Analysis of Lignin from Archaeological Waterlogged Woods by Direct Exposure Mass Spectrometry (DE-MS) and PCA Evaluation of Mass Spectral Data

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Abstract

The chemical characterisation of waterlogged archaeological wood is of fundamental importance to understand the degradation processes undergone by wood objects and consequently to develop suitable consolidation and conservation procedures. The characterization of lignin from archaeological waterlogged wood samples has been performed using direct exposure electron ionisation mass spectrometry (DE-MS) and the results compared with non-aged reference lignin from birch and spruce. Mass spectral data have been put in relation with lignin molecular composition and evaluated by means of principal component analysis (PCA).

Introduction

The recovery, consolidation and preservation of waterlogged wooden artefacts, such as shipwrecks and archaeological objects recovered from underwater environments, is a particularly arduous conservation problem. Under favourable conditions of low temperature and low oxygen, wood artefacts can survive underwater in surprisingly good condition. Nevertheless, it has been showed that some species of anaerobic bacteria can slowly degrade waterlogged wood even under near anoxic conditions, eroding mainly the cellulosic components as source of nutrients. This leads to the formation of pores and cavities filled with water and transforms the wood into a soft and fragile structure which is likely to collapse when drying [1]. Due to the almost complete loss of cellulosic components, the chemical characterisation of lignin is an aspect of primary importance in the diagnosis and conservation of waterlogged wood artefacts [2-4].

In this contribution, following a paper published by Saiz-Jimenez et al. [5], we attempted to characterise lignin from archaeological shipwrecks using a direct mass spectrometric technique, namely direct exposure electron ionisation mass spectrometry (DE-MS), in order to explore the potentiality of this technique in the study of degraded waterlogged wood.

Materials & Methods

The archaeological lignin were obtained from four waterlogged wooden objects: two bollards recovered in the archaeological site of Pisa S. Rossore (Tuscany, Pisa), sample DD1 (elm) and sample SR (broad-leaf); the shipwreck Epave du Grand Congloué recovered in Marseille (France), sample B44 (oak); a shipwreck recovered in the Tantoora Lagoon (Israel), sample IS (pine). The results have been compared with those obtained for recent lignin from spruce (soft wood) and birch (hard wood), extracted in the laboratories of DISAT (University of Milano Bicocca) by Prof. Marco Orlandi using a recently published procedure [4].

The instrumentation (Thermo Electron Corporation, USA) was made up of a Direct Probe Controller and a Direct Exposure Probe (rhenium filament, current programmed mode 0 mA to 1000 mA in 2 s then 1000 mA for 60 s) , coupled with a Polaris Q ion trap mass spectrometer (E.I. ionisation 70 eV).

Unsupervised pattern recognition analysis of DE-MS spectral data corresponding to replicated samples of recent and archaeological waterlogged lignin was performed by principal component analysis (PCA, Nipals algorithm) on centred data after row normalisation using MatLab 6.5.

Results and discussion

The mass spectra of reference spruce lignin and sample IS from Israel (Figure 1) show the occurrence of mass fragments indicative of a guaiacyl lignin by the presence of m/z 124, 137, 151 and 272 [5]. Birch lignin, samples DD1, SR and B44 show the presence of mass fragments characteristic of guaiacyl-syringyl lignin with m/z 124, 137, 151, 167, 181, 208, 210, 358, 418 [5].

DE-MS spectra of the samples have been compared by mean of PCA analysis and the following three clusters have been highlighted: spruce and IS, birch and DD1, SR and B44.

The results show that the differences in the mass spectra are be related not only to the difference between guaiacyl lignin (spruce and IS) and guaiacyl/siringyl lignin (other samples), but also to the ratio between guaiacyl and syringyl components and to the degree of demethylation undergone by lignin monomers in the course of degradation processes (m/z 153 and 196) [2].

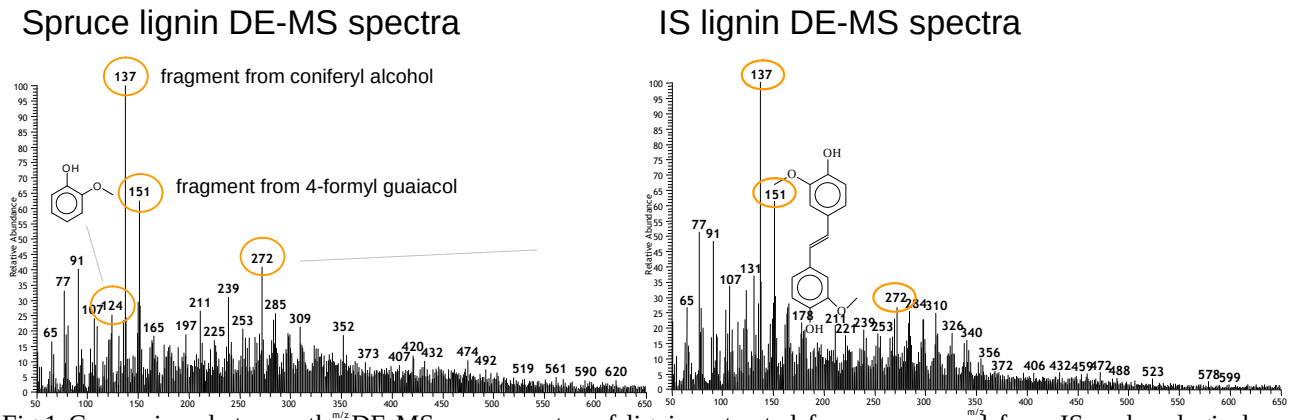

Fig.1 Comparison between the DE-MS mass spectra of lignin extracted from spruce and from IS archaeological wood.

Conclusions

From this preliminary study it is evident that DE-MS is a fast fingerprint tool able to discriminate between hardwoods and softwoods archaeological wood and sensitive to differences in the chemical structure of lignin. Further comparative investigation are in course, involving a larger number of archaeological and reference samples, aimed to establish the value of this technique in determining the extent of degradation of wood.

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