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A Novel Instrument for Spatially Resolved Surface Analysis with Laser Desorption Quadrupole Ion Trap Mass Spectrometry

A new instrument for Laser Microprobe Mass Spectrometry with a quadrupole Ion Trap Mass Spectrometer is described. The instrument is designed to achieve a spatial resolution of 10 μm. Analytical data on preliminary measurements of the distribution of pigments in a paint cross section are presented. These demonstrate a spatial resolution of approximately 25 μm. Also the possibility to perform spatially resolved structural studies by utilization of MS² experiments is shown.

8.1 Introduction

A large number of commonly used and fullgrown techniques is available for the spatially resolved analysis of surfaces. For example, techniques as Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) lead to detailed information on the surface morphology. Various forms of electron spectroscopy are available if instead information is required on the identity of the elemental composition of the surface. For example, Auger Electron Spectroscopy (AES) and Xray Photoelectron Spectroscopy (XPS) are widely used techniques in this field. Surface information on a more molecular level is provided by techniques as Raman and Fourier Transform Infra-Red (FTIR) spectroscopy, because also the presence of specific functional groups in the surface molecules can be detected. However, the only analytical method that provides information on the composition and the structure of large organic molecules is mass spectrometry.

The first step in the examination of solid surfaces by mass spectrometry is the conversion of solid matter into gas phase ions. This conversion can be problematic if knowledge on the masses of the intact molecules is desired, because then the energy deposited into the molecules has to be minimized to prevent decomposition. This is even worse if the surfaces consist of large polar, nonvolatile or thermally labile substances. During the
past two decades, various so-called “soft” ionization techniques have been developed to address this problematic conversion step (Chapter 1). Of these techniques, laser desorption is the most promising ionization technique for the study of organic compounds. The spatially resolved version of laser desorption MS, which has become known as “laser microprobe mass spectrometry” (LMMS), has proven to be very successful in characterizing both the organic and the inorganic constituents at the surface of a broad range of samples [10–14].

The pulsed nature of the ion production in the LMMS technique makes it a natural partner for a mass analyzer which is also operating in a pulsed manner, such as Time-of-Flight (TOF), Fourier Transform Ion Cyclotron Resonance (FTICR), and quadrupole Ion Trap (IT) mass spectrometers. Especially TOF mass spectrometers are widely used in LMMS instruments, as these are relatively inexpensive and easy to couple to laser desorption techniques. These systems provide a large mass range over which the samples can be analyzed and a high sensitivity. If the mass resolution and mass accuracy of the TOF-MS instruments are insufficient or multistage mass spectrometry experiments (MS^n) are required to fully characterize the samples, it is preferable to couple the laser microprobe technique to FTICR-MS instruments. Concessions with respect to the sensitivity provided by TOF instruments are however unavoidable. A rather unexplored area is the use of quadrupole ion traps in LMMS instruments. Laser desorption experiments in ions traps have demonstrated that this combination is very attractive as the IT-MS combines MS^n possibilities with high sensitivity.

This chapter deals with the development of a new ion source for specially resolved laser desorption experiments with FTICR-MS and ITMS. The design of the ion source and the hardware and software for sample manipulation are described in detail. Results of preliminary experiments with the ion source coupled to the ITMS instrument are presented to illustrate its performance.

8.2 Instrument Description

The design of the novel LMMS instrument is based on the following criteria:

- The spatial resolution in the LMMS analyses must be better than 15 μm.
- Spatial resolution is to be achieved by focusing laser beams to a spot size of approximately 15 μm on the sample surface for localized desorption.
- The laser and sample viewing optics are fixed and situated entirely outside the vacuum system.
- Samples are micropositioned inside the vacuum system in order to specify the desorption area.
- Desorbed neutrals should be post-ionized by electron impact ionization (EI) or photon ionization (PI) to obtain maximum ion yields.
The ions are analyzed according to their mass in a quadrupole ion trap mass spectrometer in order to ensure high detection sensitivity in combination with the possibility of high-efficiency tandem mass spectrometry experiments.

The hardware required for spatially resolved laser desorption experiments must be compatible with the existing FTICR-MS instrument in case of ultra-high resolution LMMS experiments in the future.

Figure 8.1 shows a schematic representation of the instrument that was build on basis of these criteria. To summarize the operating principles briefly, a sample that is mounted on a sample holder is introduced into the vacuum system via the sample exchange chamber and placed on the sample table. After pumping down the manipulator and the sample exchange chamber, the separation valve is opened and the sample is transported to the ion source by the manipulator. There, it is micropositioned underneath a small ionization chamber in the focus of the laser beam to select the desorption area. This selection process is aided by visual images, which are recorded by a video camera mounted on the long distance microscope and captured by in-house developed software that controls the manipulator. Four different types of laser light are available for desorption. A diode pumped Nd:YAG laser delivers cw laser light at 1064 nm, whereas a Q-switched Nd:YAG laser produces short, intense pulses of light at 1064 nm, which can be frequency doubled or tripled if desirable. The same optics are used to focus either of these laser beams on the sample surface. The laser light is coupled into the line of view of the microscope with a dichroic laser mirror, which reflects only light at the laser’s operating wavelength. Upon
desorption, surface material is converted into gaseous neutrals and ions. The neutrals expand into a small ionization chamber, where they are post-ionized by electron impact or photo ionization. The ions are extracted orthogonal to the desorption plume and then transferred from the external source into the ITMS with an electrostatic ion optical system.

In this instrument, the ITMS (including electronics and data acquisition software) and the XYZ-manipulator are commercially available and were obtained from Bruker-Franzen Analytik GmbH (Bremen, Germany) and VG instruments (Fisons Instruments Vacuum Generators, East Sussex, England), respectively. The remaining components were designed and/or constructed in-house and are described in more detail in the following subsections.

8.2.1 Vacuum System

It can be seen in Figure 8.1 that the vacuum system consists of four sections: the XYZ-manipulator, the sample exchange chamber, the ion source region, and the ITMS. The sample exchange chamber is pumped by a Balzers 56 l/s turbo molecular pump and the ion source region by a Balzers 520 l/s turbo molecular pump, both backed by oil-free membrane pumps. A separation valve is installed, which allows the venting of the sample exchange chamber and the XYZ-manipulator without braking vacuum in the source and ITMS regions. The base pressure in the ion source region is $10^{-7}$ mbar (with closed separation valve and no Helium introduction). Helium is introduced into the ion trap to a level that increases the pressure in the ion source to typically $2 \times 10^{-6}$ mbar. After venting the sample exchange chamber, it is pumped down in approximately half an hour to a pressure $< 1 \times 10^{-5}$ mbar before the separation valve is opened. During operation, the pressure in the ion source is typically $4 \times 10^{-6}$ mbar.

8.2.2 Ion Source and Ion Optics

A top view of the ion source is schematically shown in Figure 8.2. The core of the ion source is the source chamber, which consists of a source housing (internal dimensions $2 \times 2 \times 4.5$ cm$^3$), a movable pusher electrode and an extraction electrode. Holes in the top and bottom of the source housing of 5 mm and 4 mm diameter, respectively, allow the focusing of the laser light onto the sample surface that is located typically 1 mm underneath the source chamber (see also the inset in Figure 8.1). In the configuration depicted in Figure 8.2, neutrals that expand into the source chamber via the bottom hole are subjected to electron bombardment for post-ionization. These electrons are emitted by the filament that is mounted on the side of the source housing and are accelerated by a potential difference of 1-100 V between the filament and the source housing. This causes the electrons to move along the magnetic field lines between the two permanent magnets towards the collector at the other side of the source housing, and thus to cross the desorption plume. The complete assembly for the electron beam can be removed easily. This allows to direct a laser beam through the desorption plume for photo-ionization.
The repeller electrode consists of a thin layer of CrN that is deposited on a 2 mm thick plate of macor. The extraction electrode consists of a pair of such plates. However, the CrN layers on these plates were milled to yield specially shaped patterns, as is depicted in Figure 8.3 A. These plates were connected together to obtain the electrode structure that is shown in Figure 8.3 B. Three voltages are applied to this electrode assembly: the left-hand side extraction voltage $E_L$, the right-hand side extraction voltage $E_R$, and the voltage that is applied to the source housing. Resistors are placed in between the two electrode plates to connect the different CrN segments with these external voltages according to the scheme that is shown in Figure 8.3 C. This causes the voltage on the CrN segments to change gradually from the extraction voltage (which is the average of $E_L$ and $E_R$) to the source housing potential, as is illustrated in Figure 8.3 D. SIMION ion trajectory calculations [186] indicate that this arrangement provides a hundred percent efficient extraction field for ions that are created around the center of the source chamber. Additionally, these numerical simulations show that optimization of the source potentials allows the efficient extraction primary ions that are produced by the laser desorption process at the sample surface.

Extracted ions are transported to the ion trap by the ion optical system that was already presented in Figure 7.1 of Chapter 7. In this system, a set of eight cylindrical electrodes is used to alternately accelerate and decelerate the ions between typically 80 eV and 30 eV. A set of three plate electrodes (typically operated at $-40$ V, $-150$ V, and $-10$ V, respectively) is installed at the end of these transport electrodes to focus the ions onto the entrance of the ion trap. This system was designed with the aid of ion trajectory calculations using the SIMION computer program. The results of the numerical simulations indicate a high transport efficiency for low kinetic energy ions ($< 30$ eV).
Figure 8.3: Specially shaped extraction electrode for an optimal extraction field. Shown are the milled patterns in the CrN layers of the component plates that face the source and ITMS, respectively (A), a cross section of the extraction electrode assembly (B), the wiring scheme that connects the different CrN segments, the voltage applied to the source housing and the externally applied extraction voltages EL and ER (C), and the voltage scheme near the source side plate (D).

8.2.3 Sample Viewing System and Laser Optics

Sample viewing during desorption experiments is provided by a Leica (Heerbrugg, Switzerland) MZ12 microscope equipped with a Donpisha XC-003P color video camera (fabricated by Sony, Japan). This system attains a maximum magnification of 220× at a working distance of 190 mm. The output of a cold-light source is coupled into the vacuum system for sample illumination with a 10 mm diameter flexible fiber optic light guide that is sealed in a stainless steel tube.

Laser light is produced by two different Nd:YAG lasers. A diode pumped Nd:YAG laser (Adlas DY301 Q DII, Adlas GmbH & Co. KG, Lübeck, Germany) delivers laser light of 0.6 mm beam diameter at 1064 nm. In the cw mode, the output power is adjustable between 0 and 200 mW. Alternatively, a Q-switch mode is available, in which it produces pulses of laser light of minimally 13 ns length and maximally 7 µJ pulse energy. The second laser is a Quanta-Ray GCR-11 pulsed Nd:YAG laser (Spectra Physics Inc., Mt View, CA). It produces 6.4 mm diameter intense laser beam pulses at 1064 nm, which can be frequency tripled if desirable. At 1064 nm, the pulse length and energy are 9 ns and 257 mJ, respectively; at 355 nm, these are 6 ns and 60 mJ, respectively.

The optical system that is used to focus the laser beams must have a numerical aperture (i.e., ratio between the input beam diameter at the focusing lens and the focal distance) of approximately 0.18 in order to achieve a spot diameter of ~ 10 µm on target [187]. On the other hand, the minimal distance between the optical system and the sample surface is approximately 200 mm in order to keep all optics outside the vacuum. Therefore, two beam expanders are used to expand the laser beams with a factor of 16 and 4, respectively (see
A doublet laser collimator lens (240 mm focal length) is used for focusing. The beam expanders and focusing lens were fabricated by Optics for Research (Caldwell, NJ). The focused laser light is coupled into the line of view of the sample viewing system with a 1 mm thickness $62 \times 82$ mm$^2$ sapphire laser mirror (Eksma Co, Vilnius, Lithuania). A mirror is available for each of the two laser wavelengths. Special mirror mounts were in-house constructed to exchange the mirrors whilst reproducing the position of the laser focus at target within 20 $\mu$m.

### 8.2.4 Sample Manipulation

The sample manipulator is based on a Fisons Omniax MXY25 and MZ200 high precision XY-translation and Z-translation stage. It consists of a bellows XY-stage on which a 200 mm bellows for the Z-movement is mounted. This arrangement provides a maximum XY-motion of $\pm 12.5$ mm and a maximum Z-motion of 200 mm to a 50 mm diameter support tube (see Figure 8.1). The sample table on which the sample holder (that carries the samples) is clamped, is mounted at the end of this tube.

The translation stages are driven by DC motors. Rotations of these motors are detected by optical increment encoders and are fed back to the motorization controller unit. The controller unit uses this information to keep the position of the sample table with respect to a reference position (defined by optical marks which are automatically traced by optical sensors) updated during sample translations. The controller unit supports two modes of sample translation: a number of relative translations from an actual sample position, each initiated by an external trigger signal, and absolute translations to a specified sample position. The resolution of the encoders in combination with the gear boxes attached to the motors and the reproducibility of the Fisons components allows the reproduction of sample positions well within 1 $\mu$m.

Software was developed in-house for communication with the motorization controller and the calibration of the different degrees of freedom. The software provides a graphical user interface in which sample translations can be defined on basis of visual images of the sample. These images are captured life from the video signal that is recorded by the sample viewing system.

### 8.3 Experimental

#### 8.3.1 Instrumental

Preliminary spatially resolved experiments were carried out with the newly constructed instrument that was described in the previous section. Details on the operation of the ion trap, the ion optics, and the laser can be found in Chapter 7.

Line scans were performed in this instrument by moving the samples with a constant velocity of 3 $\mu$m/s underneath the spot of the desorption laser in the direction perpendicular to the layers. The 355 nm beam of the frequency tripled Q-switched Nd:YAG laser was
used, which was focused to 20 \( \mu m \). The desorbed neutrals were post-ionized by means of 25 eV electron ionization. During the movement over the sample, the laser was fired and mass spectra were recorded by the ITMS every \( \sim 1 \) s.

### 8.3.2 Sample Preparation

Multilayered paint samples were produced from two Liquitex acrylic paints (Lefranc & Bourgeois, Le Mans, France), which contained phthalocyanine blue (C\(_{32}\)H\(_{16}\)N\(_{8}\)Cu) and phthalocyanine green pigment (C\(_{32}\)Cl\(_{16}\)N\(_{8}\)Cu), respectively. An alternating stack of twelve approximately 100 \( \mu m \) thickness layers was created. Spacers were used to control the layer thickness. The sample was dried at \( \sim 100^\circ \)C under air for 15 min. every time a new layer was applied. The final sample was cut to a size of \( 2 \times 5 \) mm\(^2\) and clamped on its side onto the sample holder.

### 8.4 Results

#### 8.4.1 Spatially Resolved Measurement of the Pigments in a Multilayer Paint Sample

The performance of the novel ion source was tested with measurements of the multilayer paint sample. Figure 8.4 shows the results of a line scan over this sample. The intensities in the individual mass spectra were summed over the mass ranges \( m/\bar{z} 574-576 \) and \( m/\bar{z} 1000-1150 \) (i.e., the mass ranges in which molecular ions of the phthalocyanine blue and phthalocyanine green pigment are respectively expected). These ion currents are plotted in Figure 8.4 A and B, respectively. These plots show that the different layers are clearly resolved. The spatial resolution in the measurements was estimated by comparison of the ion currents. It was determined from Figure 8.4 A and B that the shortest distance over which both pigments are detected was approximately 25\( \mu m \) (which applied to roughly half of the layer boundaries) and represents the spatial resolution. This is in good agreement with the observed crater diameter of 20 \( \mu m \). Around some of the layer boundaries (for instance, the boundary between layer 1 and 2), both pigments were detected over distances up to 80\( \mu m \). It was observed that in these cases the line scan was not perpendicular to the layer boundary due to imperfections in the sample.

The spectra averaged over the third and the sixth layer are plotted in Figure 8.4 C and D, respectively. Both spectra comprise a total of 20 laser shots and exclusively show the molecular ions of the respective pigments. Given the number of laser shots that is averaged, the spectra exhibit a very large signal-to-noise ratio. This is indicative for a high sensitivity of the new ion source. Of course, quantification of the sensitivity is not possible on basis of these measurements. Nevertheless, the present experience is that the configuration for spatial resolved laser desorption offers a higher sensitivity than the MALDI configuration that was presented in Chapter 7.
Figure 8.4: Line scan over a multilayer paint sample, which consisted of 10 acrylic paint layers containing alternately phthalocyanine blue and phthalocyanine green pigment. The top graphs (A & B) show the ion currents over the two mass ranges where the molecular ions of the two different pigments are expected as a function of the position on the sample. The spectra corresponding to the third and the sixth layer (as determined from the ion currents) are plotted in the lower graphs (C & D).
Figure 8.5: Spatially resolved MS$^3$ laser desorption experiment on phtalocyanine green. After isolation of the molecular ions around $m/z$ 1093 (A), the higher mass part of the cluster was fragmented (B), and the resulting daughter ions were again fragmented (C).

In Figure 8.5, an example of structural information obtained from spatially resolved MS$^3$ experiments is given. For these spectra, 25 consecutive laser shots were fired at the same position on a layer that contained phtalocyanine green pigment and were averaged. After isolation of the cluster around $m/z$ 1093 (Figure 8.5 A), the higher mass part of the cluster was kinetically excited to induce fragmentation by means of collisional induced dissociation. The excitation waveform comprised a small frequency band, which corresponded to the resonance frequencies of the mass interval $m/z \sim 1089 - 1099$. The amplitude was 3.5 V and the time associated with the excitation event was 100 ms. The spectrum in Figure 8.5 B demonstrates that the excited ions were effectively fragmented and that a loss of Cl$^-$ was the result. Furthermore, there is no significant decrease in ion signal observed for the unfragmented molecular ions ($1080 < m/z < 1089$). This demonstrates that the excitation event leaves ions outside the excitation range unaffected. Note that the shape of the isotopic clusters around $m/z$ 1024 and $m/z$ 1088 in Figure 8.5 B are complementary and resemble the shape of the original isotopic cluster of the molecular ion in Figure 8.5 A. Similar fragmentation of the daughter ions around $m/z$ 1024 ($m/z > 1019$) again led to a loss of Cl$^-$ (Figure 8.5 C). Losses of Cl$^-$ are to be expected from fully chlorinated aromatic systems, such as phtalocyanine green.
8.5 Summary and Conclusions

A new instrument for Laser Microprobe quadrupole Ion Trap Mass Spectrometry with a spatial resolution of 10 $\mu$m was designed, built, and tested. Preliminary measurements of the pigments in a paint cross section demonstrated an actual spatial resolution of approximately 25 $\mu$m and the possibility of structural studies by MS$^n$ experiments. It is expected that the spatial resolution can be further improved by realignment of the laser optics and optimization of the applied power densities.