.

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