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AN EASY PROTOCOL FOR THE DETERMINATION OF THE BOTANICAL ORIGIN OF NATURAL RESINS FROM *BURSERA* THAT JOINS THE USE OF FTIR SPECTROSCOPY AND X-RAY DIFFRACTION

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Introduction

Natural products are known to be complex mixtures of organic molecules. Certain spectroscopic techniques are advantageous when identifying these materials, as they do not require the destruction of the sample.

Bursera species are the source of oleoresins that have been used in different fields and cultures. In the Pacific slope this botanic genre numbers more than 80 species. In the patrimony field, they were used by pre- Columbian cultures, such as the Aztecs and the Mayas, as adhesives, and by outstanding painters such as Diego Rivera and D. Alfaro. Chemically these resins are highly valuable because of their triterpen content of oleanane-, ursane-, lupane- and hopane-like molecules. It has been found that considerable variability in terpenoid composition is genetically determined, therefore terpenoids can be often act as biochemical markers for chemotaxonomic classification.

During the 2009 archeological excavations in Templo Mayor site, many fragments of resin were found which presented differences in color and texture. For conservation professionals many questions arise, from both archeological and fresh materials (used in restoration treatments), concerning botanical origin and the impact of different preservation conditions.

In this context, non-destructive techniques such as XRD (X-ray diffraction) and FTIR (Fourier Transformed Infrared) are invaluable for the professionals that are responsible for the conservation and the restoration of cultural objects, as it is generally difficult to identify such substances only by physical characteristics and olfactive observations. Moreover, processes of deterioration often make the interpretation of observations carried out on archaeological materials difficult. Such sample analysis is of great interest for scientists working towards the understanding of the techniques employed in the fabrication of an object.

In this work we present a time-efficient technique for the botanical identification of these materials by means of FTIR and XRD, aiming to be useful as a first approach to these techniques for non-chemist

Fig 1. Mexican copal A) archeological samples, B) certified origin samples C) Commercial samples

About the author:
Paola LUCERO is a conservation scientist. She firstly obtained a Masters degree diploma in Molecular chemistry at Rennes University (France) and by July 2012 she will hold a Ph.D. diploma from Avignon University (France). The focus of her Ph.D research was the study of organic materials used in archeological context as adhesives, molding materials and binders by Aztec and Maya cultures.

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Materials of Investigation

In this research two types of samples of copal resin were studied:

A) Fresh resins represented by certified origin samples from 6 species: *B. bipinnata, B. excelsa, B. laxiflora, B. stenophylla, B. grandifloia* and *B. penicillata* and commercial samples from markets in different geographical locations in Mexico.

B) Archeological resins from the "Templo Mayor" site and from Chichén Itzá.

Methodology: FTIR Spectroscopy plus PCA (Principal Component Analysis) and LDA (linear discriminant Analysis)

After the collection of IRTF spectra of certified botanical resins, some spectral band positions were used chosen owing to its contribution to differentiate IRTF spectra from one species to another

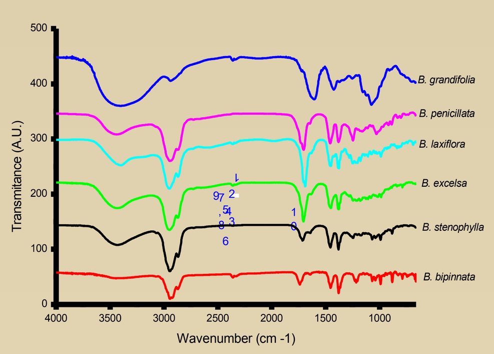


Fig 2. Comparative of FTIR spectra of the different species

	Band position	Interpretation
a	3425	Tension O-H broad band
b	2945	Tension C-H from alkans CH3, and alkens CH2
c	1710-1720	Stretching C=O from carboxylic acid
d	1638	Tension C=C
e	1454	Symmetric deformation CH2
f	1380	Deformation of def ection CH3
g	1242	Tension C-O-C
h	1037	Tension C-O simetrical from alcohol
i	883	
j	687	
k	584	

This data was then used in chemometric analysis. Sample distribution patterns were investigated with principal component analysis (PCA); this is a well known pattern recognition technique which projects the data in a reduced hyperspace, defined by the principal components, this allows the construction of a model able to predict the property of a sample to a category previously defined. Score graphics, using the first two components, revealed a sample agglomeration with good differentiation in 5 out of the 6 species (*cf* Fig 3). As a validation method, our research used LDA (Linear discrimination analysis. This method calculated a 95,2% positive recognition for the PCA model. The aim of this work was to establish a spectral databank in order to identify the botanical provenance of unknown resin samples.

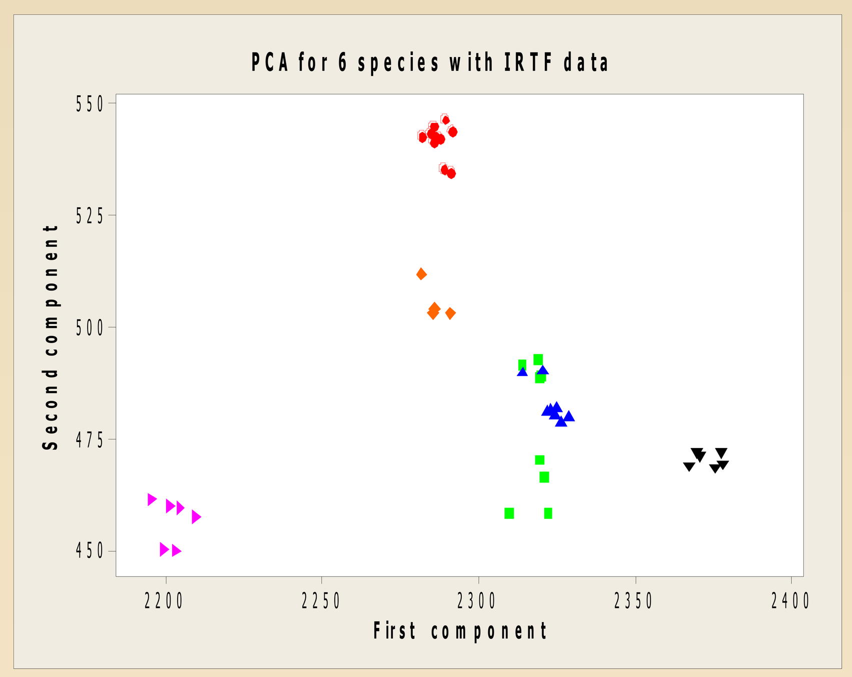


Fig 3. Distribution in the hyperspace of the first two components of the species according their botanical origin. Variables are shown with different symbols: ● *B. laxiflora*, ♦ *B. excelsa*, ■ *B. stenophylla*, ▲ *B. bipinnata*, ► *B. grandifloia*, ▼ *B. penicillata.*

Methodology: XRD

When crystalline components are present in a significant amount in a sample (10% or more), X-ray diffraction will reveal these molecules and may assist with identification.

X ray diffraction patterns for botanically certified origin resins were obtained and differences arising from chemical structure of the resin were noted. As X-ray can detect the presence or absence of amorphous matter (correlated to the presence of volatile compounds) this data, may be used as a reference to estimate the relative age of commercial samples.

Previous studies have shown that when copal is heated (Frondel, 1967) or ground (Amaro, 2007) it loses its crystalline structure, therefore our team hypothesized that X-ray diffraction could provide some insights into sample history which would contribute to determining whether a sample was heated or ground during anthropogenic activities.

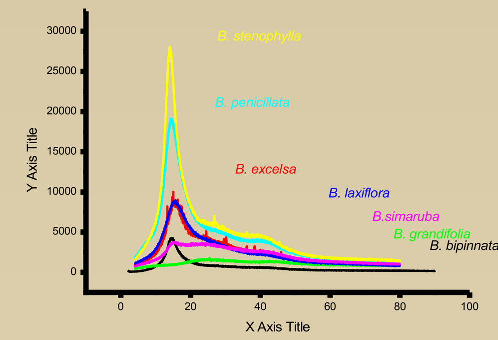


Fig 4. X-ray Diffraction patterns by species for fresh resins

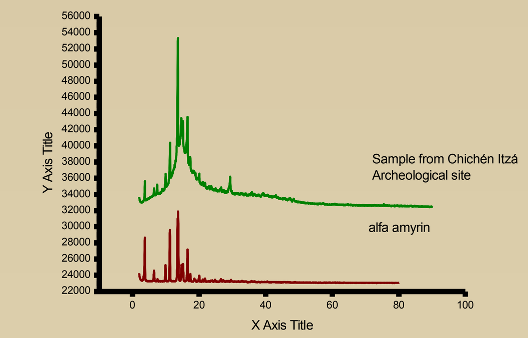
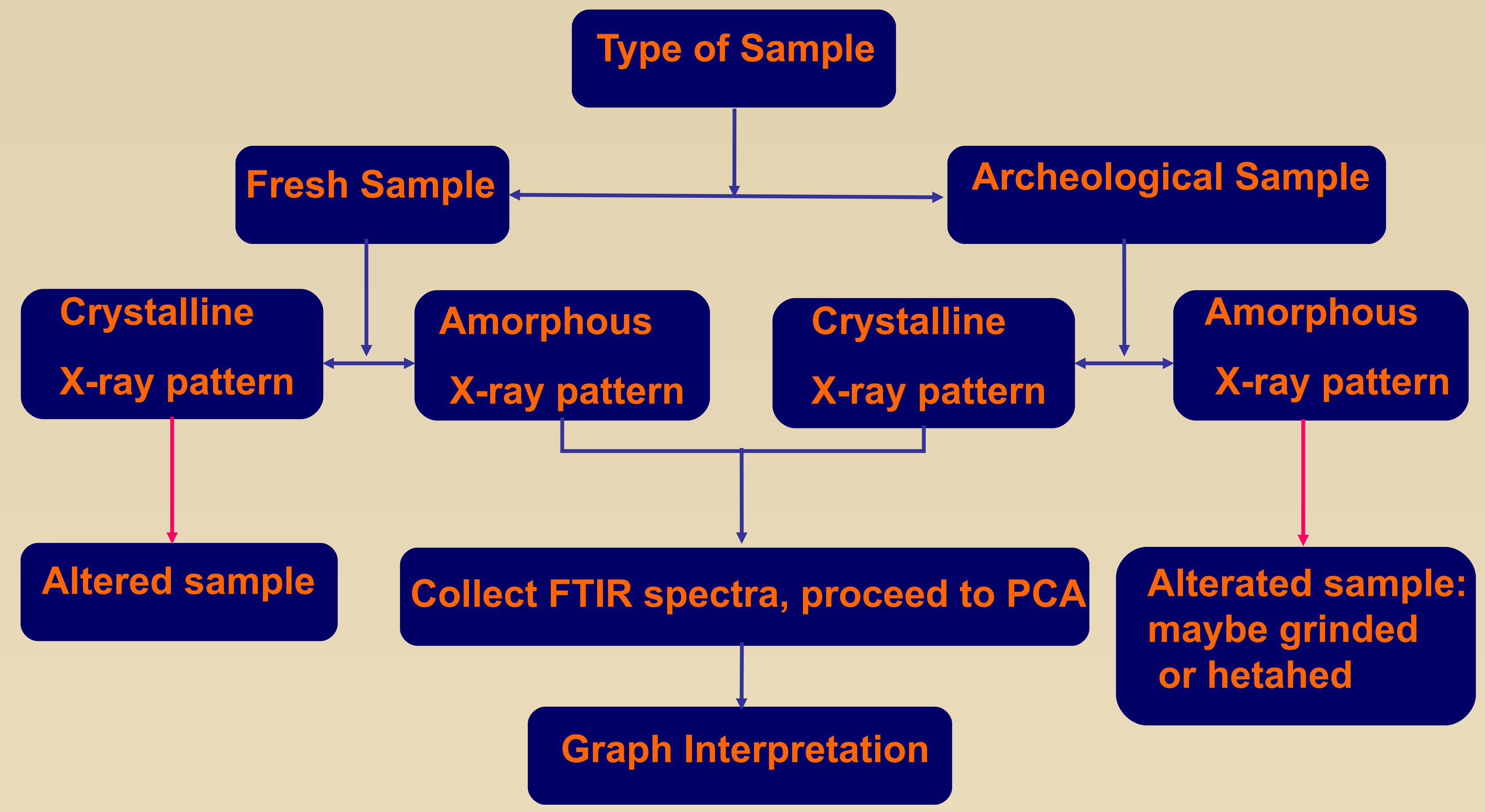


Fig 5. X-ray Diffraction pattern For an archeological resin

Application of the methodology to samples



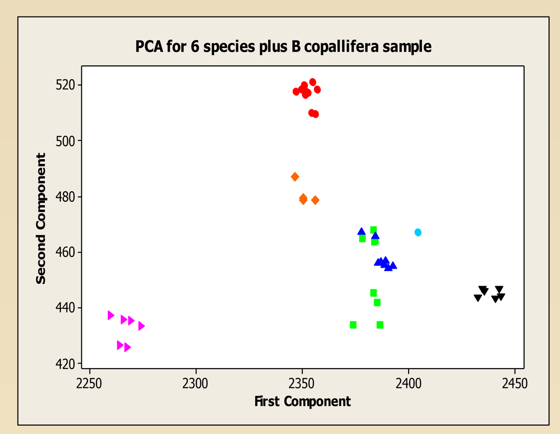


Fig 6. PCA for a fresh resin from *B.copalifera* botanical origin (●)

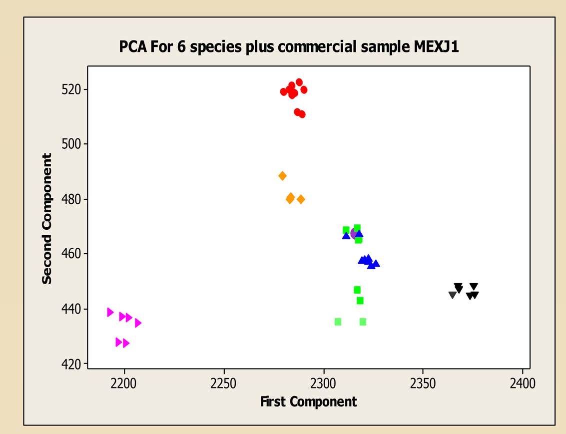


Fig 7. PCA for a commercial sample (●) possible botanical origin: *B stenophylla* or *B. bipinnata*

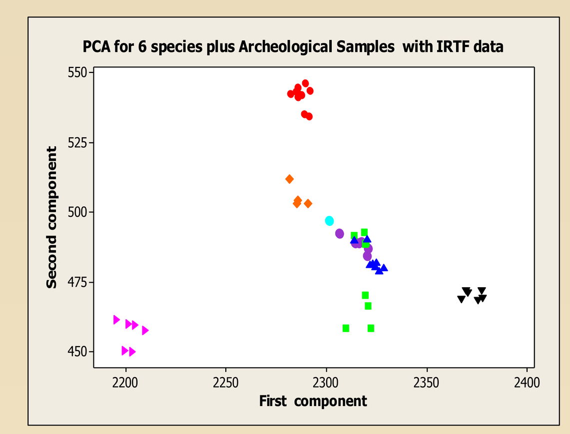


Fig 8. PCA for archeological resins (●)from Templo Mayor (Aztec) (●)from Chichén Itzá (Maya)

Conclusions and Perspectives

This method is a quick and efficient tool, that may help in identifying the botanical origin of unknown samples of Mexican resins. It can also provide information regarding sample history. Nevertheless some limitations exist and a better understanding of the degradation process of the resin is needed. In the meantime further separative techniques, such as Gas Chromatography coupled to Mass spectrometry (GC/MS) and High Performance Liquid Chromatography (HPLC) may be used in order to accurately interpret the information obtained by these means.

In the authentication field this method can be used to distinguish between botanical origins for archeological samples from different archaeological sites.

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