GC-MS Spectroscopy as Valuable Tool for the Study of Archaeological Ceramics

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The identification of organic materials present in archeological findings by spectroscopic methods is important due to the information that can provide useful data both in archeological research and in the restoration and preservation activities. Organic materials can be easily preserved on a ceramic support. This paper presents analytical results of microsamples taken from the surface of two neolithic ceramic fragments, found at the “Porţ Corău” archaeological site. The fragments are decorated with a black colored layer, assumed to be natural bitumen due to the geographic area in which the fragments were excavated. The microsamples were characterized by means of gas chromatography coupled with mass spectrometry (GC-MS) and compared with reference samples. The analysis strategy being based on the detection of characteristic biomarkers. The results presented in this study were also supported by Fourier transform-infrared spectroscopy (FT-IR). Based on the analysis it can be concluded that the black layer is organic in nature, being a mixture of birch bark tar with natural bitumen. This mixture is predominantly composed of birch bark tar.

Keywords: GC-MS, birch bark tar, natural bitumen, Neolithic decorated ceramic

In this paper we present the identification and composition analysis of the black material used on decorated archeological ceramic objects found at “Porţ Corău” site. Preliminary research on the aforementioned ceramic fragments was performed by means of by optical microscopy and X ray diffraction, characterizing the ceramic paste. Samples were collected from two ceramic fragments (C 137 and C 137 M) and subject to GC-MS and FT-IR spectroscopy.

Located in the northwest of Romania, within the current Sălaj and Bihor counties, the archaeological site at “Porţ Corău” is one of the most important Neo-Eneolithic sites in this geographical area. The first systematic research here began in 1973 and continued until 1990. Due to the start of a construction project (dam reservoir) partially affecting the site from “Porţ Corău”, preventive research was required for the investment approval. This research began in 2002-2003 and was resumed in 2010 - 2011.

The archeological research conducted in 2010 led to the identification of levels of habituation belonging to the Starčevo – Criş culture, the Pişcolt culture, the so-called Suplac group, the Coţofeni culture, the later bronze Hallstatt culture, the Vekerzug Szentes culture and from the Roman period (second and third centuries A.D.). A possible deepened dwelling (2.60 m x 2.60 m) was identified in the S5/2010 area. This residence, called Cx. 137, belongs to the early Suplac housing level (4800-4500 B.C.) and exhibits a rich ceramic inventory [1].

Several fragments stand out among the discovered items; these fragments belong to a large bowl with vertical, glossy black stripes, 2 to 2.3 cm wide. The archaeological material obtained from the last two research campaigns has not yet been scientifically exploited or restored. The black colored layer is very well preserved and it is, by macroscopic appearance, a bituminous substance. It is well known that a surface shale exploitation area was present in the immediate geographical region from where the fragments were excavated. Furthermore, it is well established from archaeological reports that black colored layer used for Neolithic ceramic decorations was often natural bitumen, obtained from shale. Birch bark tar was also used as black material, alone or mixed with natural bitumen.

Natural bitumen is found at surface level, as native deposits resulting from the seepage of crude petroleum through fissures or exposure by erosion, followed by evaporation of the more volatile components [2].

Depending on the geological era and location, the associated minerals and local water sources there are many different bitumen compositions. Petroleum and bitumen composition determinations were and still remain an important topic, out gas chromatography coupled with mass spectrometry consistent results have been obtained in this field [3]. Another useful characterization technique is represented by FT-IR spectroscopy which can provide efficient structural confirmation.

In addition to the alkanes and cycloalkanes, there are several other classes of compounds which constitute important biological markers helpful in ‘fingerprinting’ particular bitumen.

Biological markers (biomarkers) are complex molecular compounds once found in living organisms [4]. Biomarkers are very useful because they can provide information about the entire petroleum or bitumen geology [5]. Due to their general resistance to weathering, biodegradation and other possible transformations, biomarkers are commonly employed as indicator of the contamination of petroleum as a result of its environment.

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It is of real importance to make the correct assignment if all black paint or layer found on archaeological objects originates from natural bitumen. Other sources of black layers could be from burnt natural resins [6]. Such resins, for example pine pitch or birch bark, contain a huge number of cyclic or acyclic terpenoid hydrocarbons and derivatives [7, 8].

Experimental part

Materials

Chloroform and hexane of spectroscopic purity were used as received from Riedel and Merck, respectively, 60-230 mesh chromatography alumina was purchased from Fluka. Helium, purchased from Linde, was used as carrier gas. Gravimetric measurements were performed on an AX 210 Mettler electronic balance. A Towson&Mercer ultrasonic bath was used for samples dissolution. Syringe equipped with 0.2 μm disposable cellulose filters were purchased from Schleicher & Schuell.

Gas chromatography was performed on a Trace GC Ultra gas chromatograph fitted with an AS 2000 automatic injector and a 10 μL Hamilton syringe, equipped with a TR 5 MS column of 30 m length, 0.25 mm diameter and 0.25 μm film thickness from Thermo. Detection was performed on a Polaris Q ion trap mass spectrometer, all fitted modules being provided by Thermo. Data was processed with the help of the Xcalibur software suite, version 1.3 and for spectral identification was performed by employing the NIST '02 library.

Procedure

Reference samples of natural bitumen from the collection of Organic Chemistry Technology Department from the Politehnica University of Bucharest, approximately 50 years old, were used. Reference samples of birch bark tar from the collection of Brukenthal National Museum, were used.

The reference sample (1000 mg) was dispersed into hexane by sonication for 10 min and subject to a chromatographic filtration onto an open tubular column (30 mm diameter and 40 mm height) loaded with alumina and using as solvent hexane. The hexane fraction was concentrated under vacuum up to a volume of 2 mL and then subjected to GC-MS analysis. The black residue was eluted with 100 mL chloroform and analyzed.

The black deposit from the C 137 M and C 137 fragments surface were labeled sample 1 and sample 2, respectively. These samples of very small size (around 1 mg) were dissolved under sonication (10 min) in 0.5 mL chloroform and filtered using cellulose filters fitted to a luer lock syringe. The resulting solutions were analyzed by GC-MS.

Chromatographic separation was performed at 1 mL/min helium carrier gas flow rate using the following temperature program: start at 100° C, ramping up to 320 ^{0} C at a 10 degrees/min rate and then isothermal regime up to a final time of 60 min. Pressure increased from 81 psi at the analysis start up to 165 psi at the finish. Injector port was heated to 250 ^{0} C and the injection volume was 5 μL with a split flow of 10 mL/min. The high injection volume coupled with low split flow assured a good sensibility and reliable detection. Electron impact provided the ionization source, at 70 eV. The scanning range was set at 50-650 atomic mass units for 0.41 s, at 300 V multiplier offset. Infrared spectra were recorded on Tensor 21 infrared spectrophotometer with ATR module from Bruker.

Results and discussions

The chromatogram of the reference sample solution obtained after hexane elution from open column can be noticed in figure 1. At the short retention time were expected the most volatile components, consisting mainly of linear or branched terpenoid hydrocarbons (fig. 2 A is an extended part of chromatogram from figure 1 up to min 14). The mass spectra were almost identical and consist of fragmentation patterns characteristic for alkanes (fig. 2 A and 2 B).

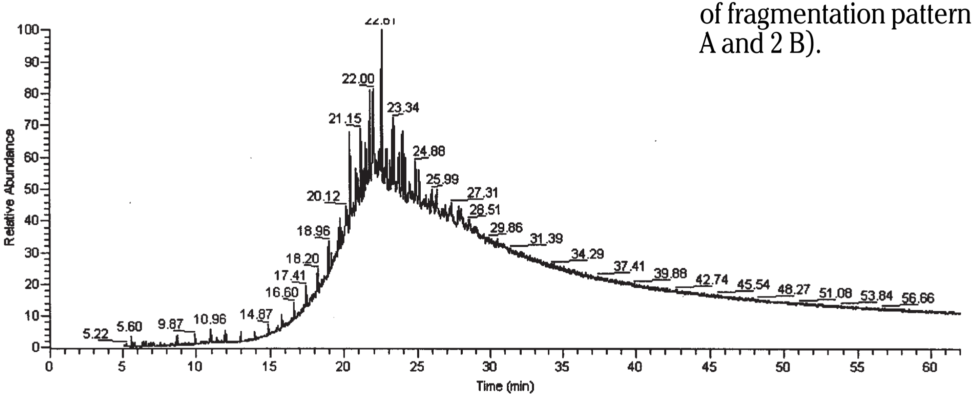


Fig. 1. Total ion chromatogram from the hexane solution of bitumen reference sample

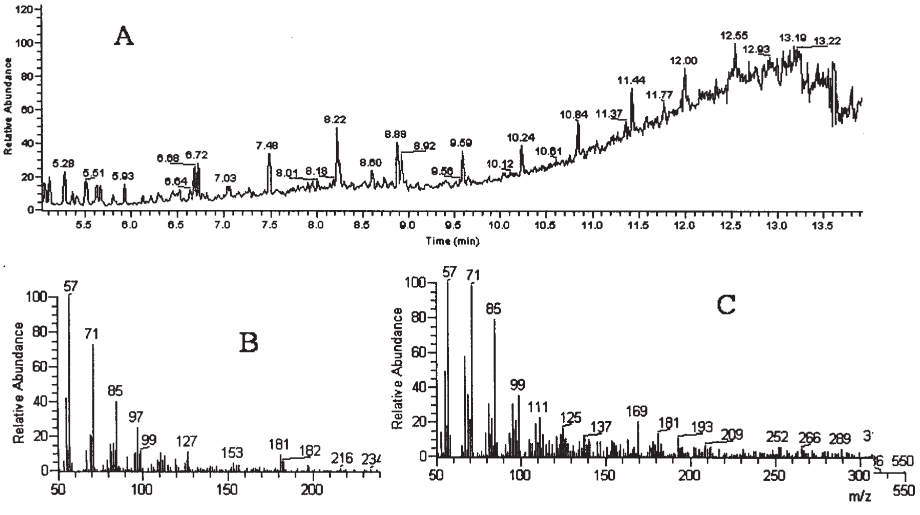


Fig. 2. Extended part up to min 14 (A) of chromatogram from figure 1, mass spectrum of the 7.48 min peak (B) and mass spectrum of the 11.44 min peak (C).

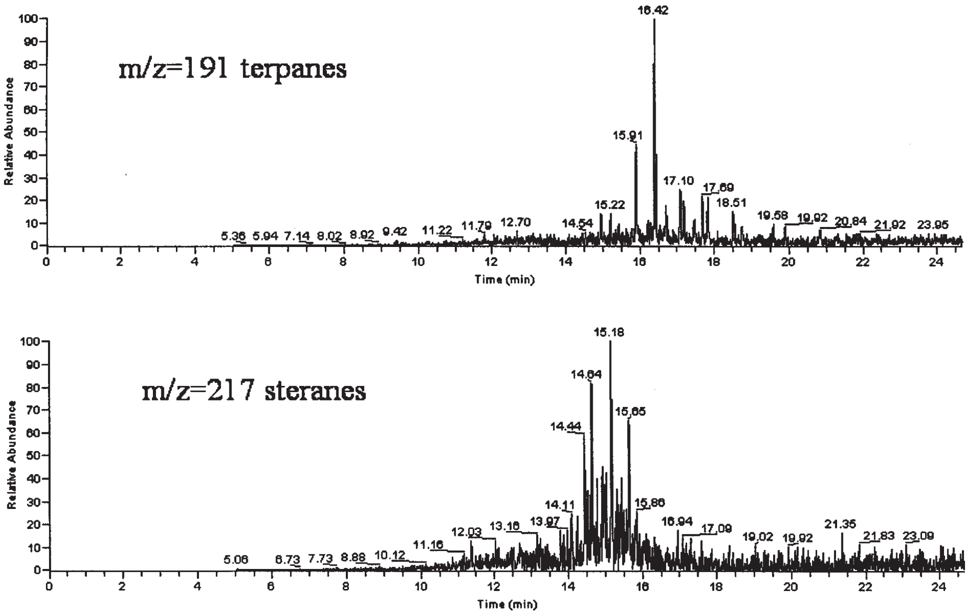


Fig. 3. Reconstructed ion chromatograms from figure 1 for m/z=191 indicating terpanes and reconstructed ion chromatograms m/z=217 indicating steranes

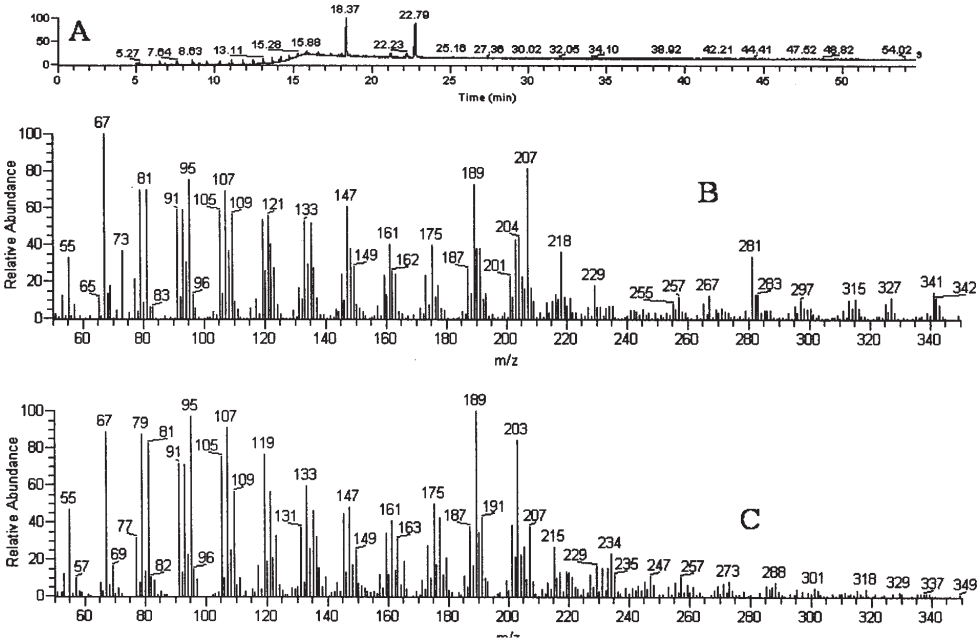


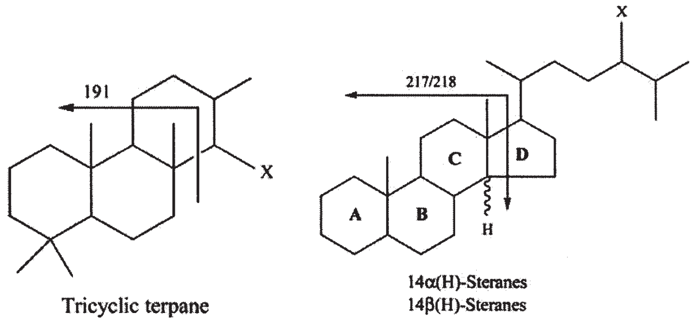
Fig. 4. Chromatogram for sample no 1, fragment C 137 M. Total ion chromatogram (figure 4 A) with major peaks: 18. 37 min., figure 4 B the corresponding spectrum and 22.79 min. - figure 4 C the corresponding spectrum.

The reconstructed ion chromatograms, presented in figure 3 (the first 25 min), were obtained by using the characteristic biomarkers for terpanes (m/z=191) and steranes (m/z=217). As these biomarkers are characteristic to a large number of petroleum types, it was concluded that this sample originates from petroleum source.

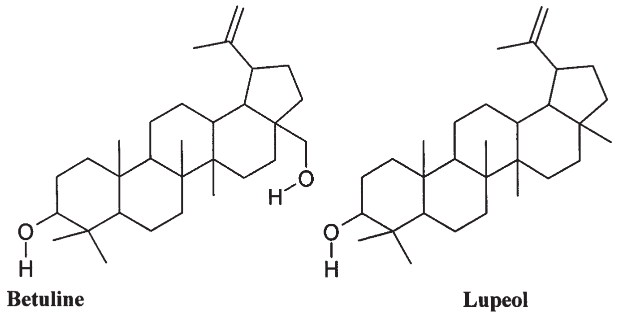
Identical results were obtained for sample 1 and 2, with better amplitude for the former. The total ion chromatogram of the chloroform solution from fragment C137 M, named sample 1, is presented in figure 4 A. Two major peaks, corresponding to retention times of 18.37 and 22.79 min can be noticed. The other peaks are due to column bleeding and their spectra consist mainly of m/z=73 and m/z=281 ions, characteristic for silanes. The normalized current ion level of this chromatogram is around 10^5 counts, which is two orders of magnitude lower than that of the reference sample. The baseline subtraction of this weak signal is presented in figure 4 B (for the 18.37 minutes peak) and in 4 C (for the 22.79 min peak). The base peak intensity of 10^4 counts, characteristic for these peaks, indicates the low concentration of the main components in the mixture. The characteristic peaks of 4 B, found at 189 and 207 m/z were assigned to lupeol (scheme 2) using the library search function [8]. Similarly, the 189 and 203 m/z peaks of 4 C were assigned to betuline (scheme 2). These two substances are known biomarkers for birch bark tar, especially when found together [9]. The lupeol mass spectrum has characteristic peaks at 189 and 207 m/z but also at 55, 69, 81, 95, 109 and 121 m/z [9]. A careful analysis of 4 B and 4 C spectra has shown the presence of the former series of peaks shifted. This can be explained by the dehydration of lupeol and betuline [10].

To a more careful analyze of chromatogram from figure 4 up to retention time to 15 min we can see a series of peaks due to of column bleeding. However chromatogram has very small peaks with normalized level of ion current about 10^3 counts that correspond to alkanes (fig. 5 chromatogram and spectra). These facts shows a mixture of birch bark tar with natural bitumen.

IR spectrum of lupeol presents a very intensely broad band at 3384 cm^{-1} was observed for the O-H bond vibration



Scheme1. Characteristic fragmentation of polycyclic terpenoid hydrocarbon



Scheme 2

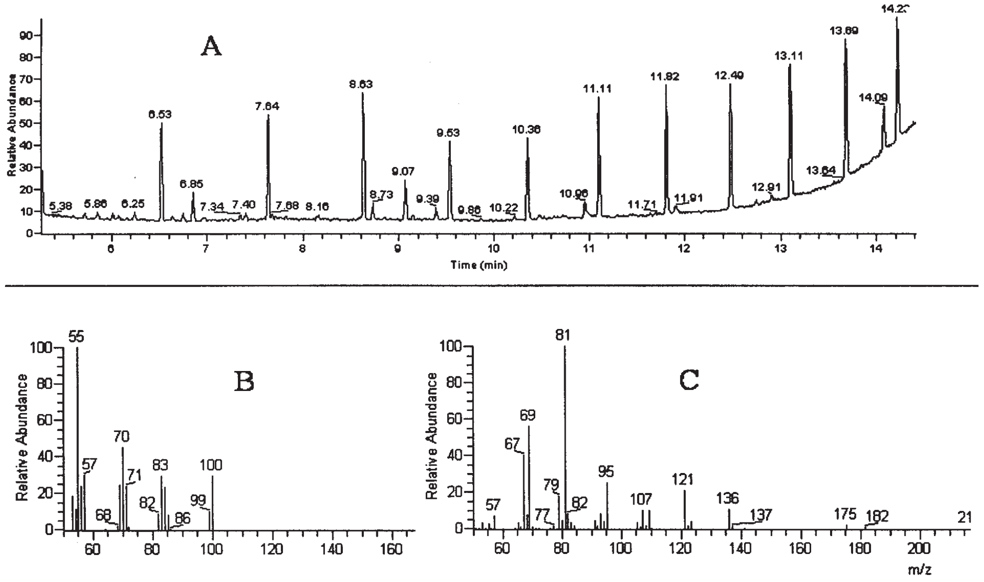


Fig. 5. Extended chromatogram from sample no. 1, fragment C 137 M. (A) and alkanes mass spectra (B, C)

of hydroxyl group and moderately intense band at 1192 cm^{-1} was observed for the C-O bond vibration of C-OH group. The out of plane C-H vibrations of the unsaturated part was observed at 826 cm^{-1}. The corresponding C=C vibrations were shown around 1654 cm^{-1} as weakly intense band. The stretching and bending vibrations of methyl part were noticed by the intense band 2916 cm^{-1} and medium intensity band at 1460 cm^{-1}. Vibration of the methylenic part was shown by the band at 2851 cm^{-1} and the medium band at 1548 cm^{-1}. The moderate intense band at 764 cm^{-1} was attributed to the rocking movement of methylenic part. The corresponding C-C vibration was shown as weak intense band at 1033 cm^{-1} [11, 12].

IR spectra of an extract of birch bark tar were compared with IR spectrum of black organic layer used on Neolithic decorated ceramic. Both spectra contains specific bands to 2850 cm^{-1} and 2919 cm^{-1} corroborated with medium intensity band from 1458 cm^{-1} confirm that the black organic layer from Neolithic decorated ceramic containing mainly birch bark tar than natural bitumen.

Conclusions

The black colored layer found on neolithic ceramic fragments, excavated from the “Porţ Corău” archaeological site was analyzed by GC-MS and FT-IR. The layer was found by comparison with the reference samples to be composed of a mixture of birch bark tar and natural bitumen. This mixture is predominantly composed of birch bark tar.

The analysis of this ancient material represented a challenge due to the chemical complexity of the material. The results obtained in this study are in accordance with historical data and come to enrich our knowledge about the past, being of great importance for future archeological research. The results presented in this paper are also highly relevant for the choosing of restoration methods and materials as well as in making the right choice of adequate preservation conditions for the ceramic fragments.

GC-MS has proved as a tool suitable for the analysis of the very small samples of archeological materials. Based on the target analysis of characteristic biomarkers we have demonstrated the organic nature of the samples. Moreover, the biomarker analysis has enabled the determination of the chemical composition of the investigated samples. This instrumental analysis approach, presented herein, is part of a larger ongoing study aimed at the identification and characterization of black layers found on various ceramic fragments, found in different Romanian archeological sites.

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