Analysis of Triterpenoid Resinous Materials by Direct Exposure Electron Ionization Mass Spectrometry (DE-MS): PCA Evaluation of Mass Spectral Data

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Abstract

A systematic study of triterpenic resinous materials (frankincense resin, mastic resin, dammar resin and birch bark pitch) was performed using direct exposure electron ionisation mass spectrometry (DE-MS). DE-MS provides a mass spectral fingerprint of organic materials in a few minutes which highlights the main components in the sample. The application of principal component analysis (PCA) on DE-MS data enabled us to distinguish between different triterpenoid materials. The DE-MS analytical approach has been applied in the characterisation of organic residues from archaeological findings.

Introduction

Natural resinous materials are some of the most common organic substances present in archaeological findings and art objects. They have been used as adhesives, varnishes, sealing agents, and also as ingredients for cosmetics, medicines, incenses and mummification balms[1,2]. Frankincense, mastic, birch bark pitch and dammar were between the most widely used triterpenoid resinous materials.

Analytical procedures based on GC/MS have been applied successfully in the characterization of archaeological organic residues and paint varnishes containing terpenic resins. Nevertheless, they require time-consuming sample pre-treatment, which normally entails extraction, purification, chemolysis and derivatisation before injection into the gas chromatographic system. Thus, the adoption of direct mass spectrometric techniques, such as DE-MS, that reduces sample manipulation, seems to be advisable [3,4]. In this study, DE-MS has been applied in the characterisation of four triterpenic resinous material and for their identification in archaeological findings.

Materials & Methods

A systematic study of standard triterpenic molecules and of modern raw materials of a known origin (frankincense resin, mastic resin, dammar resin and birch bark pitch) has been carried out by DE-MS (Direct Probe Controller, Direct Exposure Probe and Polaris Q ion trap Mass Spectrometer by Thermo Electron Corporation, USA). GC/MS analysis after wet chemical treatment has been performed on the same materials in order to compare and evaluate DE/MS results. To discriminate between the four materials, pattern analysis of DE-MS mass spectral data was performed by principal component analysis (PCA) on the covariance matrix after row normalisation of the data, by using Xlstat 6.0 (Addinsoft, France).

The results relative to two archaeological samples are also presented [4]: the first was collected from a ceramic censer from Roman times found in Antinoe (Egypt) and the second from a flint-flake from the Palaeolithic period recovered at the Campitello site (Arezzo, Italy).

Results

The DE-MS spectra of frankincense, mastic, dammar and birch bark pitch and of archaeological samples have been collected and interpreted on the base of the comparison with

standard molecules and with GC/MS data. The results show that DE-MS enables to highlight significant differences and to provide evidence of the presence of the most abundant components of the materials.

Due to the relatively difficult interpretation of complex DE-MS mass spectra, PCA was applied to selected significant regions of the DE-mass spectra which contain all the fragments that in the analysis of standard compounds were assigned to triterpenes: the range m/z 181- 260 and m/z 331-500. The four reference materials are located in distinct areas of the scatter plot of the first two PCs (67% of the variance). The sample from the censer is located in the area of the mastic resin cluster, while the sample from the flint flake is located next to birch bark pitch reference samples.

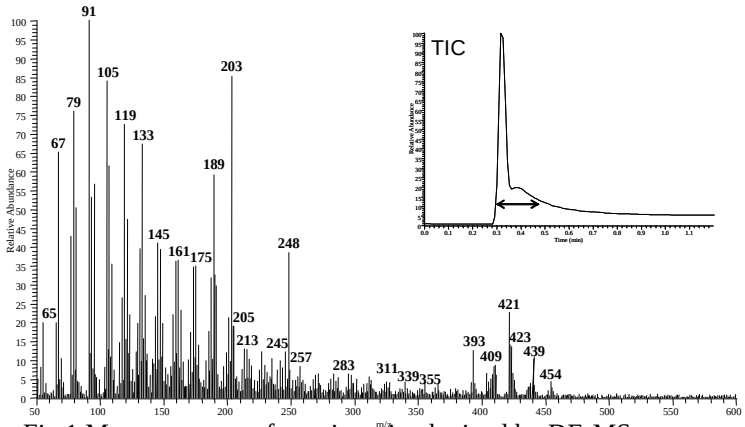

Fig.1 Mass spectrum of mastic resin obtained by DE-MS.

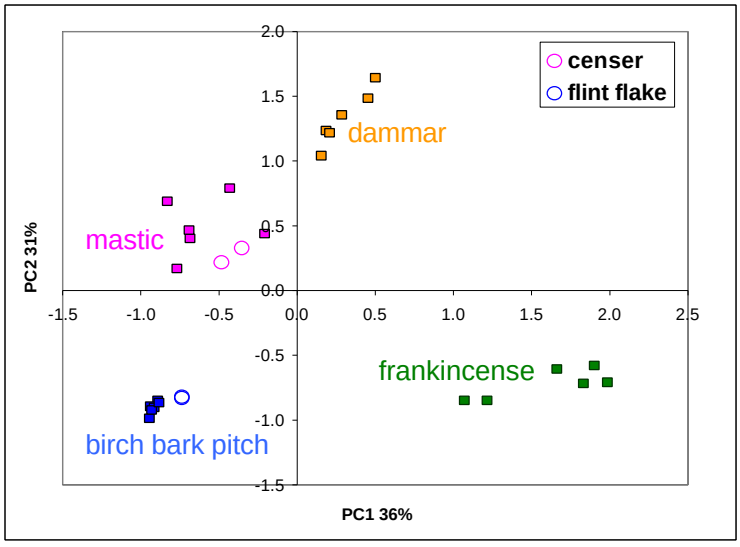

Fig.2 PCA scatter plot of DE-MS mass spectral data

Conclusions

Principal component analysis on DE-MS mass spectral data of triterpenic materials at selected mass ranges permits to differentiate between very similar triterpenic resins and to highlight chemical differences and similarities between samples. Examination of the loadings for the first two PCs permitted to highlight the more significant m/z fragments in the differentiation of the triterpenoid materials. DE-MS was found to be a fast screening analytical tool suitable to archaeological samples, but it failed to give information on the presence of less abundant compounds, in fact only mastic resin was found in the residues from the Roman censer, whereas GC/MS analysis identified the presence of a vegetable oil from Brassicaceae seeds and Pinaceae resin [4]. Birch bark pitch as a pure material was identified in the sample from the Palaeolithic flint flake using both procedures.

References

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