

## Isomer and Species Selective Ionization and Detection of Chlorinated Aromatics by means of Laser Mass Spectrometry: First Results for Dichlorinated Dibenzodioxins

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### ABSTRACT

The applicability of resonance enhanced laser ionization for substance and isomer selective ionization of aromatic compounds is demonstrated. Laser induced mass spectra and UV spectra of some unchlorinated and chlorinated aromatics (e.g. 2,8- and 2,3-dichlorodibenzodioxin) are presented.

### INTRODUCTION

The isomer selective determination of unchlorinated and chlorinated aromatics in complex matrices often requires extensive sample clean up prior to instrumental analysis. Hence it is important to develop analytical methods which perform higher selectivity. A new promising technique is the combination of resonance enhanced laser ionization with a time-of-flight mass analyzer (laser mass spectrometer), which represents a two-dimensional analytical method with the parameters ionization laser wavelength (i.e. the UV spectroscopy is involved in the ionization process) and molecular mass<sup>1,2</sup>. Laser mass spectrometry is already established for inorganic trace analytics<sup>3</sup>. New improvements have been made for example in the field of time resolved exhaust gas analysis<sup>4</sup>, trace analysis of polycyclic aromatic hydrocarbons (PAH's) from geological samples<sup>5</sup>, and laser desorption of biomolecules<sup>6</sup>.

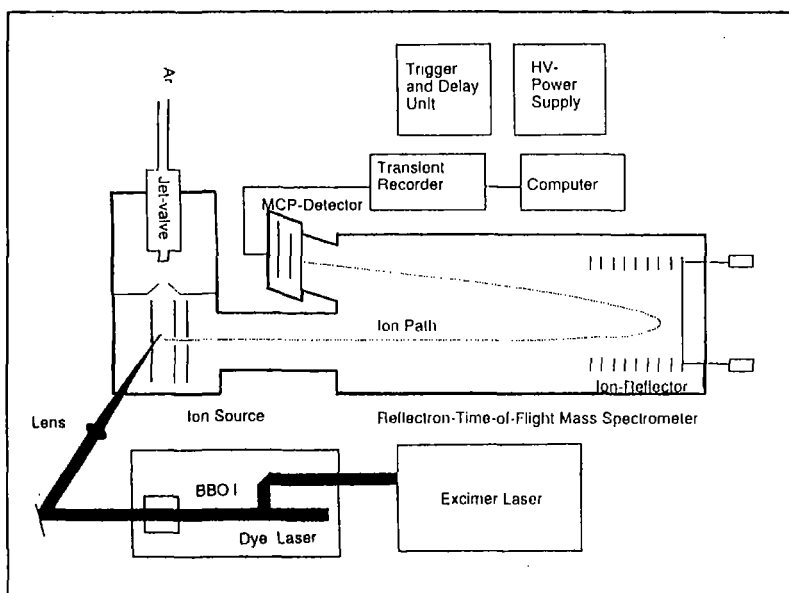
The prerequisite for substance or isomer selective laser ionization is that the molecules should have a well structured gas phase UV spectra (vibronic finger-

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print). The use of a special supersonic molecular beam inlet system cools down the sample temperature to typically  $10^0\text{K}$  in the gas phase without condensation, leading to a drastic reduction of the number and width of lines in the spectrum. This technique has been used previously for isomeric discrimination<sup>2</sup>. Here we present the initial results of the application on chlorinated Dibenzodioxines<sup>7</sup> and other compounds.

## METHOD AND EXPERIMENTAL

Fig.1 gives a survey of the experimental setup, which has been described in detail elsewhere<sup>8</sup>. A reflectron time-of-flight mass spectrometer, an excimer laser pumped, frequency-doubled dye laser and a special heatable inlet system have been used<sup>7</sup>. In this inlet system samples were vaporized, seeded in 2 atm of argon and injected in pulses through a  $200\ \mu\text{m}$  orifice into the vacuum, creating a supersonic molecular beam.



**Fig.1 Experimental Setup**

In the ion source the supersonic molecular beam is intersected by the ionization laser beam and ions are formed by a resonant multiphoton ionization process. Resonant multiphoton ionization utilizes the excited electronic states of the neutral

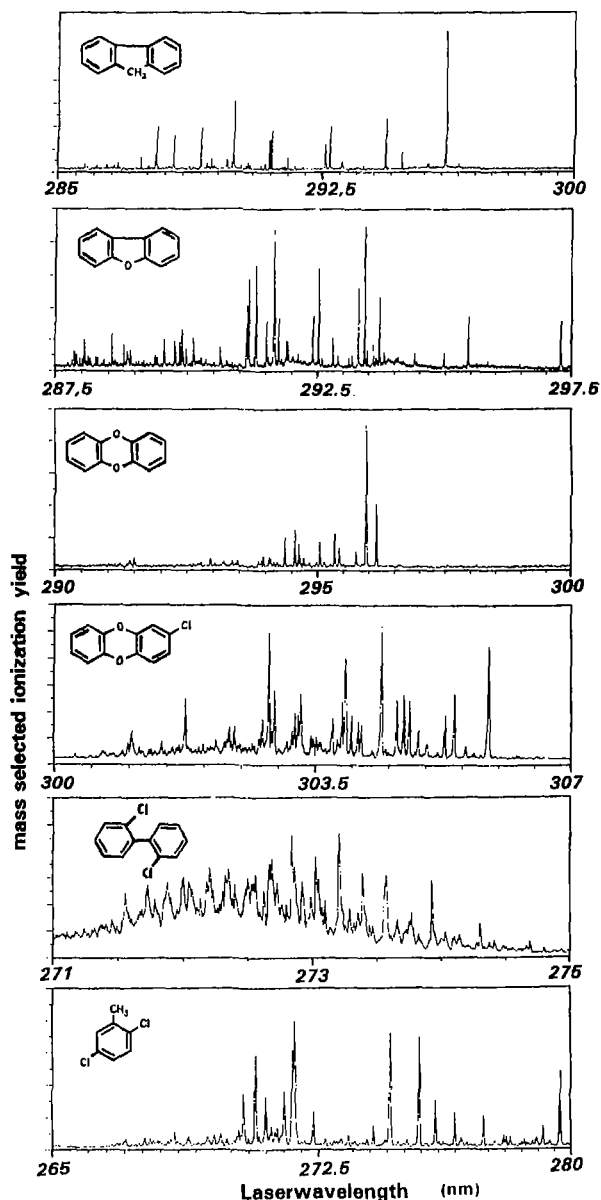


Fig.2 REMPI-spectra of some molecules

molecules, thus the highly resolved UV-spectroscopy is involved in the ionization process.

For cold molecules in the gas phase such UV spectra are dominated by a vibronic finestructure that represents a moleculespecific "fingerprint pattern" (analogous to IR spectroscopy). If the ionization laser wavelength is in resonance with such a moleculespecific fine-structure peak, the two photon absorption necessary for this ionization process is enhanced dramatically; this results in a high species selectivity of ionization. The formed ions are detected in an reflectron time-of-flight mass spectrometer<sup>9</sup>.

The great advantages of time-of-flight mass analysis are the simultaneous detection of the whole mass spectrum on a 100 $\mu$ s time scale, high transmission and good mass resolution (10000 and better).

A prerequisite for substance or isomer selective ionization is the knowledge of the highly resolved absorption UV-spectra of the target compounds. This UV-spectrum can be obtained by registering the ionization signal of the mass of interest as a function of the laser wavelength. The so called resonant enhanced multiphoton ionization spectra or REMPI-spectra contain the wavelength depended information of the ionization yield. Through comparison of REMPI-spectra (see fig.2

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and fig.4) the wavelength for selective ionization can be found.

## RESULTS AND DISCUSSION

Fig. 2 shows the REMPI spectra (i.e. highly resolved UV spectra) of six organic compounds representative of the substance classes of PAH's, PCDD's, PCDF's, PCB's and PCBz's. All spectra are well structured and are partly located in different wavelength domains. Thereby the condition for substance selective ionization is fulfilled. By tuning the ionization laserwavelength in resonance with an absorption peak of a target compound in a substance mixture, the ionization rate of the selected compound is enhanced. Other substances do not exhibit any recognizable ionization at this wavelength and therefore the mass spectra is simplified and mass interferences are reduced. For example it should be possible to discriminate PCDD/F's from PCB's or chlorinated diphenylethers spectroscopically by selective ionization.

A demonstration of substance selective ionization is given in fig. 3, where the mass spectra of a mixture of six substances (2-chlorodibenzodioxin, dibenzofuran, fluorene, 2,2'-dichlorobiphenyl, 4,4'-dichlorodiphenylether and 2,5-dichlorotoluene) are shown. The first three traces show respectively selective ionization of fluorene, dibenzofuran and 2-chlorodibenzodioxin out of the mixture (for wavelength see fig.3). The bottom trace displays an overview mass spectrum, generated by reduced cooling and a relatively short ionization wavelength, showing all compounds except of 2-chlorodibenzodioxin. Furthermore fig.3 demonstrates another important property of resonance enhanced laser ionization for analytical applications; the possibility of "soft", fragmentation

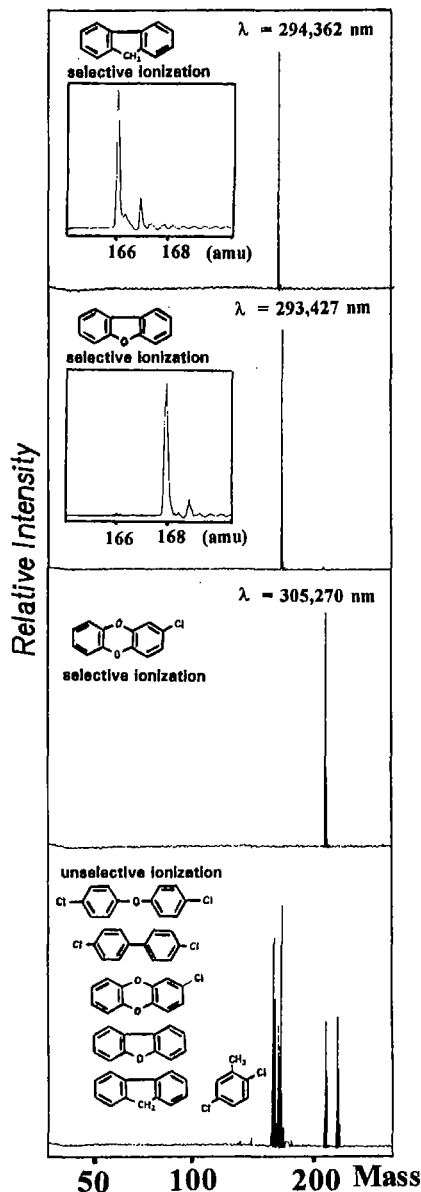
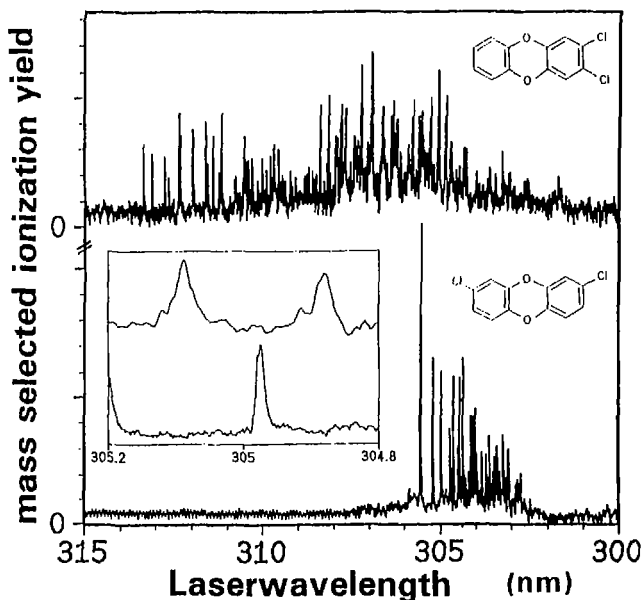


Fig.3 Species selective ionization out of a mixture

free ionization.

The practicality of isomer selective ionization for PCDD's is demonstrated in fig.4 that shows the REMPI spectra of 2,8- and 2,3-dichlorodibenzodioxin. The spectra are well structured and show isomere typical sharp peaks, furthermore the origin of the bandsystems are shifted about 10 nm in respect to one another.



**Fig.4 Isomer selective ionization of two dichlorodibenzodioxins**

There is no problem in finding a wavelength where one isomer can be selectively ionized (see insert of fig.4). Regarding the structure of the spectra (great number of sharp, spaced peaks, band-shift) it should be possible to ionize a single isomere out of 10-20 homologous PCDD/F compounds. In addition to selectivity, sensitivity is also essential for analytical applications. For PAH's detection limits in the 100 fg range have been achieved within laser mass spectrometric experiments<sup>9</sup>.

## CONCLUSION

Resonance enhanced laser ionization as an ion source for time-of-flight mass analysis offers a highly selective and sensitive method for organic trace analysis. In this work it has been demonstrated that laser mass spectrometry is able to discriminate

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substance classes that may interfere with dioxins in analysis (PCB's etc.). Furthermore first results on dichlorinated dioxins promise the possibility of isomer selective detection of PCDD/F's with high sensitivity. The combination of a separation step, such as gas chromatography or supercritical-fluid-extraction/chromatography (three dimensional method!), followed by laser mass spectrometry may allow the analysis of very complex mixtures with dramatical reduction of the costly sample preparation procedure (clean up) due to conventional analytical methods of polychlorinated aromatics. Of course this method is not limited to PCDD/F's but generally applicable to aromatic pollutants. Thereby it should be possible to get an overview of organic pollutants (PCDD/F, PCB, PAH, other chlorinated aromatics, pesticides etc.) in environmental samples very quickly.

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