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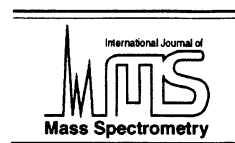
Influence of the substrate on the ion yield in direct laser desorption–ionization for thin organic layers

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Abstract

The ion yields for direct (no matrix) desorption-ionization with a nitrogen laser (0.5 ns pulse width) were studied for 3 organic molecules deposited as thin layers on different metallic substrates. These molecules have a low absorption coefficient at the laser wavelength (337 nm). One molecule (aminotriazole) forms positive $(MH)^+$ ions, the two other molecules (dinoterb and ioxynil) form negative $(M-H)^-$ ions. The yields were measured at 240 MW/cm^2 ($\sim$120 mJ/cm^2) for dinoterb on Al, Au, Co, Cu, CuZn, Fe, Mo, Pd, stainless steel, Ti and Zr. The yield variation was also studied for the three molecules, on brass (CuZn) and on stainless steel, between 50 and 250 MW/cm^2. It was observed that the yields are strongly substrate-dependent, with very low yields for the noble metals Au and Pd. For the three molecules, the yield is higher for CuZn than for stainless steel, with the difference becoming smaller as the irradiance (MW/cm^2) increases. The observed phenomenon cannot be explained in terms of heating due to absorption of light by the metal alone; it is proposed that the superficial oxide layer plays a major role in the observed phenomenon. (Int J Mass Spectrom 177 (1998) 217–223) © 1998 Elsevier Science B.V.

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1. Introduction

During studies on the detection of some pesticides (aminotriazole, dinoterb, ioxynil) using laser desorption/ionization techniques, we have observed that in direct (no matrix) desorption/ionization, for thin organic layers deposited on metallic substrates, the ion yields were strongly substrate dependent under otherwise identical experimental conditions. A substrate dependence for the ion yields is expected for thin layers and/or for molecules that do not absorb much at

the used wavelength. In the case of two widely different substrates—quartz and stainless steel—ion yields differing by more than one order of magnitude were reported, at the same laser irradiance (MW/cm^2), within a limited irradiance range [1]. This effect was attributed to different temperatures being reached at the beam spot, because of different absorption and thermal properties of the two materials. These results were obtained with a CO$_2$ laser at 10.6 μm, and for a 200 ns pulse width, conditions which are quite different from the present ones. In another work [2], desorption/ionization of absorbing and of nonabsorbing molecules has been studied, and the substrate effect (again for two very different materials, silver

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and quartz) has been discussed, on a qualitative basis. In another study [3], for molecules deposited on a thick gold substrate or on a very thin gold layer resting onto an insulating substrate, a thermal and a nonthermal mechanism were evidenced, depending on the laser wavelength. Other substrate effects, on the desorption yield of neutral molecules [4] and on the internal energy of these molecules [5], have also been reported.

In our studies, where metallic substrates only were used, we also observed ion yields that could vary by a factor higher than 10. Ion yields observed on a brass (CuZn) substrate for instance, could be more than 10 times higher than on a stainless steel substrate, and this was true as well for MH^+ ions as for $(M-H)^-$ ions. This large ion yield variation for similar substrates, seemed difficult to interpret in terms of energy absorption and dissipation by the metal (or alloy) alone. It is the purpose of this work to investigate in more detail the observed phenomenon.

2. Experimental

2.1. Mass spectrometer

The spectrometer is a time of flight mass analyzer, based on the TRIFT system [6]. We purchased the three 90° quasihemispherical electrostatic sector analyzers placed in a circular chamber and several electrostatic lenses from the C. Evans and Associates company, which built the TRIFT at that time. The rest of the spectrometer was assembled in the laboratory [7]. The sample holder can accept up to four disc shaped substrates (1 cm in diameter), onto which the samples are deposited. An X-Y stage (there is a Z movement also), can bring any part of each of these four samples at the laser beam spot, so that the entire sample(s) can be analyzed. For these experiments, the samples were held at 4.5 kV (+ or −), and the ions were detected by two multichannel plates (MCP) in a chevron configuration, with the front of the first MCP at ground. For data acquisition, a Lecroy 9354 digital oscilloscope (450 MHz analogic bandwidth, 2 gigasamples/s maximum) was used.
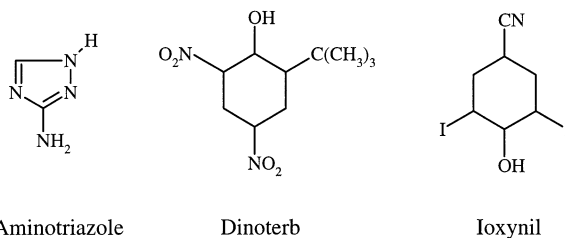

Fig. 1. Schemes of the structure of the three analytes.

2.2. Laser system

A nitrogen laser (ILEE AG laser innovation, Urdorf, Switzerland), with a pulse energy of 140 μJ delivered in 0.5 ns at 337 nm was used. The laser beam is transported using mirrors, and focused to a spot of 4.10^{-4} cm^2 using a UV grade silica lens; the angle of incidence on the samples is 30°, with respect to the normal to the surface. Beam attenuation is achieved by means of absorbing colored glasses and of collimators. Pulse energies from microjoules to tens of microjoules were measured with a pyroelectric detector (Molectron J9LP).

2.3. Substrates

The 1 cm diameter discs adapted to the sample holder were made out of polished stainless steel. The sample holder itself, made out of polished brass, was also used for sample deposition around and in between the four stainless steel discs. Other metals, A1, Au, Co, Cu, Fe, Mo, Pd, Ti, Zr and also a brass sample, were thin rolled metallic foils (10 to 25 μm thickness).

2.4. Sample preparation

Solutions of aminotriazole ($C_2H_4N_4$, M = 84.08), dinoterb ($C_{10}H_{12}N_2O_5$, M = 240.2, vapour pressure at 20 °C: 20 mPa), and ioxynil ($C_7H_3I_2NO$, M = 370.9, vapour pressure at 20 °C:55 nPa), with a concentration of 100 mg/L in methanol were prepared. A volume of 0.5 μL is deposited with a micropipette and left to evaporate by itself. Schemes of the structure of these three molecules are shown in Fig. 1.
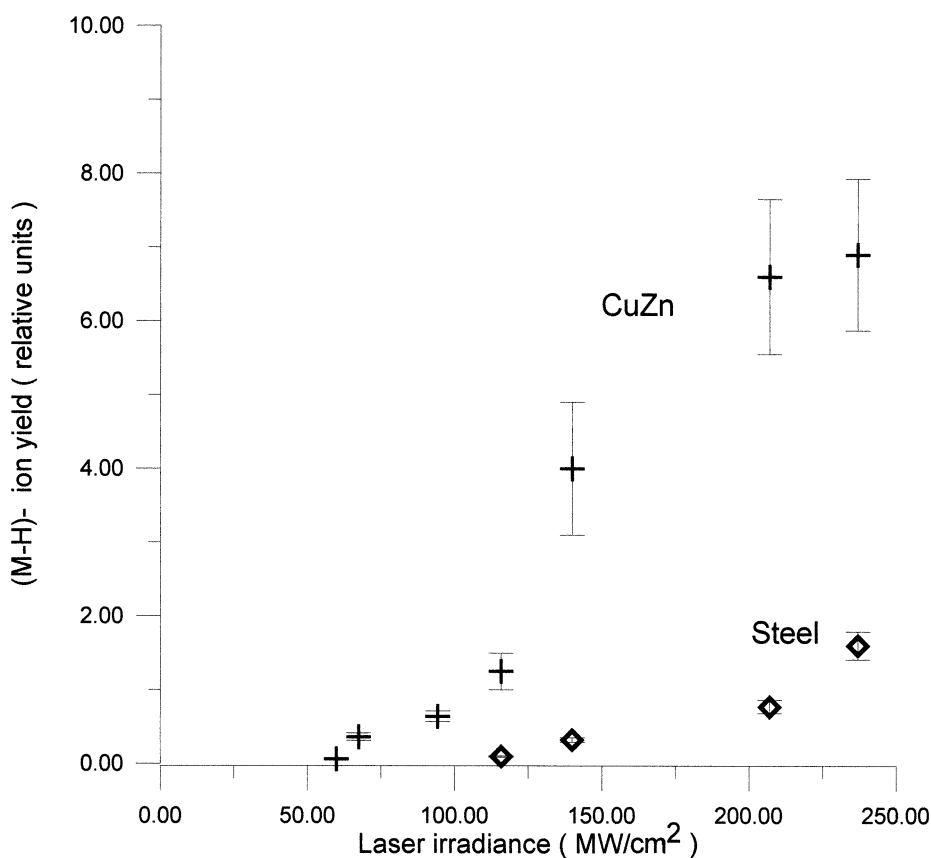
Fig. 2. Variation of the (M-H)$^{-1}$ ion yield with the laser irradiance, for DINOTERB on CuZn and stainless steel.

3. Results

3.1. Ions obtained

The MH$^+$ ion is obtained for aminotriazole, whereas it is the (M-H)$^-$ ion for dinoterb and ioxynil; these are the same ions which are observed for these compounds using MALDI [8].

3.2. Variation of the ion yields with the laser irradiance

Ion yields were measured from ~50 up to ~250 MW/cm^2, for each of the three molecules of interest, on two different substrates for which a pronounced difference had been observed: stainless steel (18% Cr-8% Ni) and brass (63% Cu-37% Zn). A volume of

0.5 μL of sample solution (methanol with 100 mg/L of organic molecule), is deposited on the substrates; it spreads over ~0.5 cm^2, which represents ~0.1 μg/cm^2 of organic matter, assuming a homogeneous repartition. It was noted that due to sample sublimation under vacuum (the pressure is 10^{-6}–10^{-7} torr in the sample chamber), the ion yields are almost insensitive to the sample concentration in methanol, between 0.1 and 10 g/L. It seems that at the time the operating pressure is reached, most of the sample has sublimed. Some edge effects due to the drying process are observed: on the edges of the dried deposits, a higher ion yield is always observed. This means that after drying there is significantly more matter on the edges than on the rest of the area; this more abundant deposit needs more time to sublime. We have checked that sublimation does indeed take place, by analyzing
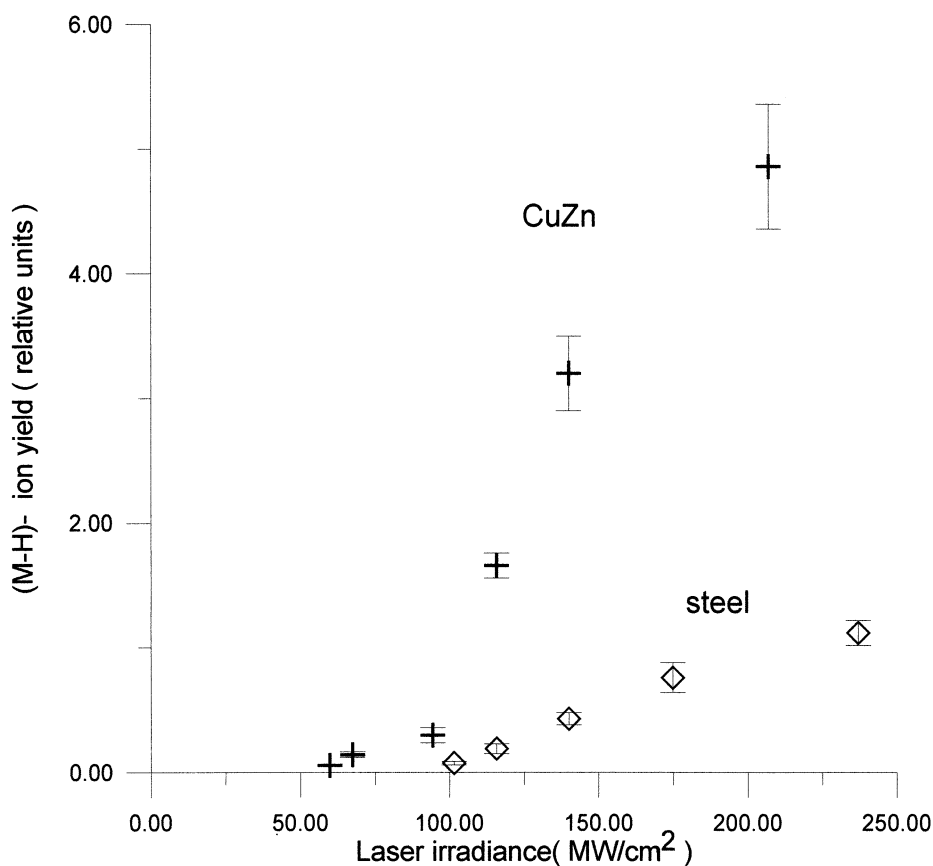
Fig. 3. Variation of the $(M-H)^{-1}$ ion yield with the laser irradiance, for IOXYNIL on CuZn and stainless steel.

places of the sample holder where no deposit had been made, before hitting any of the deposits to avoid removing and redepositing matter: ion yields very similar to those obtained on the deposits themselves are observed. The phenomenon just described is actually beneficial for our measurements, because we can easily obtain rather uniform layers, even if there are some variations in the areas of the dried deposits. It was also noted that the ion yield decreases very rapidly as the number of shots on the same spot increases, which is normal considering the small thickness of the layers (in the monolayer range). Thus, for the measurements shown in Figs. 2–4, only one measurement per spot was taken, moving to a fresh spot after each measurement with the X or Y movement of the three axis stage. Each data point is the average of at least 20 shots, with the associated

standard deviation; the peak height was used here, and a better precision would be obtained by integrating the peak area. A striking difference can be seen between the two substrates: the threshold is lower and the yield higher for the brass substrate, in the range of irradiances investigated, the difference in yield decreasing as the irradiance increases. This behavior is observed for the three molecules studied, two of which produce negative ions, the third one producing positive ions. The threshold for the production of positive ions on CuZn, is also higher than the threshold for negative ions (100 MW/cm^2 instead of ~50 MW/cm^2).

3.3. Comparative ion yields at fixed laser irradiance

Table I shows the ion yields for dinoterb, measured under identical experimental conditions, for a number
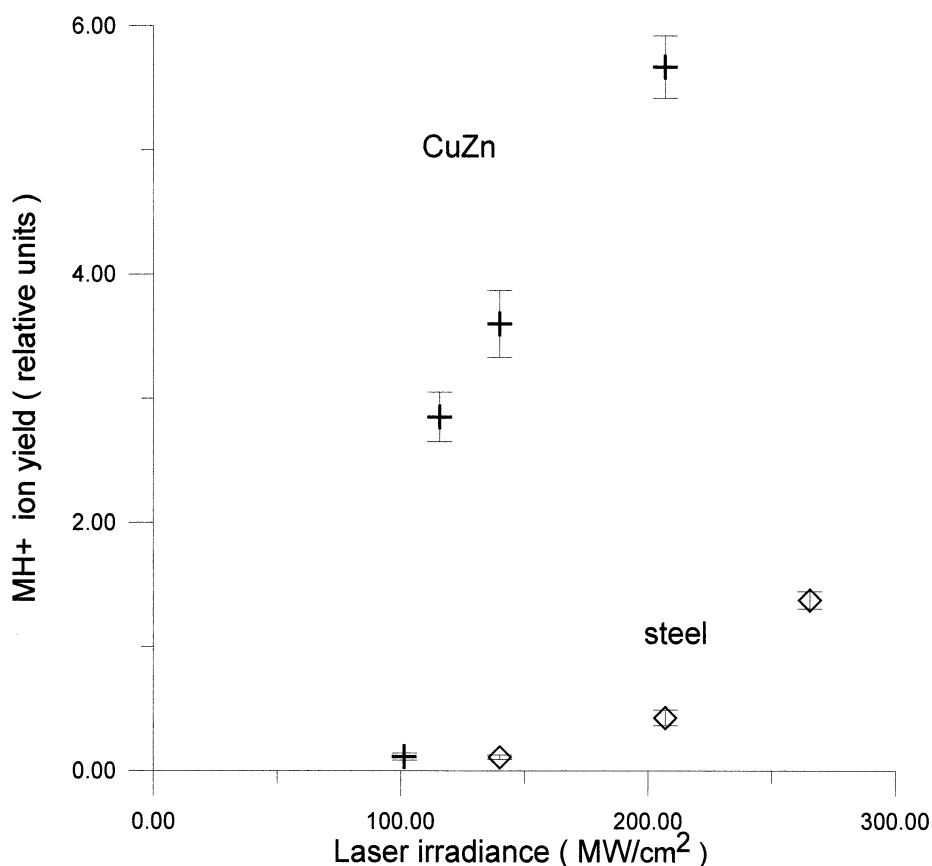
Fig. 4. Variation of the MH^+ ion yield with the laser irradiance, for AMINOTRIAZOLE on CuZn and stainless steel.

of metals and alloys. The laser irradiance was ~240 MW/cm^2, corresponding to a total energy of ~50 μJ; it was calculated by measuring the laser energy at the beam spot (somewhat out of focus to avoid deterioration of the pyroelectric detector), and by measuring the area (4×10^{-4} cm^2) of the beam spot (as was done for the curves in Figs. 2–4). This area was measured

by optical observation of a thin layer of alpha-cyano-4-hydroxycinnamic acid, a matrix commonly used in MALDI experiments and which absorbs well at 337 nm, after damaging by submission to a large number of laser shots. It appears that even though the measurements were made on the high irradiance side, where differences between substrates are smaller (cf.

Table 1
Ion yields for DINOTERB on different metallic substrates at 240 MW/cm^2, and calculated surface temperature for these substrates

Substrate	Al	Au	Co	Cu	CuZn	Fe	Mo	Pd	Stainless steel	Ti	Zr
Ion yield[a]	25	<2	34	32	100	48	17	<2	23	83	42
	(11%)		(7%)	(27%)	(16%)	(11%)	(33%)		(13%)	(9%)	(12%)
Surface temperature (K)[b]	460	1470	1545	1120	[c]	1745	1557	1885	***	4250	7534

[a]Average and standard deviation (%) for at least 20 shots, normalized to CuZn (taken equal to 100).
[b]Calculated surface temperature (K), at 240 MW/cm^2, see text for more information.
[c]Not calculated because of unknown absorption of light at 337 nm.

Figs. 2–4), very different yield values are obtained. These yields are normalized to 100 for brass (CuZn), which gives the highest value. The data points are the average of at least 20 shots, moving to a fresh spot after each shot, as explained earlier; again, the peak height only was used here.

4. Discussion

To determine if there was a correlation between the ion yields and the temperature at the beam spot, the temperatures were calculated using a known theory [9] and an existing computer program [10]. For the calculations, the relevant parameters for the laser are the pulse length, the energy per unit area, the angle of incidence, the wavelength and the polarization; for the metals, they are the specific heat, the thermal conductivity, the density and the absorption of light at the wavelength of interest. The parameter that is the most difficult to measure and to find in the literature, is the absorption of light; in these calculations, the data were found in [11].

Unfortunately, the temperatures for CuZn and stainless steel, which were much used as substrates, could not be calculated because the absorption coefficient of light at 337 nm in these materials could not be found in the existing table [11]. There is clearly no correlation between the calculated temperatures and the ion yields, as shown in Table I. This is especially obvious for Au and Pd, which give a very low ion yield at temperatures which are higher than (or similar to) those reached by metals giving a much better yield (A1, Co, Cu, Fe, Mo). A possible explanation could be that the actual temperatures are different from the calculated ones, not only because of uncertainties in the parameters used for the calculations, but also because the sample surfaces are not clean. Indeed, there is the deposited organic layer and also the native oxide layer (except for Au and perhaps for Pd). The organic layers are of the order of the monolayer, and for two molecules (dinoterb and ioxynil) it was checked that the absorption at 337 nm was very low, respectively, 213 and 44 L mol^{-1} cm^{-1} [12].

The organic layer does not absorb significantly, but it may change the amount of energy absorbed, by changing the reflectivity of the surface. As for the oxide layer, its thickness and its optical, thermal and chemical properties are different from one metal to another. We think that the observed ion yield variation is in fact linked to the oxide layer, in a way that we do not yet fully understand: it could be partly thermal, and partly due to an exchange of protons between the absorbed molecules and the OH radicals and/or the H_2O molecules contained in the oxide layer. There are several ways in which the oxide layer could have an effect on the temperature at the beam spot: intrinsic absorption of light, modification of the reflectivity, or creation of a hot spot because of poor thermal conductivity. On the other hand, the oxide layer could exchange protons with the organic molecules, more or less easily depending on the relative proton affinities and/or acidities. The fact that Au, which does not have an oxide layer, behaves quite differently from all other tested materials (except Pd), supports this hypothesis; Pd, also a noble metal, probably also does not have an oxide layer, although it is more likely than Au to oxidize. Finally, comparative (and preliminary) measurements were made on Cu, CuZn, Fe, Ti and Zr, for samples freshly etched chemically versus samples prepared as usual (only cleaned ultrasonically in water, then in methanol): the ion yields are systematically lower by a factor two to five for the etched samples, which is also in favor of a major role played by the oxide layer.

In conclusion, we believe that we have demonstrated that the production of ions under laser impact, for thin nonabsorbing organic layers, does not depend upon the heating of the sole metallic substrate; there are reasons to believe that it strongly depends upon the presence of an oxide layer, for thermal reasons but also perhaps for chemical reasons (proton exchange). This is presently being investigated.

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