B100 Laser Desorption Mass Spectrometry: Part II. A Tool for the Analysis of Inks and Pigments on Written and Printed Documents of Historical and Archeological Interest

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At the conclusion of this presentation, the participant will understand how laser desorption/ionization mass spectrometry (LDMS) can be used to distinguish between contemporary and historical inks, as well as how isotopic distribution pattern analysis in mass spectrometry aids in the LDMS identification of inorganic pigments.

LDMS can be used to detect dyes found in inks and pigments found on illuminated old manuscripts directly from a paper substrate. In these experiments, a PE Biosystems matrix-assisted laser desorption/ionization (MALDI) mass spectrometer was used to perform direct LD experiments, without using a matrix. Old documents were analyzed as part of investigations concerning authenticity. The documents include a page of the Koran (17th century), currency (18th century), and publications (late 19th century). The samples were introduced into the MALDI source using a modified sample plate, which is typically designed to hold electrophoretic gels. The instrument is equipped with a pulsed nitrogen laser (337nm, 2ns, 3Hz), which can be focused directly onto the width of a pen stroke. Positive and negative ion spectra were obtained and calibrated using dye solutions on paper (Rhodamine 6G and an ink containing Solvent Black 29, respectively).

A page of the Koran, allegedly from the 1600s, served as the primary target for this project. The manuscript was written with black ink, calligraphy style, and was illuminated with gold, red, and possibly green pigments. The goal is to determine whether or not the document could have been created in the 1600s. Colorants used at this time were primarily inorganic pigments or organic dyes from vegetable or insect matter, precipitated onto an inorganic substrate, such as alum. The latter are referred to as lakes. Red pigments used at this time for illuminating manuscripts included vermilion (HgS), madder lake (alizarin), and red lead (Pb_3O_4). Expected yellow ("gold") pigments included orpiment (As_2S_3), lead tin yellow (Pb_2SnO_4), and a variety of yellow lakes. After subjecting the document to both positive and negative ion LDMS analysis, the red and "gold" pigments were identified as containing vermilion and orpiment, respectively. The positive identification of these two pigments was accomplished by comparing theoretical isotopic distribution patterns to the isotopic patterns present in the mass spectra, generated by the red and gold samples. Both vermilion and orpiment were used during the 17th century to illuminate Islamic calligraphy, lending support to the authenticity of the manuscript. LDMS has previously been used to detect organic dyes, such as methyl violet and copper phthalocyanine, commonly found in contemporary ink formulations. Historical inks, including carbon black, iron gallotannate, and sepia, have very different compositions, and are not detected as easily. The LDMS spectra produced from both contemporary and historical ink are very different, enabling one to easily distinguish between the two. The positive and negative ion spectra of the black ink on the manuscript indicate that the ink is not contemporary, lending support to the authenticity of the document.

LDMS serves as a minimally invasive analytical tool for the *in situ* analysis of inks and pigments on printed and written documents. The ability of LDMS to detect a variety of colors, both organic and inorganic in nature, demonstrates the importance of this analytical technique in the analysis of both ancient and contemporary documents and works of art.

Inks and Pigments, Mass Spectrometry, Art Authentication

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