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-photon ionization with UV laser (FHS NaD/YAG, 266 nm)

Analysts: VOCs, toluene in N<sub>2</sub>, toluene in H<sub>2</sub>

Experimental Setup

1 MHz

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<sub>2</sub>

Sample chamber pressure 18.5 mbar
- Decreasing toluene concentration
- RF voltage ca. 700 V<sub>pp</sub>
- Trapping field is deactivated temporally, before ionization → no accumulation of ions
- SNR at 10 ppb still at 50 dB

VOC in dry air

Problem:
- N<sub>2</sub> and O<sub>2</sub> 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<sup>6</sup> or more is achieved

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
  - S 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<sup>6</sup> is obtained
- High resolution in single-shot measurements
  - At low pressures of about 10<sup>-6</sup> mbar the measured ion oscillation times reach several seconds, resolution exceeding 100000 is feasible

Future aspects:
- Improved mass accuracy / radio-frequency amplitude measurement technique

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References


Appendix

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 DP-amp with ultra low noise input stage
- Adding of an anti-phase compensation signal to amplifier input \( V_{\text{amp}} \)
- Trapping frequency 1 MHz, ion frequency range 0-250 kHz

Resolution / Storage

Residual gas measurement at < 5 · 10<sup>-4</sup> mbar

SNR at 10 ppb still at 50 dB

Future aspects:
- Improved mass accuracy / radio-frequency amplitude measurement technique