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ANALYSIS OF DAMMAR RESIN WITH MALDI- AND APCI-FT-ICR-MS

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Dammar resin is one of the most important components of painting varnishes. It is a terpenoid resin (dominated by triterpenoids, but also containing sesquiterpenoids and polymeric fraction based on cadinene units) with very complex composition. This complexity further increases on ageing (oxidizing, polymerizing, etc).

The composition of dammar resin (and dammar varnishes) has been previously investigated by different instrumental techniques: FT-IR spectroscopy, GC-MS, HPLC-MS, MALDI/GALDI-TOF-MS. Still, only limited information has been obtained for the aged dammar resin. This is because most of the separation (LC, GC) and analysis techniques are not well suited for the oligomeric fraction containing condensation products or give only very general information (FT-IR). Due to this the requirements for the analysis method are high (high resolution and mass accuracy etc). [1]

Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer offers the highest resolution and m/z measurement accuracy presently possible and Matrix-Assisted Laser Desorption/Ionization (MALDI) and Atmospheric Pressure Chemical Ionization (APCI) can be used for a wide variety of complex materials, including those that are (partly) polymeric, non-volatile etc. Surprisingly MALDI- and APCI-FT-ICR-MS have to date found limited use in analytical studies related to cultural heritage, although the above mentioned properties of FT-ICR-MS match very well with the needs of complex mixture analysis. [1]

Methods for analyzing dammar resin with MALDI- and APCI-FT-ICR-MS were developed. Suitable sample preparation and mass spectrometer parameters (numerous voltages, pulse lengths and amplitudes, frequencies, laser intensity, etc) were found for each ionization method. Also for MALDI, several solvents and solvent systems (altogether 10) were tested for preparing the sample solution. A suitable solvent system is one that readily dissolves the resin, readily dissolves the matrix and is volatile.

As a result, the obtained mass spectra were of high resolution and high mass accuracy. The MALDI-FTMS spectrum contains 9 clusters of peaks in the m/z range of 420-2200 and the APCI-FTMS mass spectrum contains 3 clusters of peaks in the m/z range of 380-910. The peaks in the clusters correspond to the oxygenated derivatives of terpenoids differing by the number of C_15H_24 units. The clusters in turn are composed of sub-clusters differing by the number of oxygen atoms in the molecules. [1]

In conclusion, it was shown that MALDI and APCI are complementary ionization sources for the analysis of natural dammar resin. In the MALDI source preferably polar (extensively oxidized) components of the resin are ionized (mostly as Na^+ adducts), while in the APCI source preferably non-polar (hydrocarbon and slightly oxidized) compounds are ionized (by protonation).

References: