

# Development and characterization of an FT-QIT with in situ electron ionization for residual and trace gas analysis



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## Introduction

Process-, residual-, and trace gas measurements are currently mostly done with linear quadrupole based mass analyzers. Ever increasing demands, such as challenging gas matrices (e.g. H<sub>2</sub> gas) or recording of entire mass spectra within very short time ask for new approaches in this area, however not at the expense of significantly larger footprints.

### Current challenge:

Development of a compact mass spectrometric setup for residual and trace gas analysis in different gas matrices (e.g. nitrogen and hydrogen) showing a better analytical performance than existing residual gas analyzer technology.

Figures of merit are mass resolution, limit of detection and linear response.

### Realization:

- In-trap ionization with filament driven 70 eV electron ionization
- Pulsed gas inlet with a fast switching valve sampling from up-to 10 mbar recipient pressure
  - Gas load of the QIT is sharply rising and quickly depleting
  - ✓ Enabling efficient ionization
  - ✓ Reaching optimum pressure for storage and detection phase within short time
- Broad-bandwidth excitation and detection
- Linear dynamic range over several orders of magnitude

## Methods

### Mass Analyzer:

Zeiss Fourier Transform Quadrupole Ion Trap (based on iTrap-Technology)

### Ionization Method:

70 eV electron ionization

### Chemicals:

- Custom gas mixtures:
  - Toluene in nitrogen (10 ppmV and 10 ppbV)
  - Toluene in hydrogen (10 ppmV)
  - Xe and Kr in nitrogen (10 ppmV each)
- Dynamic dilution stage (up to 1:10000)

### Data Analysis:

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

### Further equipment:

Pulse Function Arbitrary Generator, Model 81150A, Keysight, Böblingen, Germany

## Experimental Setup

The mass spectrometric setup consists of a quadrupole ion trap working with a non-destructive ion detection based on FT technique.

For optimum measurement conditions base pressure in the QIT vacuum chamber is reduced to  $p < 10^{-8}$  mbar.

Gaseous samples are introduced into the trap with a fast switching valve. Sample pressures are in the range of 0.1 – 10 mbar.

A filament driven 70 eV electron ionization source allows an in-trap ionization.

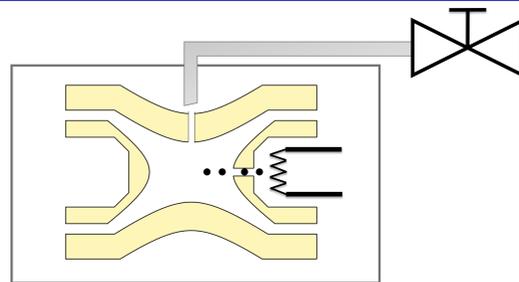


Figure 1: Schematic of the experimental setup. Quadrupole ion trap with pulsed gas inlet and filament driven electron ionization.

## Residual Gas Measurements

For residual gas measurements at pressures  $< 10^{-6}$  mbar the ion trap is operating at optimum pressure conditions needed during storage and detection phase.

As the resolving power of FT instruments scales with the length of the observed FT analysis window and as ions can be trapped for long periods of time under optimum conditions, a mass resolution  $> 5000$  is achievable.

Figure 2 depicts a mass spectrum recorded at  $1 \cdot 10^{-8}$  mbar residual gas pressure showing water and nitrogen as residual gas components. Mass resolution is determined to 5200 for water and 5900 for nitrogen, respectively.

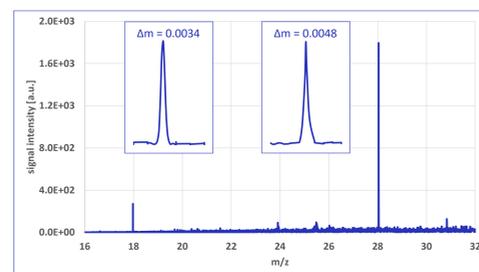


Figure 2: Spectrum of a residual gas measurement recorded at  $10^{-8}$  mbar residual gas pressure.

## Advanced ion excitation schemes

When trace gas analysis is considered, advanced ion excitation schemes become inevitable.

70 eV electron ionization is a non-selective ionization method and thus ionizing matrix compounds in large excess when analytes are present at e.g. ppbV-levels.

The analysis of small analyte mixing ratios becomes feasible when matrix ions are removed from the ion trap to avoid space charge and ion suppression effects.

To remove ions from the trap, they need to become unstable within the rf field. This approach is realized with the application of targeted ion excitation schemes, e.g. resonant ion excitation, broad bandwidth excitation and/or Stored Waveform Inverse Fourier Transform excitation (SWIFT).

Figure 3 a) shows the extract of the mass spectrum of 1 ppmV krypton diluted in nitrogen. In contrast to the expected isotopic distribution a single signal is observed. With krypton diluted to 100 ppbV no corresponding ion signal is observed in the mass spectrum (see. Fig. 3 b) as those signals are entirely suppressed.

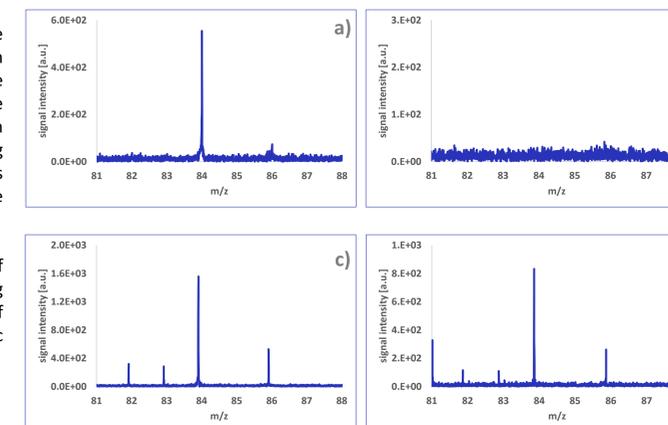


Figure 3: Extract of the mass spectrum of 1 ppmV (a and c) and 100 ppbV (b and d) without the application of SWIFT signals (a and b) and applying SWIFT signals (c and d). Consider the enhanced signal-to-noise ratios.

In both cases the application of synthesized SWIFT signals removing matrix ions allows the measurement of krypton with the correct isotopic pattern (c): 1 ppmV and d): 100 ppbV)

Isotopic distribution of krypton[1]:

<sup>82</sup>Kr: 11.6 %  
<sup>83</sup>Kr: 11.5 %  
<sup>84</sup>Kr: 57.0 %  
<sup>86</sup>Kr: 17.3 %



## Benchmark Measurements: Toluene in N<sub>2</sub> and H<sub>2</sub>

Benchmark measurements were carried out with toluene (T) diluted in either nitrogen or hydrogen with respect to limit of detection, dynamic range and mass resolution.

The analyte containing gaseous sample is pulsed via a fast switching valve at a backing pressure of a few mbar into the QIT, held at  $10^{-9}$  mbar base pressure. This leads to a pressure pulse that is sharply rising and then depleting within a few seconds.

What does this imply for the current measurements?

- An efficient ionization requires sufficient number of analyte molecules
  - ✓ Given at maximum gas load
- For detection phase pressure  $p < 10^{-6}$  mbar is required
  - ✓ Reached within approx. 1 sec

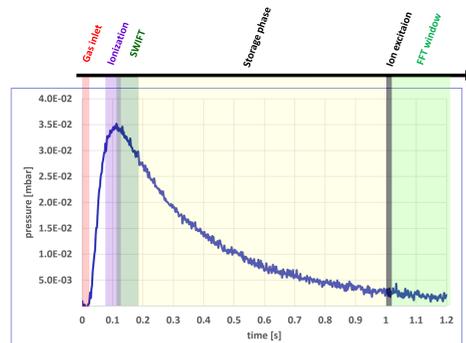


Figure 4: Qualitative trend of the gas pulse let into the trap with highlighted points of interest within a measurement sequence.

- Depending on the analyte mixing ratio the length of the ionization pulse is adjusted to avoid an ion overload of the trap (space charge effects etc.)
- For the following dilution series of toluene in nitrogen the ionization time was varied between 0.5 and 35 ms
- Signal intensities were corrected by normalization of the signal intensities to the ionization time, resulting in a highly linear response.

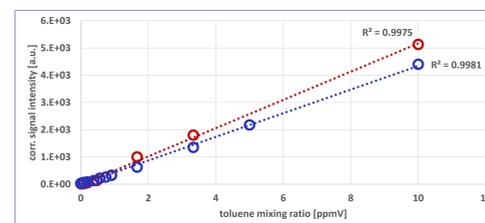
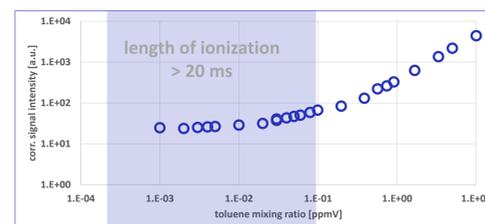


Figure 5 and 6: Dilution series of toluene in nitrogen (blue) and toluene in hydrogen (red) while varying the toluene mixing ratio in the range of 1 ppbV and 10 ppmV. Commonly plotted in figure 5 and logarithmized on both axes in fig. 6.



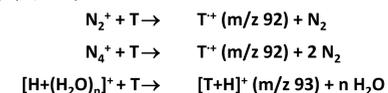
How is the non-linear behavior at lower mixing ratios rationalized?

With electron ionization mainly  $m/z$  91, which is the  $[T-H]^+$  and  $m/z$  92, which is  $T^+$  as well as a small amount of  $m/z$  93 reflecting the C-13 isotopic peak are expected.

In figure 7 the mass spectra obtained for 10 ppmV and 100 ppbV are compared, showing a significant greater amount of  $m/z$  93 at lower toluene mixing ratios.

Chemistry at work:

Lower mixing ratios correspond to longer ionization times and thus prolonged times for ion-molecule interactions inside the ion trap. Matrix ions ( $N_2^+$ ,  $N_4^+$ ,  $[H+(H_2O)]^+$ , ...), that are generated in great excess, lead to the formation of  $T^+$  ( $m/z$  92) and  $[T+H]^+$  ( $m/z$  93):



Further chemical conversion is invoked by subsequent reactions of toluene species with neutral molecules:

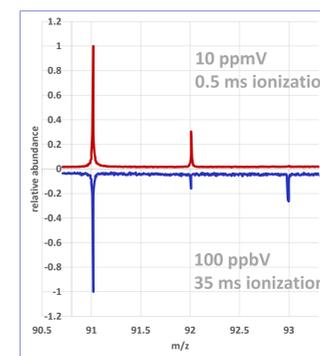


Figure 7: Comparison of mass spectra obtained with short and prolonged ionization times.

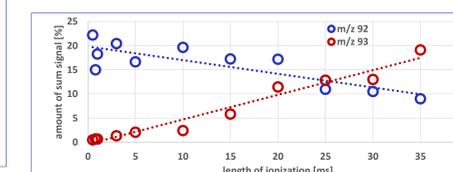


Figure 8: Amount of  $m/z$  92 and  $m/z$  93 on the sum signal of  $m/z$  91 - 93 in dependence of the length of the ionization, showing a great influence on the signal distribution due to chemistry ongoing at elevated ionization times.

## Conclusions

- The FT-QIT with in-trap electron ionization represents a compact and powerful analytical tool
- Residual gas measurements are feasible, showing mass resolution well above 5000
- A pulsed gas inlet enables analysis of gaseous samples with a temporal resolution of currently 10 sec in a continuously sampling mode
- Upon normalization of obtained signal intensities to the length of the ionization, a linear behavior over several orders of magnitude is observed
- Limits of detection have not been calculated yet, as the chemical conversion of the ion species is affecting the analyte response, but are expected to be well below 1 ppbV
- Ion excitation schemes such as SWIFT are powerful and inevitable tools to enhance QIT performance and to enable MS<sup>n</sup> experiments

## Outlook

For each measurement:

- Determination of total ion load
  - Adjustment of ionization length to avoid space charge and ion suppression
- Determination of matrix and background ions
  - Adjustment of SWIFT signals and with SWIFT applied energies to remove disturbing ions present in large excess
- Renewed record of dilution series in both matrices (nitrogen and hydrogen)
  - Determination of limits of detection

## Literature

- [1] D.R. Lide, (ed.), *CRC Handbook of Chemistry and Physics 1999-2000 - A Ready-Reference Book of Chemical and Physical Data* (CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, Florida, USA, 79th edition, 1998)
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- [4] Brachthaeuser, Y.; Mueller, D.; Kersten, H.; Brockmann, K.; Benter, Th.; Aliman, M.; Fedosenko, G.; Reuter, R.; Laue, A.; Derpmann V.; Chung, H. Y.; Micro-plasma based pulsed direct charge transfer stage coupled to a FT-IT mass spectrometer; 63rd ASMS Conference on Mass Spectrometry and Allied Topics; St. Louis, MO, USA (2015)

## Acknowledgement

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