

Micro-plasma based pulsed direct charge transfer stage coupled to a FT-IT mass spectrometer

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Introduction

Challenge

Direct coupling of a DC micro-plasma source to a Fourier Transform – Ion Trap (FT-IT) mass spectrometer

- Pulsed sampling from 10-1000 mbar
- FT-IT requires trap pressures < 10⁻⁶ mbar to achieve:
 - Optimum mass resolution
 - Strongly reduced ion-molecule reactions during the storage and detection phase since
 - such reactions change the initially injected ion population
 - analysis of the recorded spectra is rendered much more difficult
- Stable operation of the micro-plasma by continuous delivery of primary discharge gas flow

Realization:

- Direct coupling of a reaction chamber and the FT-IT mass analyzer via a quartz capillary
- Application of a fast switching valve to adjusting the pulse duration depending on the upstream gas pressure
- Three-channel-valve allowing pulsed inlet of the analyte and subsequent swift pumping of the gas load to quickly lower the trap pressure
- Spatial separation of the continuous delivery of the primary discharge gas flow and the pulsed analyte flow

Benchmark Measurements:

- Carried out with toluene in nitrogen; figures of merit are limit of detection and dynamic range
- Observations of the extent of ion-molecule reactions using Kr/Xe mixtures in nitrogen and toluene in hydrogen

Methods

Mass analyzer:

Zeiss Fourier Transform Ion Trap (FT-IT)

Ionization Method:

- Custom DC micro-plasma source (initially developed for applications in the low pressure regime)
- Operated with Helium 5.0 (Messer Industriegase GmbH, Bad Soden, Germany)
- Quartz capillary (GC column, uncoated, ID 0.5 mm)

Chemicals:

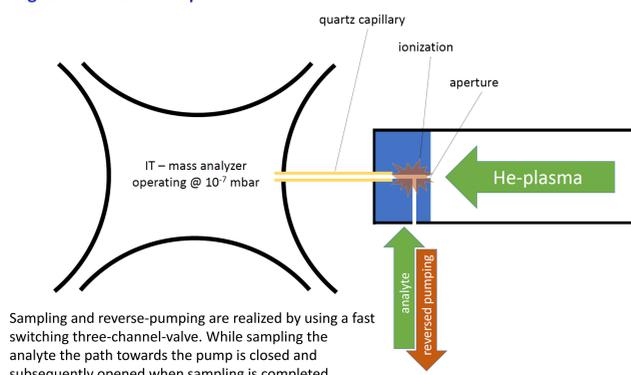
- Custom gas mixtures:
 - Toluene in nitrogen (10 ppmV and 10 ppbV)
 - Toluene in hydrogen (10 ppmV)
 - Xe and Kr in nitrogen (6 ppmV each)
- Dynamic dilution stage (up to 1:1000)

Data Analysis:

Analysis of the mass spectra were performed with mMass (Version 5.5.0; open source software)

Experimental Setup

Fig. 1: Schematic Setup



Sampling and reverse-pumping are realized by using a fast switching three-channel-valve. While sampling the analyte the path towards the pump is closed and subsequently opened when sampling is completed.

This leads to an elevated pressure within the trap upon sampling (10⁻³ to 10⁻² mbar), which has a favorable ion „cooling“ effect. As the pump rate through the quartz capillary is rather low and the trap requires a local pressure of at least 10⁻⁶ mbar for measurement, a swift reduction of the gas load by reverse-pumping of the sample is favorable.

Heart of the setup: “T-piece” arrangement

Why?

- DC micro-plasma generated He-metastables (He^M) are quantitatively reacting to form reagent ions in very close vicinity to the aperture, minimizing any He^M losses
- High pressure conditions while ionizing the analyte, thus the analyte molecule density is still elevated (as compared to e.g. gas expansions)
- Small and defined reaction area including a reaction volume inside the quartz capillary
- Direct transfer of analyte ions into the trap via the quartz capillary (GC column, ID 0.5 mm)

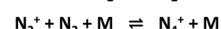
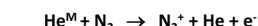
Chemistry @ work: Reagent Ions and Analyte Ions

Initial He^M – formation:

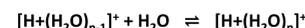
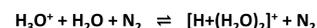
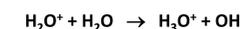
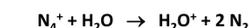
The operation of the DC micro-plasma in helium leads to the generation of helium meta-stables (He^M; 19.8 eV):

Formation of reagent ions:

In N₂ as main background gas N₂⁺ and N₄⁺ are generated due to Penning ionization induced by He^M



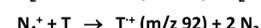
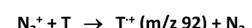
In presence of elevated water mixing ratios protonated water clusters rapidly form



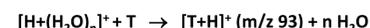
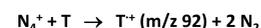
Depending on the water mixing ratio and temperature n = 3 ... 6

With toluene as analyte

Under „dry“ conditions only charge transfer from N₂⁺ and N₄⁺ towards toluene (T) is observed:



At elevated water mixing ratios charge transfer and protonation by proton bound water clusters is observed



Why do we measure m/z 91?

Collisional ion activation within the trap under H₂-loss leads to formation of C₇H₇⁺ (m/z 91) ions.

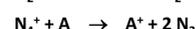
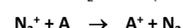
Summary: Which reagent ions do we generate?

Under „dry“ conditions: N₂⁺ and N₄⁺

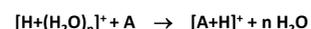
At elevated water mixing ratios: N₂⁺, N₄⁺ and [H+(H₂O)_n]⁺

Formation of analyte ions:

Charge transfer reactions of N₂⁺ and N₄⁺



After activation of the protonated water clusters (n → 0, 1) in the ion trap, protonation of the analyte molecules is observed



(strongly simplified reaction scheme)

Analyte	IP [eV]	Analyte	IP [eV]
Nitrogen	15,6	Xenon	12,1
Water	12,6	Krypton	14,0
Oxygen	12,1	Toluene	8,8

Table 1: Ionization potentials of selected analytes

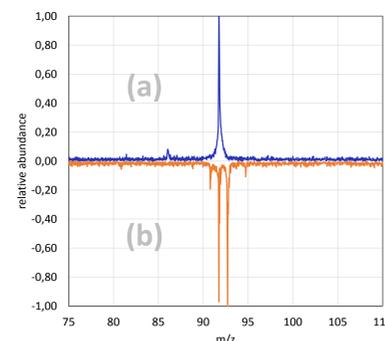


Fig. 2: Mass spectra of 1 ppbV toluene in nitrogen under a) purified and b) non-purified conditions

Benchmark Measurements

Benchmark measurements were carried out with toluene diluted in nitrogen at elevated water mixing ratios and sampling the analyte from 100 mbar back pressure.

In this case formation of M⁺, [M+H]⁺ and [M-H]⁺ is expected. For toluene these analyte ions refer to m/z 91, m/z 92 and m/z 93, respectively (compare fig. 2b and 3).

The dynamic range shows a highly linear signal dependence on the mixing ratio over 5 orders of magnitude.

The signal dependence on the toluene mixing ratio is exemplarily demonstrated for the range 100 pptV to 1 ppbV.

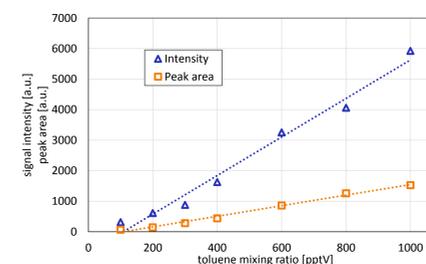


Fig. 4: Signal intensity and peak area of m/z 91 depending on the toluene mixing ratio varied between 100 pptV and 1 ppbV

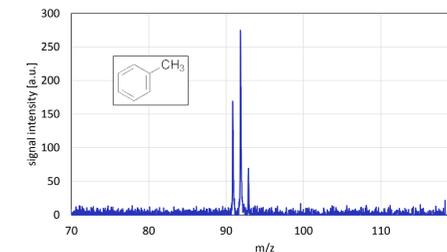


Fig. 3: Single-shot mass spectrum of 100 pptV toluene in nitrogen; total measurement time (gas pulse delivery, ion trapping, pumping, analysis, FFT) is 30 s

Using S/N = 6 the limit of detection (evaluated for m/z 91 as analyte base signal) is determined to 130 pptV.

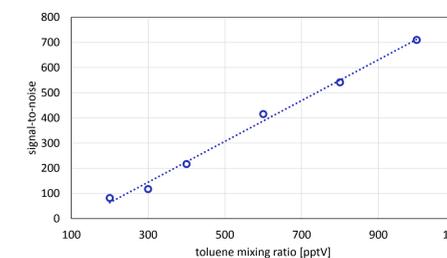


Fig. 5: Signal-to-noise ratios of m/z 91 depending on the toluene mixing ratio between 200 pptV and 1 ppbV

Conclusions

General conclusions:

- The DC micro-plasma source was successfully coupled to the FT-IT-mass analyzer
- Direct coupling was realized using a quartz capillary (GC column, length: 15 mm, ID 0.5 mm)
 - Adjustable valve opening times and reverse-pumping of the gas load allow sampling at gas pressures up to 1000 mbar
- Optimum trap pressure is reached within seconds after sampling, thus the temporal resolution of measurements in the pptV-range is about 30 s
- The system allows temporally resolved observations of ion-molecule reactions by multiple stimulation of the ion population held inside the trap.

Analytical Performance:

- Limit-of-detection: 130 pptV toluene in nitrogen @ S/N = 6
- Highly linear dynamic range over 5 orders of magnitude

Outlook

- Benchmark measurements (LOD, dynamic range) in other gas matrices
 - e.g. in hydrogen with protonation with H₃⁺
- Further investigations on ion – molecule reactions
- Is a simplification of the setup possible?
 - Up to now an additional pumping stage is necessary for reverse-pumping to reduce trap pressure swiftly
- Improvement of the temporal resolution

Literature

- [1] Anichich; An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics; JPL-Publication-03-19, 2003, Pasadena, CA, USA
- [2] Schmidt, M.; Brockhaus, A.; Brockmann, K.; Benter, Th.; Laue, A.; Aliman, M.; Using a Fourier-transform quadrupole ion trap operating with advanced ion excitation methods for high performance mass analysis of organic hydrocarbons; 62nd ASMS Conference on Mass Spectrometry and Allied Topics; Baltimore, MD, USA (2014)

Acknowledgement

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Ion – Molecule Reactions

The extent of ion molecule reactions is investigated by temporally resolved experiments as the ion population remains trapped in the FT – IT. Experiments were carried out with an 1:1 mixture of Xe/Kr in nitrogen as well as toluene in hydrogen.

Xe/Kr – experiments

Charge transfer from N₂⁺ to the rare gases initially leads to a uniform ion distribution.

This initial ion distribution changes as charge transfer from Kr⁺ to Xe occurs.

Mass spectra of this gas mixture only exhibit Xe⁺ signals even if the reaction time is held as short as possible.

In case of elevated reaction times and in presence of several ppmV water, quantitative charge transfer occurs from the rare gases to water. In this case neither Kr⁺ nor Xe⁺ is detected at all.

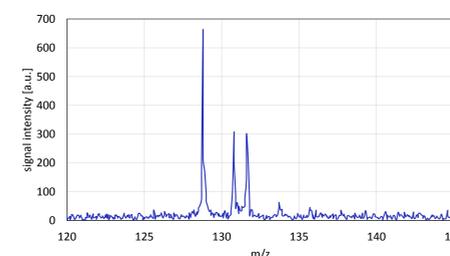


Fig. 6: Mass spectrum of Xe @ 600 ppbV in good agreement with the isotopic distribution (¹²⁸Xe: 1,91%; ¹²⁹Xe: 26,4 %; ¹³⁰Xe: 4,1 %; ¹³¹Xe: 21,3 %; ¹³²Xe: 26,9 %; ¹³⁴Xe: 10,4 %; ¹³⁶Xe: 8,9 %)

Toluene – experiments in hydrogen

The primary generated toluene species will be the M⁺, the [M-H]⁺ and in quiet large extent the [M+H]⁺ due to protonation from initially generated H₃⁺ - ions.

In subsequent ion – molecule reactions the following reactions will occur:

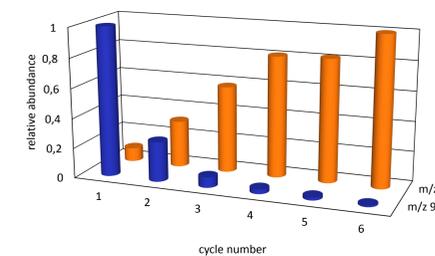
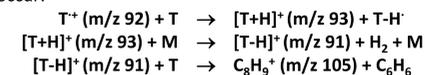


Fig. 7: Temporal evolution of the signal distribution while applying the stimulus pulse of the FT-IT in cycles of 9 sec. [M+H]⁺ is the base signal in H₂ matrix when analyzing swiftly after ionization. At longer reaction times m/z 105 becomes more dominant and the intensity of m/z 93 decreases drastically.