

# Measurement of Distribution of Ion Acceptance (DIA) in ESI and APCI Ion Sources

Physical & Theoretical  
Chemistry

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## Introduction

Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) are commonly used ionization methods in mass spectrometry. Since both methods are used under atmospheric pressure, they are particularly affected by matrix effects. A spatial and temporal resolved ion acceptance distribution (DIA) was used to observe the trajectories of analytes in more detail as a function of matrix effects and physical effects due to the source parameters. For this purpose, analytes located in both the liquid and gas phases, can be selectively ionized by a moving laser to get information about the spatial distribution of observed ion signal. This method can be used to investigate how the ion distribution varies under different chemical conditions and different instrument parameters.

## 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)

## Experimental Setup

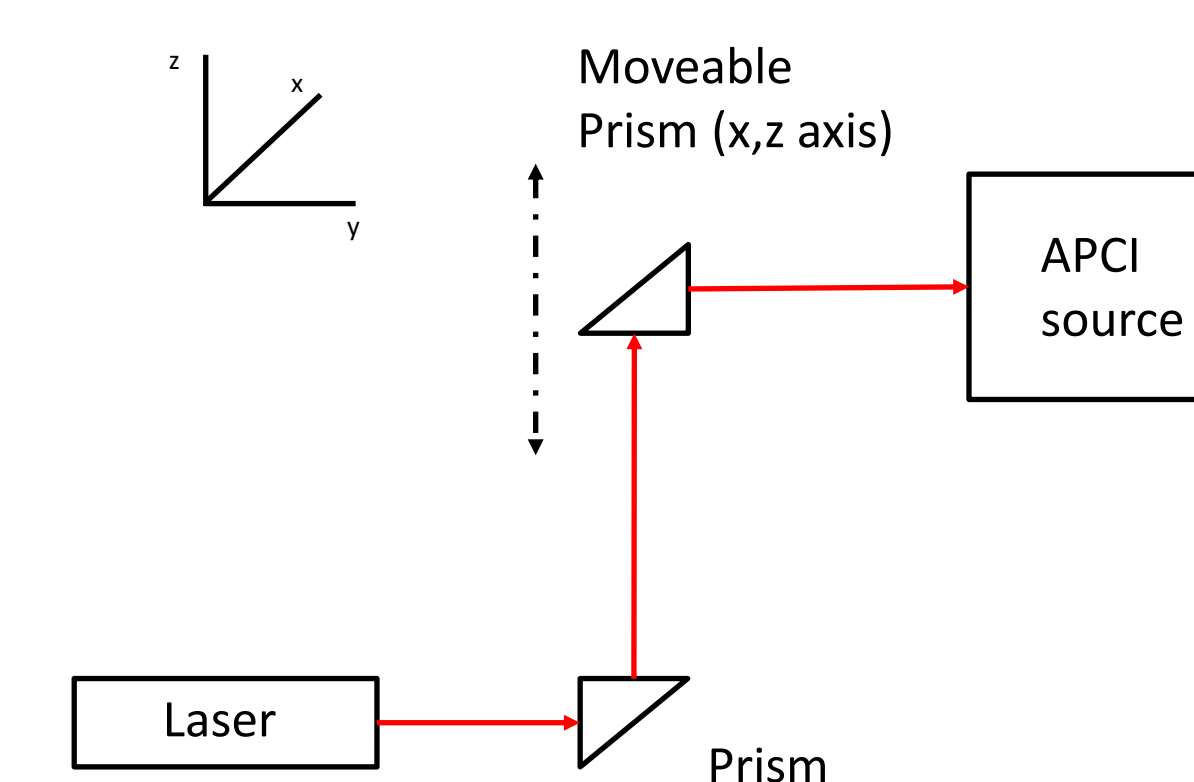


Fig. 1: experimental setup

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.

## Validation of the Experimental Setup

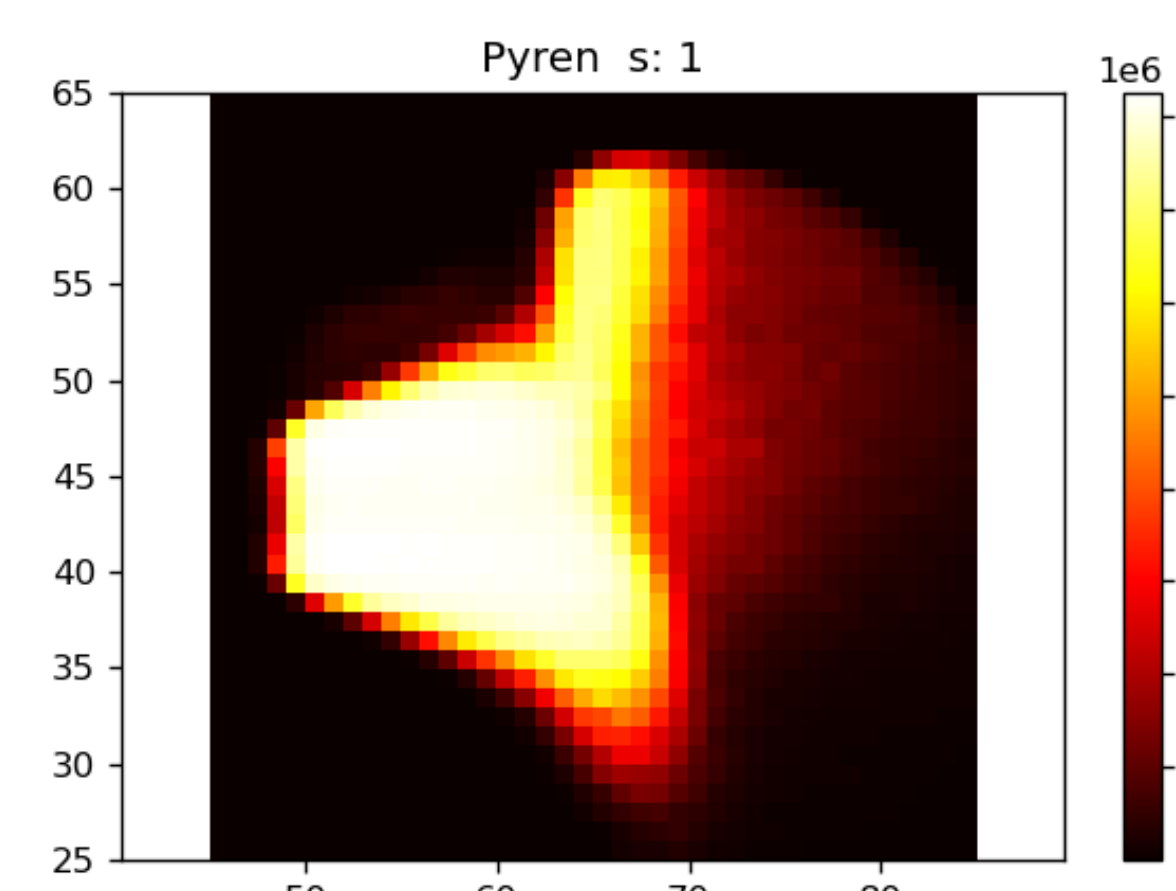


Fig. 2: DIA of Pyrene in MeOH

The first measurements was used to align the coordinate system and to obtain a good overview of the analyte signal (Fig. 2). 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.

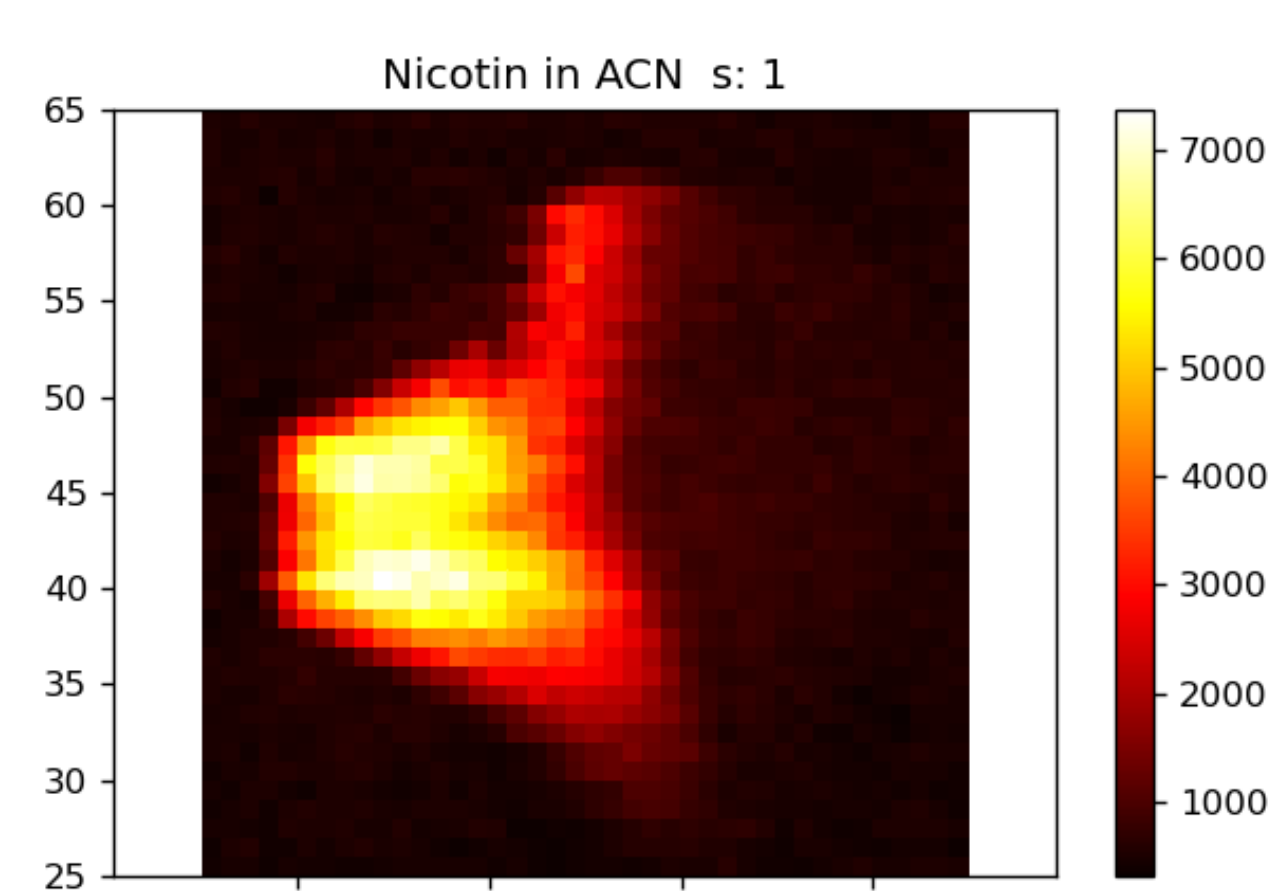


Fig. 3: DIA of Nicotine in ACN

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 Analyte and Source Parameters

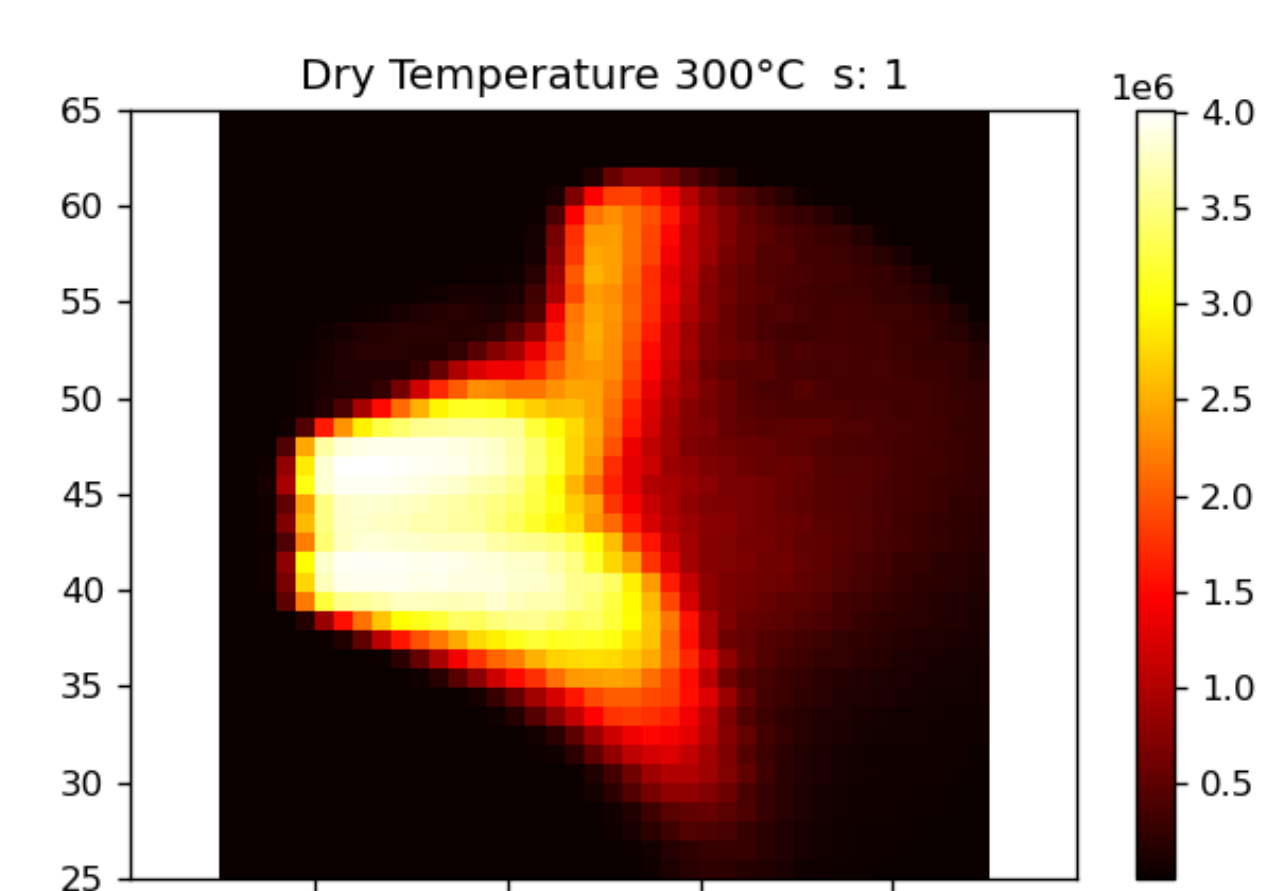


Fig. 4: DIA of Pyrene with 300°C Dry Temperature

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

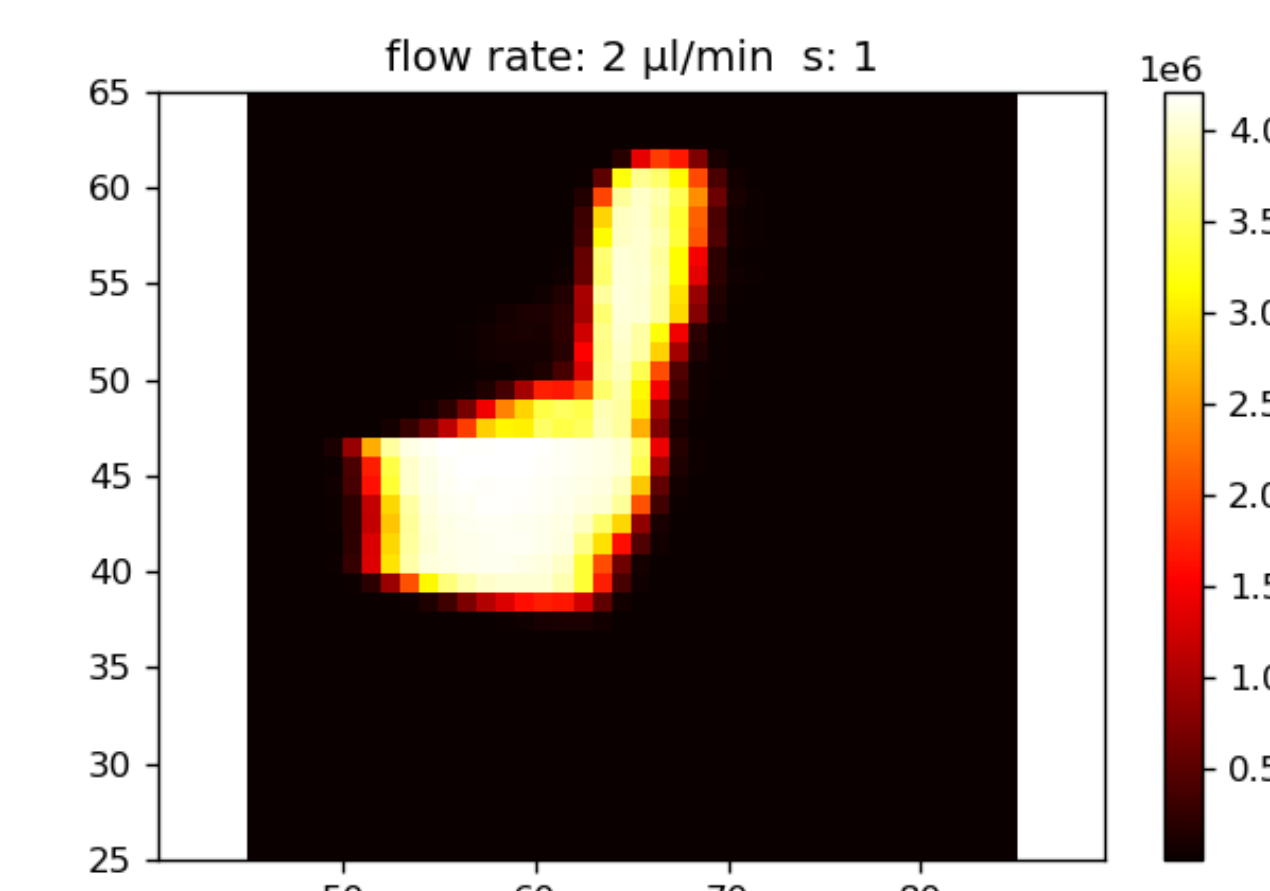


Fig. 5: DIA of Pyrene with a dry gas flow rate of 2 µl/min

- Dry Gas flow rate: 2 µl/min (previously: 5 µl/min)
- The maximum of the signal intensity didn't changed
- Shape of DIA changed with decreasing flow rate and becomes significantly more asymmetric

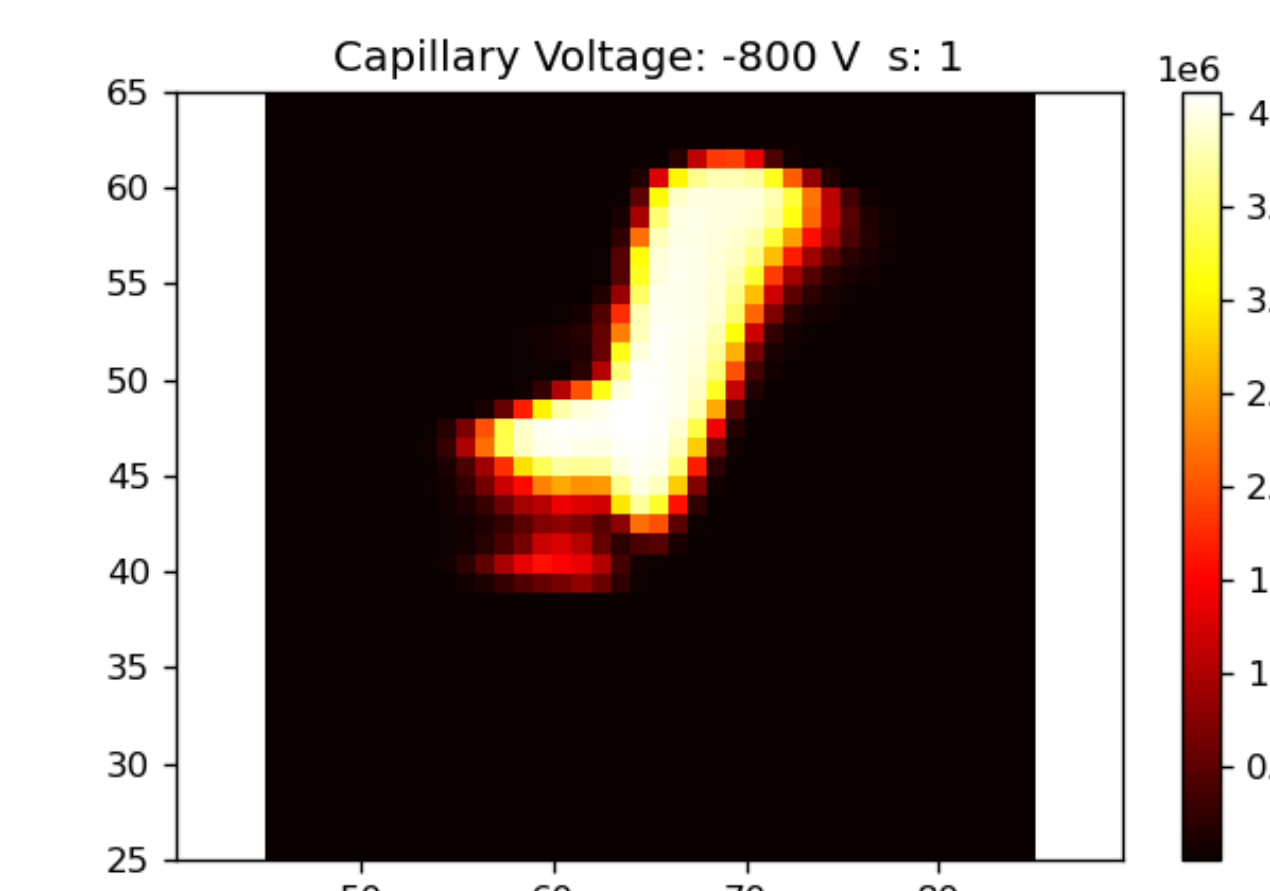


Fig. 6: DIA of Pyrene with Capillary Voltage of -800V

- Capillary Voltage: -800V (previously: -500V)
- The maximum of the signal intensity didn't changed
- Shape of DIA also changed to an asymmetric shape with increasing Capillary Voltage. Loss of signal intensity directly in front of the spray shield

## 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..
- 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, e.g. using ESI, 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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