Fourier Transform Raman and Statistical Analysis of Thermally Altered Samples of Amber

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We report the experimental results that refer to a Fourier transform Raman (FT-Raman) survey of thermally altered Baltic and Romanian amber and the related statistical interpretation of data using principal component analysis (PCA). Although FT-Raman spectra show several small changes in the characteristic features of the investigated amber samples which may be used for discrimination, their visual recognition is relatively difficult, especially when interpreting data from archeological samples, and thus multivariate data analysis may be the solution to more accurately assign the geological origin based on overall characteristic spectral features. The two categories of amber have different behavior in terms of degradation during the experimental alteration, and Romanian amber is more susceptible to physico–chemical transformations by the aggressive environment when compared with Baltic amber. The obtained data were in accordance with the Fourier transform infrared (FT-IR) remarks published previously in a dedicated journal. The Raman technique is an alternative method that requires little to no sample preparation, water does not cause interference, and the spectra can be collected from a small volume (1–50 μm in diameter).

Index Headings: **Baltic and Romanian amber; Raman spectroscopy; Statistical analysis; Thermal alteration.**

INTRODUCTION

The necessity of using the physical sciences to answer the questions of archeology, such as where an object was made (provenance) and the details of its manufacture, dates back to the 18th century. An important demand in the investigation of archeological materials is that unnecessary damage should be avoided, preserving the integrity of the sample.

Amber is a natural polymer, which is derived from the fossilization of resins produced by different trees, and it has been appreciated from ancient times as a precious gemstone used for the manufacture of jewelry, household goods, and ceremonial items.[1–3] The amber objects came to the attention of archeologists because they reveal the economic, social, and religious values of the people that made and wore them. This material is susceptible to progressive degradation and complete disintegration due to its sensitivity to physico–chemical environmental factors (light, moisture, air pollutants, and heat). Amber chemical properties are the result of both its biological origin and the geological environment in which it was deposited and has subsequently matured. For this reason, it is important to take these factors into account when assessing the properties and characteristics of amber objects.

Infrared and Raman spectroscopy are extremely powerful analytical techniques, for both qualitative and semi-quantitative analysis, which offer the possibility to identify inorganic and organic molecular species, therefore, any kind of sample, large or small, optically perfect or imperfect, colorless or colored.[4–7] Both methods can be used with microscopic techniques. The key advantage of Raman spectroscopy is that it requires little to no sample preparation, while the Fourier transform infrared (FT-IR) method has constraints on sample thickness, uniformity, and dilution to avoid saturation. An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference and thus can be used as a solvent, and the spectra can be collected from a small volume (1–50 μm in diameter). Whether Raman or FT-IR spectroscopy is used, both methods have advantages and limitations, but when combined, these two methods become a powerful tool in performing materials characterization.

Combining two complementary techniques, such as IR and Raman spectroscopy, can lead to a decrease in uncertainty of a single analysis, in our case, induced by the great similarity between Baltic amber and Romanian amber, and processing the data obtained by means of statistical analysis allows the establishment of criteria for distinguishing between the two varieties of resins.

In recent years, a series of papers on Raman and micro-Raman spectroscopy applications were published in order to characterize the molecular structure of fossil resins, allowing nondestructive and rapid interpretation of geological origin of the samples investigated.[8–26]

Studies on accelerated alteration and specific changes that occur on altered matter, such as archeological amber, were previously published but focused on conservation issues within the repositories of the museum.[13,27–31] It was also suggested in the specialist literature that chemometrics techniques could be applied with the advantage of improving the spectral recognition from the background interference.[19,25,27,32]

Name, provenance	Sample ID	Sample ID in statistical analysis	Experimental conditions
Baltic amber	B345	B345	Initial stage, unaltered
Kaliningrad, Russia	B1001	BW	Water
	B1003	BD	Air
	B1026	BS	Salt
	B1034	BA	Acid
	B1036	BK	Alkaline (basic)
Romanite	R134	R134	Initial stage, unaltered
Colti, Buzau, Romania	R933	RD	Air
	R956	RW	Water
	R961	RS	Salt
	R964	RA	Acid
	R968	RK	Alkaline (basic)

In this paper, we discuss the experimental results that refer to Fourier transfer Raman (FT-Raman) analysis on thermally altered Baltic and Romanian amber and the related statistical interpretation of data using principal component analysis (PCA) in order to define which environmental factors, if any, initiated or catalyzed the degradation of fresh Baltic and Romanian amber in good condition. These data were in accordance with the FT-IR data already published in a dedicated journal.[27] To our knowledge, no Raman survey was conducted on these two types of amber (Baltic and Romanian) for this purpose.

EXPERIMENTAL

Amber Samples Preparation. The material considered in this paper was Baltic amber, one of the most common and investigated kinds of amber due to the abundance of its deposits, and romanite (Romanian amber), a less studied material collected along the length of the Carpathian Mountains, particularly in the region Colţi, Buzău County, Romania. From two large pieces of raw amber material (Baltic amber labeled B345 and Romanian amber labeled R134), a number of ten fragments were selected (five for each origin) weighing between 7 and 14 mg and subjected to thermal alteration at a constant high temperature (80 ± 2 °C) for a period of 12 weeks in a Memmert UFB 400 drying oven. The other two pieces of amber (one for each source—Baltic amber and Romanian amber from the raw material) were kept in ambient conditions and were considered as initial stage. The raw material was not relatively fresh and has been in the collection of the museum for at least 30 years. The conditions simulating environmental medium were created by adding the pieces of amber into 50 mL flasks with Teflon caps filled with deionized water, salted water, alkaline solution (0.2 M Na_2HPO_4, pH = 8), and acid solution (0.2 M NaH_2PO_4, pH = 5.5), and in the last case, the sample was suspended in an empty flask. The origin and identification of each sample is reported in Table I.

Therefore, the aging experiment was performed on two experimental sample sets (Baltic and Romanian amber) for five different media of degradation.

Instrumentation. The experiments were performed using a FT-Raman RFS 100/S (Bruker) instrument equipped with a Nd : YAG laser excitation source (laser wavelength of 1064 nm, and adjustable output power between 1 and 500 mW), a liquid nitrogen cooled germanium detector, a standard sample compartment, dispersion by Michelson interferometer, notch filter and a macro- and micro-interface.

The laser power was set at 500 mW, the beam diameter at sample position was ∼50 μm, and the power on the sample approximately 190 mW due to the lenses and optic fiber attenuation. Each sample was analyzed at three different positions (36 spectra acquired), and for each measuring spot, 2000 spectral scans per sample at 4 cm^{-1} resolution over the wavenumber region 3500–50 cm^{-1} were co-added in order to improve signal-to-noise ratio.

Data analysis. In order to enhance the fingerprinting capabilities of FT-Raman spectroscopy on thermally aged amber samples, statistical analysis was performed on several spectral regions using PCA via the covariance matrix incorporated in Statistica software, version 12.0.[33,34]

From past experience, we have learned that the extreme variability—which makes the data almost impossible to interpret—can be reduced by the elimination method of the eccentric results. The results of FT-Raman analysis performed on 12 amber samples were submitted to statistical analysis in triplicate (36 spectra acquired), but in order to have a better homogeneity of data, from these 36 spectra, we decided to remove the triple eccentric experimental result of all the samples, leaving for the statistical interpretation only a doublet with more homogeneous values (24 spectra) due to the high variability of amber, previously proven by numerous measurements on the same samples. Prior to the application of PCA methods, data underwent a pretreatment procedure, one of the most common operations also well known as mean centering, with the purpose of transforming the data into a suitable form for the analysis.

Another preparatory step was to eliminate the wavenumber domain with very weak signal intensity, at the level of background noise, to avoid making statistical analysis on areas where the "noise" could be dominant. Fourier transform Raman spectra were prepared for multivariate data analysis by atmospheric compensation (H_2O and CO_2), baseline correction by concave rubber band correction with eight iterations, and normalization using the min-max normalization method of the OPUS software on the 3500–50 cm^{-1} wavenumber domain.

RESULTS AND DISCUSSIONS

Fourier Transform Raman. The FT-Raman spectra of the amber samples before the accelerated aging process are shown in Fig. 1. Each spectrum is the average of the spectra of three spots analyzed on the sample, and for the simplicity of presentation, the wavenumber regions presented are 1800–400 cm^{-1} and
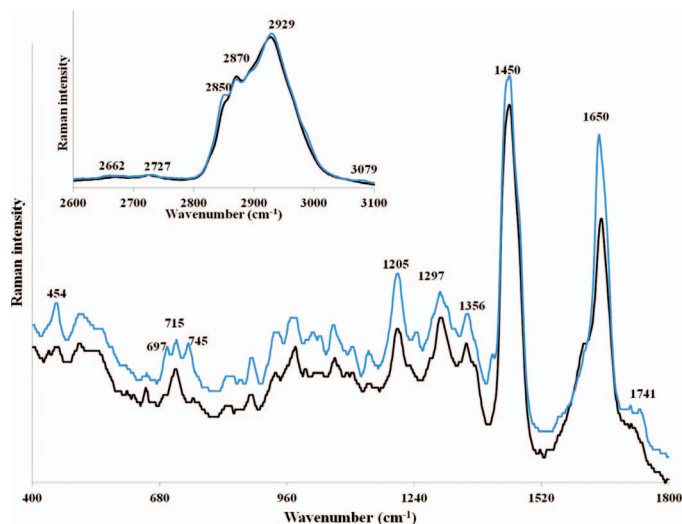
Fɪɢ. 1. Fourier transform Raman spectra of Baltic (B345-blue) and Romanian (R134-black) amber initial stage; 1064 nm excitation, region 1800–400 cm^{-1} and 3200–2600 cm^{-1} (inset).

the inset 3200–2600 cm^{-1}. As it can be observed in Fig. 1, FT-Raman spectra of romanite and Baltic amber presented several common signals assigned to out-of-plane vibration on the exocyclic methylene bond of compounds with labdane skeleton (827–882 cm^{-1} of weak intensity),[14,35] to bond vibrations of ν (C–O) type (1002–1065 cm^{-1} of weak intensity), ν (C–C) aliphatic, aromatic type (1205–1299 cm^{-1}, both of medium intensity), δ (CH$_2$) and δ (CH$_3$) type (1356–1375 cm^{-1} of weak intensity), δ (–CH) scissoring type (1450 cm^{-1} of high intensity), ν (C=C) type (1648–1660 cm^{-1} of medium-high intensity), ν (–CHO) type (2662–2727 cm^{-1} of weak intensity), ν (–CH) type (2870–2929 cm^{-1} and 2910–2950 cm^{-1} of strong intensity). However, significant differences were seen between the spectra of these two varieties of amber; for example, romanite presents in the spectral region corresponding to ν (C=C) type bond vibrations, a broader band at 1650 cm^{-1} with a weaker shoulder at 1617 cm^{-1}, a single broad band assigned to ν (C–C) isolated type centered at 715 cm^{-1} accompanied on both sides by two shoulders and correlated to the central band in the triple of the Baltic amber spectra. This change in the spectral profile in the wavenumber region 800–600 cm^{-1} was previously noted by Brody et al.[14] and also correlates with the degree of maturation for fossil resins. They observed that, as the fossil resins mature, a doublet at 745 and 697 cm^{-1} becomes a triplet at 745, 720, and 697 cm^{-1}, which then becomes a single broad band with a weak shoulder and correlated to the central band of the triplet. Furthermore, Baltic amber spectra presents in the wavenumber region 3200–2600 cm^{-1}, some additionally undefined bands accompanying the characteristic signal at 2929 cm^{-1} assigned to ν (–CH) type bond vibrations,[14,20] such as a weak intensity band at 3079 cm^{-1} and a shoulder at 2988 cm^{-1}, features that are much reduced in intensity or absent in romanite spectra. Although both ambers present a medium intensity signal between 1430 and 1470 cm^{-1}, in most reference Baltic amber samples, this signal is not well resolved, appearing

as one band at 1450 cm^{-1} with a weak shoulder at around 1469 cm^{-1}. Moreover, Winkler et al.[22] observed this unresolved band mostly in the spectra of recent resins, and based on their observations, they stated that the transformation of the two peaks into one clear defined band is also a sign of resin maturation. The shape of FT-Raman spectra for both investigated fossil resins shows several other small characteristic features that may be used for discrimination, but their visual recognition is relatively difficult, especially when interpreting data from archeological amber.

All forms of organic matter undergo changes in sedimentary systems over geological time. This general phenomenon is referred to as maturation. In the literature, it was suggested that the relative intensity measurements of the most characteristic bands in the Raman spectra of amber, the alkene stretching band at around 1650 cm^{-1}, and that of the methylene (C=CH$_2$) deformation at 1450 cm^{-1}, represent a definitive method to assess the extent of resin maturation and, hence, the age of the resins.[20] The ratio was referred to as the index of maturation (I_m) and presented values < 1 for resins with a higher degree of maturity. The ratio decreases as the sample matures, and the explanation for that is the depletion of the alkene functional groups due to cross linking and oxidation processes. The calculation of this parameter was done on a variety of fresh and fossil resins, and later, it was found that the fossilization process is not the major contributor on the Raman intensity ratio, but other influences (climatological, burial environment, or botanical) might affect the relative intensities of these bands.[14,20,23,24,28,35,36]

The weathering-related changes of amber samples subjected to alteration experiment have been investigated by FT-Raman spectroscopy and the peaks to be compared where chosen according to the maximum values of the standard deviation on the range of intensity: the one at about 1450 cm^{-1}, actually corresponding with the maximum of the first band, and that at about 1660 cm^{-1} were divided by each other to obtain the values for the maturation index, which presented lower values for Romanian unaltered amber (0.36 ± 0.02) compared to Baltic amber (0.91 ± 0.08). These values together with the spectral differences presented previously conclude that romanite is Baltic amber that suffered thermal degradation, a fact also suggested by Stout et al.[37] through the gas chromatography–mass spectrometry (GC-MS) method. The index of maturation (I_m) ranges between 0.70 and 0.76 for the weathered Baltic amber and between 0.15 and 0.35 for the weathered Romanian amber samples. It was not only confirmed that romanite has a lower I_m value than Baltic amber, but also it was pointed out that artificially weathered fragments have lower I_m values with respect to the fresh ones, indicating that the weathering induces the same kind of transformation caused by natural maturation of fossil resins. For the romanite, it is also interesting to note that there seems to be a difference of behavior between fragments subjected to degradation in air and water and those exposed to saline, acid, and alkaline environments, since the former are much closer or even overlapped to the I_m values obtained for the unaltered samples, leading to a
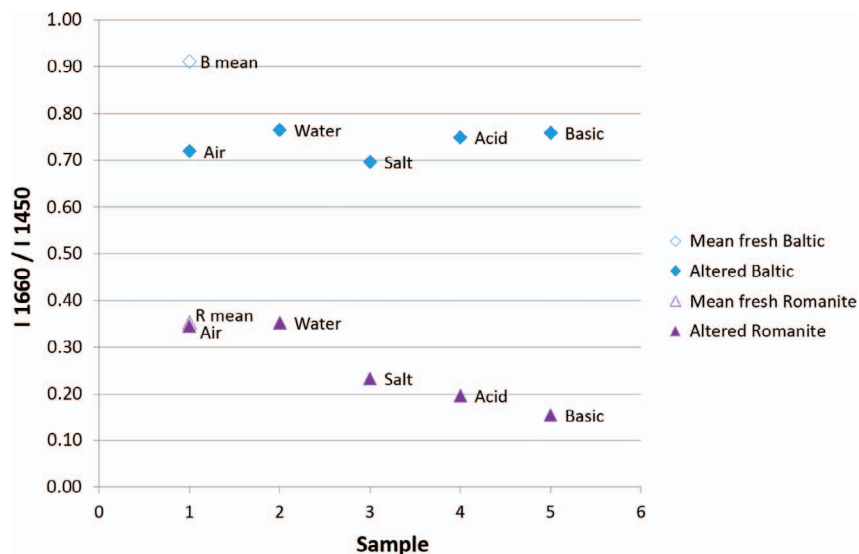
FIG. 2. Plot of the intensity ratio ($I_m = I_{1660}/I_{1450}$); Baltic (rhombi) and Romanian amber (triangles).

hypothesis of a stronger form of alteration in the latter three conditions (see Fig. 2).

On the basis of a qualitative examination of the spectra, it appears clear that Romanian amber shows a bigger difference between the before and after weathering spectra: in particular, the background increases in the altered fragments; this could be connected to the increasing fluorescence with a stronger coloration of amber that, in these samples, is in fact much darker by visual appearance (see Supplemental Material).

The spectral region most affected by the alteration is that included between 1540 and 1700 cm^{-1}.

In Fig. 3, this region is normalized to the not-varying broad band at approximately 2900 cm^{-1}, assigned to the CH stretching vibration. An increment in the intensity of the components at approximately 1580 and 1610 cm^{-1}, associated to the aromatic CH or C=C stretching,[18,22] can be observed. This is more evident for Romanian amber, in particular for the spectrum acquired on the fragment subjected to acid conditions, with the appearance of a shoulder at around 1590 cm^{-1} (Fig. 3a).

This shoulder is present also on the spectrum of the fragment treated in basic conditions and is less evident for spectra related to water and salt treatment, while it seems absent for amber altered in air. For Baltic samples, the alteration of the spectra results is less evident, and the differences between the spectra are

FIG. 3. Fourier transform Raman baseline subtracted spectra in the region 1540–1700 cm^{-1} of (**a**) Romanian and (**b**) Baltic amber samples, initial stage and weathered conditions.

attenuated with respect to romanite (Fig. 3b). The same observations can be made if the normalization is made with respect to the 1450 cm^{-1} δ (CH) band.

The influence of atmospheric conditions (role of oxygen-enriched atmosphere, changes of temperature, presence of water) and also the duration of these kinds of processes (heating, pressure effects) in weathering can cause drastic transformations in amber composition, such as oxidation or even elimination of specific functional groups. It has been proposed[13] that the major process of maturation of the resins is olefinic polymerization, leading to the formation of high molecular weight compounds, with a reduction in the number of functional bonds and increase in aromaticity. After the observation of the spectral modifications consequent to thermal alteration, the increase in aromaticity can be confirmed, and it can be affirmed that it is more consistent when the alteration or maturation, which are apparently comparable processes, happens in acid environments and affects more the Romanian amber with respect to the Baltic one.

Statistical Data Evaluation. Before starting the statistical analysis, a pre-processing step such as mean-centering for the spectral data was performed in order to gain in the interpretability of the model for a PCA.[38,39] Statistical analysis was first applied on the 3500–50 cm^{-1} Raman spectral region (895 variables) which presented the most informative spectral features of the samples. Looking further at the table of variable contributions, the 3500–3100 cm^{-1} region was removed from exploration because it had very weak signal intensity, at level of background noise (< 0.005 in this interval). Each of the 12 samples was measured three times, having thus 36 spectra. In order to have better homogeneity of data and to avoid any possible spectra acquisition errors, we removed the eccentric triplet result of all samples and performed further statistical analysis with 24 spectra.

Statistical tests showed that PC 1 tends to cover about 80% of the variation of the dataset. Figure 4 presents a plot of PC1 and PC3, where it can be seen that all Baltic
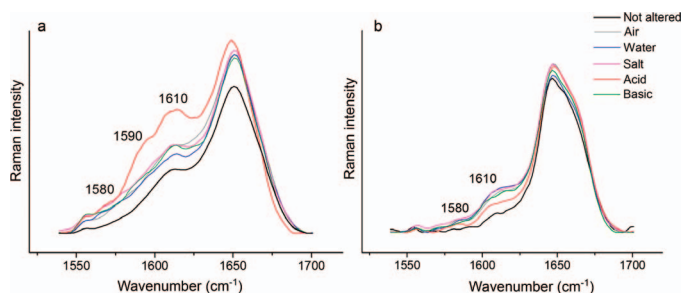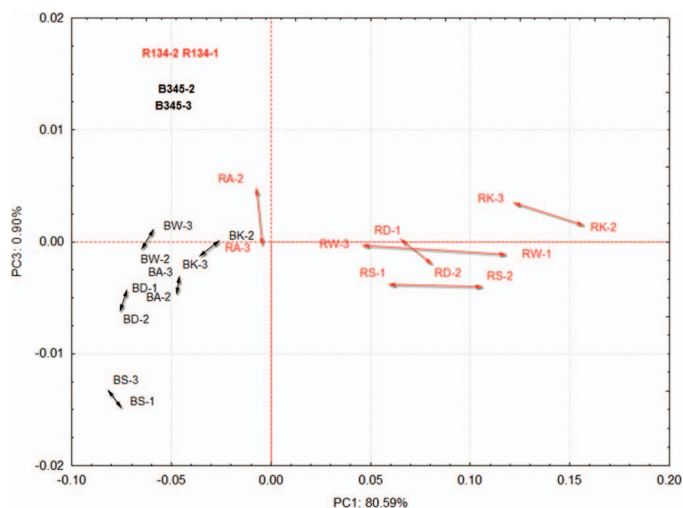
FIG. 4. Principal component analysis score plot for wavenumber domain 3100–50 cm^{-1}: B345-Baltic amber, R134-Romanian amber, unaltered; B* and R* -altered amber (*D-air; *W-water; *S-salt; *A-acid; *K-alkaline); arrows are showing the duplicate relationships.

TABLE II. Variable contributions to the PC1-4 constitution (1700-1570 cm^{-1}).

Wavenumber (cm^{-1})	PC 1 (%)	PC 2 (%)	PC 3 (%)	PC 4 (%)
1701	1.800	0.651	10.213	1.313
1697	1.851	0.649	9.175	0.957
1693	1.905	0.600	6.995	0.499
1689	1.966	0.418	6.442	0.119
1685	2.036	0.203	5.449	0.013
1681	2.049	0.026	2.960	0.355
1678	1.884	0.031	1.585	2.383
1674	1.531	0.485	1.068	3.597
1670	1.081	2.065	1.109	3.052
1666	0.760	4.801	1.135	2.740
1662	0.694	7.767	0.614	3.223
1658	0.837	10.483	0.015	5.436
1654	0.988	13.171	0.119	9.546
1651	0.872	15.122	0.012	3.924
1647	0.619	15.069	0.511	3.093
1643	0.697	11.617	0.849	22.362
1639	1.354	5.647	0.001	20.306
1635	2.330	1.533	1.676	8.396
1631	3.089	0.283	3.302	3.535
1627	3.637	0.029	4.168	1.514
1624	4.033	0.011	4.915	0.542
1620	4.227	0.101	4.785	0.055
1616	4.433	0.215	4.333	0.035

samples are grouped along the left side of the graph, while the romanite ones are being spread on the rest of the plot. The strong separation of the results for altered Romanian amber samples is not something new.[27] PC3 was chosen instead of PC2 because it provides a closer location for the duplicates (see the arrows from Fig. 4), although PC3 accounts for less than 1% from all the processed data. Looking at the results, the samples of romanite altered in acid environment (RA) seem less affected, but the pair altered in alkaline environment (RK) is quite far from the unaltered samples (R134). The Baltic experimental set of samples is generally less affected, with the notable exception of the pair altered in saline environment (BS).

The separation made within the thermally altered samples was convincing in the diagram from Fig. 4, but does not show a reasonable discrimination between the raw materials. An improved separation of unaltered
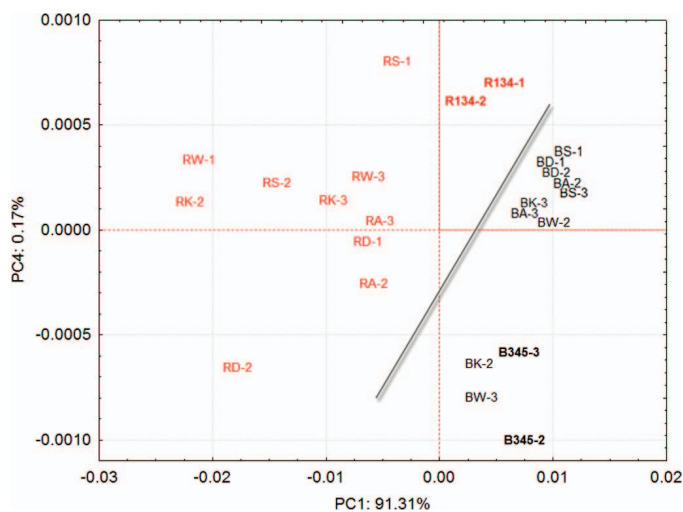

FIG. 5. Principal component analysis score plot for wavenumber domain 1700–1570 cm^{-1}: B345-Baltic amber, R134-Romanian amber, unaltered; B* and R* -altered amber (*D-air; *W-water; *S-salt; *A-acid; *K-alkaline).

amber samples could be realized taking into account the wavenumber domain 1700–1570 cm^{-1} starting from the suggestion given by the sequence of spectra from Fig. 3.

Figure 5 illustrates the PC1 and PC4 score plot in which the unaltered Baltic amber and romanite are clearly located on divergent sides of the graph, due to the fourth component (PC4). The pairs of samples are located more randomly compared to Fig. 4, but with an obvious advantage of a clear distinction between the two sets of samples. The rate of separation for the samples of romanite is also greater than for the entire set of Baltic amber, confirming our previous observations (see Raman analysis and Ref. 27) about the tendency of Romanian amber to alter faster than Baltic amber.

In order to find out what specifically contributes to the discrimination between Baltic amber and romanite, we took into consideration the variable contributions in the range 1701–1570 cm^{-1} (Table II) with a noticeable improvement due to the wavenumber domain 1670–1631 cm^{-1} assigned to ν (C=C) type bond vibration, not only on PC4 (see Fig. 5), but also on PC2.

In order to assess other possible sequences of data that might give a discriminator clue, we plotted the loadings (variable coordinates based on correlations) for the principal components (PC1 to PC4) and presented them in Fig. 6. There were two spectral regions of interest, at both ends of the wavenumber domain, especially at PC1 and PC2, but they statistically did not provide additional information regarding a clear separation of the samples investigated.

We can emphasize that the results of the statistical analysis applied on Raman data are similar to those on FT-IR-reflectance data previously reported;[27] however, they are more clear and convincing having the advantage that Raman data were used for statistical analysis without additional treatment compared with FT-IR data.[40]
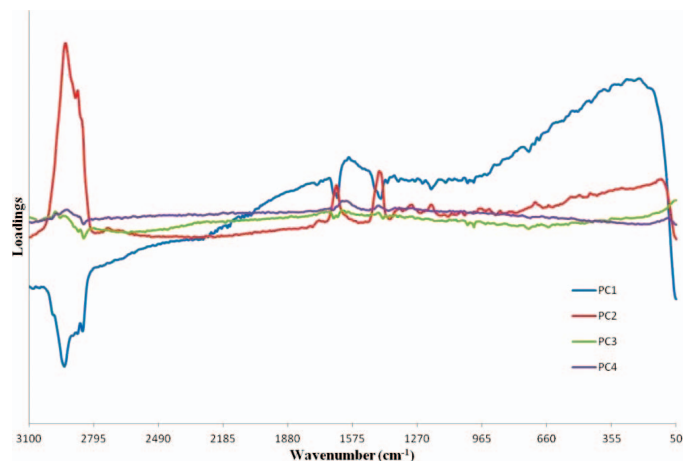
FIG. 6. Loading plots of the principal components (PC1 to PC4) for the investigated Raman spectral region.

We can conclude that this optimized Raman technique (laser 1064 nm, power on sample ~190 mW, and 2000 scans per sample) coupled with statistical analysis represent a promising set of tools for amber artifacts analysis.

CONCLUSIONS

In order to determine new differentiating criteria for altered matter such as archeological amber, the non-destructive FT-Raman technique was applied on two categories of amber samples (Baltic and Romanian amber) subjected to thermal alteration in five different media for a period of 12 weeks. Raman spectra qualitative observations demonstrate that the two categories of amber have different behavior in terms of direction and degree of alteration during the experiment, and Romanian amber is the most affected by the hostile environment when compared to Baltic samples. The statistical analysis performed on FT-Raman data results successfully confirm that the two types of amber subjected to analysis responded in different ways to the various alteration conditions. These results can be used to develop a preventive conservation strategy based on the control of climatic and atmospheric conditions in the environment where archeological objects are placed during storage, transport, and exhibition.

SUPPLEMENTAL MATERIAL

All supplemental material mentioned in the text, including a stack plot of FT-Raman spectra of one representative fresh fragment and the weathered fragments of Romanian and Baltic amber in the wavenumber region 100–4000 cm^{-1}, can be found in the online version of the journal at http://www.s-a-s.org.

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