Using a Fourier-transform quadrupole ion trap operating with advanced ion excitation methods for high performance mass analysis of organic hydrocarbons

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Introduction

Overview:

In modern mass spectrometry quadrupoles are commonly used as transfer stages and mass filters.

Operating the quadrupole in the instability mode with a particle detector has some constrains:

- Limited mass resolution
- Low scan speed

Approach:

A three-dimensional Paul trap is used as a compact Fourier Transform mass analyzer.

- Detection of induction charges of stored ions
- In-situ ion generation with pulsed gas inlet

  ⟶ Very compact setup
- Ion oscillation frequencies are mass dependent
- Improved dynamic range using advanced ejection and excitation techniques

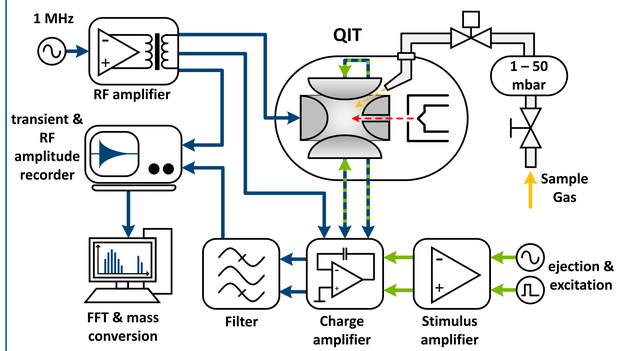
Applications:

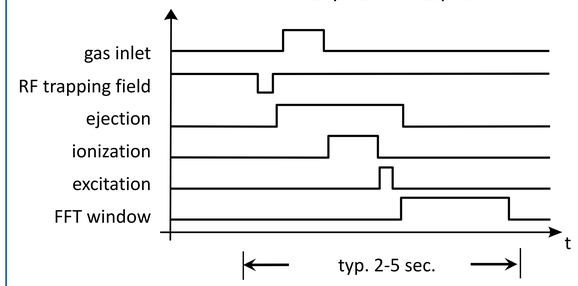
- High resolution/sensitivity MS
- Industrial environments (robust design)

Methods

Detector	Custom quadrupole ion trap (QIT), image current measurement (FTMS)
Electronics	Custom designed: • RF push-pull amplifier • Filter amplifier • Charge amplifier • Stimulus amplifier
Transient recorder	Standard 4 MS/s scope
Ionization	• Electron ionization • Multi-photo ionization with UV laser (FHG Nd:YAG, 266 nm)
Analytes	VOCs, toluene in N_2, toluene in H_2

Experimental Setup





- Sample gas is pulsed into the main chamber
- Ions are generated in-situ
- Electron or multi-photon ionization

no need for a transfer stage

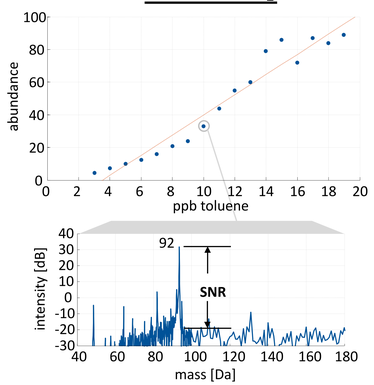
High pressure regime (main chamber)

- \+ Efficient ionization
- \+ High ion signal/number
- – Space charge effects
- – Short ion signal

trade-off between signal amplitude and resolution has to be found

Dynamic Range

Toluene in H_2

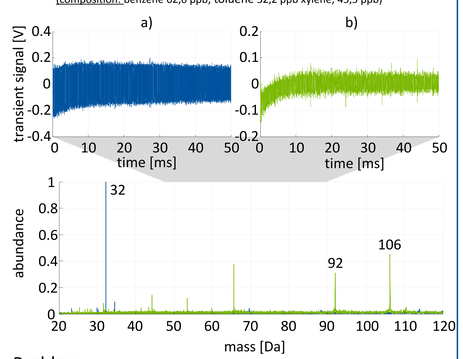


- Sample chamber pressure 18.5 mbar
- Decreasing toluene concentration
- RF voltage ca. 700 V_{pp}
- Trapping field is deactivated temporarily, before ionization ⟶ no accumulation of ions

➡ SNR at 10 ppb still at 50 dB

VOC in dry air

(composition: benzene 62,6 ppb; toluene 52,2 ppb xylene; 45,5 ppb)



Problem:

- N_2 and O_2 ions fill the ion trap a), all other components in lower concentrations are suppressed

Solution:

- Increase RF trapping voltage, lighter ions become unstable
- Eject dominant ion species b)

dynamic range of 10^8 or more is achieved

Sensitivity

Key component of Paul trap FTMS ⟶ charge amplifier

Requirements:

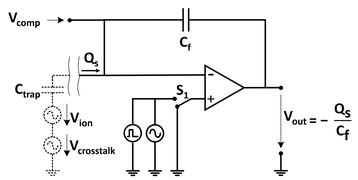
- Conversion of induction charges into scaled voltages without adding significant noise
- Distortion-free transfer of ejection & excitation waveforms to end-cap electrodes

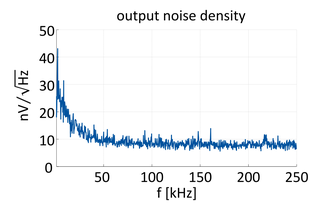
Challenges:

- Ion signal 140 dB smaller than crosstalk signal
- Keeping the detection electrodes at virtual ground

Solution:

- Application of modern OP-amp with ultra low noise input stage
- Adding of an anti-phase compensation signal to amplifier input $\mathbf{V_{comp}}$
- Trapping frequency 1 MHz, ion frequency range 0-250 kHz





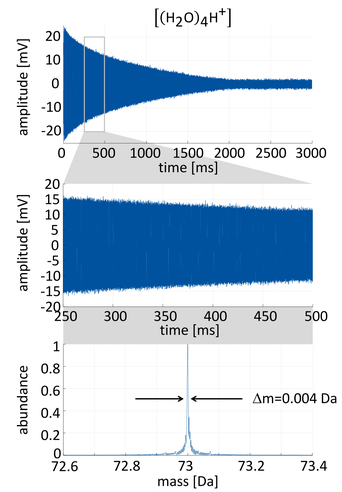
- Charge corresponding to the measured noise level is given by:

$$Q_{noise} = C_f \cdot v_{noise} \cdot \sqrt{\Delta f} \quad \text{with} \quad \Delta f = \text{FHWM}$$

$$Q_{noise} = 20\ \text{pF} \cdot 10\ \frac{\text{nV}}{\sqrt{\text{Hz}}} \cdot \sqrt{5\ \text{Hz}}$$

➡ $\approx 4.5^{-19}$ As $\overset{!}{\leq}$ N · e = **3** elementary charges !

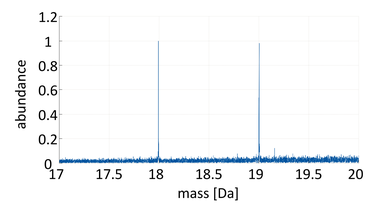
Resolution / Storage



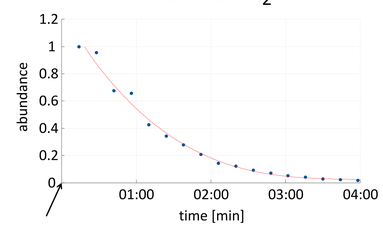
- long ion transient times ⟶ high single-shot resolution (no signal processing)

➡ $R = \frac{m}{\Delta m} = \frac{73}{0.004} \approx 18000$

residual gas measurement at $< 5 \cdot 10^{-9}$ mbar



toluene in N_2



gas inlet and ionization

Conclusions

A custom-made electrical quadrupole ion trap in Fourier Transform mode is demonstrated. Non-destructive ion detection based on a sensitive ultra-low noise induction charge amplifier enables advanced mass analysis:

- The system allows for i) long-term ion accumulation, ii) stable ion storage, and iii) multiple ion excitation and observation cycles
- Signal-to-Noise ratios exceeding 60 dB are readily achieved

  ⟶ Sensitivities in the low ppb range are established as shown here for toluene samples
- If the analyte is present in a complex gas mixture then unwanted ion species may be ejected from the trap by selected destabilization of their oscillations

  ⟶ A high dynamic range exceeding 10^8 is obtained
- High resolution in single-shot measurements

  ⟶ At low pressures of about 10^{-8} mbar the measured ion oscillation times reach several seconds, resolution exceeding 100000 is feasible

Future aspects:

- Improved mass accuracy / radio-frequency amplitude measurement technique

References

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Acknowledgement

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