

MULTI-INSTRUMENTAL ANALYSIS OF ASPHALTS OF ARCHAEOLOGICAL INTEREST

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Use was made of thermal and other techniques to characterise three native asphalt samples. The purpose was to support archaeological investigations reconstructing their thermal history and composition. The first sample (from a Roman quarry in central Italy) proved to have 37% impurities, no sign of oxidation or degradation and to have never been heated to above 100°C. The second sample (from a Roman ship sunk south of France) was pure, but partially oxidised, with a saturated fraction in its structure. Analyses of the latter sample, obtained from the eye of a Thracian bronze head, revealed that the asphalt had been heated to over 100°C and then mixed with natural wax.

Keywords: asphalt, archaeology, DTA-TG, FTIR, TMDSC, XRD

Introduction

Native asphalt is composed of an organic fraction (bitumen) and an inorganic fraction. Bitumen is a viscoelastic substance composed of a mixture of hydrocarbon molecules of different molecular mass. Bitumen may be subdivided into four organic fractions: saturated, aromatics, resins and asphaltenes. Bitumen derives from the decomposition of organic material; at low temperature (T), it is solid and brittle; however, at increasing T and before melting, it has an elastic behaviour. Native asphalt occurs in nature as impregnations, pockets, layers or large volumes in sedimentary clastic or carbonate formations of continental, transitional and near-shore environments.

Since the Middle Palaeolithic (40000 BC) [1], asphalt has been employed as adhesive, sealant for containers, canoes, boats, flaming agent for torches or offensive weapons, pigment for pottery, etc. A good review of its applications from antiquity to date is given in [2].

Chromatography (CG) and mass spectrometry (MS) are used to analyse the chemical and isotopic composition of asphalts of archaeological interest, trace their provenance and reconstruct trade routes [3–5]. To characterise asphalt properties, reliance is made on thermal methods, such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG) [6–11] and, more recently, temperature modulated differential scanning calorimetry (TMDSC) [12–15]. The composition of ancient asphalts may be complex, depending on pro-

cesses of oxidation, degradation and impurities. They are often mixed with other organic substances, such as resins, pitch, wax and mineral matter.

This study reports the results of analyses conducted with powder X-ray diffractometry (XRD), diffuse reflection infrared Fourier transform spectroscopy (DRIFT or FTIR), DTA, TG and TMDSC methods on three samples of archaeological interest coming from Italy, France and Bulgaria. Multi-technique analysis revealed to be essential to identify the composition and technology used to prepare ancient mixtures based on asphalt. The combined results offer to archaeologists new elements for the interpretation of the history of the analysed samples.

Experimental

Three samples were analysed. Sample CH (250 mg) was detached from a 1-cm thick layer of asphalt, which covered a limestone block (26×36×10 cm) dated of the 1st century AC. The sample was found at Manoppello, 19 km SE of Chieti (Abruzzi, central-eastern Italy), where it is kept in the Museo La Civitella. Engraved on the asphalt layer is the Latin inscription 'ALONI C (ai) F(ili) ARN(iensis) SAGITTAE' (Caius Aloni Sagitta of the Arniensis tribe, probably the owner of the asphalt quarry).

Sample FR (350 mg) is made up of vitreous, shiny asphalt fragments, which were collected from the remains of a Roman ship sunk off Cap d'Agde (southern France).

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Sample BG (600 mg) is part of an incrustation adhering to the left eye of a splendid bronze head found in 2004 inside a 4th century BC Thracian tomb at Kazanlak (central Bulgaria). During restoration work, the incrustation was studied together with the casting core found inside the head.

Methods

XRD

XRD was carried out on 50–100 mg samples. Data were collected on a Siemens Seifert MZIV equipped with monochromator and a Philips 1840, in the 2–60° range of 2θ angles, at 1° min⁻¹ speed, using a CuK_{α1} radiation.

FTIR

FTIR spectra were recorded using a Bruker Vertex 70 equipped with solid reflection cell. 20 mg samples diluted in KBr were analysed with 36 scans at a resolution of 4 cm⁻¹ in the 400–4000 cm⁻¹ region.

Thermal analysis

TMDSC analyses were performed using a TA Instruments Model No. DSC 2920 on 7–10 mg samples, from -50 to 150°C, at a flow rate of 50 mL min⁻¹ of N₂, a heating rate of 5°C min⁻¹ and a modulation amplitude of ±0.5°C every 60 s. The instrument was calibrated for *T* using indium at heating and cooling scanning rates of 5°C min⁻¹. The heat flow was calibrated with the heat of fusion of indium; the heat capacity constant was calibrated with the heat capacity of sapphire. DTA (TA Instruments Model No. DTA 2920) and TG (TA Instruments Model No. TG 2950) experiments were conducted in an oxidising atmosphere using an open crucible with 5–10 mg samples and a 10°C min⁻¹ heating rate. The inorganic components of one of the sample were identified by embedding them in epoxy resins and preparing a thin section for analysis under the petrographic microscope.

Results and discussion

The XRD pattern of Italian sample CH (Fig. 1) reveals that the asphalt has a sizeable number of mineral impurities, with dominant calcite associated with dolomite and quartz. Calcite is the main component of the local limestone formation, where impregnations and pockets of asphalt are found.

The FTIR spectrum (Fig. 2a) is typical of native asphalt: *i*) in the 2800–3000 cm⁻¹ range, the stretching effects due to methyl and methylene vibrations; *ii*) at 1600–1500 cm⁻¹, the structural bands of the benzene

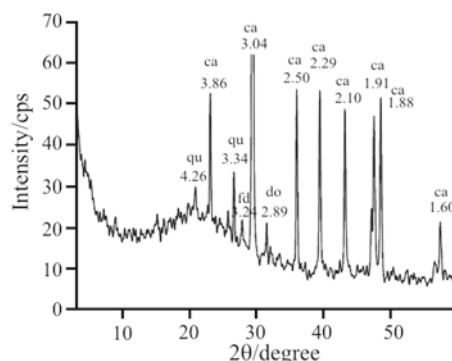


Fig. 1 XRD of sample CH, rich in inorganic impurities. The *d*_{hkl} corresponding to the main peaks are indicated. qu=quartz; ca=calcite; fd=feldspar; do=dolomite

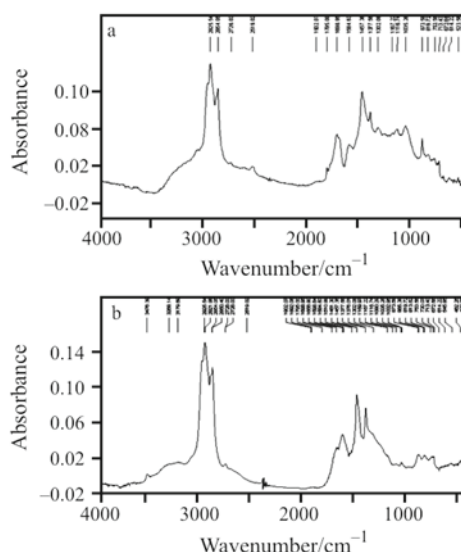
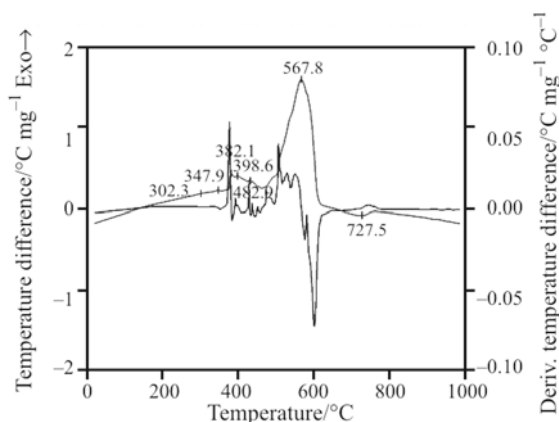
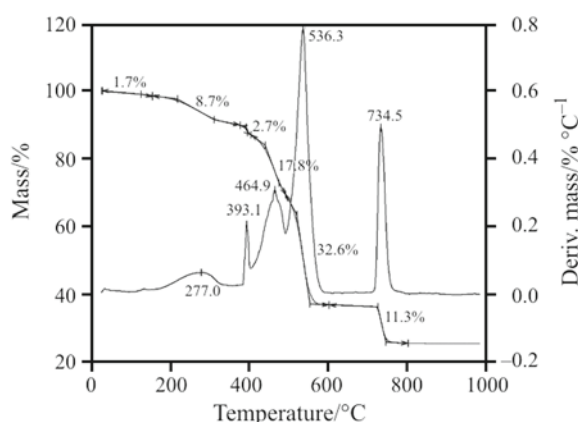


Fig. 2 FTIR of a – sample CH and b – a natural bitumen from Sicily (Italy)

rings; and *iii*) at 1800–1700 cm⁻¹, the broad bands of the carbonyl groups. At lower wavenumbers, stretching and banding may be observed: at 1300–1400 cm⁻¹, those due to CH₂ and CH₃ vibrations and, at 1116 cm⁻¹, the effects of the hydroxyl groups. The triplet between 800 and 700 cm⁻¹ is typical of native asphalt, such as one from Sicily, which was analysed under the same experimental conditions (Fig. 2b). FTIR results testify the good state of conservation of the ancient sample.

The DTA curve (Fig. 3) is dominated by the effects of bitumen decomposition, with major peaks at 382, 433 and 568°C, corresponding to a total mass loss of 63% on the TG curve (Fig. 4). On the DTA curve, the small endothermic effect at 727°C is ascribable to decomposition of calcite impurities. The corresponding mass loss on the TG (at 734°C) is equal to 11.3%. The total mass loss indicates that the bitumen content in the sample is 63%.

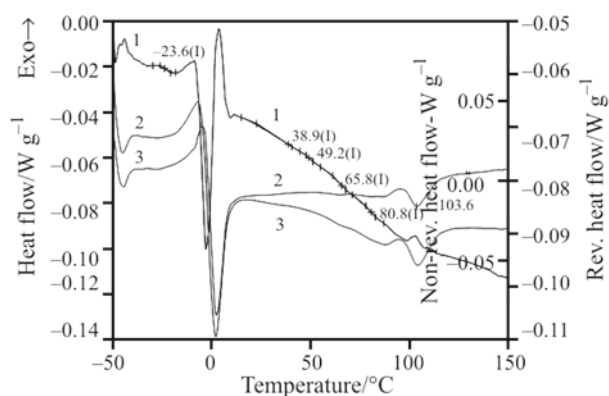
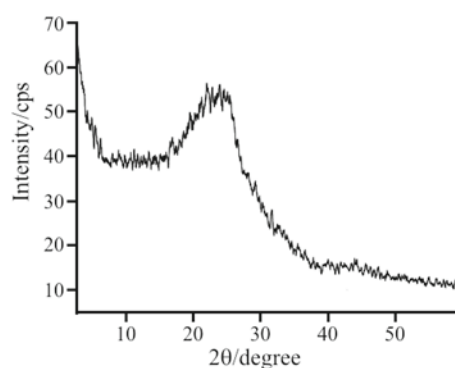
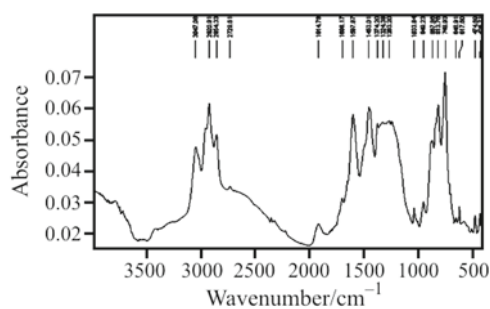

Fig. 3 DTA and DDTA of sample CH

Fig. 4 TG and DTG of sample CH

The TMDSC pattern (Fig. 5) is typical of bitumen [16]. The T_g is at -24°C and the sequence of the softening intervals, between 39 and 81°C , is related to the different organic fractions, the saturated at low T and the asphaltenes at higher T . The peaks at approximately 0 and at 104°C are due to humidity of the sample, as shown by both the reversible and non-reversible curves.

The combined results from analyses infer that the features of sample CH are typical of native asphalt, containing 37% inorganic impurities. Despite the fact that the sample is 2000 years old, it shows no signs of degradation or oxidation. The asphalt layer was applied on the limestone block at low T , as thermoanalytical data suggested that the sample had never been heated to more than a few tens of degrees.

The XRD pattern (Fig. 6) of the French sample FR is typical of a pure amorphous substance and shows no inorganic impurities.

The higher wavenumber section of the FTIR spectrum (Fig. 7) has a marked analogy with sample CH and is typical of native asphalt; however, in the $800\text{--}700\text{ cm}^{-1}$ region, the peaks are much more pronounced. These peaks may be attributed to the saturated compounds contained in the sample.


Fig. 5 TMDSC of sample CH. 1=reversible heat flow; 2=total heat flow; 3=non-reversible heat flow

Fig. 6 XRD of pure sample FR

Fig. 7 FTIR of sample FR

The DTA curve (Fig. 8) only displays minor endothermic effects (at 280 , 392 and 417°C), which are associated with the decomposition of the lighter fractions of the sample. Decomposition occurs at relatively high T (631°C). Although the overall pattern is typical of an oxidised product, the sample retains the behaviour of bitumen, as part of its lighter fractions are still present.

The TG curve (Fig. 9) exhibits two main mass losses: 30.5% with DTG peak at 164°C and 65.5% with DTG peak at 516°C . The T ranges are relatively high and testify the presence of an oxidised, but not carbonised bituminous compound. The total mass

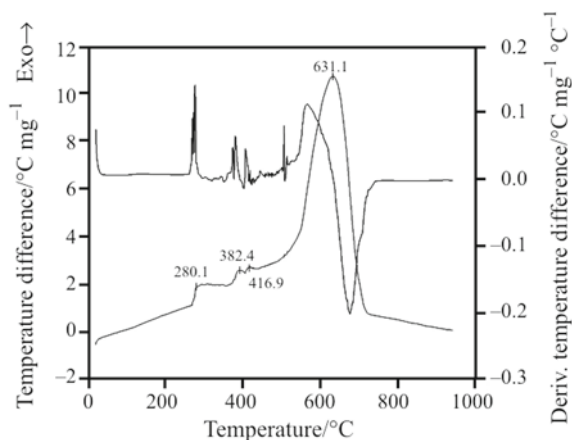


Fig. 8 DTA and DDTA of sample FR

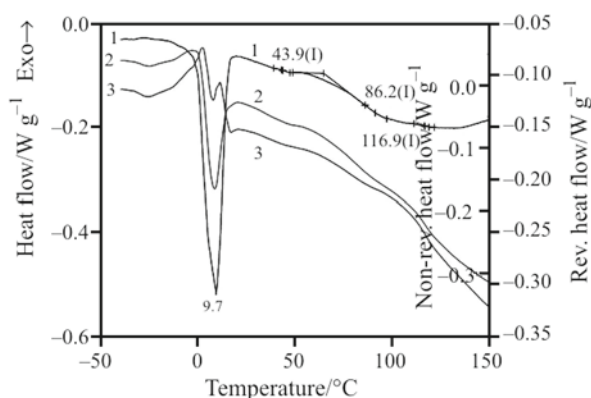


Fig. 10 TMDSC of sample FR. 1=reversible heat flow; 2=total heat flow; 3=non-reversible heat flow

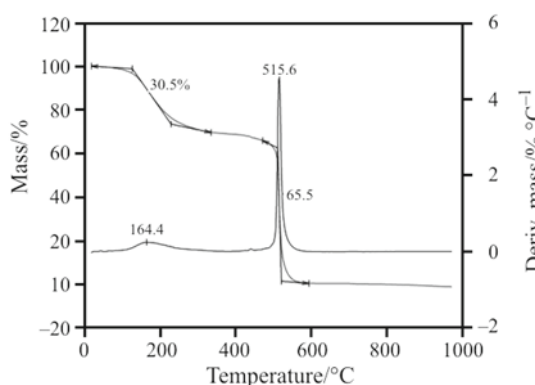


Fig. 9 TG and DTG of sample FR

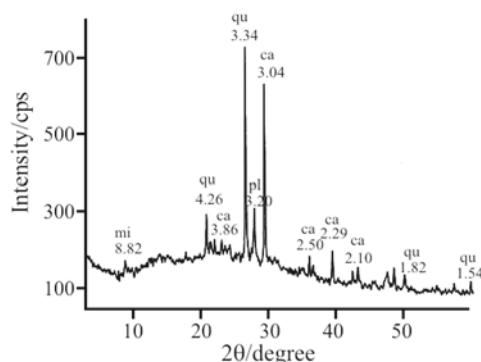


Fig. 11 XRD of the bitumen aggregate BG. The d_{hkl} corresponding to the main peaks are indicated. mi=mica; qu=quartz; ca=calcite; pl=plagioclase

loss (100%) confirms the purity of the sample, in accordance with FTIR and XRD data.

The TMDSC curve (Fig. 10) is typical of bitumen, with softening transitions (T_s) at 44, 86 and 117°C. The relatively high T_s of the last transition is typical of partially oxidised bitumen fractions, in agreement with the high softening T measured with DTA and TG. The endothermic effect at 10°C on the reversible curve is related to the fusion of the saturated fraction identified on the FTIR spectrum.

The data from analyses reveal that sample FR is a partially oxidised pure bitumen with a saturated fraction in its structure. TG and XRD confirm that it contains no inorganic impurities. The decomposition peaks on the thermal curves are shifted towards relatively higher T_s than for bitumen. This finding is consistent with the assumption of a treatment at low T , maybe to enrich the sample.

Stereoscopic microscope, thin-section and XRD (Fig. 11) analyses of the Bulgarian sample BG indicate a brownish-black matrix, binding chiefly silicatic and subordinately carbonate rock fragments and minerals.

The FTIR curve (Fig. 12) shows asphalt peaks (e.g. at 2919, 2851 and 1457 cm^{-1}) related to CH_3 and CH_2 vibrations, but also vibrations in the field of sil-

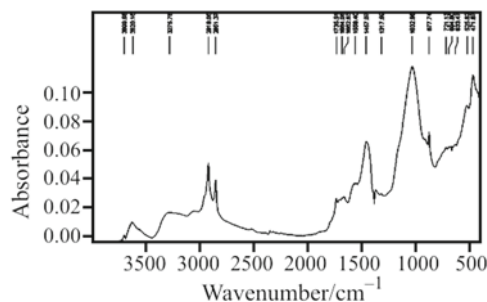


Fig. 12 FTIR of sample BG

ica (e.g. at 1033 and 472 cm^{-1}) due to the inorganic component. FTIR also displays the absorption peaks (at 1736 and 721 cm^{-1}) of a natural wax.

A complex exothermic effect is visible on the DTA curve (Fig. 13); this effect, which is due to bitumen decomposition, corresponds to a mass loss of approximately 37% on the TG (Fig. 14). The peaks T_s of 321°C on the DTA and of 282°C on the DTG are much higher than for bitumen. Moreover, the TG does not indicate three different mass loss steps, but only a continuous mass loss between 181 and 430°C. This finding suggests that the sample underwent strong

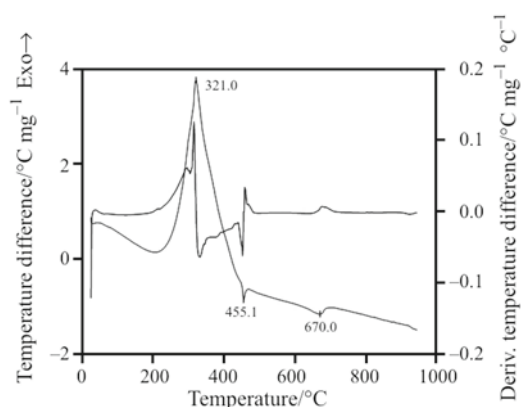


Fig. 13 DTA and DDTA of sample BG

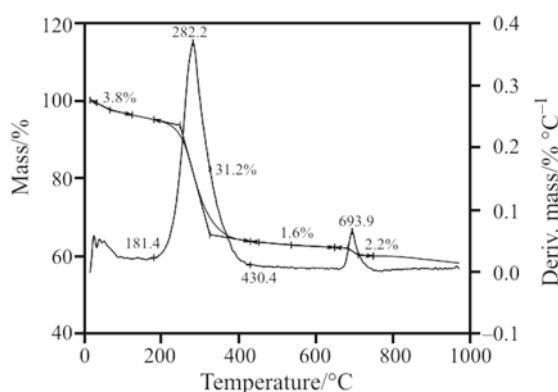


Fig. 14 TG and DTG of sample BG

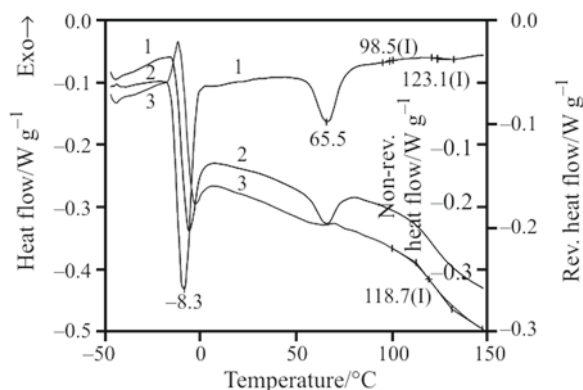


Fig. 15 TMDSC of sample BG. 1=reversible heat flow; 2=total heat flow; 3=non-reversible heat flow

heating, which induced oxidation and structural degradation. The low total mass loss of the asphalt (and wax) testifies the high content of inorganic impurities of the sample.

The DTA endothermic peak at 455°C occurs within the range of T that is typical of the degradation of iron hydroxide compounds, which are present in small amounts in the sample. The endothermic effect at 670°C on the DTA, which corresponds to a mass

loss of 2.2% (DTG peak at 694°C), is related to CO₂ emissions from the calcite (~5%) identified by XRD.

The TMDSC curves (Fig. 15) show two transitions T_s from the viscoelastic to the liquid state, at -8 and at 66°C. The T and morphology are characteristic of wax, a substance identified on the FTIR spectrum. Bitumen-related effects only occur above 100°C, as is typical of strongly oxidised samples. These T_s occur when high-molecular mass structures are derived from a heating process. The non-reversible heat flux curve shows (at 119°C) the solid to liquid transition due to the softening of the bitumen.

In conclusion, this sample, dated of the 4th century BC, consists of an inorganic fraction associated with a 37% organic fraction composed by an oxidised bitumen mixed with wax. The TMDSC analysis shows that this bitumen was heated to above 100°C and then mixed with natural wax. Therefore, the contact and adhesion of the asphalt to the eye of the bronze head occurred close to ambient T .

Conclusions

The characteristics of asphalt in archaeological samples may be very different, depending on: origin of the raw material, processes of ageing and oxidation and mixing with other substances. The three samples analysed in this study demonstrate the need for conducting multi-instrumental analysis in order to fully understand their composition and thermal history. The main components of the inorganic matter impurities were identified via XRD, while the organic compounds of the asphalt and other substances were detected by FTIR. TG provided quantitative data on the composition of the samples, permitting to assess their purity. DTA and TMDSC offered a detailed picture of the thermal evolution of organic compounds and made it possible to obtain valuable data for interpreting the history of the samples.

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