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 < 10^4 mbar to achieve:
- Optimum mass resolution
- Strongly reduced ion-molecule reactions during the storage and detection phase since
- Ion-molecule 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 adjust the ion 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 limited and direction dependent
- Observations of the extent of ion-molecule reactions using TIC mixing in nitrogen and toluene in hydrogen

Methods

Mass analyzer:
Zeus 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 Salzuflen, Germany)
- Quartz capillary (GC column, uncoated, 0.05 mm)

Chemicals:
- Custom gas mixtures: Toluene in nitrogen (10 ppmv and 10 ppbv), Toluene in Hydrogen (10 ppmv), and Air in nitrogen (5 ppmv each)
- Dynamic dilution stage (up to 1:1000)

Data Analysis:
Analysis of the mass spectra were performed with m/z Mass (Version 5.0, open source software)

Experimental Setup

Fig. 1: Schematic Setup

Heart of the setup: T-places arrangement

Why?
- DC micro-plasma generated He-mesotatals (He³⁺) are quantitatively reactive towards forming ions in very close vicinity to the aperture, minimizing any He³⁺ escape.
- High pressure conditions while sensing the analyte, thus the analytic 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 analytic ions into the trap via the quartz capillary

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 analytic ions refer to m/z 91, m/z 93 and m/z 95, 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 ppbv to 1 ppbv.

Literature

[1] Anich; An Index of the Literature for Biomolecular Gas Phase Chemical Reaction Kinetics; JPL-Publication-03-15, 2005, Pasadena, CA, USA

Using a Fourier-transform quadrupole ion trap operating with advanced ion excitation methods for high performance mass analysis of organic and inorganic compounds; GDCh AAMCS on Mass Spectrometry and Allied Topics, Baltimore, MD, USA (2014)

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, 0.05 mm)
- Adjustable valve opening times and reverse-pumping of the gas load allowing 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 ppbv-range is about 30 s
- The system allows temporally resolved observations of ion-molecule reactions by multiple stimulation of the ion population inside the trap.

Analytical Performance:
- Limit of detection: 130 ppbv toluene in nitrogen at 5% S/N
- Highly linear dynamic range over 5 orders of magnitude