

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 constraints:

- 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

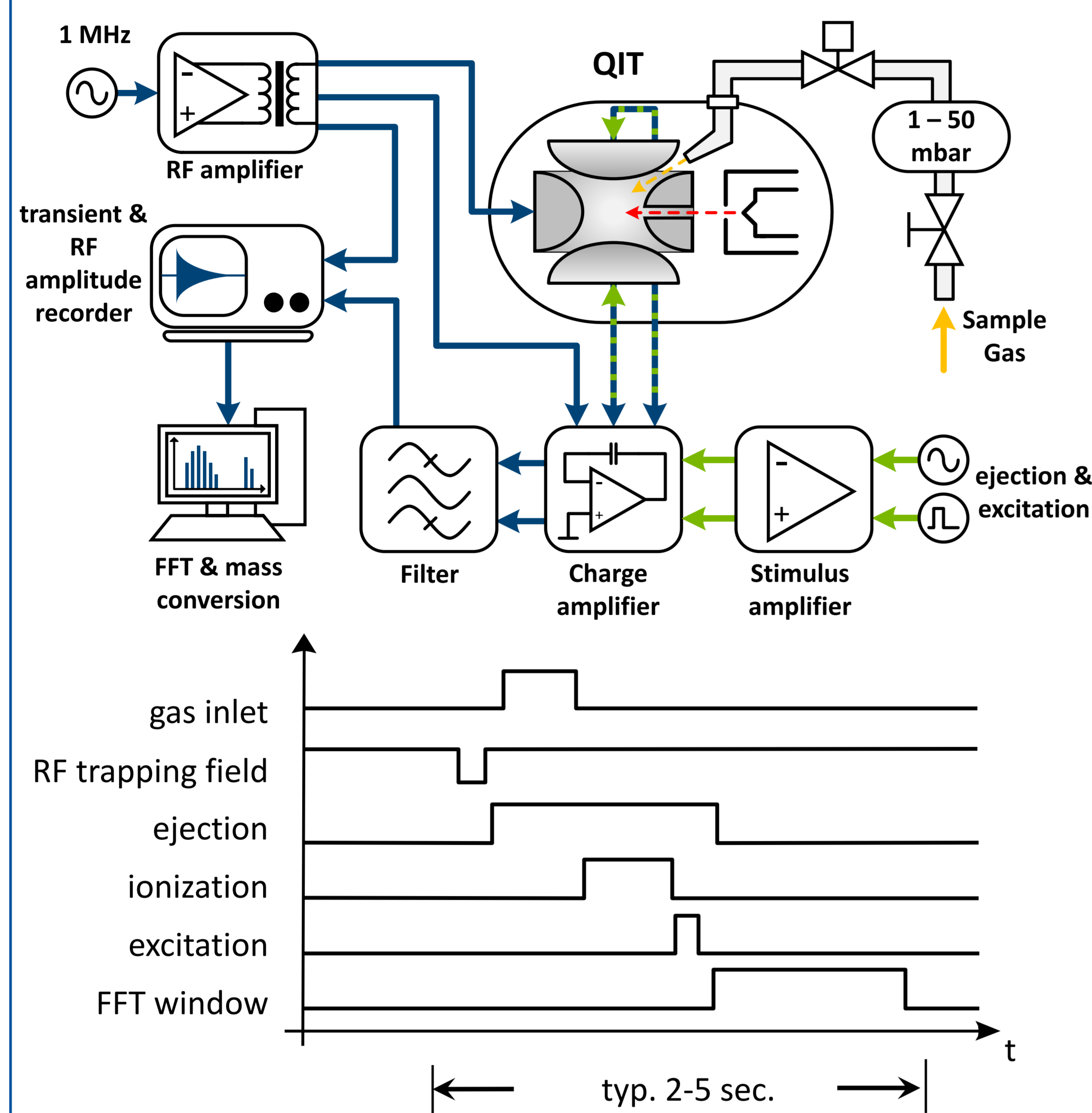
Transient recorder Standard 4 MS/s scope

Ionization

- Electron ionization
- Multi-photo ionization with UV laser (FHG Nd:YAG, 266 nm)

Analytes VOCs, toluene in N₂, toluene in H₂

Experimental Setup



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

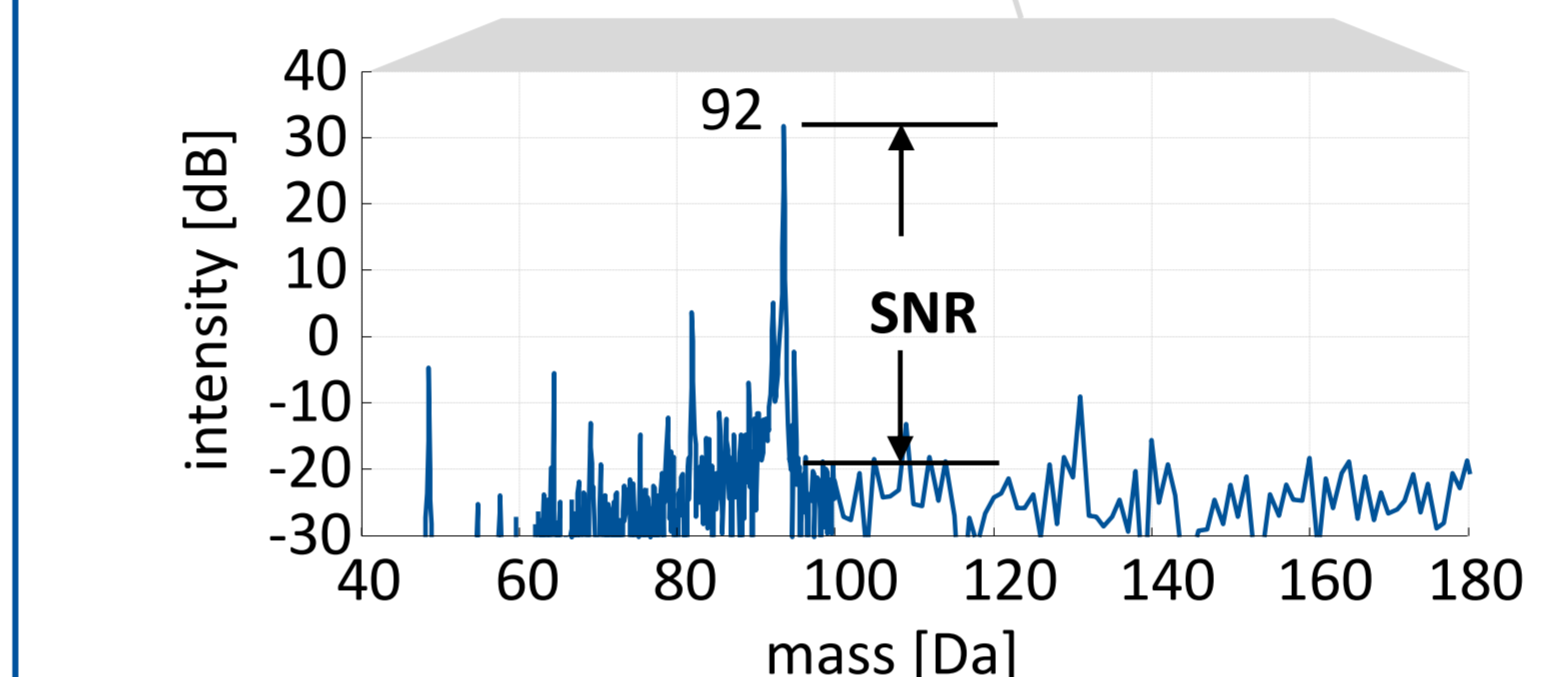
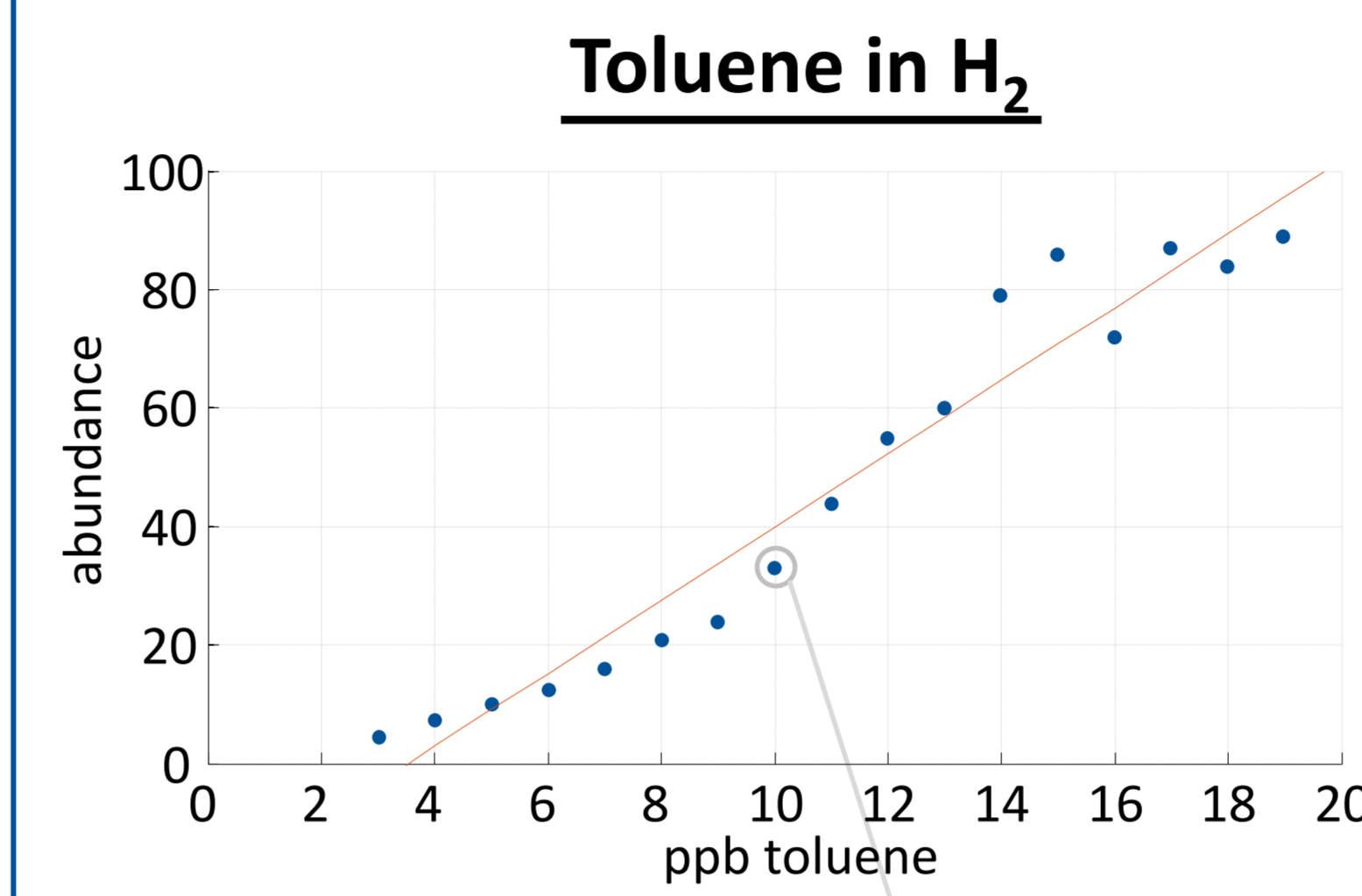
no need for a transfer stage

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

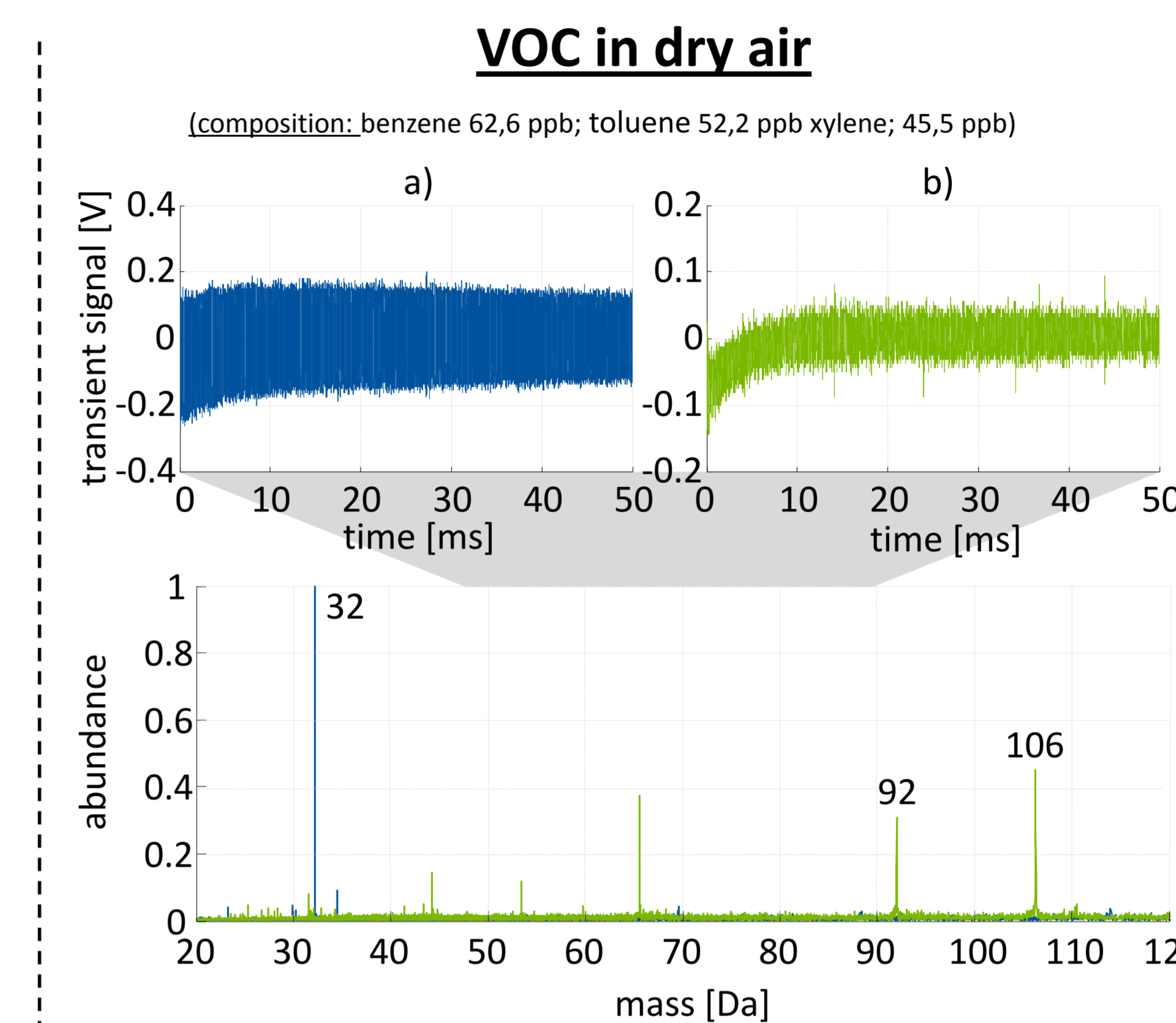
Dynamic Range



- 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

dynamic range of 10⁸ or more is achieved



Problem:

- N₂ and O₂ 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)

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 10⁸ 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

Sensitivity

Key component of Paul trap FTMS → charge amplifier

Requirements:

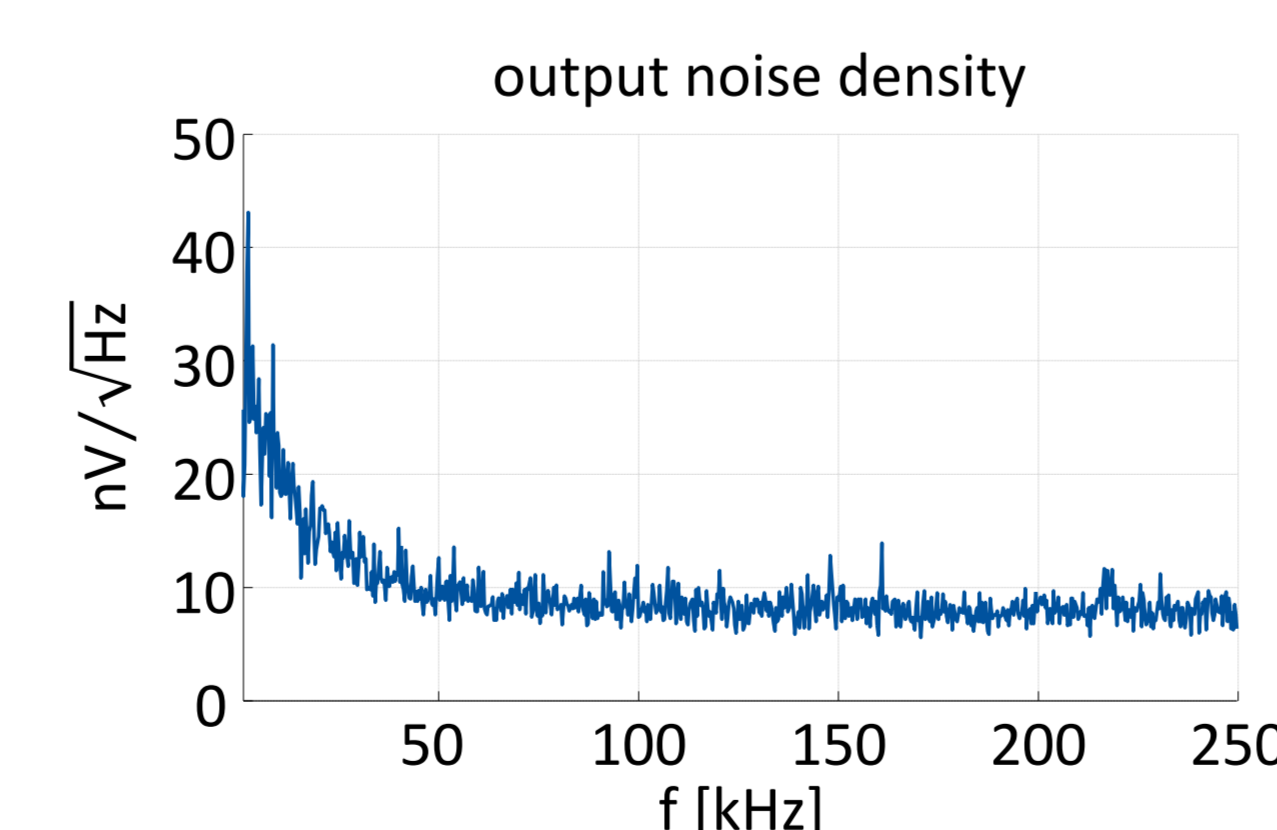
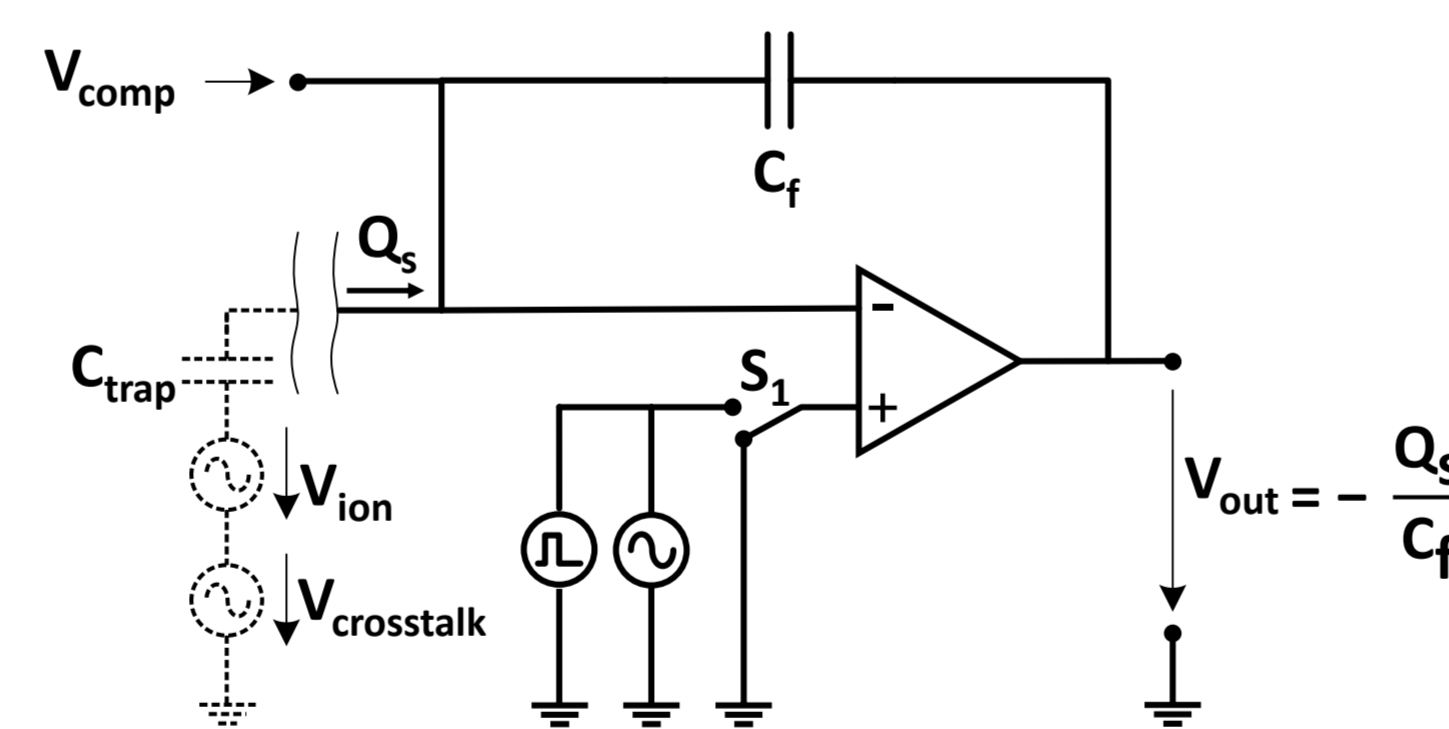
- Conversion of induction charges into scaled voltages without adding significant noise
- Distortion-free transfer of ejection & excitation waveforms to end-cap electrodes

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 V_{comp}
- Trapping frequency 1 MHz, ion frequency range 0-250 kHz



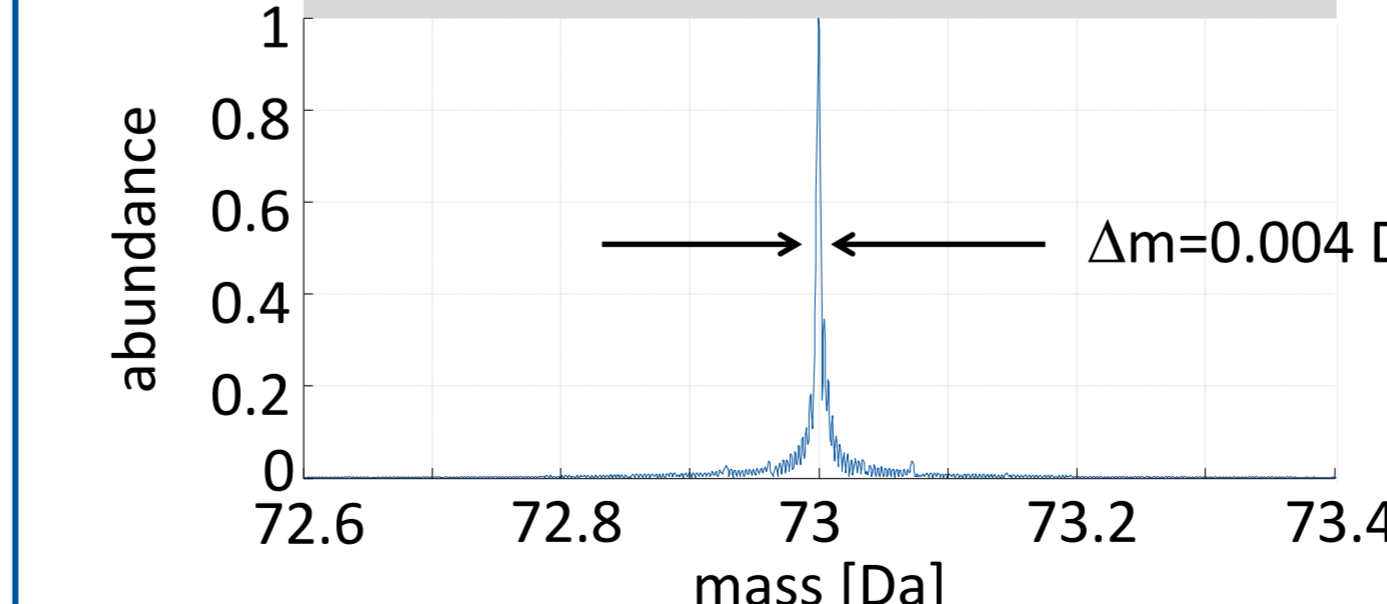
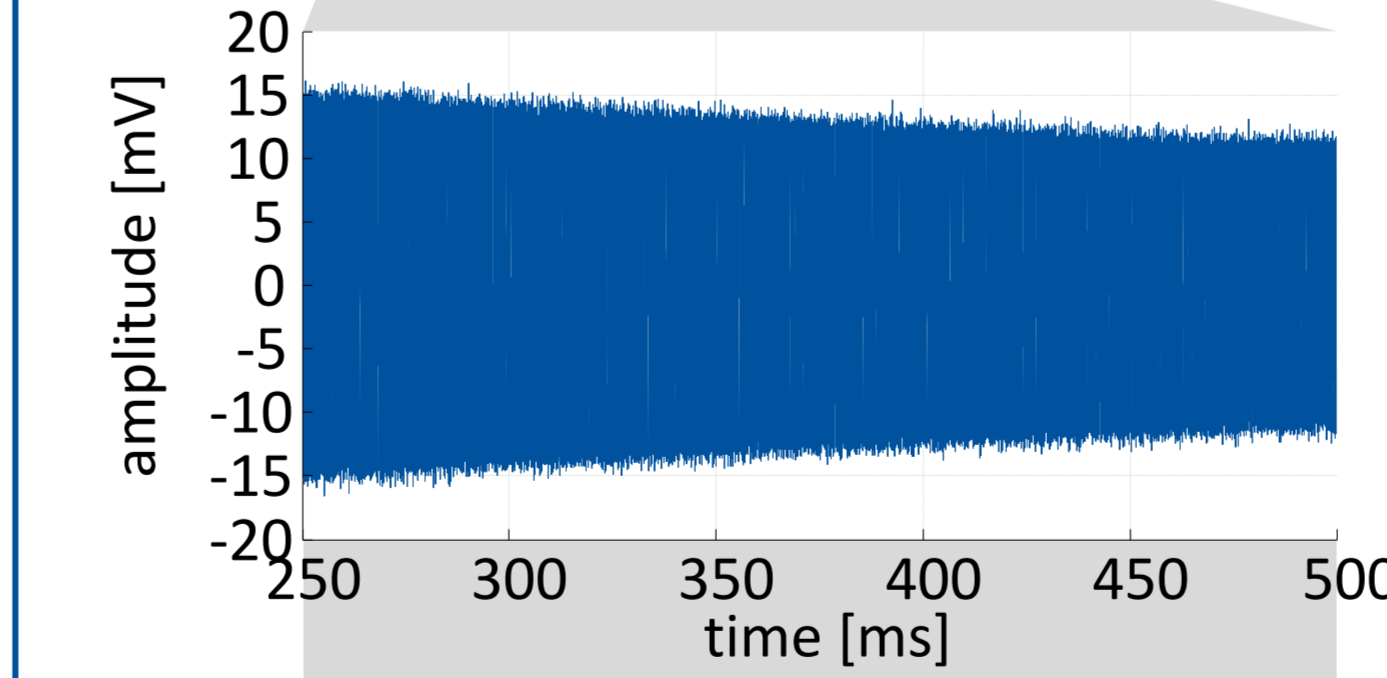
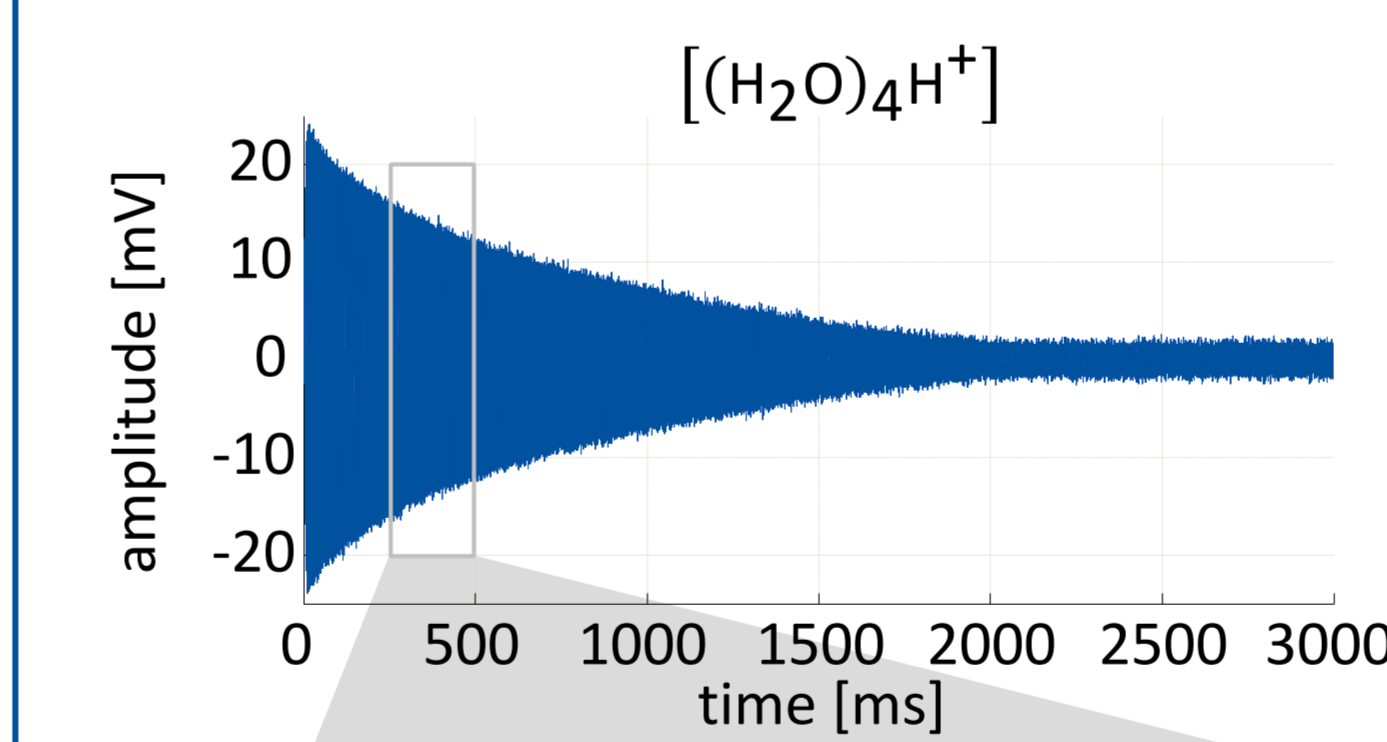
- Charge corresponding to the measured noise level is given by:

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

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

→ $\approx 4.5 \cdot 10^{-19} \text{ As} \lesssim N \cdot e = 3 \text{ elementary charges!}$

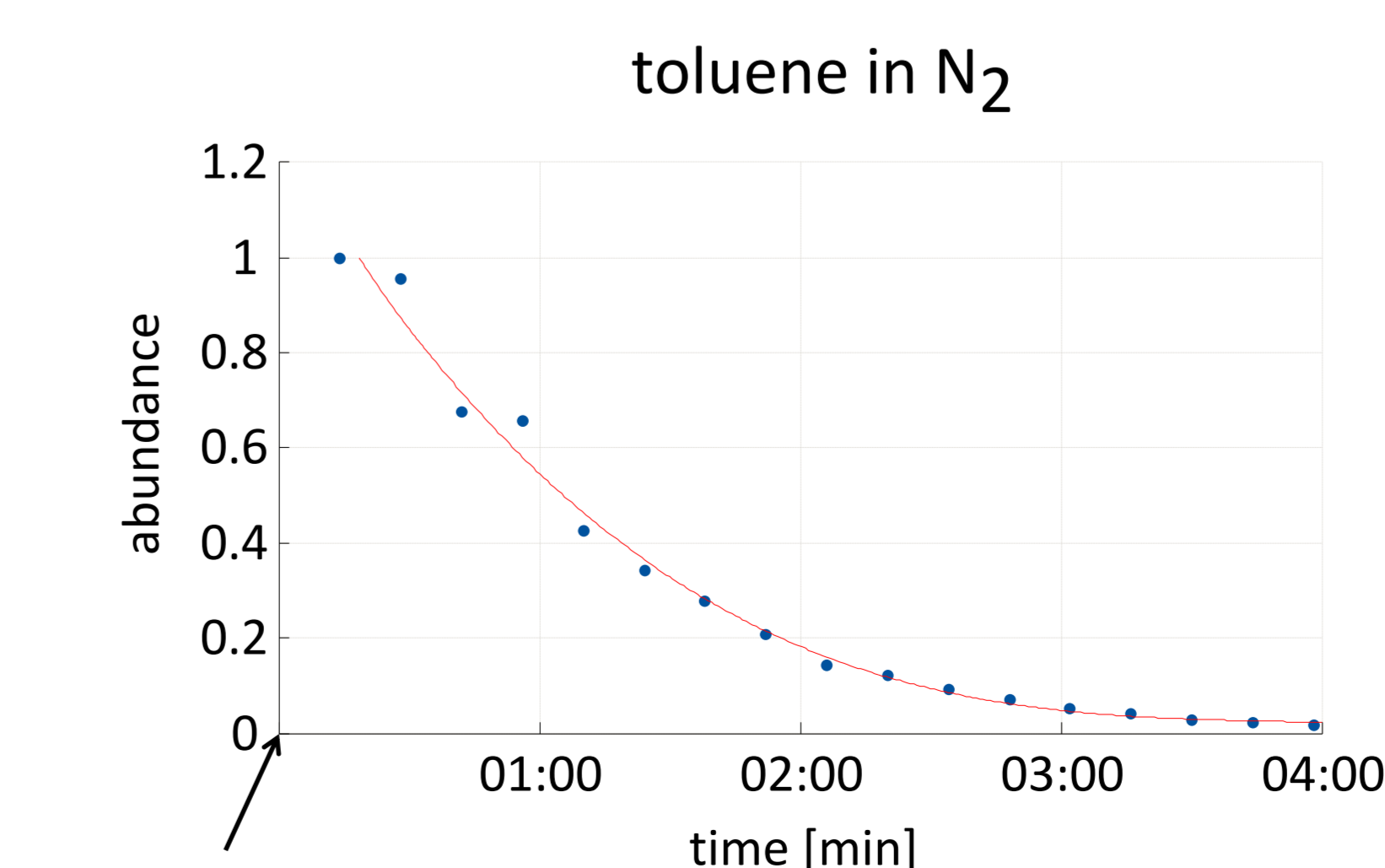
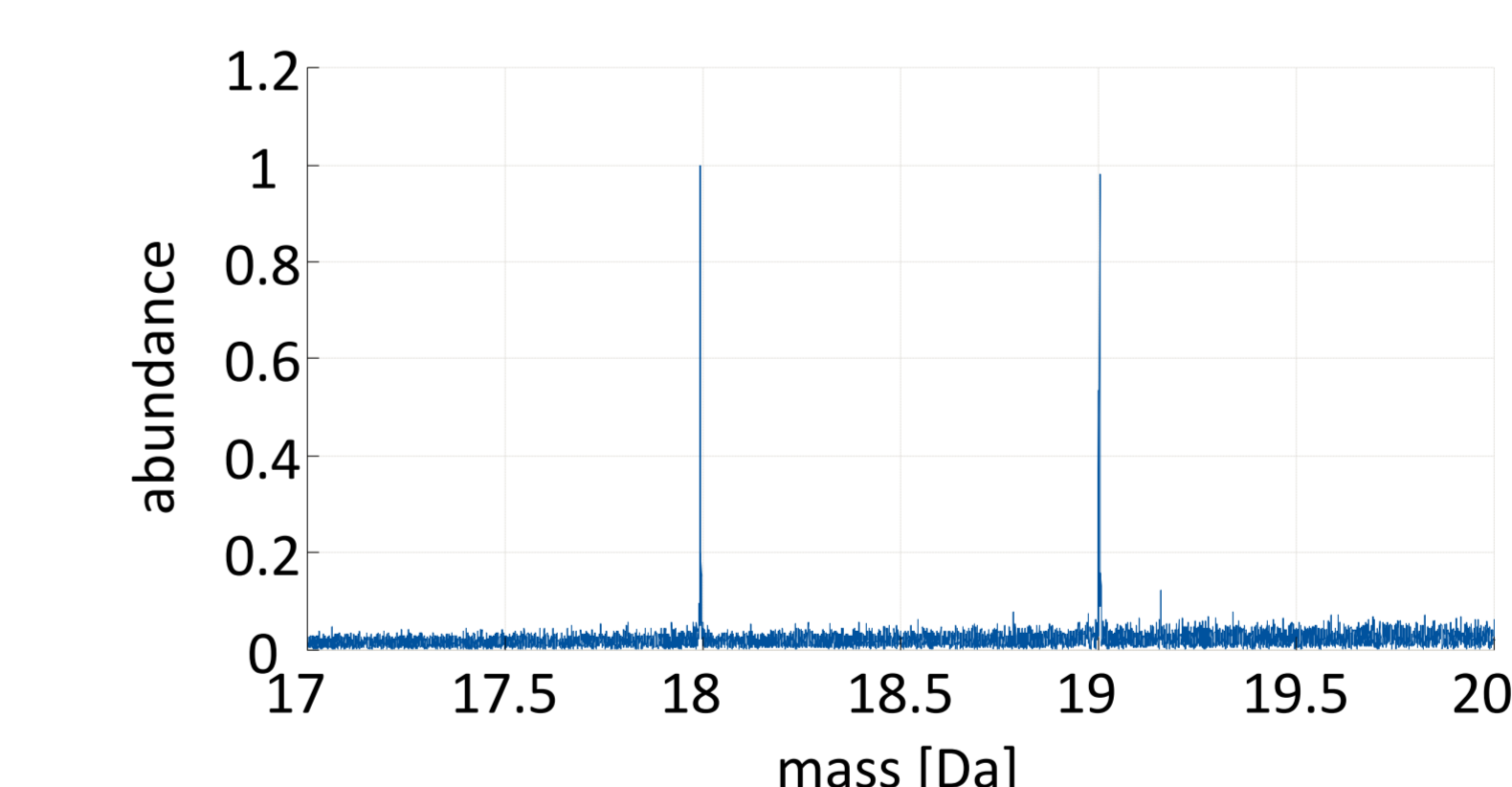
Resolution / Storage



- 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



gas inlet and ionization

References

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