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Romanian Archaeological Amber Artefacts Characterisation Using Vibrational Spectroscopy and Multivariate Data Analysis

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Abstract

Principal component analysis (PCA) has been applied to FTIR and FT-Raman data in order to determine the provenance of the amber used for an archaeological artefact discovered at Noşlac (Alba county, Romania), now preserved in the Romanian National History Museum collection. As reference materials were used Romanian and Baltic amber from various locations. Similarities among the spectra displayed with PCA indicated a local origin for the archaeological amber beads.

Introduction

Fourier transform infrared (FTIR) or Raman spectroscopy has been used to characterise the amber [1,2,3] but little has been reported about their utility in combination with multivariate statistical analysis [4]. Here, FTIR and FT-Raman spectral data were used for principal component analysis (PCA) in order to find out the origin of the raw material used for the amber artefact from Noşlac (Romania), dated to seventh century. The characterisation and differentiation of archaeological amber samples according to their source is essential for further studies concerning amber routes and distribution across Europe.

Materials & Methods

Twenty-five amber samples with different origin were analysed. Five samples of archaeological amber were from Noşlac, Alba county (a string of amber beads; inventory number 84879), three from archaeological Baltic amber (Stone Age), five from Baltic area (geologic amber from Poland, Kaliningrad - Russia and Bitterfeld – Germany) and twelve from Romania (geologic amber from Colţi and Sibiciul de Jos, both located in Buzău county).

FTIR analyses in transmission were performed on a Bruker Tensor 27 spectrometer, using a small quantity of amber (about 0.5 mg) for KBr pellets (5 mm diameter). For each sample, FTIR spectra were collected in the range 4000–400 cm^{-1}. In order to remove disturbing H_2O and/or CO_2 bands in the spectra, a straight line was generated between 2500 and 1880 cm^{-1}.

FT-Raman spectra were collected using a Bruker Vertex 70 instrument with Nd: YAG laser excitation source (1064 nm). The samples were not pre-treated for Raman measurements.

OPUS software (version 4.2, Bruker Optics) was used for spectral acquisition, instrument control and preliminary file manipulation (smooth, baseline and normalization). PCA was performed using MATLAB software package (version 7.10, R2010a, The MathWorks www.mathworks.com). The Euclidian distance method in the principal component space was also used.

Results

Principal component analysis (PCA) was performed to each data set (FTIR and FT-Raman spectra) in order to display the data and to reduce the dimensionality of the spectral data to a small number of components. Only the PCA scores plot for the infrared dataset is presented below. Figure 1 shows some of the FTIR spectra used for the dataset. As can be seen from Fig.2 (a), on scores plot of PC1 versus PC2, explaining 88.9% of the total variance, amber is classified in two main groups: archaeological amber on the left and geological amber on the right. The most important absorption bands which differentiate the amber samples are those corresponding to stretching vibrations of OH in (broad band at 3450 cm^{-1}) and of C=O in carboxylic acid groups for the archaeological samples, and CH in methyl/methylene groups for geological samples.

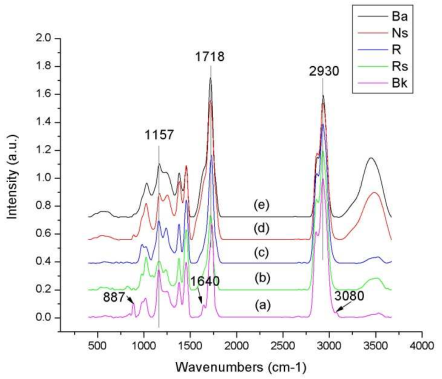

Figure 1 FTIR spectra of (a) Baltic amber, Kaliningrad, Russia, (b) amber from Sibiciul de Jos, Romania, (c) amber from Colți, Romania, (d) archaeological amber from Noşlac and (e) archaeological Baltic amber; these spectra are part of the dataset for PCA.

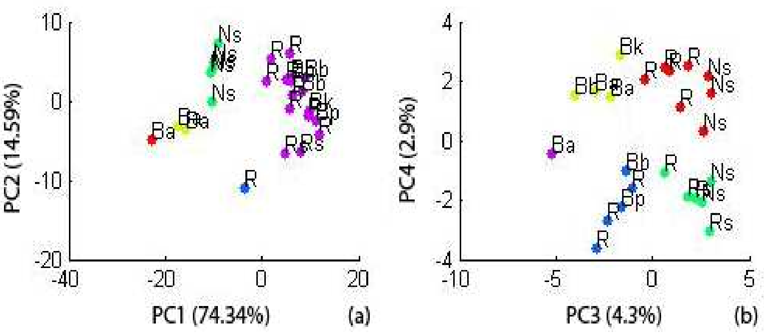

Figure 2 PCA scores plot of PC1 vs. PC2 (a) and PC3 vs. PC4 (b) for FTIR data of amber of different origin; archaeological amber: Noşlac (Ns) and Baltic amber (Ba); geological amber: Colți, Romania (R), Sibiciul de Jos, Romania (Rs), Baltic amber from Poland (Bp), Baltic amber from Kaliningrad, Russia (Bk) and Baltic amber from Bitterfeld, Germany (Bb).

PC3 axis regroups in the positive part spectra with intense bands due to C=O stretching vibration of carboxylic acid and ester groups (samples from Noşlac are grouped here, along with Romanian amber samples) while the negative zone is mainly characterised by the presence of C-O and C=O stretching vibrations of ester groups (Fig. 2, b).

FT-Raman spectroscopy revealed a new band, at 1609 cm^{-1}, attributable to C=C stretching vibration in aromatic compounds. The amber from Noşlac was distributed on PC1 versus PC2 near to Romanian amber mainly due to this band intensity.

This assignment is in agreement with the information obtained using other techniques (ROMANIT project, http://www.romanit.ro).

Conclusions

These results show the importance of multivariate data analysis for the characterisation of amber samples. The distribution of the spectra on the PCA scores plot suggests that the source of the raw material from Noşlac archaeological finds is Romanian amber.

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