

Progress in the development of a plasma based CI-source for GC-MS

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Introduction

Chemical ionization mass spectrometry (CI-MS) is a technique to generate analyte ions via ion-molecule reactions. Within the GC-MS application primary reactant ions are commonly produced by electron ionization (EI) of a reagent gas. A major disadvantage of this setup is the short operative lifetime due to filament corrosion and ion source fouling induced by reagent ions.

The chemical ionization setup in this contribution uses a hydrogen plasma, which leads to the direct production of H_3^+ , one of the strongest known gas phase acids. Subsequent quantitative transformation into other reagent ions allows less exothermic protonation of analyte molecules to obtain deliberately simplified mass spectra, often with very low loss of signal due to minimized fragmentation, which can be used for quantitative analysis of mixtures.

Recently, we introduced this custom discharge chemical ionization source [1]. In this contribution, we present an advanced version of this setup for GC-MS applications.

Methods

MS HTOF with custom ion transfer optics (TOFWERK AG, Thun, Switzerland).

Ion Source Custom low pressure RF discharge source.

Gases Nitrogen 5.0, methane 2.5, ethane 3.5, isobutane 2.5 (Messer Group GmbH, Krefeld, Germany).

Hydrogen 6.0, Hydrogen Generator NMH2 Plus (Vici AG International, Schenkon, Switzerland)

All gases were used without further purification.

Analytes Custom analyte mixtures: α -pinene (98 %), o-xylene and anisole (99 %) in hexane (99+ %), decane (99 %) in dichloromethane (99.80 %) (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany)

All chemicals were used without further purification.

Gas Chromatograph 6890A (Agilent, Santa Clara, CA, United States) equipped with a custom made transferline, carrier gas He 5.0 (Messer Group GmbH, Krefeld, Germany) purified by a HP2 gas purifier (Vici AG International, Schenkon, Switzerland), manual injection.

Chemical Ionization Setup

Approach:

- Application of one of the strongest known gas phase acids, H_3^+ , as the main primary charge carrier.
- Subsequent quantitative transformation of H_3^+ into reagent ions (XH^+) for less exothermic analyte protonation.

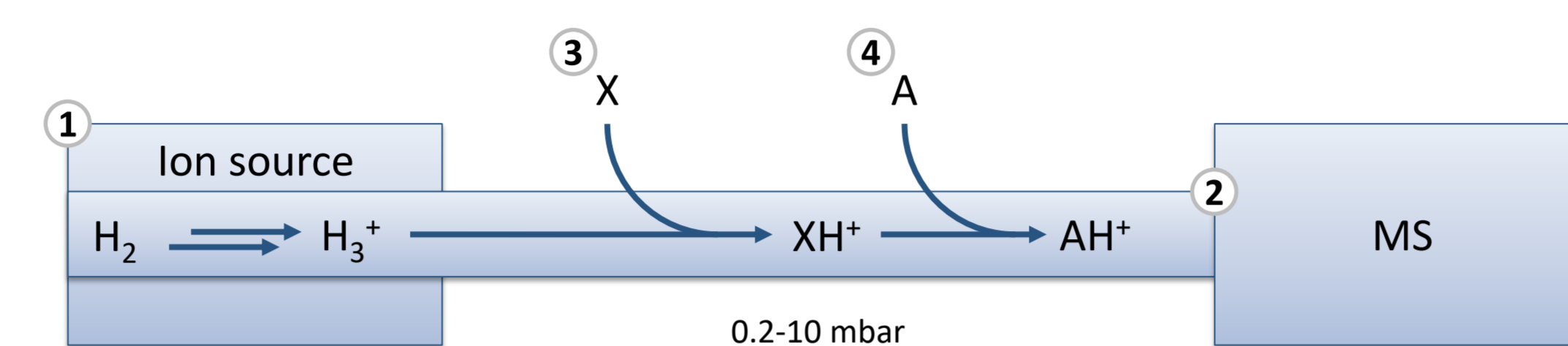


Figure 1: Scheme of the chemical ionization setup

A custom low-pressure RF discharge fed by a continuous hydrogen gas flow leads to the generation of H_3^+ ions within a hydrogen plasma (1). The discharge source consists of a helical coil resonator (HCR) providing the RF energy to sustain the discharge. The steady flow of primary reagent ions is transported through a glass tube into the first differentially pumped pressure region (0.2 – 10 mbar) of a Time-of-Flight mass spectrometer (2). A second gas flow containing a reactant gas (X) is introduced into the primary reagent ion flow to quantitatively convert H_3^+ to XH^+ as the active protonating species (3). The GC effluent containing the gaseous sample is injected directly into this reactant gas flow (4).

Reactant Gas Spectra

- Quantitative transformation of H_3^+ into reagent ions.
- Water contamination in nitrogen as reactant leading to significant proportion of H_3O^+ .

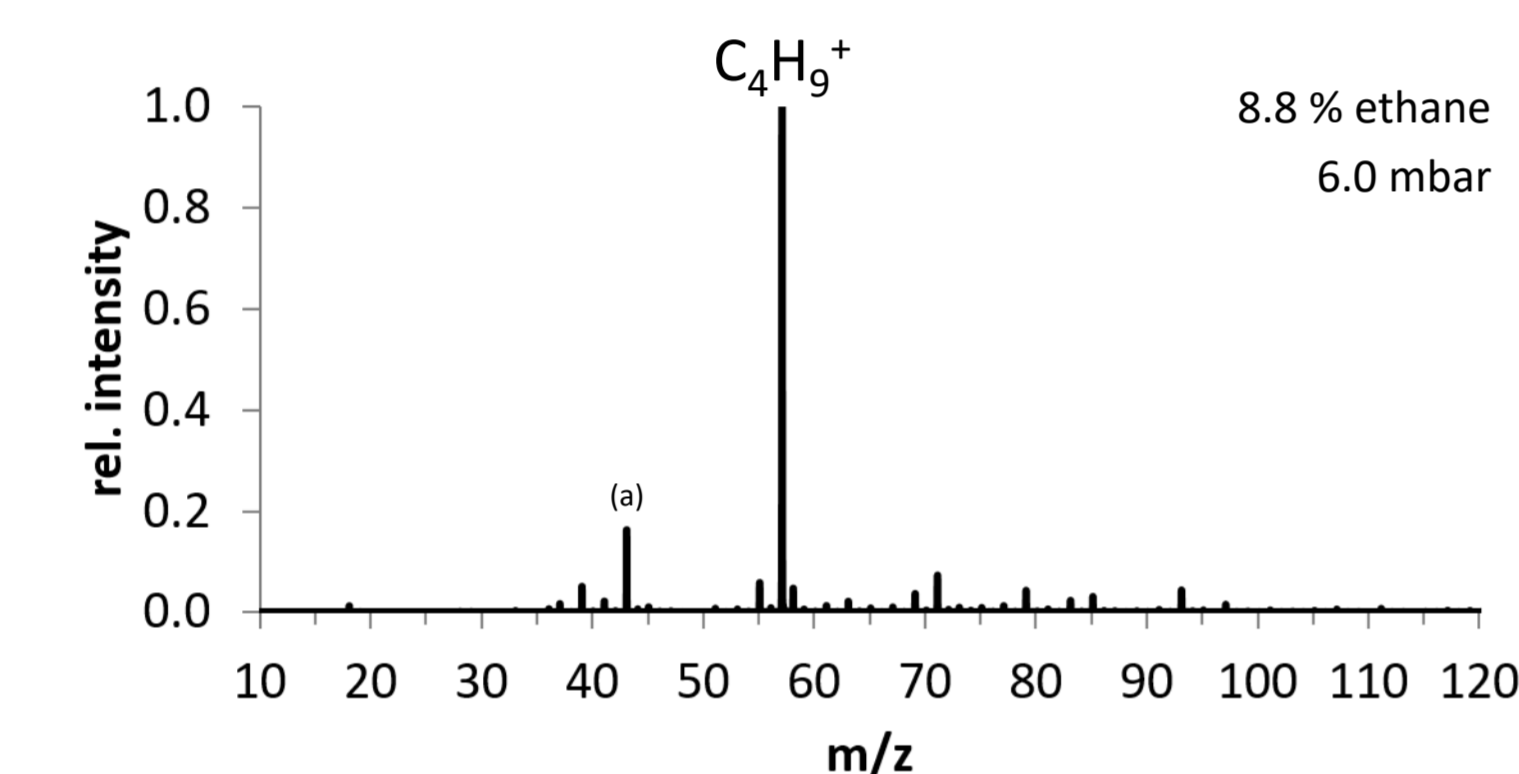


Figure 2: Mass spectrum with 8.8 % ethane as reactant gas.

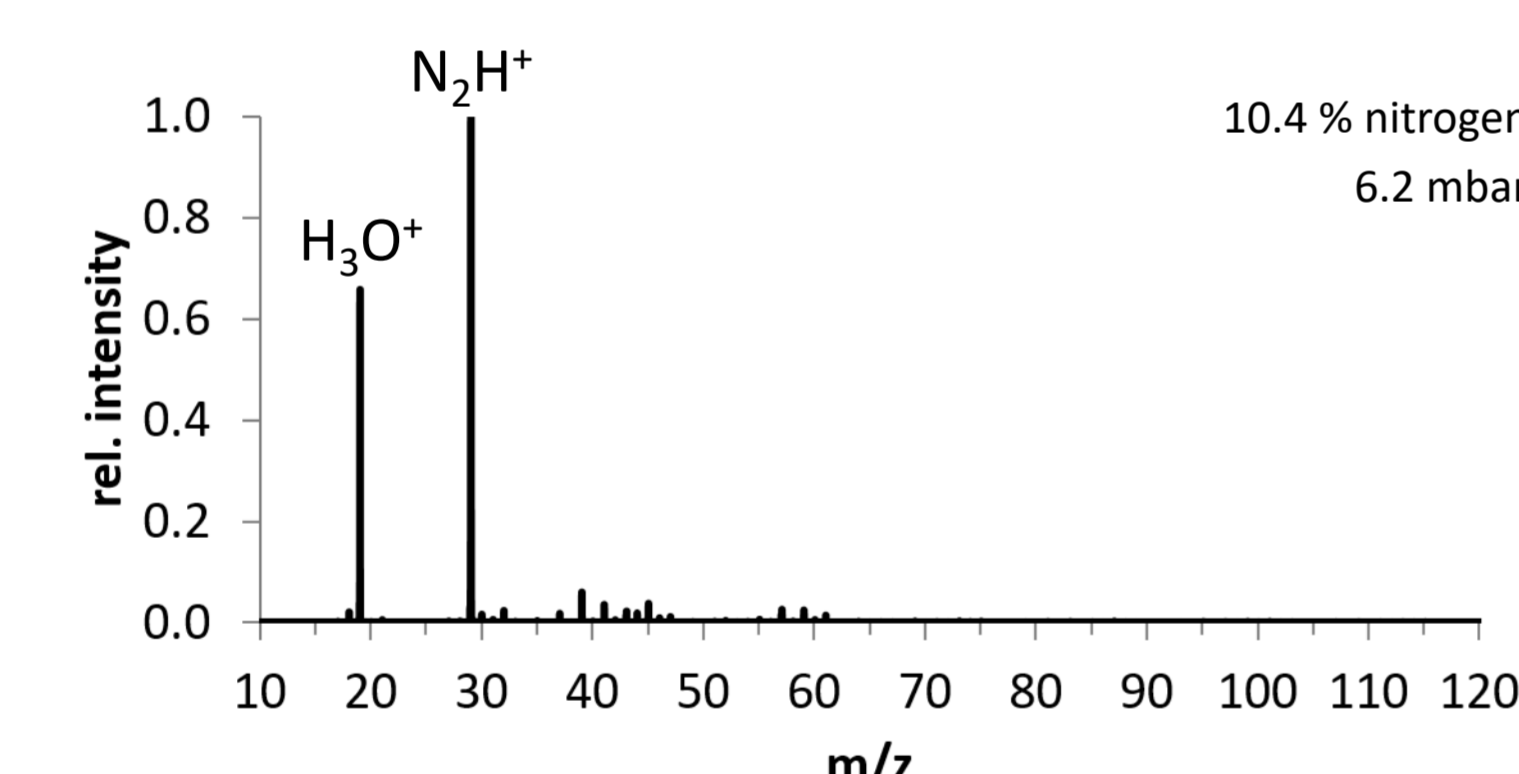


Figure 3: Mass spectrum with 10.5 % nitrogen as reactant gas.

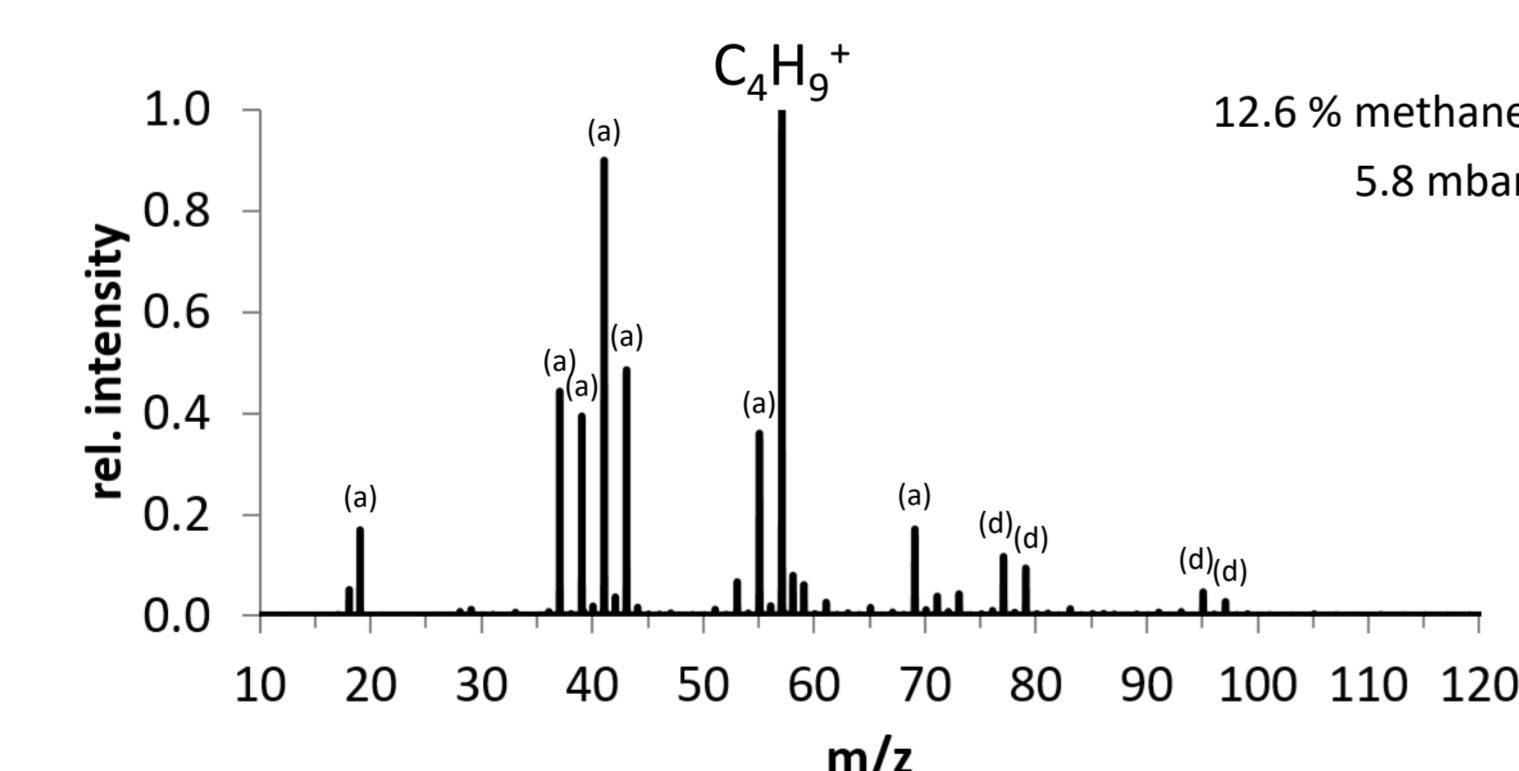


Figure 4: Mass spectrum with 12.6 % methane as reactant gas.

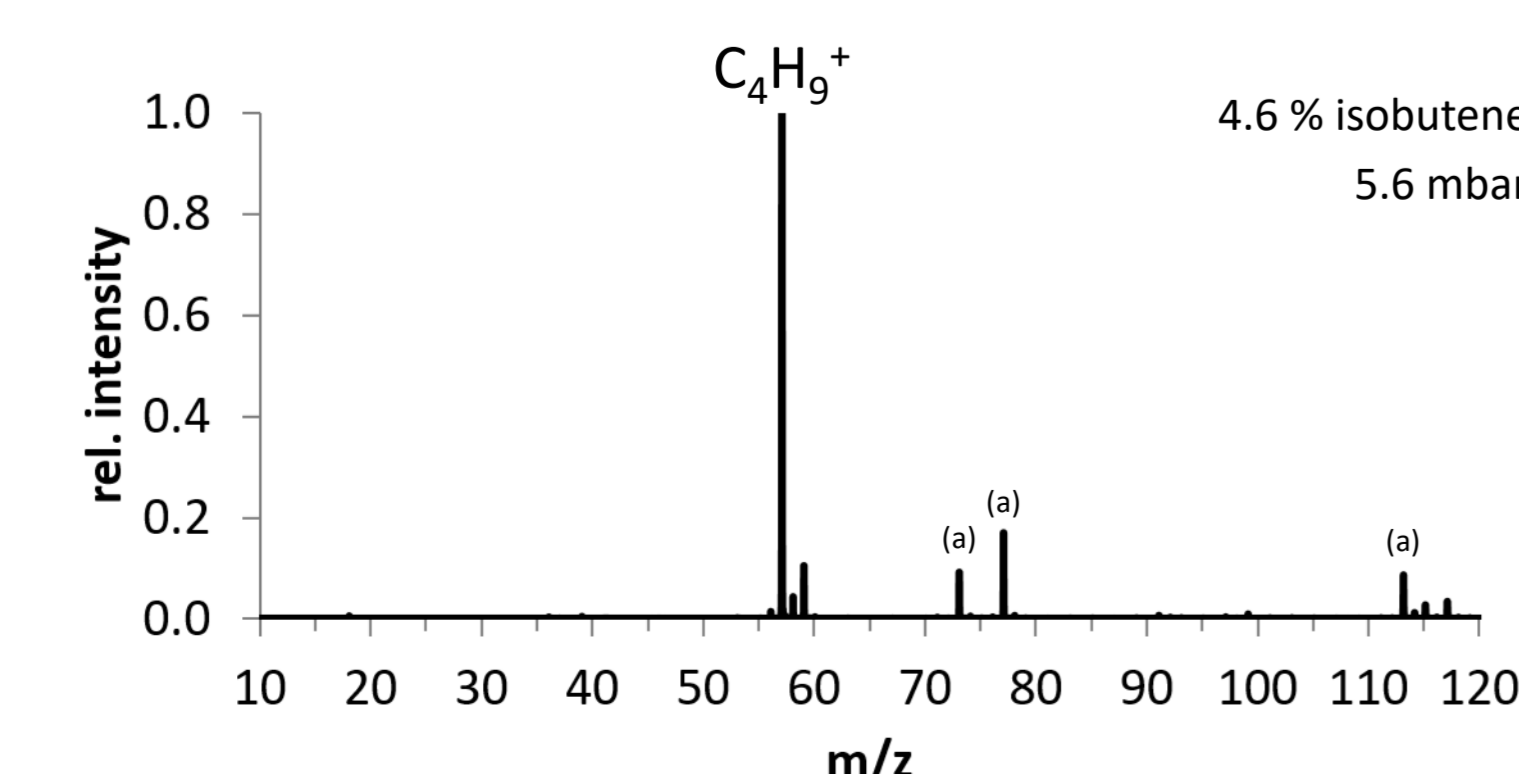


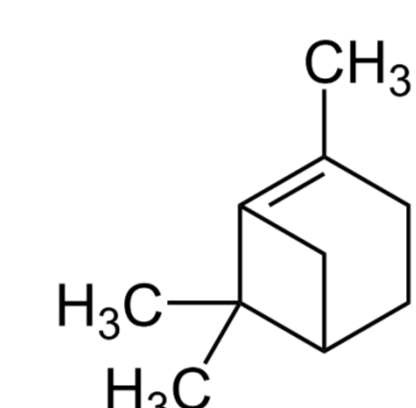
Figure 5: Mass spectrum with 4.6 % isobutane as reactant gas.

Analyte Spectra

Table 1: Proton affinities of relevant reagent gases, analytes and reactant gas ion species [2,3,4].

Analyte Proton Affinity [kJ/mol]	Hydrogen	Nitrogen	Methane	CH_5^+	Ethane	Isobutane	$C_2H_5^+$	Decane	Water	$C_3H_3^+$	o-Xylene	$C_4H_9^+$	α -Pinene
	422.3	493.8	543.5	552.3 [3]	596.3	677.8	680.3 [3]	690.4 [5]	691.0	779.5 [3]	791.2	819.7 [3]	878.6 [4]

α -Pinene



- Proportion of $[M+H]^+$ signal from 40 % with nitrogen and up to 87 % with isobutane as reactant gas.

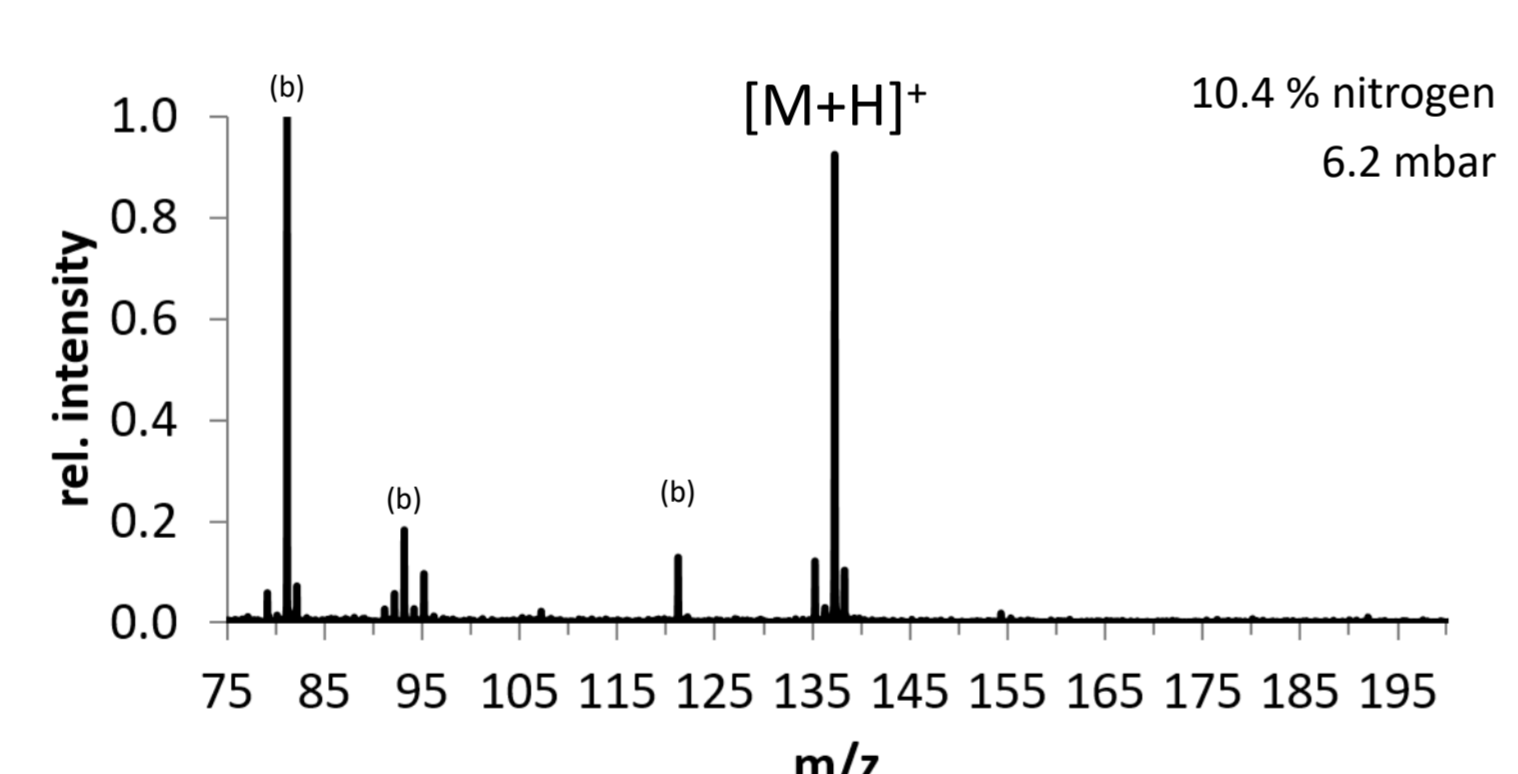


Figure 6: Background subtracted mass spectrum of α -pinene with 10.5 % nitrogen as reactant gas.

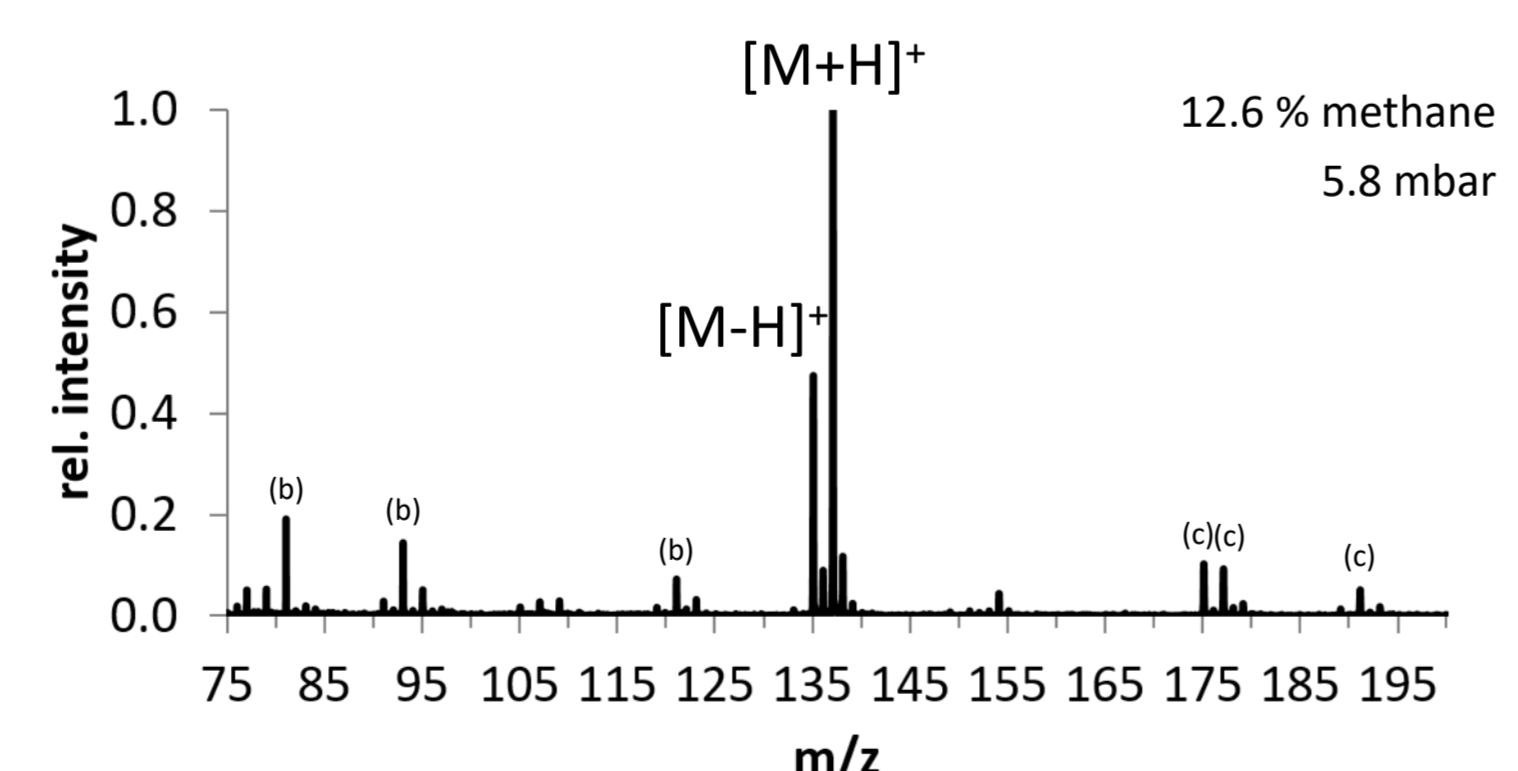


Figure 7: Background subtracted mass spectrum of α -pinene with 12.6 % methane as reactant gas.

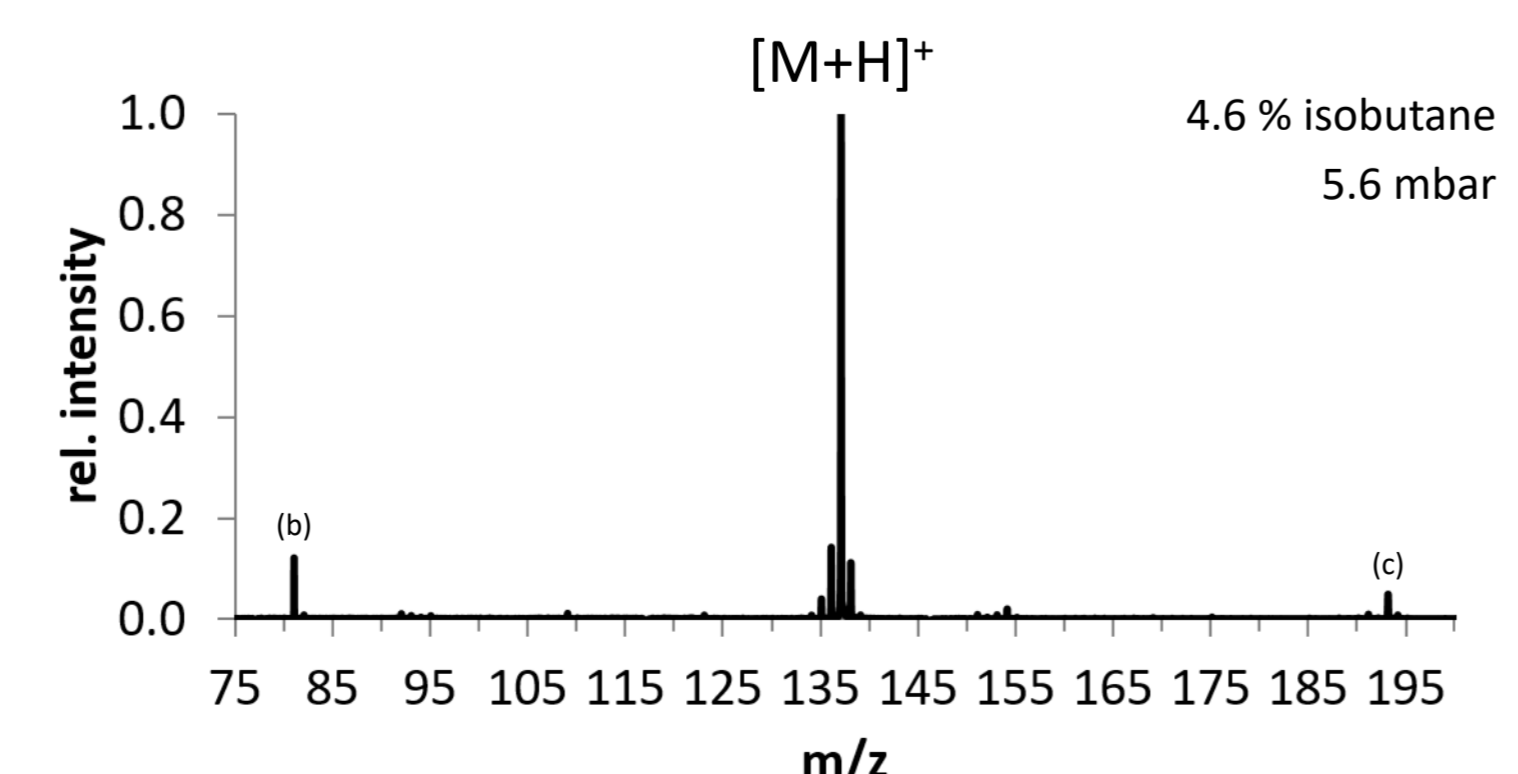
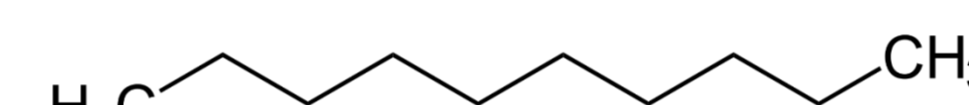


Figure 8: Background subtracted mass spectrum of α -pinene with 4.6 % isobutane as reactant gas.

Decane



- Proportion of $[M+H]^+$ signal from 36 % with nitrogen and up to 90 % with methane as reactant gas.

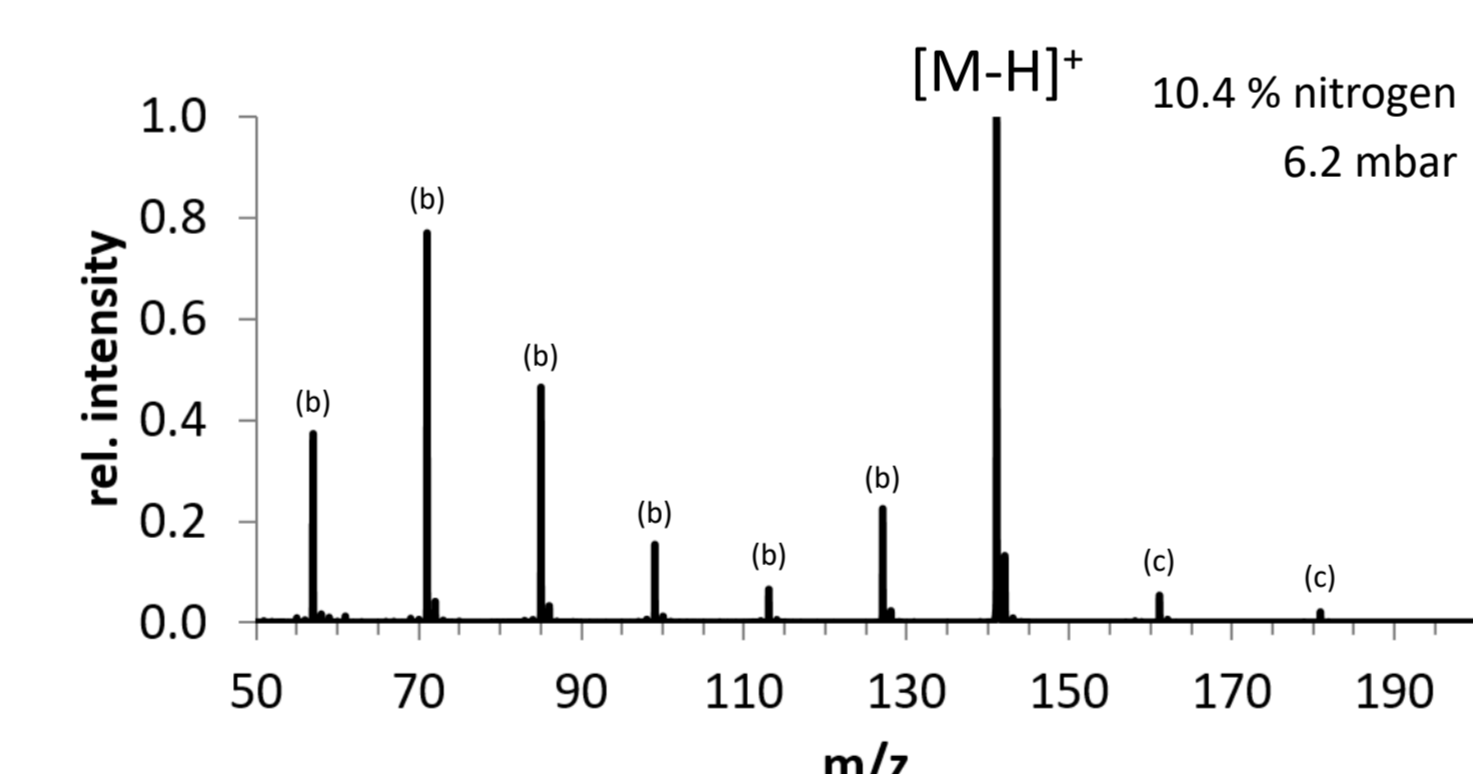


Figure 9: Background subtracted mass spectrum of decane with 10.5 % nitrogen as reactant gas.

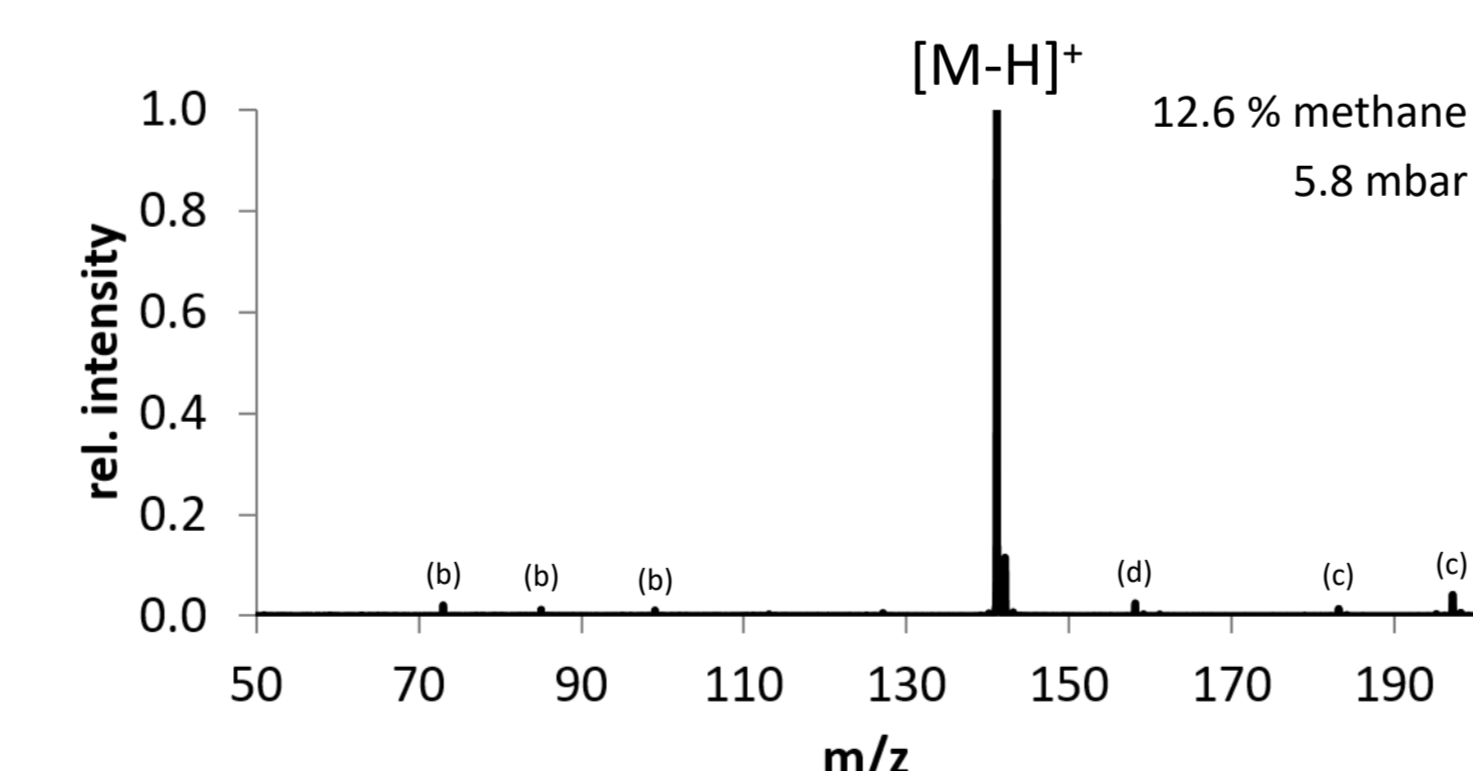


Figure 10: Background subtracted mass spectrum of decane with 12.6 % methane as reactant gas.

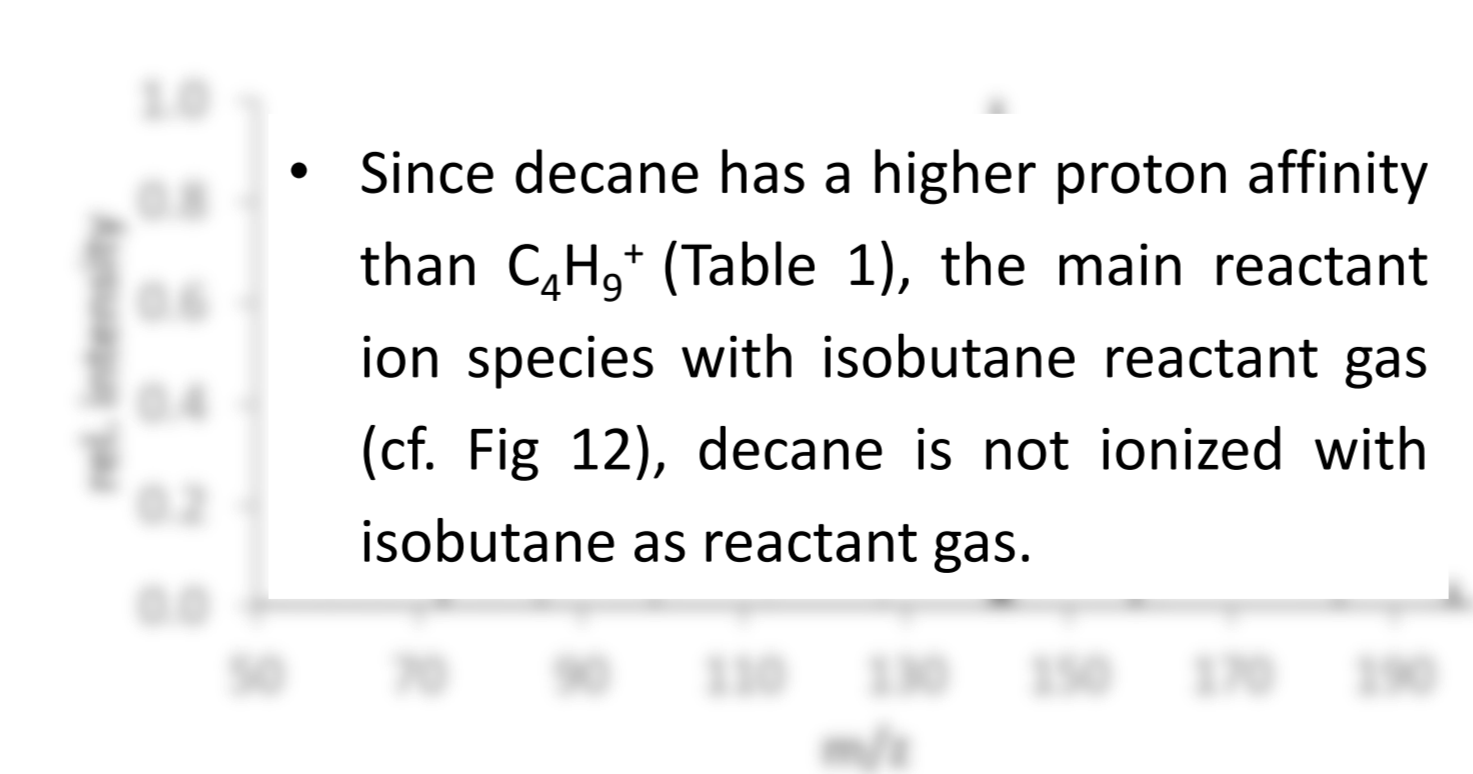


Figure 11: Background subtracted mass spectrum of decane with 4.6 % isobutane as reactant gas.

Pressure Dependency

- Reactant ion species are shifted to higher alkane species in form of $C_nH_m^+$ ions with increasing ion source pressure.
- With methane as reactant gas, $C_3H_3^+$ is the main ion species.
- With isobutane, $C_4H_9^+$ is the main ion species.

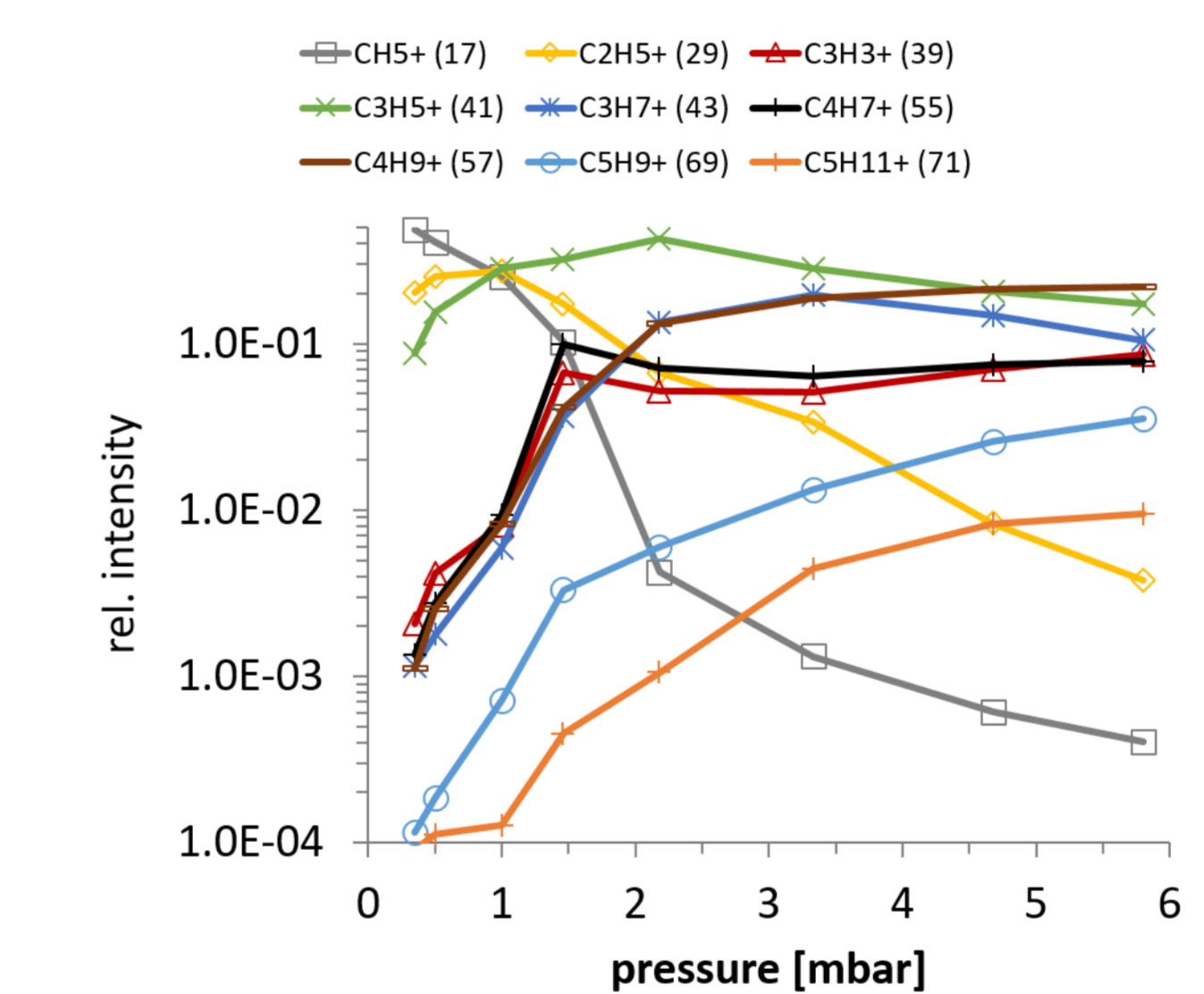


Figure 11: Pressure dependency of methane reactant ion species (TIC normalized).

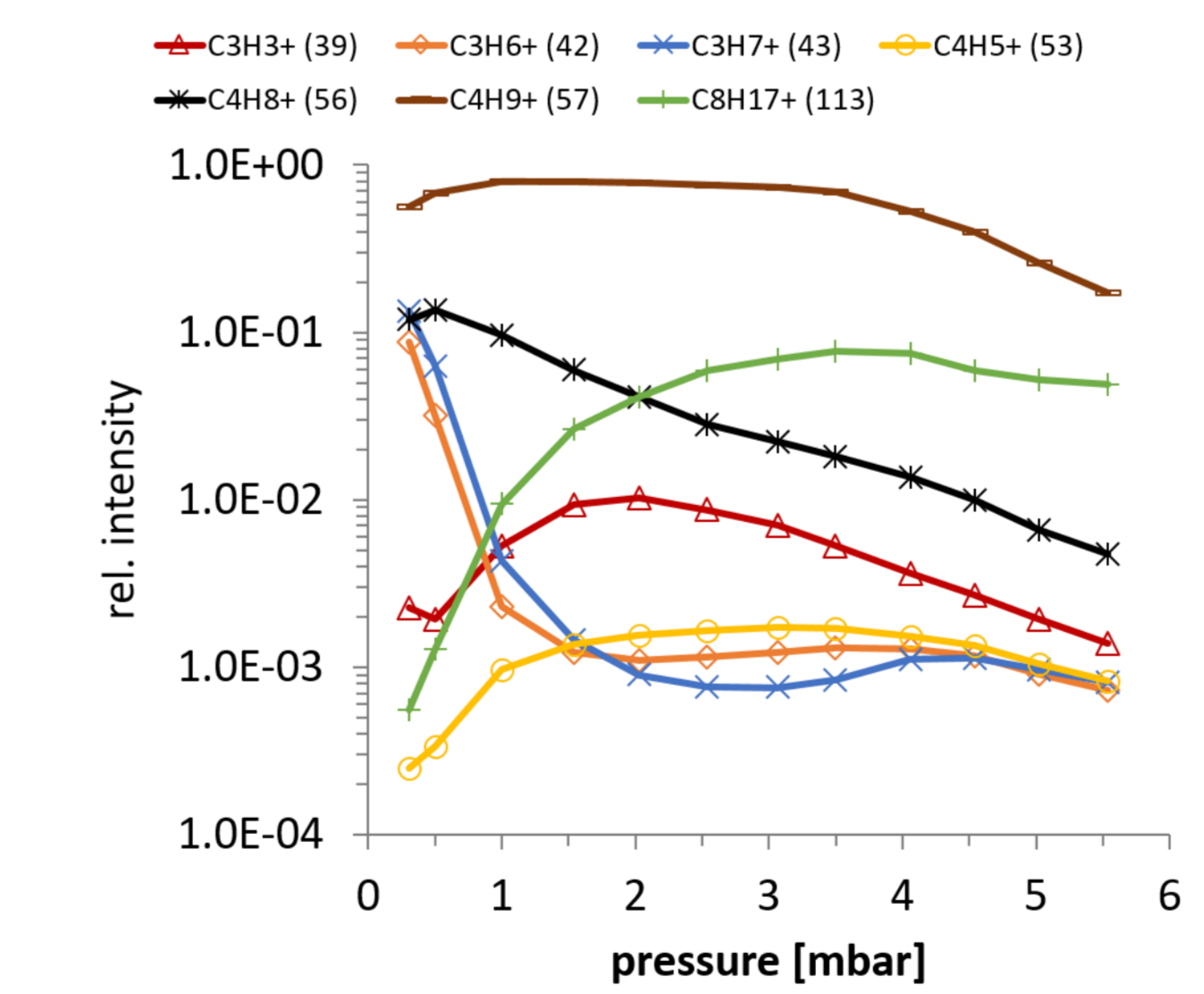


Figure 12: Pressure dependency of isobutane reactant ion species (TIC normalized).

Long Term Stability

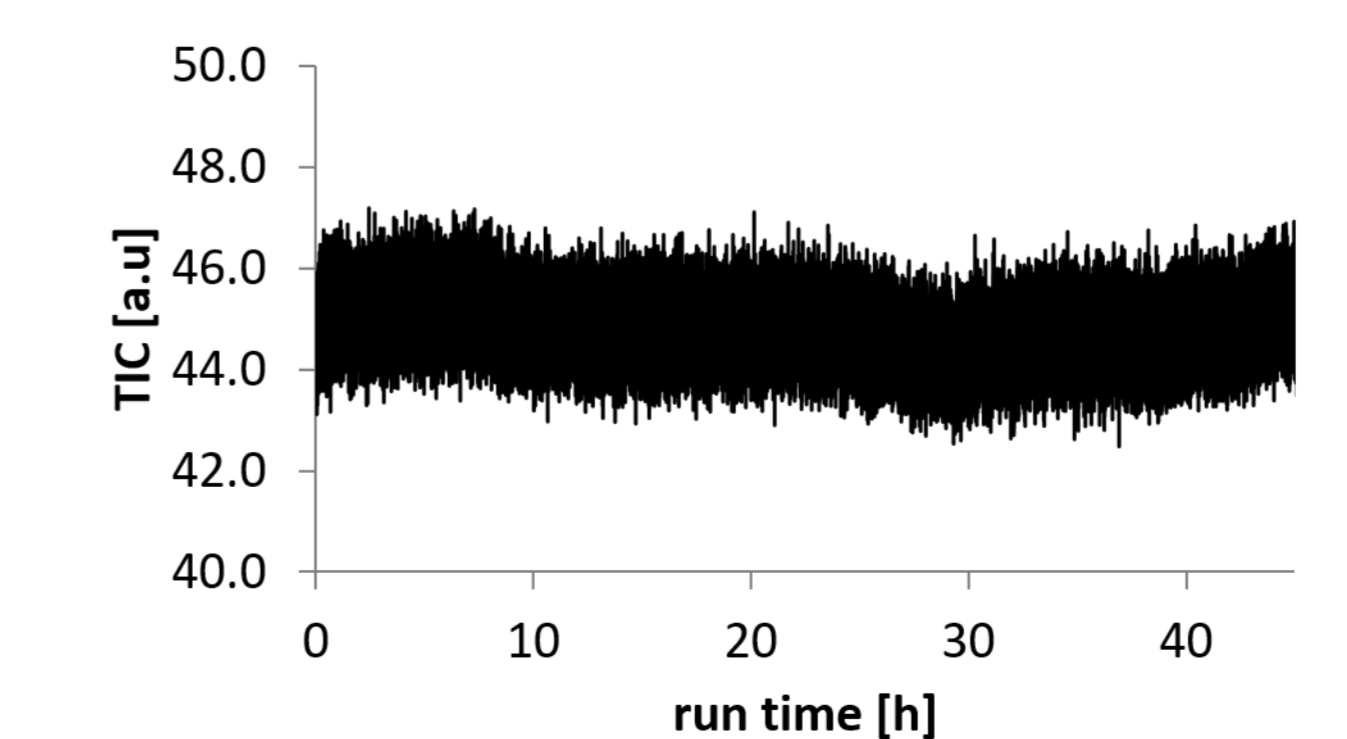


Figure 16: Total ion chromatogram over 45 h (m/z 1 – 450).

Analytical Performance

Limit of Detection

- 33 pg on column for α -pinene (estimated from $S/N = 3$, from a 84 pg sample)
- 209 fg on column for o-xylene (determined by calibration curve method according to DIN 32645).

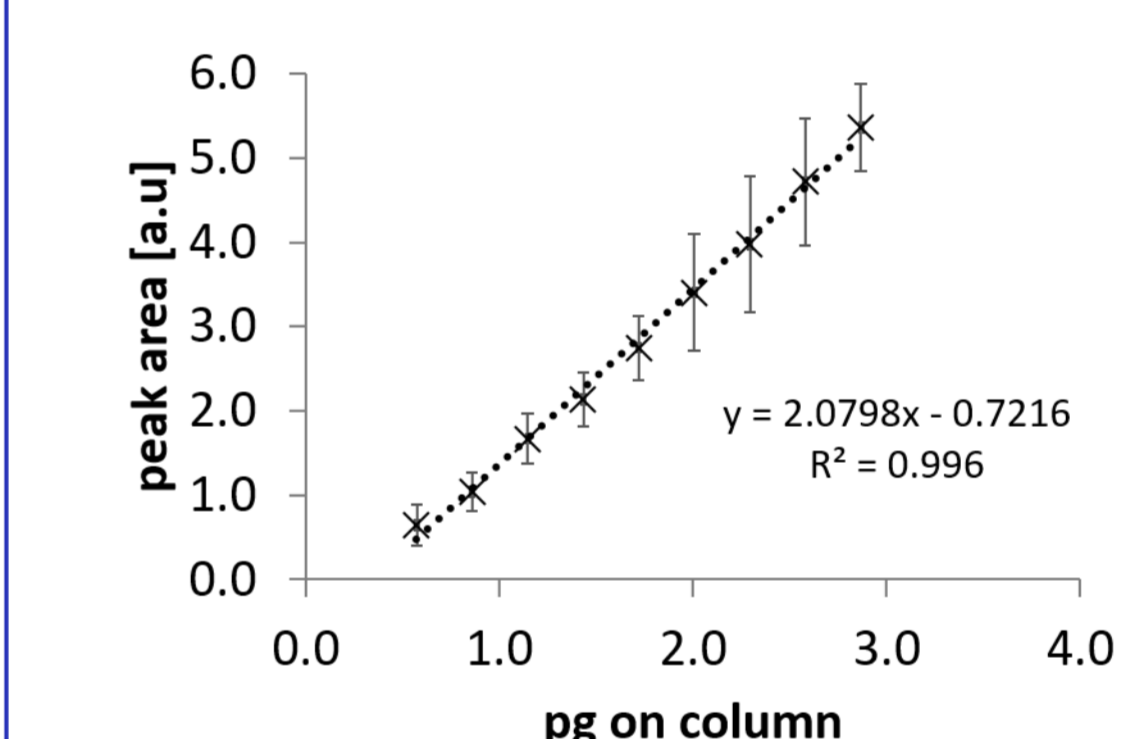


Figure 13: Calibration curve of o-xylene with nitrogen as reactant gas, split 100, manual injection, ion source not heated.

Progress in Peak Shape

- Decrease of full width at half maximum (FWHM) from 0.6 s to 0.5 s.
- Decrease of asymmetry factor from 4.7 to 1.7 (calculated by the peak half-width at 10 % peak height).

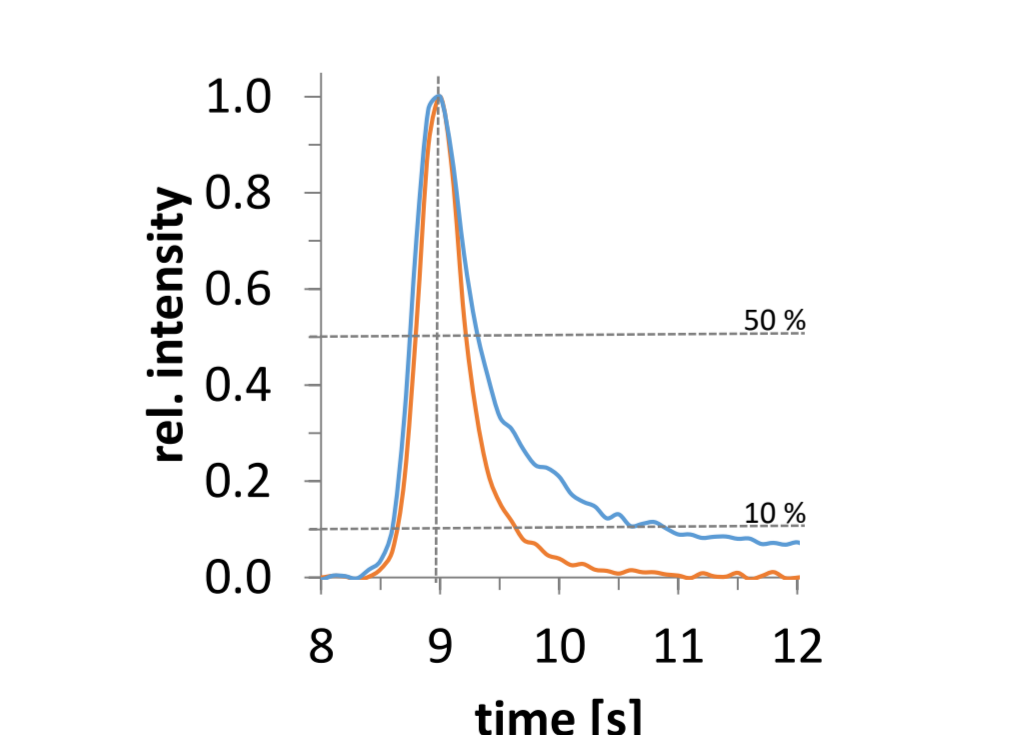


Figure 15: Extracted ion chromatogram of an isobutane GC run ($[M+H]^+$ signal). Before (blue line) and after (orange line) pressure and gas flow adjustment (ion source not heated).

- Standard deviation of the total ion current (45 h) < 1.5 % (cf. Fig. 16).
- Several weeks runtime with reagent gas without performance loss.

Conclusions

- Different reagent gases allow scaling of the exothermicity of the analyte protonation. This results in "soft" ionization and leads to quasi-molecular ions as main ion signals.
 - cf. decane + nitrogen reactant gas (Fig. 9) compared to decane + methane reactant gas (Fig. 10).
- Successful coupling of the custom build RF plasma source to a gas chromatograph with insignificant interference with the chromatographic performance (cf. Fig 15, peak tailing).
 - Ion source was not heated, due to leaks during heating.
- Low fragmentation degrees and exclusive formation of quasi molecular ions.
- Decrease in fragmentation by chemical suppression of bulk gas ions (particularly H_2O).

Outlook

- Test of different sealing materials for ion source heating up to 300 °C.
- Investigation on suitable reagent ions in addition to standard CI reactant gases.
- Avoid water cluster formation as thermodynamic sink for protons by minimizing water impurities of the chosen gases.
- Measurements and simulations of kinetic data to optimize the ionization process and suppress water cluster formation.

Literature

- Kroll, K.; Erdogdu, D.; Kutsch, T.; Wissdorf, W.; Kersten, H.; Benter, T. "Progress in the development of a kinetically controlled chemical ionization setup", 66th ASMS Conference on Mass Spectrometry and Allied Topics, San Diego, CA, USA (2018).
- Hunter, E. P.; Lias, S. G. "Proton Affinity Evaluation" in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. Linstrom P. J.; Mallard, W. G.; National Institute of Standards and Technology, Gaithersburg MD, 20899, https://doi.org/10.18434/T4D303, (retrieved May 23, 2019).
- Lias, S. G.; Liebman, J. F.; Levin, R. D. "Evaluated Gas Phase Basicities and Proton Affinities of Molecules; Heats of Formation of Protonated Molecules" *J. Phys. Chem. Ref. Data*, 13, 695 (1984).
- Solouki, T.; Szulejko, E. "Bimolecular and Unimolecular Contributions to the Disparate Self-Chemical Ionizations of α -Pinene and Camphene Isomers" *J. Am. Soc. Mass Spectrom.* 18, 2026–2039, (2007).
- Hunter, K. C.; East, A. L. L. "Properties of C-C Bonds in n-Alkanes: Relevance to Cracking Mechanisms", *J. Phys. Chem. A*, 106, 1346–1356 (2002)

Acknowledgement

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