

GC-MS and FTIR Analysis of Bitum/Kerogen as Organic Geochemistry Index

Ioana-Raluca Bunghez^{*}, Rodica-Mariana Ion^{*}, Radu Claudiu Fierascu,
Claudiu Radu^{*}, Irina Dumitriu^{*}, Mihaela-Lucia Ion^{**}, Marian Neata^{***},
Sanda-Maria Doncea^{*}

^{*} Valahia University, Materials Engineering Department, Unirii Bv., 18-20, Targoviste, Romania
& ICECHIM, Analytical Department, 202 Splaiul Independentei, Bucharest, Romania
e-mail: raluca_bunghez@yahoo.com

^{**} University of Bucharest, Art History Faculty, Bucharest, Romania

^{***} University of Bucharest, PROTMED, 90 Panduri Str., Bucharest, Romania
& RENAR, 18 Plugariilor str., Bucharest, Romania

Abstract

Archaeological samples have complex compositions consisting in bitumen organic deposit and sometimes, petroleum deposit and natural substances. The materials are usually identified by Fourier transformed infrared spectroscopy (FTIR) (for detecting the functional groups of organic substances) and gas chromatography coupled with mass spectrometry (GC-MS) (for analysis of natural substances such as vegetable resins and oils, bitumen, tar and pitch, and waxes), respectively. For the analyzed samples in this paper, all the hydrocarbons identified confirm that the black substance is a kerogen-type mixture. Moreover, the $C_{16:0}$ and $C_{18:0}$ concentrations are indicating that the compounds are native to the patina.

Key words: GC-MS, FTIR, bitum/kerogen analysis

Introduction

Flint artifacts are the most lasting objects of prehistoric sites. There are a number of interacting factors and countless natural processes working against it. For an artifact to be well preserved it must be protected from these events. Generally, caves offer a good degree of protection from many natural agents. However, every case is different and, within a site, disturbance is not spatially uniform. Attempts to date and define the depositional environments of mixed lithic assemblages have been presented in the literature [1-6]. These detailed experimental studies have been very useful in identifying the complex factors that underlie the formation of different alteration features on chert surfaces (e.g., properties of the chert, soils, environmental contexts and operating conditions) and none of these factors can be underestimated.

Studies of organic matter in solid samples include the analysis of bitumen, kerogen, organic carbon, various hydrocarbons and fatty acids. Is very important to isolate saturated hydrocarbons, normal, branched and cyclic alkanes, others hydrocarbons as n-alkanes.

Feldspars, calcite, kaolinite, illite and some smectite types mostly exist as authigenic clays, while some quartz is common as allogenic minerals.

Analytical techniques as Fourier transformed infrared spectroscopy (FTIR) spectroscopy and gas chromatography coupled with mass spectrometry (GC–MS) have been treated in this paper in order to evaluate the provenance of two collected rock flint artifacts (private collection). Analysis by GC-MS of the carboxylic acid methyl esters prepared from lipids extracted from the flint patina showed that the main organic constituents were palmitic (C_{16:0}) and stearic (C_{18:0}) acids together with minor saturated (myristic C_{14:0}, pentadecanoic C_{15:0}, palmitic C_{16:0}, iso-C_{16:0} C_{17:0}) and unsaturated (palmitoleic C_{16:1} and oleic C_{18:1}) fatty acids. Gas chromatography–mass spectrometry (GC–MS) analyses of C₁₅₊ alkanes (as C₂₃H₄₈ – tricosane, C₂₄H₅₀ – tetracosane, C₂₅H₅₂ – pentacosane, are identified, too.

Experimental details

Materials

The analyses have been achieved on two flint artifacts (private collection). The analyses were carried out on samples of macro-residues of bitumen taken from the artifact surface. A crust of black organic matter, located on both faces of artifacts was rapped from the surface. Samples extracted with chloroform or THF by ultrasonication 45 minutes at 45 °C. The methanol used was of HPLC-grade from Fluka.

Apparatus and methods

Fourier transform IR spectroscopy FT-IR standard spectra were collected by using a Perkin Elmer Spectrum GX spectrometer, by using the pellets technique in KBr from 350 to 7800 cm⁻¹ and the DRIFT accessory.

Samples were extracted twice; first, using 2 mL of acetone, in order to dissolve any resinous fraction that may have been present. After washing, the residue was extracted with the same volume of chloroform in order to dissolve less-polar and/or more polymerized substances (wax, bitumen). After drying them, the two fractions were analyzed by FTIR. Transmittance percentage (%) was collected in the range of 4000–400 cm⁻¹ with 4 cm⁻¹ resolution.

The gas chromatography–mass spectrometry (GC–MS) procedure adopted is able to simultaneously characterize natural resins, waxes, pitch and lipid materials [7]. A brief summary of the GC procedure is: samples were extracted twice with CH₂Cl₂ (1 mL) by sonication (30 min). After centrifugation, aliquots of the supernatant organic extracts were evaporated under a stream of nitrogen and were submitted to saponification with 10% hydroalcoholic KOH.

Aliquots of these extracts 2 µL were analyzed by GC–MS using hexadecane and tridecanoic acid as internal standards.

The gas chromatograph was a GC/MS/MS VARIAN Saturn 2100T instrument equipped with a split/split less injector (used in the splitless mode). The gas chromatographic conditions were as follows: the temperature program was 70°C for 1 minute, heating rate up to 300°C at 15°C/min followed by an isothermal stage at 300°C for 15 min. Carrier gas: He (purity 99.9995%), constant flow 1.2 mL/min. Injection volume: 1 µL.

Results

Kerogen is the polycondensed end-product of the diagenetic reconstitution of biological materials. It is defined as that component of the organic matter in sediments that is insoluble in

inorganic and organic solvents [8]. The soluble fraction of sedimentary organic matter is referred to as bitumen. Type I kerogen is rich in aliphatic structures, type I kerogen contains heteroatoms as sulphur (up to 6%), and type III kerogen has a high primary aromaticity. Type IV kerogen describes oxidized organic matter.

To look for the organic compounds, the artifacts have been supported to extraction in chloroform or tetrahydrofuran. The extracts were analyzed by FTIR, revealing the presence of organic components, most likely lipids (figure 1). By FTIR analysis, was possible to identify the main organic groups and their attributions.

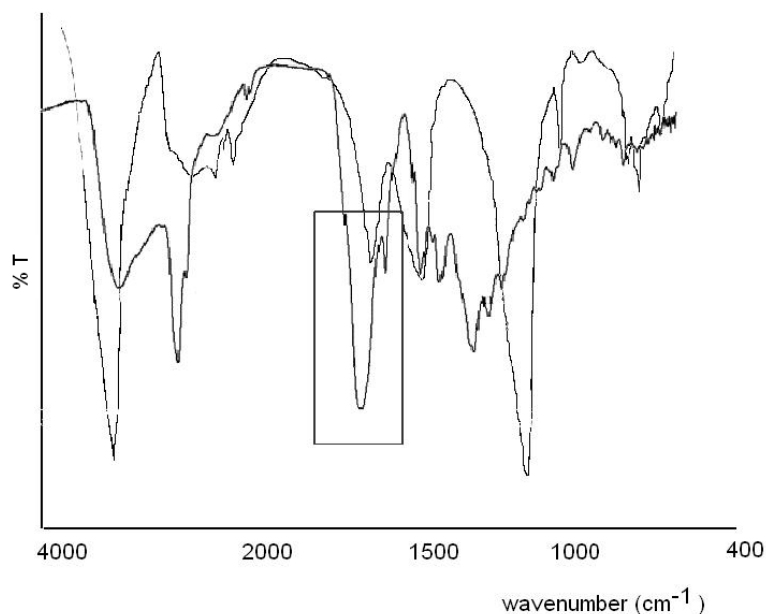


Fig. 1. FTIR spectra of the chloroform extract of the residue's substance first extracted (diluted and concentrated solutions).

The presence in these resins of several carboxylic acids with three-ring structures leads to strong C–H stretching vibration due to CH₂ and CH₃ groups at 2935 and 2871 cm⁻¹. O–H stretching bands occur at 3428 and 2646 cm⁻¹, the latter is broad and very weak due to the vibration of the dimerized carboxyl group in the solid phase. The strong C=O stretching of carboxylic acid is at 1712 cm⁻¹. Other bands are those at 1607 and 1487 cm⁻¹ due to aromatic ring stretches; at 1460 and 1385 cm⁻¹ to CH₂ and CH₃ bending; at 1240 cm⁻¹ to O–H bending in acid resins.

It is possible to presume that the black shale could belong to a bitumen sample, and this was proved by the following frequencies:

- The bands from 2929 and 1456 cm⁻¹ could be attributed to CH₃ and CH₂ vibrations from a hydrocarbonated structure;
- The bands from 1600 and 1500 cm⁻¹ are typical for aromatic structures and the band 1731 cm⁻¹ are specific to C=O group from carboxylic aromatic acids generated by aliphatic chains oxidation; generally speaking FT-IR spectra of vegetable oils and animal fats contain a strong, sharp carbonyl band at 1750-1740 cm⁻¹ due to the ester group while fatty acids from these sources show the carbonyl band at around 1715 cm⁻¹ [9, 10].
- The bands from 1242 and 1178 cm⁻¹ are typical for etheric and alcoholic groups. The most important features were the presence of a broad carbonyl absorption band at 1729 cm⁻¹ together with bands attributed to C-H stretching of CH₃ and CH₂ groups at 2934-2861 cm⁻¹ and 1466-1387 cm⁻¹. The carbonyl band at 1729 cm⁻¹ could arise from fatty acids or from acylglycerol groups. In their liquid or solid states, most carboxylic acids exist as a dimer due

to hydrogen bonding between neighboring COOH groups [11]. The dimer gives a single, sharp, intense CO stretch band near 1700 cm^{-1} . However, in dilute solutions, equilibrium exists between monomers and hydrogen-bonded dimers. The monomer CO stretch band is at a higher frequency than that of the dimer. The monomer absorbs at 1743 cm^{-1} whereas the dimer absorbs at 1705 cm^{-1} . In the preparation of calibration plots for the FTIR analyses, the peak heights at 1743 cm^{-1} and 1705 cm^{-1} are summed [12, 13] to account for the contributions of both the monomers and the dimers present at equilibrium, marked with a square inside the figure 1, detailed in figure 2.

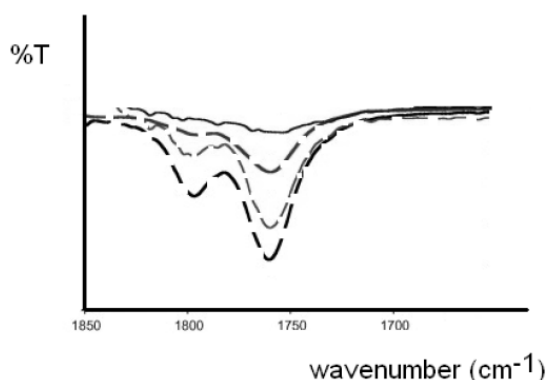


Fig. 2. The monomers and the dimers present at equilibrium

The presence of Al or Si is indicated by intense peaks located at about 473 and 566 cm^{-1} . A medium peak at 872 cm^{-1} is attributed to the OH bending mode from Al-OH and the peak at 1034 cm^{-1} is originate from Si-O stretching vibration. The shape for FTIR spectra is very similar to that of kaolinite clay [14].

Analysis by GC-MS (figure 3) of the solution prepared from lipids extracted from the flint patina showed that the main organic constituents were palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids together with minor saturated (myristic $C_{14:0}$, pentadecanoic $C_{15:0}$, palmitic $C_{16:0}$, iso- $C_{16:0}$) and unsaturated (palmitoleic $C_{16:1}$ and oleic $C_{18:1}$) fatty acids.

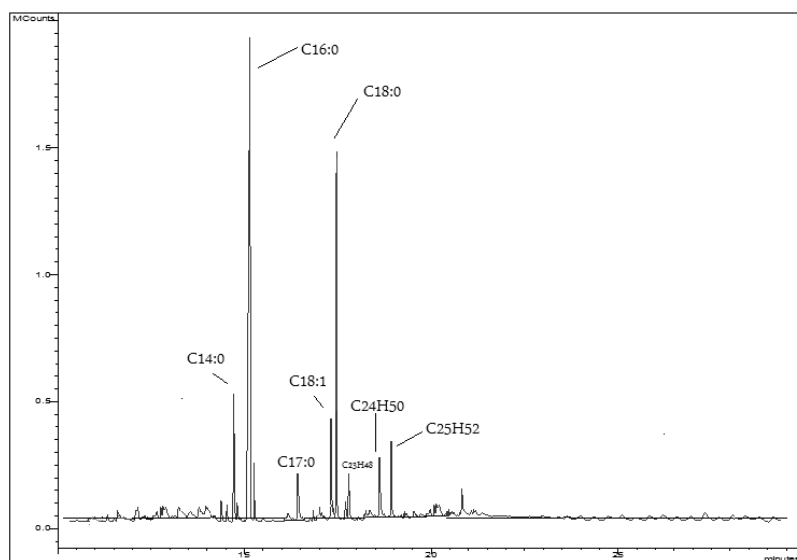


Fig. 3. GC-MS chromatogram of black deposits from flint artefacts

The shape of this black substance suggests that the organic traces are remnants of a hafting material used by people to glue handles onto their tools. Gas chromatography–mass spectrometry (GC–MS) analyses of C_{15+} alkanes (as $C_{23}H_{48}$ – tricosane, $C_{24}H_{50}$ – tetracosane,

C₂₅H₅₂ – pentacosane), are identified, too. All these hydrocarbons confirm that the black substance is highly weathered bitumen, the source of which remains unknown. The bitumen of both shale samples were removed by extraction with MeOH before and after the mineral removal step. The bitumen-free kerogen concentrates were subjected to controlled, mild, stepwise oxidation with Na₂Cr₂O₇-HOAc to yield new fractions. Analyses of the oxidation products were carried out by capillary GC and GC-MS.

Conclusions

Studies of organic matter in solid samples include the analysis of bitumen, kerogen, organic carbon, various hydrocarbons, fatty acids (n-alkanes) and minerals, too. Kerogen is defined as that component of the organic matter in sediments that is insoluble in inorganic and organic solvents, rich in aliphatic structures and sulphur. By means of both FTIR spectra, was possible to presume that the sample extract could belong to a bitumen sample, identified by absorption bands of carboxylic acids (monomers) from 1743 cm⁻¹ and carboxylic acids (hydrogen-bonded dimers) from 1705 cm⁻¹. Analysis by GC-MS of the carboxylic acid methyl esters prepared from lipids extracted from the flint patina showed that the main organic constituents were palmitic (C_{16:0}) and stearic (C_{18:0}) acids together with minor saturated (myristic C_{14:0}, pentadecanoic C_{15:0}, palmitic C_{16:0}, iso-C_{16:0}) and unsaturated (palmitoleic C_{16:1} and oleic C_{18:1}) fatty acids. Gas chromatography– mass spectrometry (GC–MS) analyses of C₁₅₊ alkanes (as C₂₃H₄₈ – tricosane, C₂₄H₅₀ – tetracosane, C₂₅H₅₂ – pentacosane), are identified, too. All these hydrocarbons confirm that the black substance is highly weathered bitumen, the source of which remains unknown.

References

1. Schnoes H.K., A.L. Burlingame, *Application of mass spectrometry to organic geochemistry in Topics in Organic Mass Spectrometry*, A. L. Burlingame (Ed.), Wiley-Interscience, New York, 1970, 471;
2. Connan J., *Use and trade of bitumen in antiquity and prehistory: molecular archaeology reveals secrets of past civilizations*, Philosophical Transactions of the Royal Society B: Biological Sciences, 354 (1379), 1999, 33–50;
3. Ion R.-M., Boros D., Piso I., Ion M.-L., Dumitriu I., Fierascu R.C., Radovici C., Florea G., Bercu C., *Combined spectral analysis (EDXRF, ICP-AES, XRD, FTIR) for characterization of corrosion products from a bronze Roman Mirror*, Metalurgia International, XIII(5), 2008, 61-65;
4. Ion R.M., Dumitriu I., Boros D., Isac D., Ion M.L., Fierascu R.C., Catangiu A., *Characterisation of corrosion products on Roman Mirror*, Metalurgia International., XIII(8), 2008, 43-55;
5. Fierascu R.C., Dumitriu I., Ion M.L., Catangiu A., Ion R.M., *Combined use of surface and micro-analytical techniques for archaeometallurgy* – Analele Universitatii din Bucuresti – Chimie, XVII (1), 2008, 9-14;
6. Fierascu R.C., Dumitriu I., Ion M.L., Catangiu A., Ion R.M., *Surface and analytical techniques studies of Romanian Coins*, European Journal of Science and Theology, 5(1), 2009, 25-34;
7. Boeda E., Connan J., Dessort D., Muhesen S., Mercier N., Valladas H., Tisnerat N., *Bitumen as a hafting material on Middle Palaeolithic artefacts*, Nature, 380, 1996, 336-338;
8. Padley D., *Petroleum geochemistry of the Otway basin and the significance of coastal bitumen standings on adjacent Australian beaches*, Pd.D Thesis, University of Adelaide, AU, 1995;
9. Vasquez C., Maier M.S., Parera S.D., Yacobaccio H., Sola P., *Combining TXRF, FT-IR, and GC-MS information for identification of inorganic and organic components in black pigments of rock art from Alero Hornillos 2 (Jujuy, Argentina)*, Analytical and Bioanalytical Chemistry, 391, 2008, 1381-1387;
10. Patterson J.H., Henstridge D.A., *Comparison of the mineralogy and geochemistry of the Kerosene Creek Member, Rundle and Stuart oil shale deposits, Queensland, Australia*, Chemical Geology 82, 1990, 319–339;

11. Lin-Vien D., Colthup N.B., Fateley W.G., Grassell J.G., *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, New York, 1991, 137–141;
12. Jivraj M.N., MacKinnon M., Fung B., *Naphthenic acids extraction and quantitative analyses with FT-IR spectroscopy*, in *Syncrude Analytical Methods Manual*. 4th Edition, Syncrude Canada Ltd. Research Department. Edmonton, Canada, 1995;
13. Holowenko F.M., MacKinnon M.D., Fedorak P.M.,. *Characterization of naphthenic acids in oil sands wastewaters by gas chromatography-mass spectrometry*, *Water Research* 36, 2002, 2845-2857;
14. Slansky E., *Minerals in some Australian oil shales*, *Fuel* 62, 1983, 469–471.

Analiza prin GC-MS si FTIR a bitumului/kerogenului ca marker organic geochimic

Rezumat

Probele arheologice au compoziții complexe, constând în depozite organice de bitum și, uneori, de petrol și alte substanțe naturale. Materialele sunt de obicei identificate prin spectrometria IR cu transformata Fourier (FTIR) (pentru detectarea grupelor funcționale de substanțe organice) și gaz-cromatografie cuplată cu spectrometrie de masă (GC-MS) (pentru analiza de substanțe naturale, cum ar fi rășini și uleiuri vegetale, bitum, gudron și ceară). Pentru probele analizate în această lucrare, toate hidrocarburile identificate confirmă că substanța neagră prezenta pe artefacte este un amestec tip kerogen. Mai mult decât atât, concentrațiile $C_{16:0}$ și $C_{18:0}$ indică faptul că acești compusi aparțin patinei.