



B99 Laser Desorption Mass Spectrometry: Part I. LDMS as a Tool for Investigating the Authenticity of Items of Historical and Archaeological Interest

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At the conclusion of this presentation, attendees will understand the basics of laser desorption mass spectrometry (LDMS), and how it can be a tool for the selective characterization of color components in a wide variety of samples. They will also gain some insights into the kinds of materials that can be characterized and the information that can be extracted from laser desorption mass spectra. Finally, they will learn that LDMS may be a versatile tool in a forensics laboratory for a variety of solid samples.

Laser desorption mass spectrometry can be performed with instruments that are now commonly sold to characterize biomolecules - matrixassisted laser desorption/ionization (MALDI) mass spectrometers. These instruments use pulsed UV lasers and time-of-flight mass spectrometers for analyzing ions desorbed from solid samples during laser irradiation. In this work, a tabletop instrument from PE Biosystems is used. This research focuses on the direct desorption and ionization of compounds that provide colors to samples, from a variety of solid supports and matrices. The analytes include organic dyes, inorganic pigments, and materials known as lakes, which are organic dyes attached to inorganic supports. In LDMS, samples are placed on a metal plate and introduced into the vacuum system of a mass spectrometer for analysis. Methods for securing the sample depend on the type of sample. A variety of approaches will be discussed for introducing small samples, such as single threads or paint chips, into the instrument.

Items of historical and artistic interest are frequently valuable because of their vibrant colors. If the authenticity of such an item is questioned, one factor that must be considered is whether the chemical components are consistent with the alleged date of its creation. The chemical composition of decorative colorants, paints, and writing inks also provides useful archaeological and historical insights into the technological skills and trade routes of the people who created them. Even in fairly recent paintings, there is considerable interest in the changing artist's palette, what paints were available, how certain effects were created, and how colors in a painting originally appeared at the time it was created.

An overview of the basic concepts associated with laser desorption mass spectrometry will be provided, followed by a demonstration of how it can be used to characterize colorants from a variety of samples. These include inks on written and printed documents, dyes and pigments used in paintings and historically significant manuscripts, dyes used in coloring fabrics (including single fibers), and printed collectables such as currency and stamps. For each type of sample, information must be collected on what colorants were available and used during a specific time period at the location where the item was made. Next, laser desorption mass spectra must be obtained for these materials, to determine what ions may be formed when the material interacts with UV laser light. Also, similar information must be collected for modern dyes and pigments that may be found if the item under study is not authentic, but a modern "recreation." Finally, positive and negative ion LDMS spectra obtained from the sample are compared with spectra of standards. At this point, data interpretation can begin, with the goal of identifying the colorants present, and possibly their age.

Many aspects of a specific "historical" item must be considered when attempting to establish authenticity. One part of such puzzles is establishing that materials used to create the item are consistent with the presumed time of origin. LDMS shines in this regard.

Dyes and Pigments, Mass Spectrometry, Art Authentication