Electrochemistry Communications 87 (2018) 18–21

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

# Polythiophenes as markers of asphalt and archaeological tar pitch aging. Characterization using solid-state electrochemistry

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ARTICLE INFO

*Keywords:*
Voltammetry
Archaeology
Asphalt
Tar pitch
Organosulfur compounds

ABSTRACT

The voltammetry of immobilized microparticles (VIMP) was used to characterize organosulfur components from ovens found at the Spanish archaeological sites of Cueva de Nerja (ca. 35,000 cal BC), la Illeta dels Banyets (4th century BCE) and Gestalgar (12th–13th CE), and asphalt probes subjected to PAV and SUNTEST aging protocols. The voltammetric responses of the archaeological samples and the asphalt probes after photodegradation were quite similar, indicating the presence of polythiophene components which could act as age/degradation markers.

## 1. Introduction

The oxidative degradation of petroleum asphalts and related materials is a phenomenon of interest in fields as widely separated as archaeology and pavement technology. In archaelogy, the characterization of birch bark materials, found from the Middle Palaeolithic up to recent times [1,2] is an important analytical challenge [3]. In today's world, the oxidative degradation of asphalt cements produces significant changes in their mechanical properties with concomitant technical and economic implications [4]. The organosulfur compounds found in asphaltic matrices are therefore being widely studied [5–8] due to their essential role in degradation processes.

In this work we report the presence of polythiophenes in samples resulting from the degradative aging of asphalt cements and archaeological pitch tar materials. Polythiophenes are widely studied polymeric materials [9,10] which display a characteristic electrochemistry when in contact with aqueous electrolytes [11,12]. Using the voltammetry of immobilized particles (VIMP) [13,14], these characteristic electrochemical signatures were detected in two sets of samples: (a) carbonaceous remains from a Palaeolithic oven from the Cueva de Nerja (Málaga, Spain) dating back to 35,320 ± 360 BP [15], an Islamic oven of 'tannur' type found in Gestalgar (12th–13th century, Valencia, Spain), and a Punic oven for preparing tar pitch from the archaeological site of la Illeta dels Banyets (4th century BCE, Alicante, Spain); and (b) a series of asphalt cement samples subjected to a range of aging tests (Rolling Thin Film Oven Test (RTFOT), Pressure Aging Vessel (PAV) and SUNTEST [9]). The VIMP response of a series of organosulfur standards has been described previously [16].

## 2. Experimental

Five Brazilian asphalt cements (**AC01** to **AC05**) were used for solid-state electrochemical evaluation of the aging processes. The samples were supplied un-aged and aged by the Petrobras Research and Development Center (CENPES), Rio de Janeiro, Brazil. They were obtained from different refineries and were used without pre-treatment or fractionation. All the petroleum asphalt cements were classified as CAP 50/70. The RTFOT and PAV standard tests were performed according to ASTM D2872-04 and ASTM D6521-08 protocols [9], respectively. Archaelogical samples from Gestalgar (**HG01** to **HG03**), l'Illeta dels Banyets (**IB01** to **IB03**) and Cueva de Nerja (**CN01** to **CN03**) consisted of brownish-black powders recovered during systematic excavation of

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https://doi.org/10.1016/j.elecom.2017.12.020
Received 2 December 2017; Received in revised form 18 December 2017; Accepted 19 December 2017
Available online 20 December 2017
1388-2481/ 

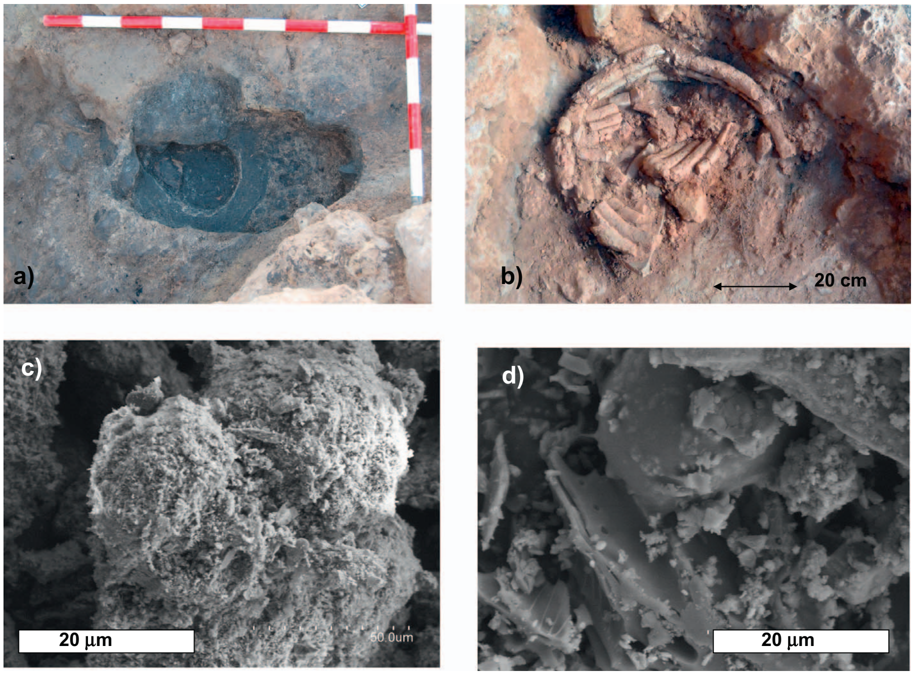


**Fig. 1.** Photographic images of (a) Punic oven at l'Illeta dels Banyets and (b) Islamic oven from Gestalgar site, and SEM images of samples (c) **IB01** and (d) **CN01**.

the sites.

VIMP, ATR-FTIR and SEM/EDX experiments were performed using methods and instrumentation described previously [16]. Electrode conditioning was performed by macerating a ca. 30 µg sample in contact with 1 mL of toluene. The resulting solution was then dripped onto the electrode surface, allowing the solvent to evaporate in air.

## 3. Results and discussion

Fig. 1 shows photographic images of the ovens found at the archaeological sites l'Illeta dels Banyets and Gestalgar, accompanied by SEM images of samples **IB01** and **CN01,** showing more or less irregular pellets tentatively assigned to bituminous organic remains. ATR-FTIR spectra of the asphalt samples included the bands characteristic of organosulfur compounds, in particular sulfones (1140, 1325 $cm^{-1}$) and sulfonic acids, as well as bands for organic components (mainly hydrocarbons). The spectra of the archaeological samples, however, were dominated by prominent carbonate and silicate bands, totally obscuring any organosulfur bands.

Fig. 2 compares the square wave voltammograms of graphite electrodes modified with sample **AC01** (a) before and (b,c) after being submitted to PAV (b) and SUNTEST (c) and (d) sample **CN01** in contact with 0.10 M $H_2SO_4$ aqueous solution when the potential was scanned in the positive direction from − 0.65 V vs. Ag/AgCl. In the voltammogram of the un-aged asphalt samples (Fig. 2a) a weak anodic peak at ca. − 0.15 ($A_{TL}$) precedes a more intense wave at + 0.50 ($A_{AD}$). There are several more or less well-defined peaks between + 0.60 and + 1.20 V ($A_{TF}$) and an ill-defined wave at ca. + 1.60 V ($A_{SO}$). The peaks $A_{TL}$, $A_{TF}$ and $A_{SO}$ can be ascribed, respectively [16], to the solid-state oxidation of different thiol/thiolate species and thiophenes to the corresponding sulfoxides and then these last to sulfones (often yielding water-soluble products). The peak $A_{AD}$ can be assigned to the oxidation of partially solubilized organosulfur compounds adsorbed onto the graphite surface. When a second positive-going potential scan was performed (red line), the peak $A_{AD}$ was consistently slightly enhanced while the other signals were, in general, diminished.

After submitting the asphalt samples to the PAV test, which simulates long-term aging of the asphalt binder in situ, i.e. during its use as a road surface at ambient temperatures, and the SUNTEST, which simulates the influence of UV radiation from natural weathering, the voltammograms were dominated by signal $A_{AD}$, accompanied, after application of SUNTEST, by a second peak at + 0.40 V ($A_{PT}$) in the second scan (Fig. 2c). Remarkably, the voltammograms of the archaeological samples produced an essentially identical profile (Fig. 2d for sample **CN01**), the signal $A_{PT}$ being increased relative to $A_{AD}$.

These results suggest that polythiophene species are markers for aging of asphalts, tar pitch and other carbonaceous materials. In order to test this hypothesis, repetitive cyclic voltammetry was carried out on microparticulate deposits of different thiophene compounds on graphite electrodes. Figs. 3 and 4 compare the results obtained for 4,6-dimethyl dibenzothiophene with those for asphalt and the archaeological samples. In all cases, anodic waves appeared above + 0.90 V ($A_{TP}$) in the initial anodic scan, giving rise to couples at + 0.40 and + 0.50 V which increase in successive potential cycles, thus yielding the typical electropolymerization pattern [9–12]. The relevant point to emphasize is that there are no anodic signals in the $A_{PT}$ potential region during the first anodic scan; i.e., there are no polythiophene species in the original thiophenes (Fig. 3a) or the un-aged asphalts (Figs. 3b and 4a). In contrast, asphalts subjected to PAV (Fig. 3c) and SUNTEST (Fig. 3d), as well as the archaeological samples (Fig. 4b–d) displayed oxidation signals at + 0.40 V in the initial anodic scan voltammograms, thus suggesting that polythiophenes were present in these samples. The ratio between the peak current for the $A_{PT}$ peak in the first scan relative to the second, $i_{PT}(1)/i_{PT}(2)$, can be seen to increase with age (see Fig. 5) and the profile of the initial signal varies from one sample to another. Accordingly, the formation of polythiophene species can be considered as an age/deterioration marker for carbonaceous materials, suggesting the possibility of using these voltammetric features to characterize different types of residuals and for dating purposes. In this regard, it is pertinent to note that (i) polythiophene formation can in principle