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► **To cite this version:**

Bin Han, Xiaopan Fan, Michel Sablier. Benefits of the use of pyrolysis-GCxGC/MS for the analysis of archaeological lacquer samples: Insights from the lacquer crafting of the Ba group through the analysis of a lacquer scabbard excavated from Lijiaba site (Chongqing, southwest China). Analytics 2022 Nantes, Société Française de Spectrométrie de Masse; Réseau Francophone de Métabolomique et de Fluxomique; Société Française de Protéomique; Association Francophone des Sciences Séparatives, Sep 2022, Nantes, France. hal-04247811

HAL Id: hal-04247811

<https://hal.science/hal-04247811v1>

Submitted on 19 Oct 2023

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Benefits of the use of pyrolysis-GCxGC/MS for the analysis of archaeological lacquer samples: Insights from the lacquer crafting of the Ba group through the analysis of a lacquer scabbard excavated from Lijiaba site (Chongqing, southwest China)

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Introduction:

The Ba group was an ethnic group living in southwest China in the upper stream of the Yangtze River during a period extending from the Shang Dynasty to the Qin Dynasty (1600-221 BCE). The associated Ba State developed a strong power in the Spring and Autumn period (770–476 BCE) and the Warring States (476–221 BCE), and had close cultural, economic exchanges and military activity with neighbouring States.

Among the typical sites of the Ba culture, the Lijiaba site located on the eastern bank of the Pengxi River (Yangtze River), Chongqing, is of outmost importance for research on Ba culture. Due to the outstanding nature of the finds, it was selected as one of the Top Ten Archaeological Discoveries in China in 1998.

The lacquer scabbard of a bronze sword dating from the Warring States excavated from a Ba tomb of the Lijiaba site was characterized by a multidisciplinary approach including microscopy, scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS), Raman spectroscopy and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS). Pyrolysis-comprehensive two-dimensional gas chromatography/mass spectrometry (Py-GCxGC/MS) was applied for the characterization of this valuable archaeological lacquer sample confirming its benefits for the description of the ingredients used in the formulation of the lacquer coating.

Materials and methods:

Analysis was conducted with a GCxGC/MS Shimadzu QP2010-Ultra mass spectrometer fitted with a two-stage thermal modulator Zoex II. Pyrolysis was performed using a FrontierLab furnace pyrolyzer PY-3030iD at 500°C. Quantities of lacquer used were ca.40-50 µg. The chromatographic separation was conducted on a set of nonpolar (30 m 5%Phe-95%Me) and moderately polar (2.8 m 50%Phe-50%Me) capillary columns with a modulation period of 9s. The oven temperature was ramped at 2°C.min⁻¹ from 100°C to 325°C. The mass spectrometer was operated at 20,000 u s⁻¹, with a scan range from 45 to 600u. Py-GCxGC/MS data treatment was achieved using GC Image software, version 2.4. The Py-GC/MS analyses were conducted under comparable conditions with a Shimadzu QP2010Plus GC/MS instrument.

Results and discussion:

The analytical results confirmed that, as expected from the lacquer technique employed at this period, two lacquer film layers and a bone-derived ground layer were present as confirmed by the detection of hydroxyapatite particles of different sizes associated to the lacquering craft. Py-GC/MS analysis allowed identification of the scabbard lacquer (*Toxicodendron vernicifluum*) and detection of potential drying oil markers, while Py-GCxGC/MS analysis unequivocally revealed the presence of a series of polycyclic aromatic hydrocarbons (PAHs) compounds non-characterized by 1D analysis. This latter observation highlights the use of soot attributed to a plant origin in conjunction with bone for the manufacture and coloring of the lacquer. Types of PAHs are correlated to the use of specific wood species as material for soot making.

Conclusion:

If Py- GC/MS analysis of the archaeological sample revealed usual data on the origin of the lacquer sap and the presence of drying oil in relation to the lacquer-making recipes, Py-GCxGC/MS, due to its sensitivity and extended resolution, demonstrated unequivocally the presence of other components specific to the lacquer crafting of the Ba group, particularly PAHs which were attributed to the use of soot of plant origin as black carbon for coloring of the lacquer.