

# Presence and Applications of Bituminous Materials on the Ancient Vaccaei Culture: a Nondestructive Spectroscopic Study

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**Abstract** – Archaeological works in the necropolis associated to the Vaccaei city-state of Pintia (Valladolid, Spain) have revealed a particularity of this culture (S. IV-I BC). A large set of bituminous objects have been found in enclosed funerary sets well contextualized. This material was first identified shaping spheres related to the Vaccaei burial rituals, a characteristic without archaeological precedents in the Iberian Peninsula.

However, recent findings demonstrate a wider use of bitumen in the Vaccaei culture, being employed in the sealing of graves, as well as to fabricate daily life utensils. Nevertheless, this apparently high availability of bitumen contrasts with the absence of known natural bitumen sources in the Vaccaei territory.

This work studied these bituminous samples using spectroscopic techniques. Their dynamic vibrational features were identified to determine if they were related to their potential use or age, as well as obtained, or not, from a unique source.

**Keywords:** archaeological bitumen, FTIR spectroscopy, funerary rituals

## I. INTRODUCTION

The Vaccaei were a pre-Roman culture which inhabited the central Duero valley (currently Castile and Leon (Spain), see Figure 1) from the IV to the I centuries BC. The origin of this culture was long believed to be on regions of Central Europe, but nowadays it has been attributed to the local substrate of the “Soto de Medinilla” culture (First Iron of the Duero Basin).[1]

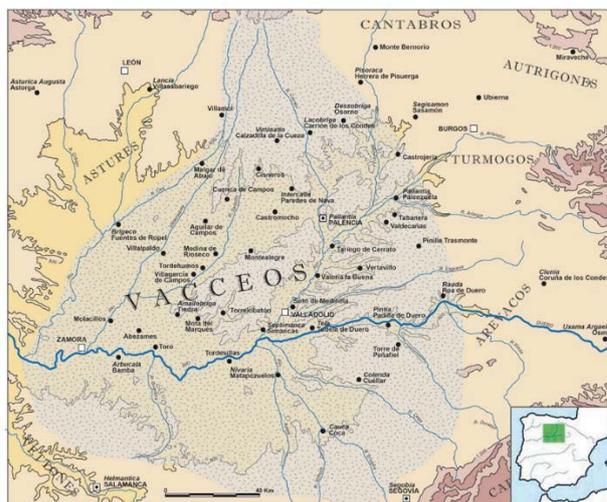


Fig. 1. Map of the Vaccaei region and its situation on the Iberian Peninsula (inset).

A significant particularity of the Vaccaei culture was their urban development, one of the earliest in the interior of the Iberian Peninsula. They constructed several cities inhabited by thousands of people, separated from each other by one or two days of road. This sparse distribution of the urban settlements allowed the creation of highly independent city-states. The best-known example of the Vaccaei' city-states has been found in Pintia (located nearby Padilla de Duero, Valladolid, Spain). The Vaccaei city-state of Pintia is believed to have held an enormous geostrategic relevance, as shown by the remaining of a complex defensive system. In particular, remainings have been found of a city wall of seven meters of width and over forty meters of a system of trenches.[2]

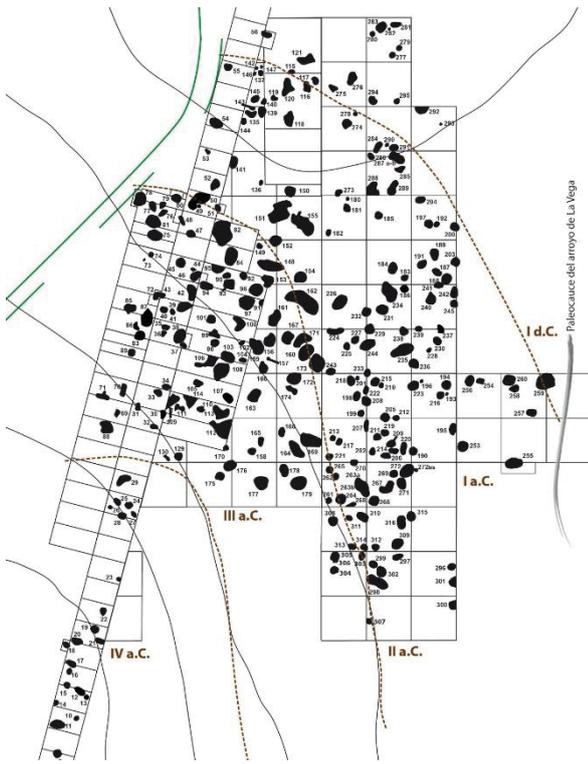


Fig. 2. Scheme of the Vaccae necropolis of “Las Ruedas” (archaeological site of “Pintia-Poblado Vacceo de las Quintanas y Necrópolis de las Ruedas” (Padilla de Duero – Peñafiel, Valladolid, Spain)).

Moreover, the former city-state of Pintia has not only allowed discovering how the Vaccae lived, but also about their beliefs and how they dealt with death. A necropolis associated to this city-state, known as “Las Ruedas”, is the only cremation cemetery excavated and studied from this culture. More than 300 graves (Figure 2) have been found since the beginning of the excavation works in 1979, being their study intensified from 2000 to the present. The successive excavation campaigns have demonstrated that this cemetery was employed by the Vaccae culture, in an orderly and continuous way, between the IV and I centuries BC. Along these centuries the main funerary ritual was the cremation of the corpse dressed with characteristic elements of its social condition. Then, the remains of cremation were placed into a cinerary urn and deposited in an open hole at the cemetery (Figure 3), together with diverse trousseaus and viatic offerings, particularly rich in the graves corresponding to the high-ranked warriors and their families. Finally, the graves were covered and indicated with stone slabs.

Among the remainings found in this Vaccae necropolis, there is a collection of objects which nature has intrigued archaeologists. A wide set of bituminous objects has been found along with the entire cemetery, proving the use of this natural material, the bitumen, during the entire history of the Vaccae city of Pintia.



Fig. 3. Trousseaus and viatic offerings placed in their original emplacement after the excavation campaign of 2009.

Bitumen, a naturally derived product from petroleum, has been widely employed by different cultures across the world and time.[3] Several civilizations employed bitumen as an expensive material useful as glue to attach the different pieces of diverse tools (fishhooks, knives, etc.) or to fix broken ceramics, sealing or waterproof coating (jars, baskets, boats, etc.). Moreover, there are proofs of their use in medical (e.g., disinfectant and insecticide) and burial practices (e.g., cosmetic, embalming), as well as with decorative purposes.[4]

However, although bituminous samples are common through human history, there is no archaeological precedent in the Iberian Peninsula for some of the bituminous objects found in Pintia. Moreover, no natural sources of bitumen are known in the territory occupied by the Vaccae culture. Therefore, the broad presence of bituminous objects became a distinctive characteristic of this archaeological site regarding the Iberian Peninsula and raised numerous questions about their origin, as well as their relevance and potential uses in the Vaccae culture.

Herein, a set of representative bituminous samples, presenting different shapes, expected uses, and provenance along with the archaeological site has been studied by Fourier Transform Infrared (FTIR) Spectroscopy, a common and powerful technique widely employed on archaeological and cultural heritage samples.[5] In a previous work (currently under consideration for publication), this technique was successfully employed to characterize bituminous samples related by their spherical shape, proving the presence of significant differences in their chemical structure which could be related to diverse origins. However, nor their shape neither their chemical composition provided useful information about their potential use. On the contrary, some of the samples included in this new work suggested diverse uses for this material, proving a more extended presence of bitumen in the Vaccae society. Moreover, the results obtained from

these new samples are compared with the previous study, trying to relate the spectroscopic signature of diverse samples with their potential origin, use, or age.

## II. MATERIALS AND METHODS

### A. Samples

Five representative bituminous samples found on the archaeological site of “*Pintia-Poblado Vacceo de las Quintanas y Necrópolis de las Ruedas*” (Padilla de Duero – Peñafiel, Valladolid, Spain) were used in this study. The selected samples were collected during excavations performed in 2014, 2017, and 2018. They have been studied and compared with thirty-two relevant samples from a previous study (currently under consideration for publication).

### B. Fourier Transform Infrared (FTIR) Spectroscopy

A Bruker Tensor 27 spectrometer was employed to collect the FTIR spectra of the studied samples. FTIR spectra were obtained in Attenuated Total Reflectance (ATR) method using an MKII Golden-Gate accessory. Each spectrum was obtained at room temperature after 16 scans, in a range  $5000\text{-}300\text{ cm}^{-1}$ , and with a resolution of  $4\text{ cm}^{-1}$ .

## III. RESULTS

### A. Morphological analysis and potential uses

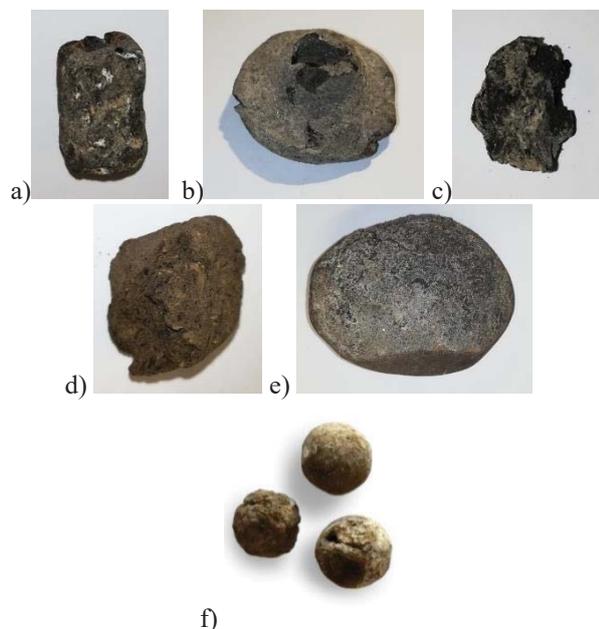


Figure 4. Images of Sample 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), and spherical samples from previous work (f).

The selected samples for this study clearly differ in shape from the spherical samples previously studied (Figure 4.f), which seems to indicate that the bitumen was employed in diverse applications by the Vaccaei.

The spherical samples previously studied still cannot be related to any specific application, but due to their wide presence in the graves could possess some symbolism during the funerary rituals.

On the contrary, Sample 1 from the present study (Figure 4.a) is a cylindrical collar bead, whereas Sample 2 (Figure 4.b) resembles a spindle whorl. Moreover, Sample 5 (Figure 4.e) is a stone found covering a grave, which was impregnated with bitumen (as well as the sand found around or below the stone). This last example suggested a potential use of bitumen as sealing during the burial ceremony.

Therefore, the bitumen seems to have been employed by the Vaccaei culture in funerary rituals, but also it could have been employed in daily life utensils (e.g. collars, spindle whorl). An alternative explanation for these samples resembling daily life utensils could be that these objects were fabricated in bitumen to be buried in substitution of actual and more valuable objects related to the deceased. This hypothesis is based on two evidence.

On the one hand, ceramic pieces have been also found in this necropolis resembling to jewelry. These pieces were buried with a symbolic value while the actual jewelry was kept by the living.

On the other hand, the spindle whorl is hollow, and its low weight suggests that it could not have fulfilled its function. This hypothesis, if true, could prove that bitumen was a common material employed in the Vaccaei culture (i.e., it was employed as a cheap substitute or more valuable objects) or that it had a strong symbolism related with the burial rituals. Future findings of new bitumen pieces could help to check the validity of these hypotheses.

In any case, the broad availability of bitumen at the Vaccaei emplacement of Pintia is still an open question for archaeologist, as finding the natural source (or sources) of this material could provide invaluable information about the trading relationships of this culture, as well as to explain the uniqueness of these remainings in the context of the Iberian Peninsula.

### B. FTIR spectroscopy

It has been possible to obtain acceptable FTIR-ATR spectra from all the studied samples (Figure 5), presenting well-defined bands that confirmed the presence of bitumen as the main component (Samples 1 to 4) or superficial impregnation (Sample 5). A common characteristic to highlight on these samples is the low relative intensity of the bands about  $800\text{ cm}^{-1}$  which correspond to polycyclic aromatic hydrocarbons (PAH). This evidence confirmed the bituminous origin of the samples, as coal-tar samples should present higher PAH contents.[6]

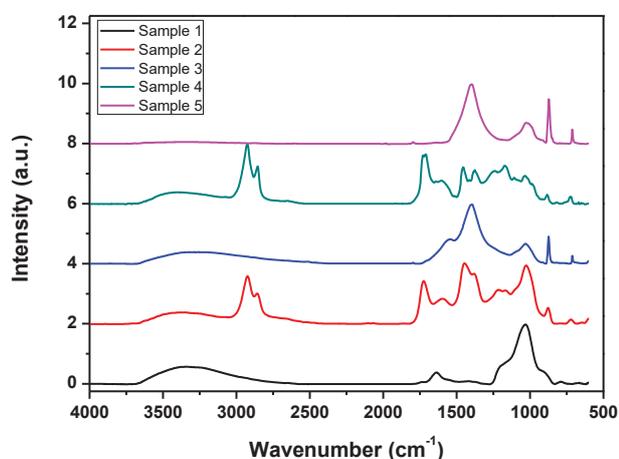


Figure 5. FTIR spectra of the five bituminous samples analyzed in this work.

Considering Sample 2 (spindle whorl) as an example, It has been possible to identify the peaks observed in its spectra (Figure 6), and perform a tentative vibrational assignment based on previous works (see Table 1).

Table 1. Infrared absorption wavenumber ( $\text{cm}^{-1}$ ) and tentative vibrational assignment of Sample 2 (spindle whorl).

Wavenumber [ $\text{cm}^{-1}$ ]	Tentative vibrational assignment
641	$\delta(\text{C-H})$ in unsubstituted aromatics
712	
729	$\delta(\text{C-H})$ in mono-substituted aromatics
	$\delta(\text{C-H})$ in orto-substituted aromatics
874	$\delta(\text{C-H})$ in tetra-substituted aromatics
1029	$\nu(\text{S=O})$ in sulfoxides
1163	$\nu_{\text{as}}(\text{C-O})$ , $\delta(\text{OCH}_2)$
1259	$\delta(\text{CH}_2)$
1379	$\delta_{\text{s}}(\text{C-H})$ in $\text{CH}_3$ , $\text{CH}_2$ of aliphatic chains
1416	
1453	$\delta_{\text{as}}(\text{C-H})$ in $\text{CH}_3$ , $\text{CH}_2$ of aliphatic chains
1595	$\nu(\text{C=C})$ in aromatics
1713	$\nu_{\text{s}}(\text{C=O})$ in enormous groups
1730	$\nu_{\text{as}}(\text{C=O})$ in carboxylic groups,

$\nu(\text{C=O})$  esters

2654	
2855	$\nu_{\text{s}}(\text{C-H})$ in $\text{CH}_3$ , $\text{CH}_2$ of aliphatic chains
2924	$\nu_{\text{as}}(\text{C-H})$ in $\text{CH}_3$ , $\text{CH}_2$ of aliphatic chains
3372	$\nu(\text{O-H})$
3396	$\nu(\text{O-H})$

Moreover, its composition seems related to one of the main groups (Group I) established for the spherical samples previously studied (Figure 6), which could indicate a related origin or age. This group is characterized by a clear tension band of sulfoxide groups ( $1029 \text{ cm}^{-1}$ ).

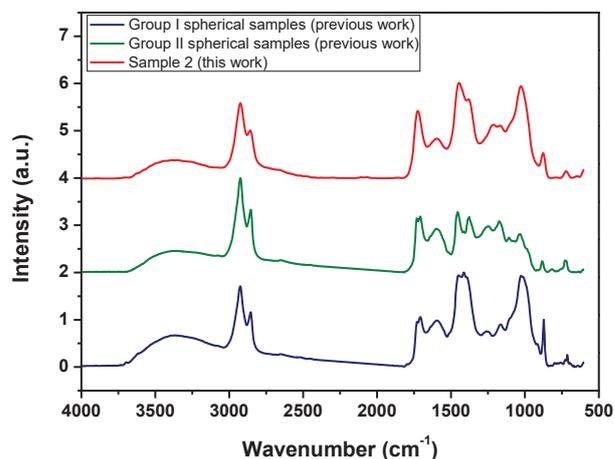


Figure 6. FTIR spectra of Sample 2 compared with the two groups of bituminous spherical samples determined in previous work.

Also, samples 1, 3, and 5 could be related to the same group of samples, although the spectra obtained by a non-invasive study were not as good. In the case of samples 2, 3, and 5 this related composition or origin is in good agreements with their origin. Samples 2 and 3 are from the same tomb, while sample 5 is from a close tomb from the same age. This results highlight the need to provide a temporal context to previous studies on these materials, and also seems to indicate that bitumen from similar origin was employed regardless of their final application (e.g., sealing of tombs (sample 5) or daily life-like objects (sample 2)).

On the contrary, sample 4 can be clearly ascribed to the other main group identified in previous works (Group II), which is characterized by the low relative intensity of the symmetric tension of sulfoxide groups, as well as by the presence of the maximum intensity peak centered at 2921

cm<sup>-1</sup> (which is related to the symmetric vs(C-H) tension mode of the methyl (-CH<sub>3</sub>) and methylene (-CH<sub>2</sub>-) groups on aliphatic chains).

### C. Potential bitumen sources identification

The absence of natural sources of bitumen in the Vaccaei territory makes the broad presence of this material and intriguing question on the study of this culture. There are few known bitumen natural sources relatively close to their territory, being the sources of the current province of Alava (Spain, situated to the northeast of the Vaccaei territory) reasonable candidates to have provided the bitumen employed by the Vaccaei.

In that region, there were numerous natural sources of bitumen, which from 1871 were commercially exploited and became the most important bitumen mines in Europe at the end of the XIX century. In 1919 up to 53 bitumen mines were operating in Alava's territory, reaching some of them up to 20% of bitumen richness in the extracted rock (Figure 7). The bitumen extraction started to decay in the 1980s, being currently most of the bitumen mines closed and the access to their facilities forbidden due to security reasons.[7]



Figure 7. Limestone impregnated with bitumen from Aaturri bitumen mines (Alava, Spain). Reproduced from: <http://veta-mineral.blogspot.com/2010/04/minas-de-la-compania-de-asfaltos-de.html>.

Currently, authorization to visit some of these mines and take some samples has been requested, looking forward to comparing the bitumen obtained from these sources with the Vaccaei bituminous objects.

## IV. CONCLUSIONS

This work demonstrates that bitumen was a widely available material for the inhabitants of the Vaccaei city-state of Pintia. Moreover, this material was employed both

with a symbolic/practical purpose in funerary rituals and daily utensils. The absence of known natural sources of bitumen in the Vaccaei territory, as well as archaeological precedents in the Iberian Peninsula, urge to identify the origin (or multiple origins) of this material to understand the Vaccaei culture and their trading relationships better.

## V. ACKNOWLEDGEMENTS

The authors acknowledge the TEMPOS Vega Sicilia group (Valladolid, Spain) for the patronage of the "Centro de Estudios Vacceos Federico Wattenberg".

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