LASER MICROPROBE MASS SPECTROMETRY: POSSIBILITIES AND LIMITATIONS

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Laser microprobe mass spectrometry (LMMS) employs an intense UV pulse from a focused high-power laser to evaporate and ionize a microvolume ($\sim$ 1 μm^3) of solid samples at relatively elevated energy density (10^6-10^{11} W cm^{-2}). The ions produced by the interaction of photons with the condensed phase are then mass analyzed in a time-of-flight mass spectrometer and yield a complete mass spectrum on each single laser shot. Depending on the operating conditions, elemental information can be obtained, extensive speciation possibilities for inorganic species are available, and organic compounds can be characterized by means of structurally relevant molecular and fragment ions. Quantitation is difficult, but LMMS remains an excellent tool for qualitative local analysis of microscopic samples, which can be dielectric or conductive. Within the range of microbeam techniques, the method is a valuable complement to the electron and ion microprobe.

The idea of combining lasers with MS is not new and has been successfully applied to a variety of analytical purposes, e.g., pyrolysis, classification of complex materials, soft ionization of organic thermolabile compounds, as an alternative to the spark source mass spectrometer, and for bulk analysis at high power density. The first part of this presentation deals with these types of instrumentation for organic and elemental analysis and surveys the functional principles of the commercially available LMMS equipment: LAMMA 500 and 1000, and the LIMA 2A.

The polyvalent nature of LMMS results from the remarkable ease of operation of the instrument under greatly varying local conditions. The applications are unlimited. Even at the present state of the art, this statement comes very close to the truth. Review of the topics of the contributions at the recently organized triennal users' meeting yields a vast panorama of the current research in various fields. The workshop's proceedings[1]

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include papers on elemental determination of trace constituents, accurate isotope measurements, inorganic speciation, surface analysis and depth profiling, organic structure characterization in microprobe applications (but primarily on pure products), and basic research on ion formation, energy distribution, and trajectory calculations. Frequently, there is an attempt to overcome the problems arising in quantitation of complex materials, by application of a statistical treatment of fingerprint spectra. This survey elaborates on the demonstration of the versatility and outstanding potential as well as the actual limitations of LMMS in practice.

The last part of the present contribution is dedicated to research examples from the author's laboratory. During the last five years, our investigations have gradually concentrated on organic compounds. A major problem in LMMS arises from the extreme dependence of the results on the locally applied (i.e., microscopic) experimental conditions, especially when particle analysis is attempted. As a matter of fact, specific (and often very important) features of the recorded mass spectra may become prominent or completely disappear, depending on the way the operator uses his feeling and experience to cope with a variety of "hidden" parameters (e.g., physicochemical properties of the analyzed material on the micron level) that are essential to the absorption and dissipation of energy. Also important are particle size and laser focus, which critically determine the actual power density in the sample region, where ionization takes place.

We elaborated an empiric protocol, based on the use of the MS parameters (resolution, calibration, peak shape) to monitor the locally achieved experimental conditions. It appears to represent a satisfactory means of insuring the reproducibility of the results, even on a long-term basis, which is not totally obvious in LMMS. Primarily intended for organic compounds, analysis is performed under threshold conditions.

The present knowledge of laser-induced ion formation is fairly limited, particularly for organic compounds. Moreover, LMMS seems to be characterized by an ambiguity: complex disintegration of very stable molecules contrasts with the soft ionization-type features observed for themolabile analogs. Generally, fragmentation is abundant, but the detected signals look unfamiliar in comparison with those from conventional MS techniques. Nevertheless, the major aim of the LMMS research remains the characterization of compounds intractable by other techniques. Hence, we started a systematic study of organic poly-

functionals, covering a wide range of polarity and structure. Interpretation was attempted initially on the basis of a model, including a set of tentative hypotheses about the desorption and ionization (DI) mechanisms in LMMS. Meanwhile, substantial experimental evidence could be obtained, sustaining some controversial aspects of our DI concepts, such as the role of electron ionization and thermal degradation. Selected examples are presented to illustrate the practical usefulness of this empiric approach in respect of organic-structure determination. Also, the application of LMMS to molecules, which traditionally cause problems in conventional MS (e.g., N oxides, salts, etc.), are discussed. The characteristic and sometimes remarkable complementary distribution of structural data obtained for both positive and negative ions remains an intriguing aspect of LMMS. At this moment, we feel that LMMS deserves an appropriate place among the already well-established methods of organic mass spectrometry.

Since our methods of procedure primarily aim at qualitative analyses, the characterization of organic mixtures also becomes an important challenge. Real quantitation cannot be utilized yet. However, principal component analysis by means of organic (i.e., structurally relevant) ions is reasonably feasible in rather simple mixtures--those containing up to, say, 5-10 constituents. Under threshold conditions, the mass spectra actually correspond to a simple superposition of the results for the individual analogs, and additional complications from plasma interactions appear to be negligible. An appropriate but not generally applicable sample preparation is required to insure a uniform particle-size distribution.

However, the ultimate goal remains the real microprobe applications, e.g., the in situ localization of a drug or metabolite in an embedded biological tissue sample. It is commonly accepted that the presence of such a complex and physico-chemically active matrix would lead to a variety of analytical problems. We therefore designed a series of model systems for sample simulation that makes provision for a stepwise introduction of the various interactions between the target and the surrounding environment. To our surprise the presence of a polymer barrier layer imposes a major inherent limitation. In other words, only targets originally present within the upper 5-10 nm of a 1μm sample effectively contribute to the detected organic ion current. Moreover, the degree of fragmentation seems to be correlated with the distance of the target from the specimen surface. This observation makes the use of selected peaks to characterize the presence of a given compound in the analyzed microvolume questionable. Nevertheless, it is feasible in a series of well-selected test cases, e.g., characterization of pigments in cryosections of microlichens and detection of organic complexes in layered silicates.

We recently found that the application of the organic protocol and operation under threshold conditions can be profitable for inorganic speciation as well. The well-known volatilization and decomposition processes that occur during the electrothermal graphite furnace atomic absorption spectrometry (ETAAS) measurement of tin in sulfate matrices were studied by LMMS analysis of the aerosols collected from the emanating smoke. From a microscopic sample, we could obtain for the first time positive evidence to support the presence of some compounds in the gas phase. Indeed, to date ETAAS mechanisms have been based primarily on oven residue characterization, molecular absorption data (which are not very specific), and thermodynamical considerations. LMMS measurement of the aerosol in the high-laser-intensity, high-power density mode of operation, according to common practice for inorganic analyses, yielded complex spectra and partly misleading information. In contrast, under threshold conditions, the majority of cluster signals could be eliminated, which led to very simple mass spectra that could be more or less directly related to the major component. The results indicate that formation of SnO_2 seems to be overestimated in comparison to the release of $SnCl_2$, whereas the sulfate matrix is primarily detected by the pyrosulfite form in the gas phase.

Finally, there has been an effort to gain a better understanding of the laser-induced ion formation by model calculations on semi-infinite targets. In accordance with the experimental data, some distinction between laser desorption and plasma ionization could be explained in terms of classical absorption at low-power density or ignition by resonant plasma interactions at high irradiances. The theoretical approach applies to the reflection geometry (instead of the transmission mode for the LAMMA 500 used in our experiments), but still provides some insight regarding the various parameters involved in the relationship between the laser output and the local energy regime in which ionization takes place. Additional information is gained about the energy distributions of the released ions, matrix assisted desorption, and formation of shock waves.

For the sake of brevity, this text must be confined to the summary of the main topics. However, complete information on the results is available in Refs. 2 and 3.

References

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