

## Introduction

Electrospray Ionization (ESI) and Atmospheric Pressure Laser Ionization (APLI) are commonly used ionization methods in mass spectrometry. Since both methods are operated at atmospheric pressure conditions, they are particularly affected by matrix effects [1]. We use the determination of the *spatial resolved ion acceptance distribution* (DIA) to observe the effects of physical source parameters on the dynamics of analyte ions

in the ion source region. For this purpose, analytes located in both, the liquid and gas phases, can be selectively ionized by an actively scanned laser beam to get information about the spatial distribution of observed ion signals. This method can be used to investigate the ion dynamics under different chemical conditions and different instrument parameters [2].

## Experimental Setup

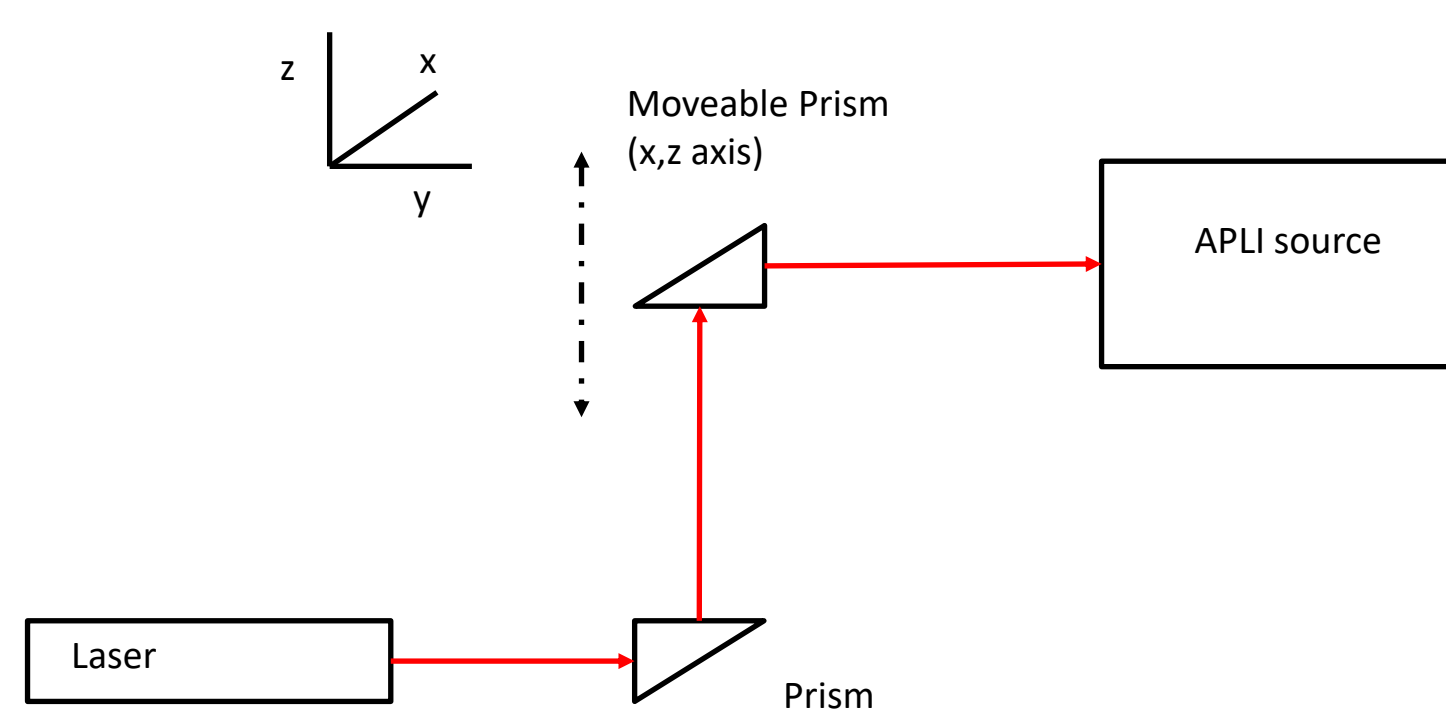


Fig. 1: experimental setup

The laser beam is diverted into the ion source using an automated laser-stage with fused quartz prisms. The prisms are moveable along the x- and z-axis and technically allows to scan wide ranges in the source. The source window currently limits the scan range to 4 x 4 cm. The laser beam has a width of 1 mm. The resolution of the DIAs and the integration time at individual spatial locations can be varied.

## Methods

**MS:** MicrOTOF (Bruker Daltonics, Bremen, Germany)  
**Laserstage:** Ender-3 3D-printer  
**Laser:** ATL Atlex-500-I Excimer laser (248 nm) (ATL-Lasertechnik, Wermelskirchen, Germany)  
**Chemicals:** - Acetonitrile and Methanol (HPLC grade, Fisher Chemicals, Germany)  
 - Pyrene and Nicotine (Sigma Aldrich, Germany)  
 - Pyrene in Methanol (5 µmol/l),  
 - Nicotine in Acetonitrile (5 µmol/l)

## Validation of the experimental Setup

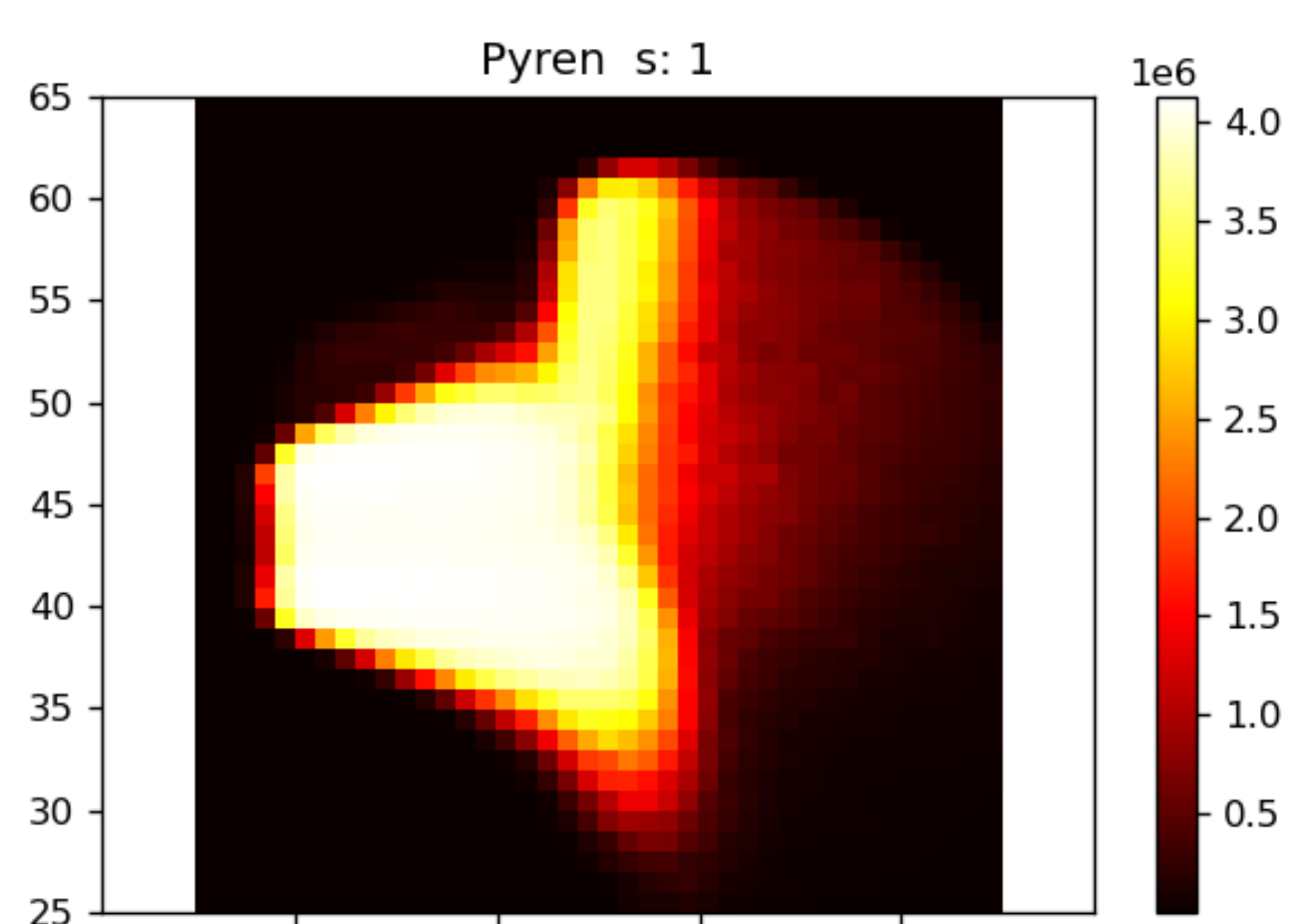


Fig. 2: DIA of Pyrene in MeOH

The first measurements was used to align the coordinate system and to obtain a good overview of the analyte signal. The coordinate at the axis are relative coordinates used for the movement of the Laserstage. The measurement shows the ion acceptance distribution (DIA) of Pyrene in MeOH. The DIA shows a almost symmetric shape along the x-axis with a high intensity in front of the spray shield.

## Variation of Analyte

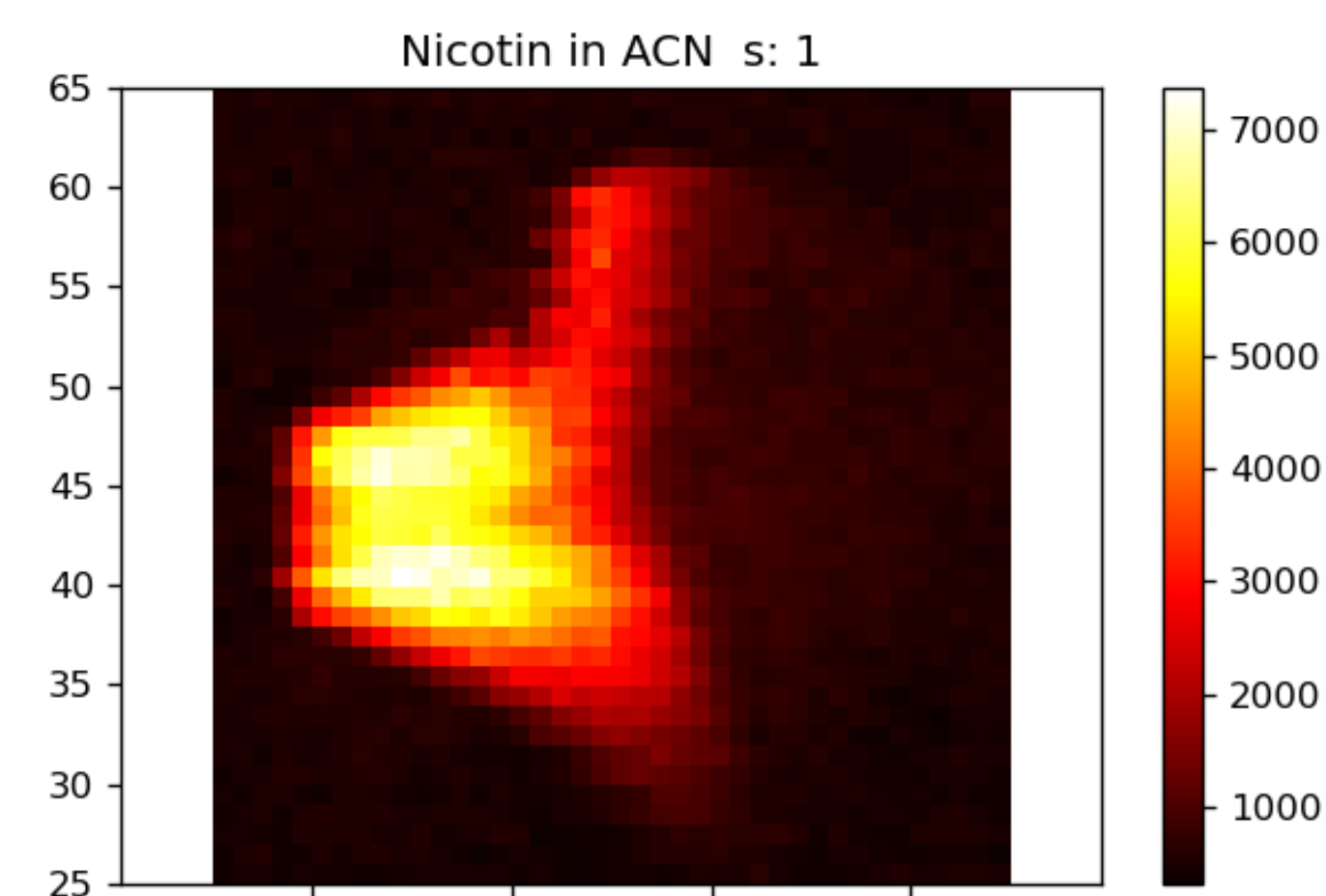


Fig. 3: DIA of Nicotine in ACN

A solution of Nicotine in Acetonitrile was used as analyte. Fig. 3 shows that the DIA of both analytes have the same symmetric shape but a much lower intensity. The intensity in front of the spray shield (x=50; y=45) has the highest value and if you move farther away, the intensity decreased but faster than the Pyrene solution.

## Variation of Source Parameters

### Dry Gas Temperature

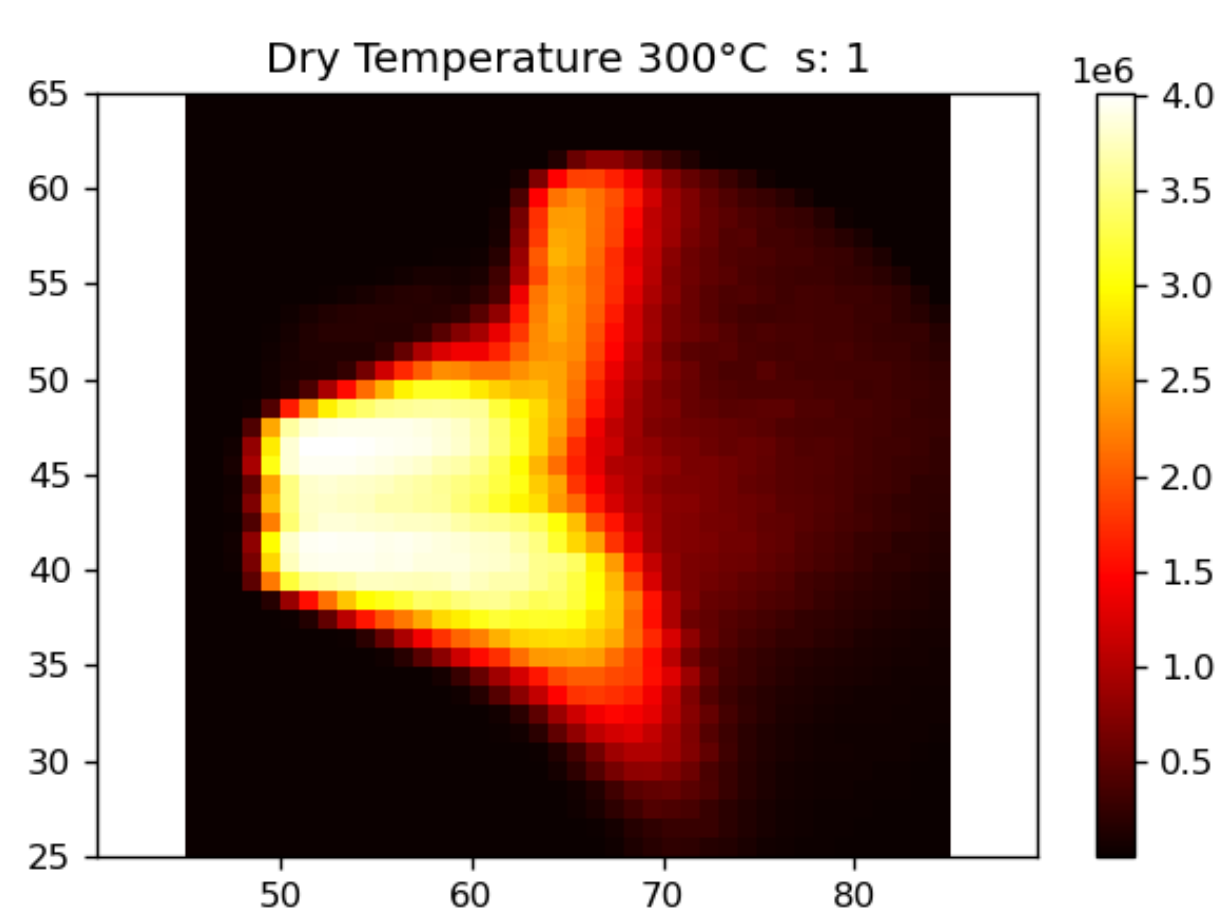


Fig. 4: DIA of Pyrene with 300°C Dry Temperature

- Dry Temperature: 300°C (previously: 100°C)
- Constant signal intensity with an almost symmetric shape along the x-axis
- No significant difference in DIA

### Dry Gas Flow rate

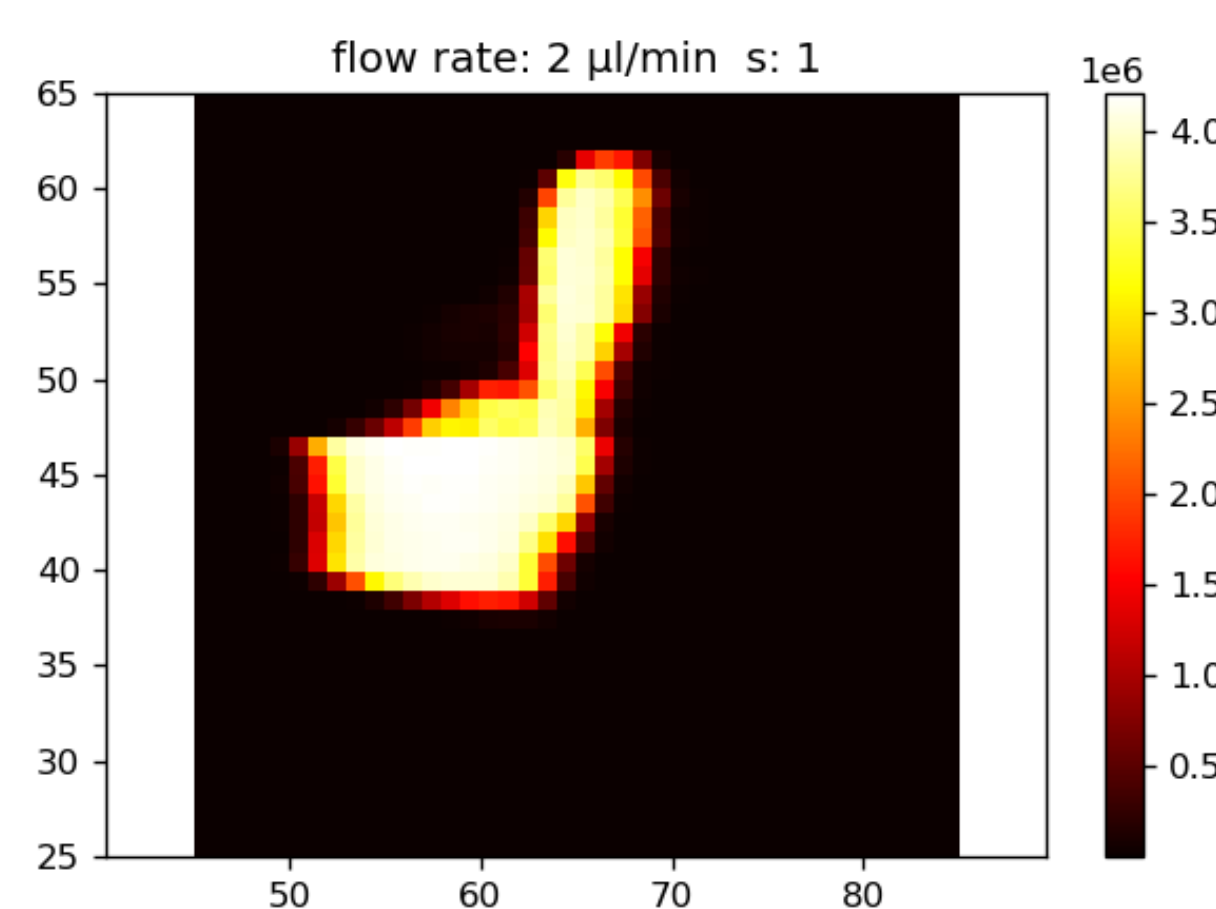


Fig. 5: DIA of Pyrene with a dry gas flow rate of 2 µl/min

- Dry Gas flow rate: 2 µl/min (previously: 5 µl/min)
- Constant signal intensity
- Shape of DIA changes with decreasing flow rate and becomes significantly more asymmetric

### Capillary voltage

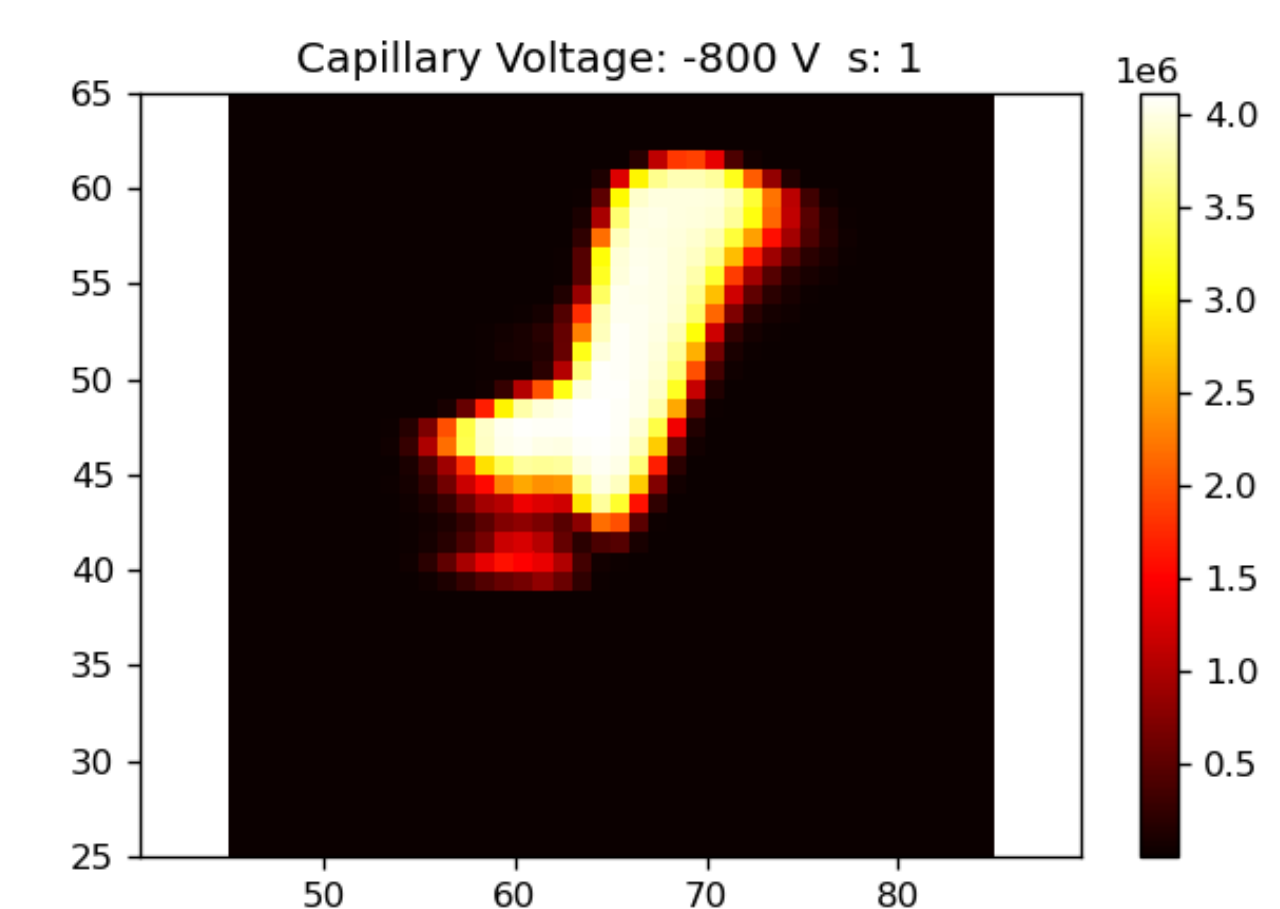


Fig. 6: DIA of Pyrene with Capillary Voltage of -800V

- Capillary Voltage: -800 V (previously: -500V)
- Constant signal intensity
- Shape of DIA also changes to an asymmetric shape when Capillary Voltage is increased

## Summary/outlook

### Summary:

- The first measurements shows that the general experimental setup is working and shows good results for the DIAs of the Pyrene solution. The DIA has a high intensity and the expected shape.
- An analyte change does not affect the shape of the DIA, but has a big effect to the signal intensity.
- The variation of the Dry Gas Temperature shows no significant effect to the DIAs
- Variation of the Dry Gas flow rate and capillary voltage induces strong changes of the DIA shape.

### Outlook:

- The measurements will be performed with different analyts and solutions.
- The source parameters can be varied to quantify the influence to the DIAs.
- It should be investigated how the DIA behave with different sources and mass spectrometers, which use e.g. different spray shields and capillaries.

## Literature

- [1] Taylor, P. J., *Matrix effects: the Achilles heel of quantitative high-performance liquid chromatography-electrospray-tandem mass spectrometry*, Clin. Chem., Vol. 38, 2005, 328-334  
 [2] Lorenz, M., *Räumlich und zeitlich aufgelöste Photoionisierung als Werkzeug zur Charakterisierung von Atmosphärendruckionenquellen in der Massenspektrometrie*, Dissertation, 2010

## Acknowledgement

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