



### C7 Comparison of Microprobe Two-Step Laser Desorption/Laser Ionization Mass Spectrometry and Gas Chromatography/Mass Spectrometry

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The goals of this paper are to present the forensic community comparisons between microprobe laser desorption/laser ionization mass spectrometry and gas chromatography/mass spectrometry in analyses of environmental samples.

Microprobe two-step laser desorption/laser ionization mass spectrometry ( $\mu\text{L}^2\text{MS}$ ) is a relatively new and powerful analytical technique used for the detection of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and other molecules having low ionization potentials.  $\mu\text{L}^2\text{MS}$  is highly sensitive, requires only small quantities of sample, and is capable of spatial mapping with a resolution of 10–40  $\mu\text{m}$ . Additionally,  $\mu\text{L}^2\text{MS}$  provides *in situ* analysis, which minimizes sample handling and the potential for contamination or chemical alteration.  $\mu\text{L}^2\text{MS}$  has been used to analyze contaminated soils and sediments<sup>1,2</sup>, interplanetary dust particles<sup>3</sup>, meteorites<sup>4</sup>, and artificial ices that simulate the interstellar medium<sup>5</sup>.

A mass spectrometric analysis using  $\mu\text{L}^2\text{MS}$  requires a two-step vaporization-ionization process, which is carried out using two independent laser sources. In the first step, a pulsed infrared (IR) laser is

focused on the sample, causing volatilization over an area as small as 10

$\mu\text{m}^2$  thereby releasing a plume of intact neutral molecules. In this step, low laser power density is used to ensure desorption of neutral, unfragmented molecules. In the second step, a single-frequency pulsed ultraviolet (UV) laser beam intersects the desorbed plume causing (1 + 1) resonance-enhanced multiphoton ionization (REMPI) of those molecules that absorb the UV radiation and have a sufficiently low ionization potential. As well as excellent selectivity, REMPI also provides a means of “soft ionization” in which very little molecular fragmentation occurs. The resulting ions are analyzed over the complete mass range in a reflectron time-of-flight mass spectrometer.

Much of the data obtained using  $\mu\text{L}^2\text{MS}$  may be compared to the more traditional mass analysis technique of gas chromatography/mass spectrometry (GC/MS), which is often used for analysis of environmental samples.  $\mu\text{L}^2\text{MS}$  and GC/MS have different strengths as analytical techniques, and they provide complementary information<sup>6</sup>. *In situ* analysis with  $\mu\text{L}^2\text{MS}$  eliminates much of the time-consuming and potentially contaminating sample preparation that is necessary for GC/MS. In addition,  $\mu\text{L}^2\text{MS}$  accommodates much smaller sample sizes and has a much lower detection limit than GC/MS. Specifically, a  $\mu\text{L}^2\text{MS}$  analysis can be completed on milligram quantities of sample in only a few minutes and can detect subattomole concentrations of analytes over the complete mass range.  $\mu\text{L}^2\text{MS}$  can only poorly differentiate isomers by changing the ionization wavelength, whereas isomers are readily separated and detected by GC/MS. Moreover, the determination of absolute values of concentrations by  $\mu\text{L}^2\text{MS}$  are quite problematic because of difficulties associated with different desorption rates and different ionization cross sections for various species. Nevertheless, the relative concentrations of an alkylation series for a given species are generally well determined by  $\mu\text{L}^2\text{MS}$ , whereas in electron impact ionization, different members of the alkylation series often show differing extents of fragmentation. Some examples will be presented of the similarities and differences of these two techniques for investigating environmental samples.

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**Laser Desorption, Laser Ionization Mass Spectrometry, Gas Chromatography**