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DETECTION LIMITS AND LATERAL RESOLUTION
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LASER MICROPROBE MASS ANALYSIS DETECTION LIMITS AND LATERAL RESOLUTION

P. Wieser, R. Wurster and H. Seiler

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Résumé - Les limites absolues de détection des éléments Li, Na, Fe, Ni, Zn, Cd, Hg, et Pb contenus dans des microparticules organiques sont mesurées avec la microsonde à impact laser (LAMMA 500, Leybold-Heraeus). La différence entre la résolution optique et analytique est discutée. Les résultats microanalytiques sont influencés par la distribution latérale de l’irradiation dans la microsonde à impact laser.

Abstract - Detection limits of the elements Li, Na, Fe, Ni, Zn, Cd, Hg and Pb obtained by lasermicroprobe massanalysis (LAMMA-R 500, Leybold-Heraeus) of organic particulate matter doped with salts are given. The difference between optical and analytical spatial resolution of the lasermicroprobe is discussed. Hints are given that lateral effects may influence the microanalytical results.

Laser induced mass spectrometry became a microanalytical technique having outstanding relative and absolute detection limits as well as a high lateral resolution /1/. Continuing preliminary studies in the field of aerosol research /2,3/ we investigated artificial micro-particulate matter well defined in size and shape by means of the lasermicroprobe massanalyzer LAMMA-R500 (Leybold-Heraeus). In order to determine detection limits the particulate matter was produced by nebulizing aqueous solutions of sucrose containing known amounts of salts. The generated droplets dried in airborne state, leaving "semi-solid", highly viscous residues, which formed flat particles on the thin substrate (20 nm pioioform foil stretched over an electron microscopic grid). A spinning spiral duct aerosol centrifuge /4/ was used in order to deposit the particles according to their aerodynamic size /5/. The experimental relationship between the ion signal (Pb^+, Hg^+) and the number concentration of atoms is fairly linear and therefore was extrapolated to the smallest detectable signal (signal to background ratio: 3). The actual laser power density was about three times the threshold irradiance of Hg^+ ion formation. Table 1 shows the results for 8 elements some of which (Pb, Hg, Cd, Zn) are involved in the discussion of environmental pollution. Table 1 shows the results for 8 elements some of which (Pb, Hg, Cd, Zn) are involved in the discussion of environmental pollution. It is most striking that with increasing ionization energy the detection limit increases and vice versa. Compared to data given in the literature, e.g. /6,7/ our results might look somewhat pessimistic but rather reflect what routinely will be possible.

As a consequence of the high power laser radiation target interaction /8/ within and near the focus a high amount of energy may be dissipated to the lattice of the irradiated solid during a very short time period. Under these conditions a non-equilibrium phase transition may nearly instantaneously form a relatively large amount of gaseous molecular and atomic ions. As pointed out by Krueger /9/ the obtained ion
formation rates are many orders of magnitude larger than expected for ordinary thermal evaporation and large quasimolecular ions can be observed even from thermolabile compounds. However, a theoretical model that can routinely be applied in the quantitative laser-microprobe mass analysis is still missing. Consequently the quantitative interpretation of the time-of-flight mass spectra obtained by analyzing samples even of partly or fully unknown composition is quite difficult.

<table>
<thead>
<tr>
<th>element</th>
<th>salt</th>
<th>ionization energy (eV)</th>
<th>detection limit (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>LiCl</td>
<td>5.39</td>
<td>2.10^-19</td>
</tr>
<tr>
<td>Na</td>
<td>NaCl</td>
<td>5.14</td>
<td>2.10^-19</td>
</tr>
<tr>
<td>Fe</td>
<td>FeSO_4·7H_2O</td>
<td>7.90</td>
<td>2.10^-18</td>
</tr>
<tr>
<td>Ni</td>
<td>NiCl_2·6H_2O</td>
<td>7.63</td>
<td>6.10^-18</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(CH_3COO)H_2·2H_2O</td>
<td>9.39</td>
<td>5.10^-17</td>
</tr>
<tr>
<td>Cd</td>
<td>Cd(CH_3COO)·2H_2O</td>
<td>8.99</td>
<td>5.10^-17</td>
</tr>
<tr>
<td>Hg</td>
<td>Hg(NO_3)_2·2H_2O</td>
<td>10.43</td>
<td>2.10^-15</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb(NO_3)_2</td>
<td>7.41</td>
<td>1.10^-17</td>
</tr>
</tbody>
</table>

Table 1 - Detection limit and ionization energy of eight elements. The elements have been added to the sucrose (matrix) in the chemical form as listed (laser energy about 5 μJ).

Besides the restrictions mentioned above the user of a laser-microprobe mass analyzer is reminded of the transient behavior of the laser-microprobe itself, being nonuniform in time and space. As e.g. pointed out by Ready /10/ only the lowest order mode, TEM_00_ of a high power solid laser represents a spatially regular output which has the desirable focusing properties. Under these conditions a high power laser radiation can be focused in a small spot size defined as the radius at which the intensity of the Gaussian like distribution is 1/e^2 of its value on the axis. Using the Zeiss Ultrafluor 32 objective the LAMMARR 500 spot size is about 0.7 μm /11/.

To determine the analytical lateral resolution the dissipation of the photon energy, the heat conductivity and the heat of formation of the material in question must be considered too. The complexity of this question is increased by the transient and nonuniform nature of the laser beam target interaction and therefore will merely be illustrated by the following scanning electron micrographs of laser induced perforations. Fig. 1a shows the effect of the laterally nonuniform laser irradiance yielding a totally perforated central area and a ring shaped region of about half the thickness of the self supporting silver foil. Clearly these two distinct regions will have contributed to the ion signal in a quite different way. In this example it will be impossible to determine the evaporated mass, since the mass of the material along the rim of the central perforation cannot certainly be estimated. Fig. 1b schematically shows a cross section through the laser induced perforation in a sandwich foil. Fig. 1c is the corresponding transmission scanning electron micrograph (dark field) showing three different perforation diameters which correspond to the three different layers. Due to their optical and thermal properties the perforation diameter increases in the following sequence: pioloform, copper and silver. A great number of obviously molten microparticles surround the point of impact, also obscuring the exact amount of the evaporated mass. Turning the sandwich foil shows that the material facing the time-of-flight mass spectrometer (TOF MS) is registered more effective than the material on the rear side by a factor which depends on the geometric dimensions of the sandwich foil and the laser irradiance. This effect must be considered when inhomogeneous structures are investigated. In order to examine the question whether or not the material leaving the interaction volume is a pure vapour, a collector foil (pioloform) was mounted in a distance of about 50 to 100 μm above a bulky brass target. The transmission electron micrograph, Fig. 2 (bright field) shows the effects caused by the interaction of
the expanding laser plume with the collector foil. It can be seen that material has left the brass target in solid/liquid state either being deposited on or passing across the collection foil. A realistic estimation of the analytical microvolume or the analytical micromass seems to be very difficult.

Fig. 1a - Scanning electron micrograph of a laser induced perforation in a self supporting Ag foil (thickness ~30 nm). The AgLα line scan demonstrates the different interaction regions.

Fig. 1b - Schematic drawing of a sandwich target consisting of a pioloform substrate foil with Ag and Cu layers deposited by evaporation.

Fig. 1c - Transmission scanning electron micrograph (dark field) of a laser induced perforation in a sandwich target, showing three different hole diameters, which correspond to the three different materials.
Due to the spatial energy distribution the ion formation in the central part of the laser spot will take place under quite different energetic conditions compared to the periphery of the laser microprobe. Laser pyrolysis may characterize the ion formation in the central part of the laser spot. In contrast in the outer regions of the high power laser radiation target interaction soft ionization such as laser induced desorption may dominate.

Due to our experiences we confirm that laser microprobe mass analysis offers a highly sensitive microanalytical tool but various difficulties concerning the atomic sensitivities (e.g. being spread over three orders of magnitude) and the analytical microvolume must be taken in mind.

References