Development of a compact multiple-ionization-stage TOF mass analyzer system for trace component monitoring within chemically challenging process gas matrices

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Introduction

Challenge

Construction of a compact mass-analyzer for qualitative and quantitative analyses:

- in N_2 as process gas matrix but also in challenging process gas matrices, e.g. H_2
- allowing a wide process gas pressure range between 10^{-2} to 10^3 mbar
- usage of several filament-free ionization methods
  - laser multi-photon ionization
  - single-photon ionization
  - chemical ionization
- quantitative analyses:
  - determination of the limit of detection
  - high dynamic range over six orders of magnitude
- qualitative analyses:
  - signal distribution depending on
    - the process gas
    - the chosen ionization method

Distribution of Ion Acceptance (DIA)

DIA measurements allow an optimization of the ion source performance and represent a powerful tool for mechanistic examinations of ion-molecule reactions. [1]

Methods

Experimental Setup

Mass Spectrometer: CTOF (TOFWerk Swi)

- Custom transfer stage with an ionization chamber operating at intermediate pressures up to 1 mbar
- Different filament-free ionization methods, in either continuous or pulsed mode
- Mass range: 1 – 5000 Da
- Resolution: 1000

Ionization Methods:

- Laser: quadrupled Nd:YAG (266 nm) for two-photon ionization
- Single-photon ionization: VUV-EBEL-lamp (128 ± 10 nm)
- Chemical ionization: induced by gas discharge

Gases:

- Custom gas mixtures [toluene in N_2 (500 ppmV; 10 ppmV and 10 ppbV) or toluene in H_2 (10 ppmV and 500 ppbV)]
- Dynamic dilution stage (up-to 1:1000)

For DIA measurements either laser or single-photon ionization is used (spatially resolved ionization)

Experimental Setup

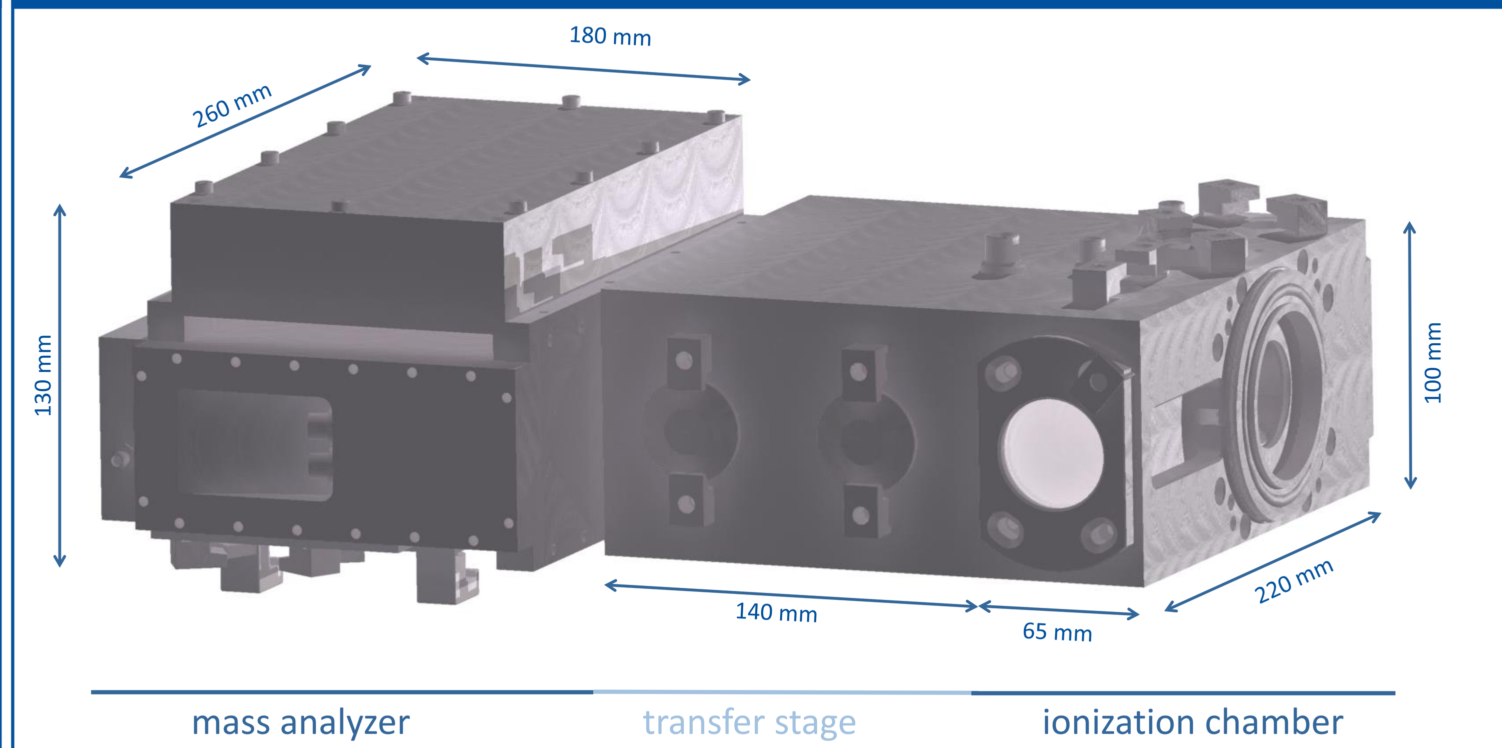


Figure 1: TOFWerk CTOF with custom ion transfer stage and shoe box sized analyzer

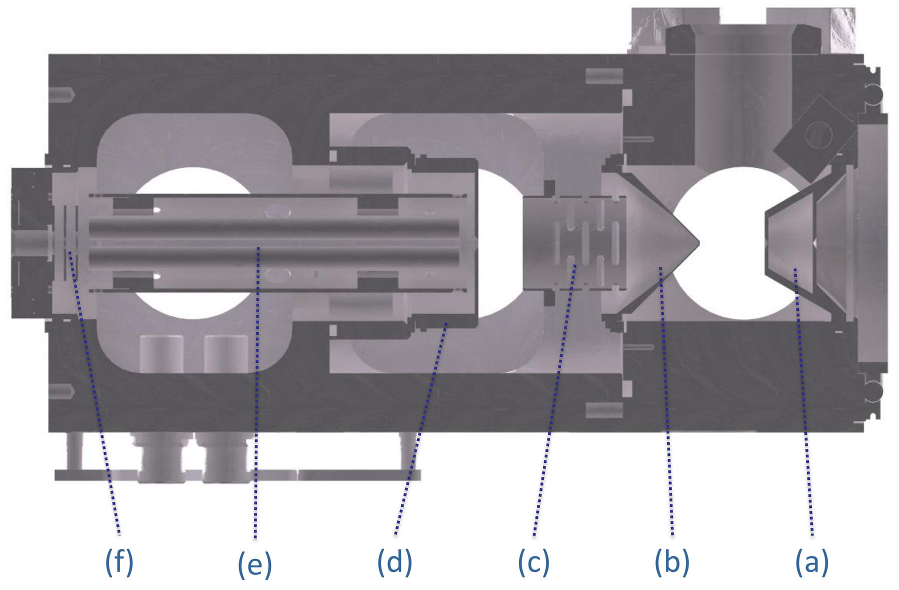


Figure 2: Ionization chamber and transfer stage with ion guiding elements. (a) sampler, (b) skimmer, (c) Einzel-lens, (d) filter orifice, (e) quadrupole, (f) lens system

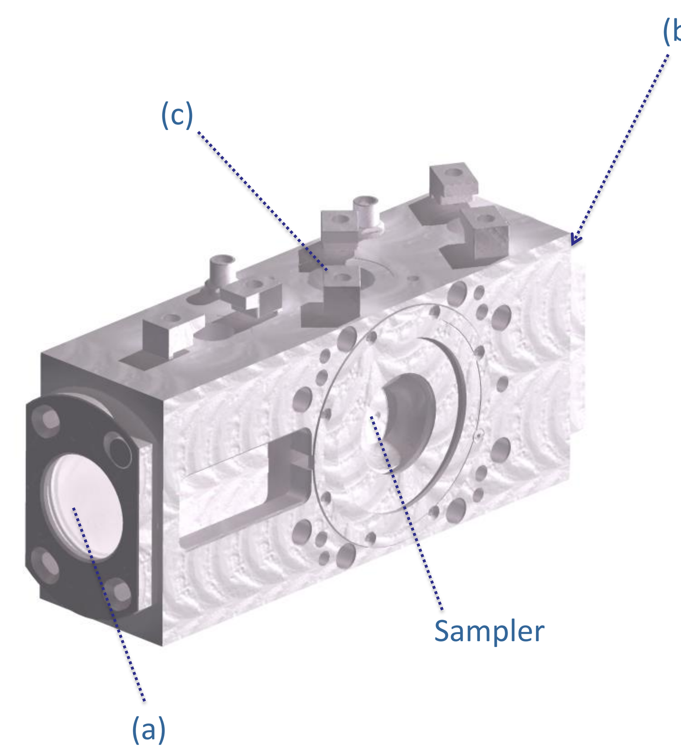


Figure 3: Ionization chamber (operating @ approx. 1 mbar),

a) equipped with MgF_2 windows for laser ionization
b) the VUV-EBEL-lamp is attached through a mirror system from the far side, replacing one of the windows
c) an opening located perpendicularly to the sampler-skimmer axis serves as gas discharge source mount

Specifications/Performance of the Setup

Best performance of the setup was obtained with gas discharge induced chemical ionization:

✓ detection limit 25 pptV with S/N 6
✓ high dynamic range over six orders of magnitude

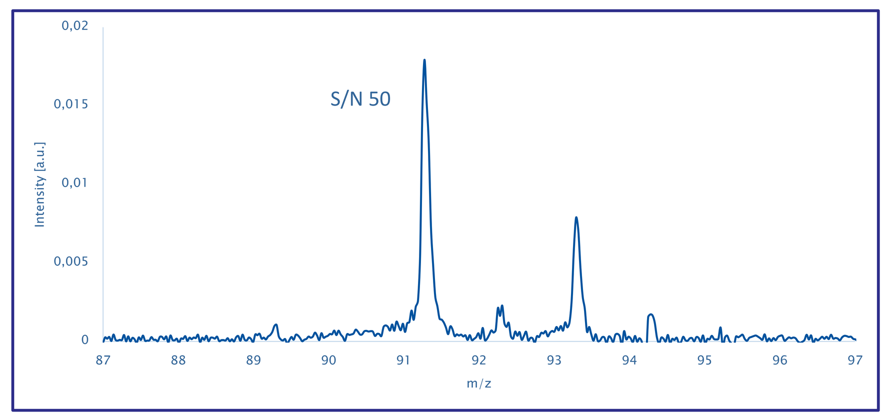


Figure 4: Mass spectrum of 184 pptV Toluene in H_2
Average of 60 s integration time leads to S/N 50 @ m/z 91

Laser ionization and single-photon ionization:

✗ higher detection limits
✗ smaller dynamic range
✓ but spatially resolved ionization possible

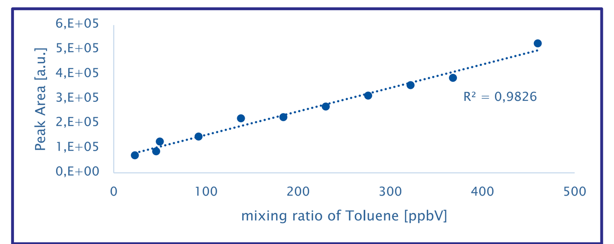


Figure 5: Peak area of m/z 91 and 93 depending on the toluene mixing ratio, dynamic range between 25 and 450ppbV

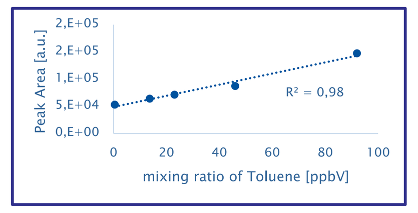


Figure 6: Dynamic range between 0.5 – 100 ppbV

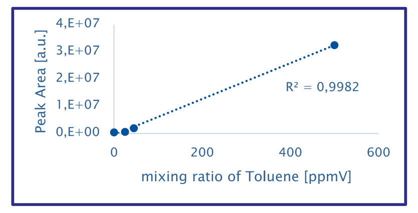


Figure 7: Dynamic range between 0.5 – 500 ppmV

Distribution of Ion Acceptance

Figure 8-10: Ion guiding voltages were optimized for maximum signal intensities while ionizing close to the skimmer.

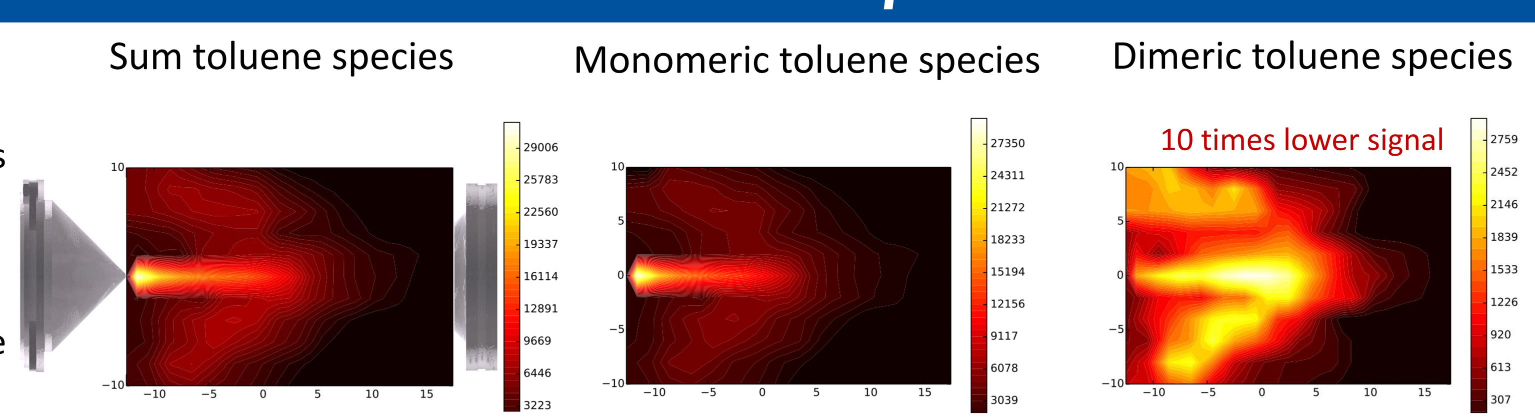
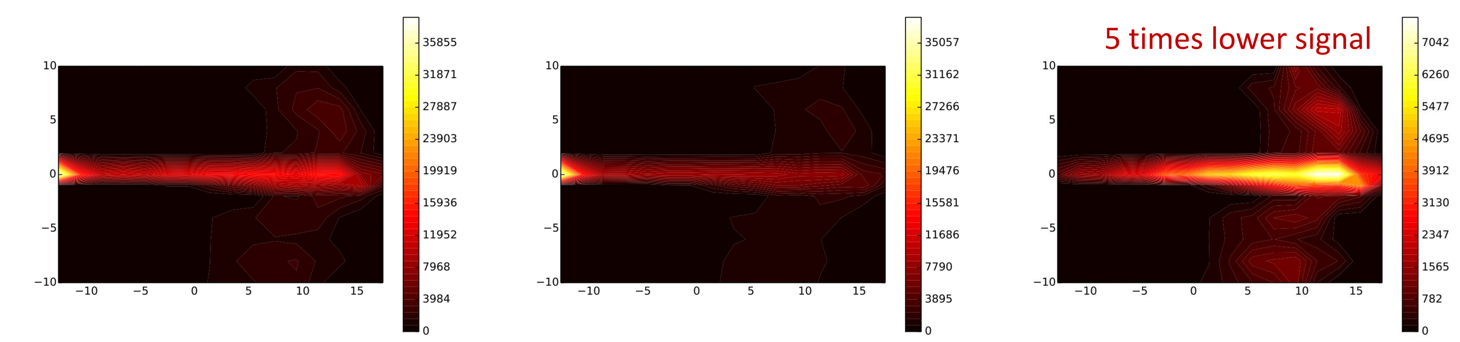


Figure 11-13: Ion guiding voltages were optimized for maximum signal intensities while ionizing close to the sampler.

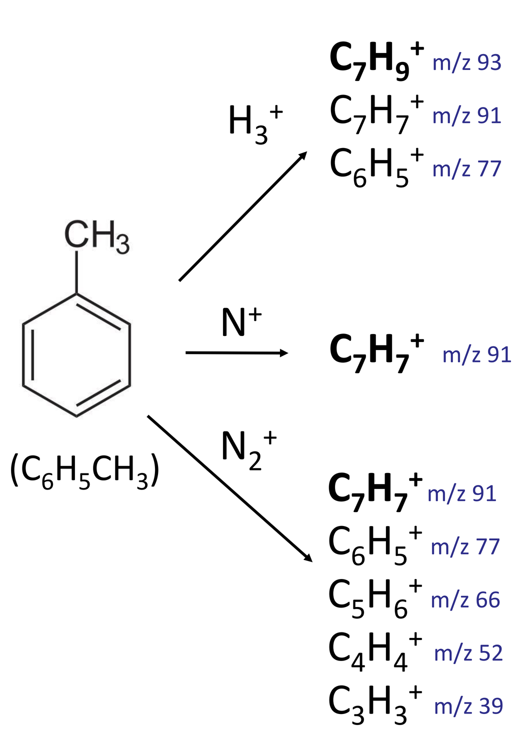


Toluene – Chemistry: Signal distribution depending on ionization method and process gas

As expected, the chosen ionization method determines the obtained analyte ion distribution.

Light-induced ionization with either the VUV-EBEL-lamp or the Nd:YAG UV laser leads to direct ionization of the analyte. In case of toluene, the primary radical cation is observed, as expected.
→ $[C_6H_5CH_3]^{\cdot+}$

Chemical ionization is induced with a point-to-plane gas discharge. The reactant ions are generated depending on the carrier gas and background species present.
→ In N_2: N^+, N_2^+, N_4^+; H_2O^+, $[H(H_2O)_n]^+$ (background water, n = 1-5)
→ In H_2: H_3^+; $[H(H_2O)_n]^+$ (background water, n = 1-5)
Subsequent ion-molecule chemistry leads to the formation of analyte ions as shown on the right.



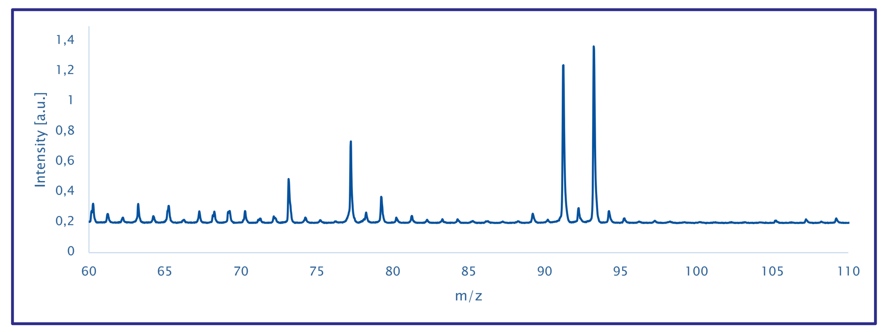


Figure 14: Mass spectrum of toluene in H_2, approx. 1 ppmV, chemical ionization

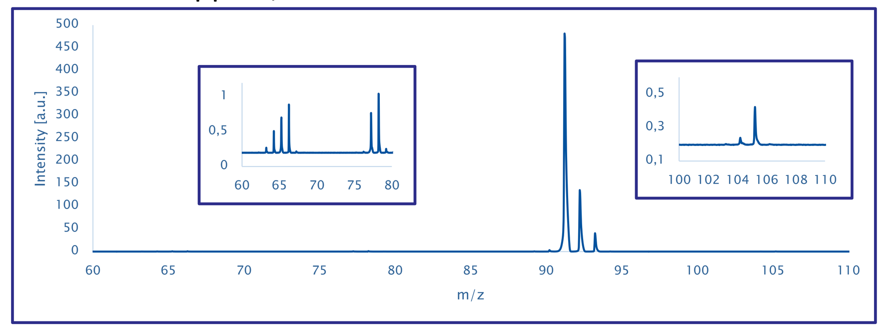


Figure 15: Mass spectrum of toluene in N_2, approx. 20 ppmV, chemical ionization

Further reactions of ionized toluene species with neutral toluene:

$$C_6H_5CH_2^+ + C_6H_5CH_3 \rightarrow C_7H_{11}^+ \quad m/z\ 95$$
$$C_6H_5CH_2^+ + C_6H_5CH_3 \rightarrow C_{14}H_{15}^+ \quad m/z\ 183$$
$$C_6H_5CH_2^+ + C_6H_5CH_3 \rightarrow C_8H_9^+ \quad m/z\ 105$$
$$C_7H_8^+ + C_6H_5CH_3 \rightarrow C_7H_9^+ \quad m/z\ 93$$
$$C_7H_9^+ + C_6H_5CH_3 \rightarrow C_7H_7^+ \quad m/z\ 91$$

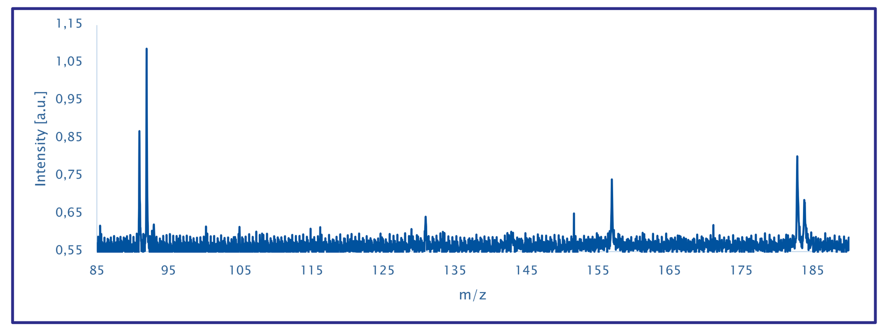


Figure 16: Mass spectrum of toluene in N_2, approx. 50 ppmV, laser ionization

Conclusions

Setup

- A TOFWerk CTOF is successfully equipped with an ion notch filter and a custom ion transfer stage.
- The ion notch filter strongly suppresses selected m/z-ranges to improve the transmission efficiency of target analyte ions.
- The ionization chamber allows usage of several filament-free ionization methods, such as two-photon laser ionization, single-photon ionization, and chemical ionization. The latter is driven by a gas discharge, which operates at intermediate pressures of approx. 1 mbar.
- With selected orifice sizes, sample pressures in the range 10^{-2} to 10^3 mbar are tolerated.

Ion Chemistry

- Depending on the ionization method employed and the process gas present, different reactant and/or analyte ions are generated.
- These ions follow distinct and well defined reaction path-ways, which are governed by the chemical nature of the process gas matrix.

DIA measurements

- Imaging the distribution of ion acceptance allowed the optimization of source and ion transfer parameters.
- Depending on the ionization *position* different analyte ion populations were observed, providing a deep insight into the ion-molecule chemistry prevailing in the sampler-skimmer region.

Literature

[1] Lorenz, Schiewek, Brockmann, Schmitz, Gäb, Benter; The Distribution of Ion Acceptance in Atmospheric Pressure Ion Sources: Spatially Resolved APLI Measurements; J. Am. Soc. Mass Spectrom. 2008, 19, 400-410.
[2] Anicich; An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics; JPL-Publication-03-19, 2003, Pasadena, CA, USA.
[3] Milligan, Wilson, Freeman, Meot-Ner, McEwan; Dissociative Proton Transfer Reactions of H_3^+, N_2H^+ and H_3O^+ with Acyclic, Cyclic and Aromatic Hydrocarbons and Nitrogen Compounds, and Astrochemical Implications; J. Phys. Chem. A, 2002, 106, 9745-9755.
[4] Bartmess; Gas Phase Ion Chemistry of 5-Methylene-1,3-cyclohexadiene (*o*-Isotoluene) and 3-Methylene-1,4-cyclohexadiene (*p*-Isotoluene); J. Am. Chem. Soc. 1982, 104, 335-337.

Acknowledgement

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