Hydrogen plasma based chemical ionization source for GC-MS

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Introduction

The main advantage of gas chromatography coupled to chemical ionization mass spectrometry (CI-MS) compared to e.g electron ionization mass spectrometry (EI-MS) is to obtain simplified mass spectra with a dominant molecule ion peak. Analyte ions are generated within the ions source via chemical reaction with previously generated reactant ions. First results on this ion source were presented by Kroll et al (1,2). This previous source version suffered from temperature limitations within the ion source and first ion transfer stage. In this version special attention is given to the chromatographic performance. A careful set up is required to avoid dead volumes and cold spots preventing peak-tailing and subsequent loss of chromatographic resolution. Commonly used materials e.g. PEEK and elastomer sealings are not suitable for temperatures (>250 °C) required to cover the entire GC temperature spectrum. Multiple parts needed to be replaced for high temperature applications. Maintaining appreciable vacuum conditions, finding low outgassing and good reusable materials for spectral reproducibility after disassembling and multiple heating cycles remains complex.

Methods

Instruments:
- HTOF (Tofwerk AG)
- Agilent Technologies 7890A GC system
- DB-5 30m x 0.250 mm x 0.25 μm (Agilent Technologies)
- Custom made heated transferline (300 °C)
- Hydrogen generator (Peak scientific)

Ion source:
- Custom made heatable CI source using a RF plasma source for primary ion generation.

Chemicals:
- Benzophenone (sigma aldrich)
- alpha pinene (sigma aldrich)
- C4 - C24 even carbon saturated FAMEs (Supelco)
- Helium (Carbagas)
- Hexane (Sigma Aldrich),
- Nitrogen 5.0 (Carbagas),
- Hydrogen 6.0 (peak scientific)
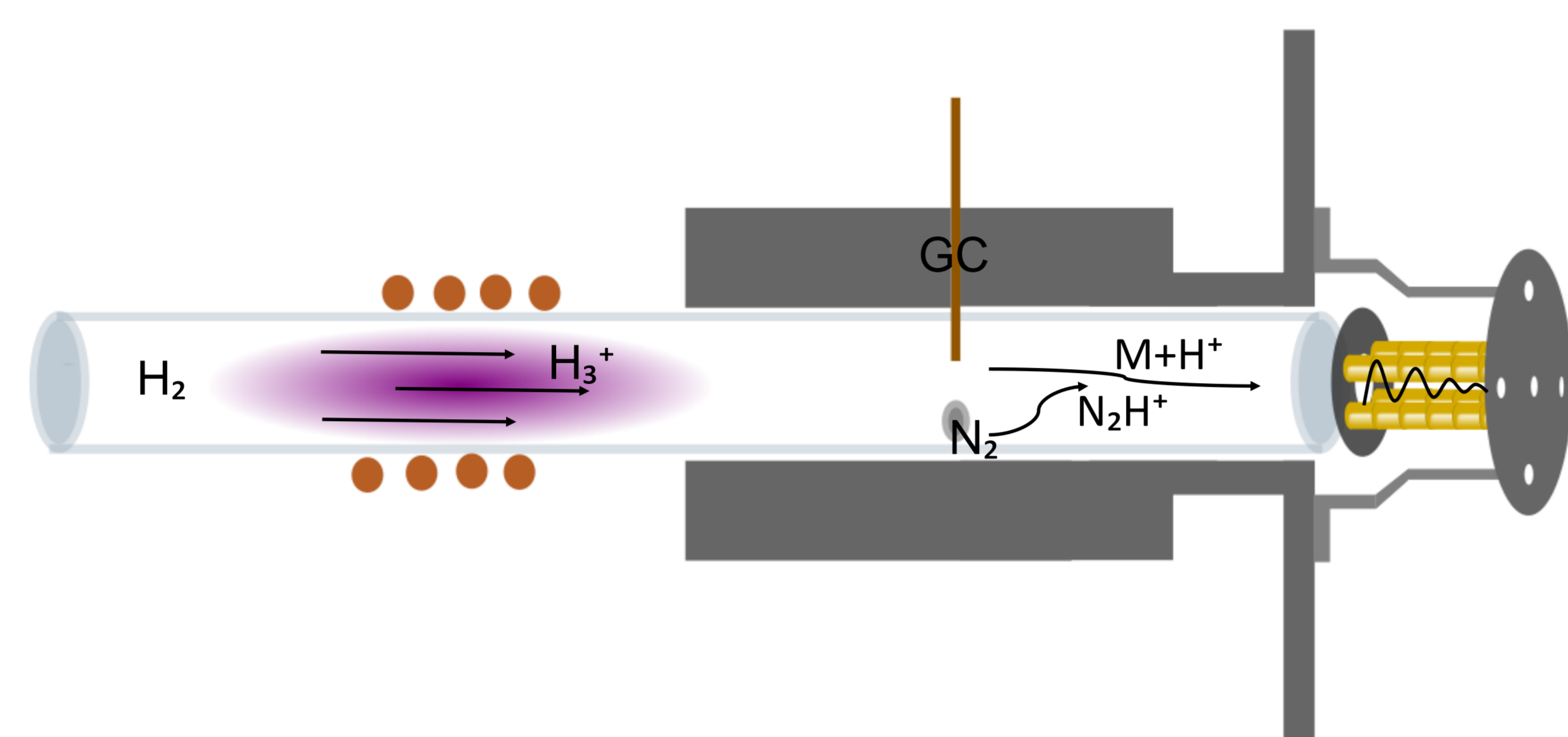
Experimental Setup

Figure 1: Schematic drawing of the CI ion source. Primary ions (mainly H_3^+) are generated within a RF plasma ignited inside of a glass tube. Operating at medium pressures of 2 - 8 mbar. Subsequent addition of N_2 and impurities of water leads to the formation of N_2H^+ and H_3O^+. An analyte protonation via these reactant ions results in less excess energy for the reaction compared to H_3^+ leading to lower fragmentation. The GC eluent is added orthogonally to the reactant gas flow. A passively heated shell surrounding the first quadrupole avoids the contact with non-heated parts of the vacuum chamber of the API mass spectrometer.
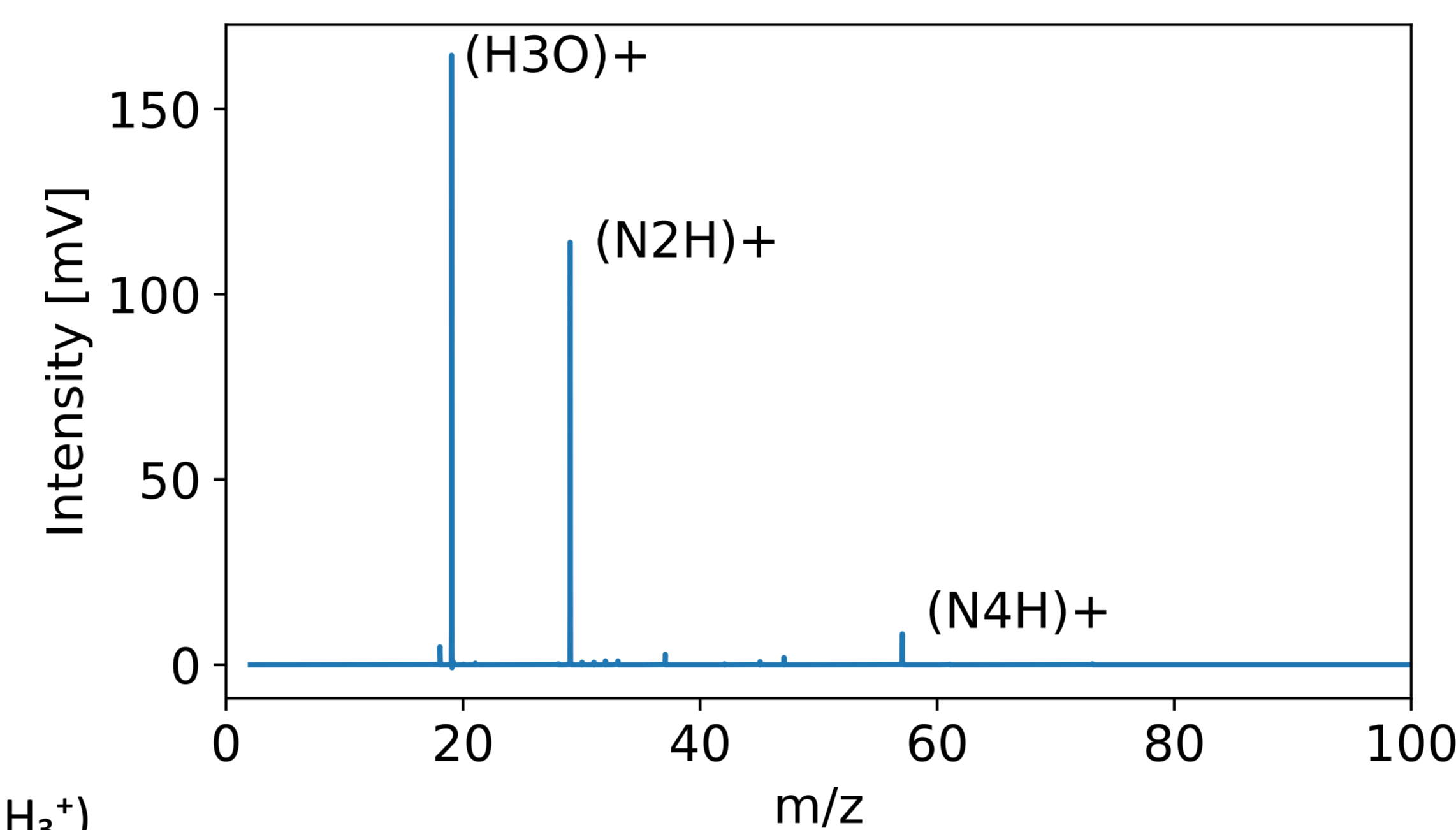

Figure 2: Reactant gas spectrum observed with the shown setup. H_3O^+ and N_2H^+ represent the main protonating reactant species. Due to their low proton affinity these species cover the protonation of a wide range of analytes without extensive fragmentation. Mainly a $(M+H)^+$ signal is generated. H_2 and N_2 are purified to water levels in the low ppb region to avoid ion-water-cluster formation.
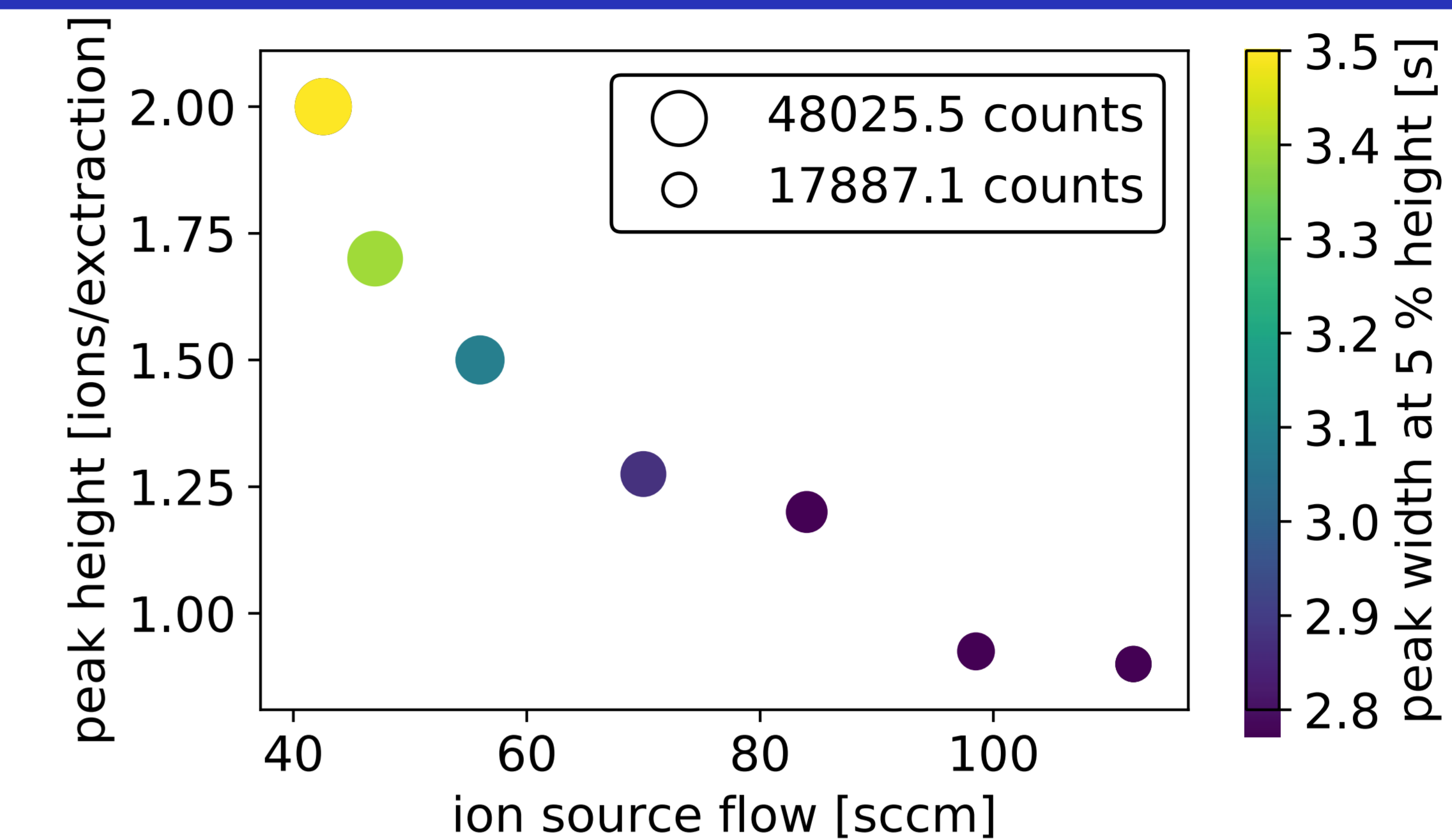
Ion source flow optimization

Figure 3: Ion source behavior for 100 pg Benzophenone GC-injections at different gas flows and constant ion source pressure. Pumping rates were adjusted via a valve between the first pumping stage and vacuum pump. Higher flow rates of CI gas in the ion source seem to sustain the chromatographic performance on a higher level, but simultaneously lead to stronger dilution and shorter residence times of the analyte molecules in the ionization region.

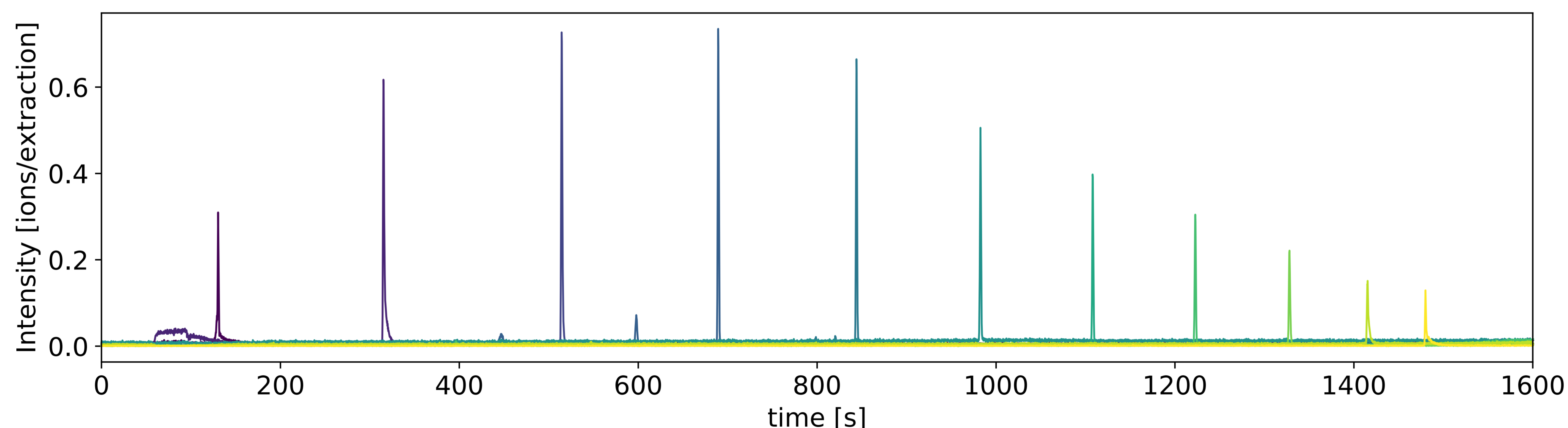## Chromatographic Performance

Figure 4: Extracted ion chromatograms of 1 ng C4 – C24 even carbon saturated FAMEs mixture sampled via GC. Showing a narrow peak shape over the whole GC temperature range. The ion source was heated to 250 °C for this measurement.
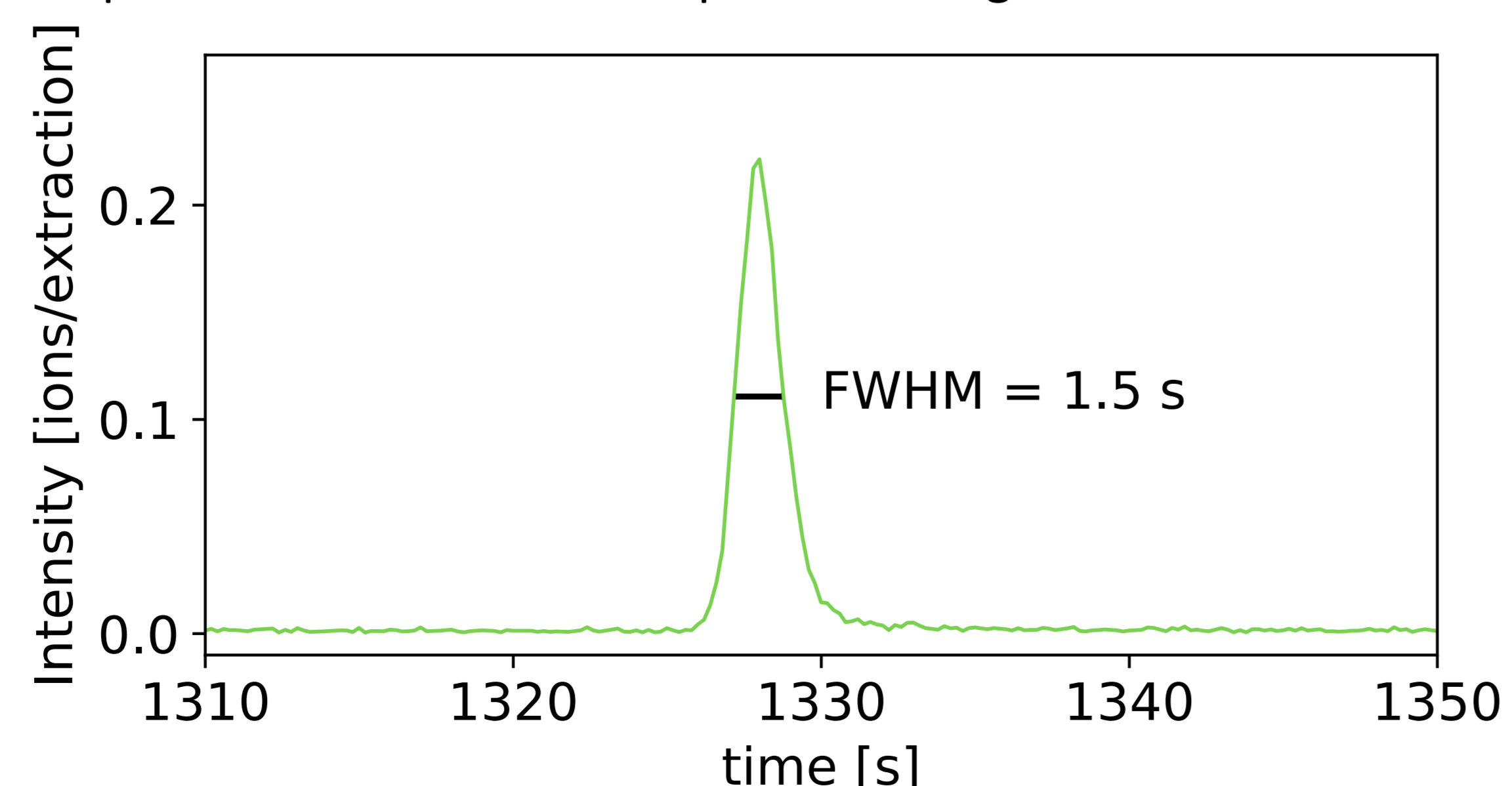

Figure 5: Zoom-in of the 9th FAMEs peak of figure 4. Methyl arachidate ($CH_3(CH_2)_{18}COOCH_3$) shows a gaussian peak shape.
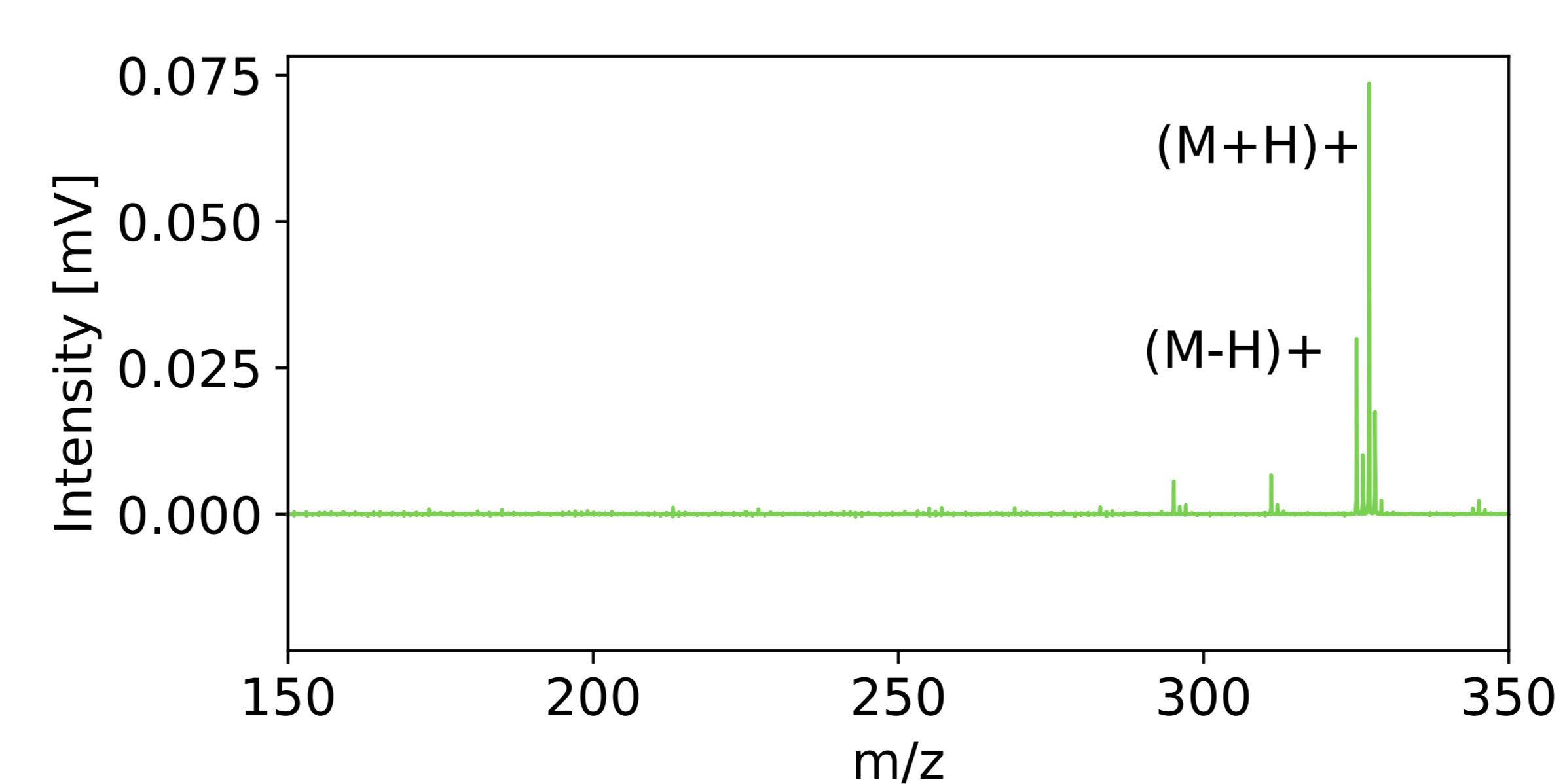

Figure 6: Background substracted mass spectrum of methyl arachidate ($CH_3(CH_2)_{18} COOCH_3$).
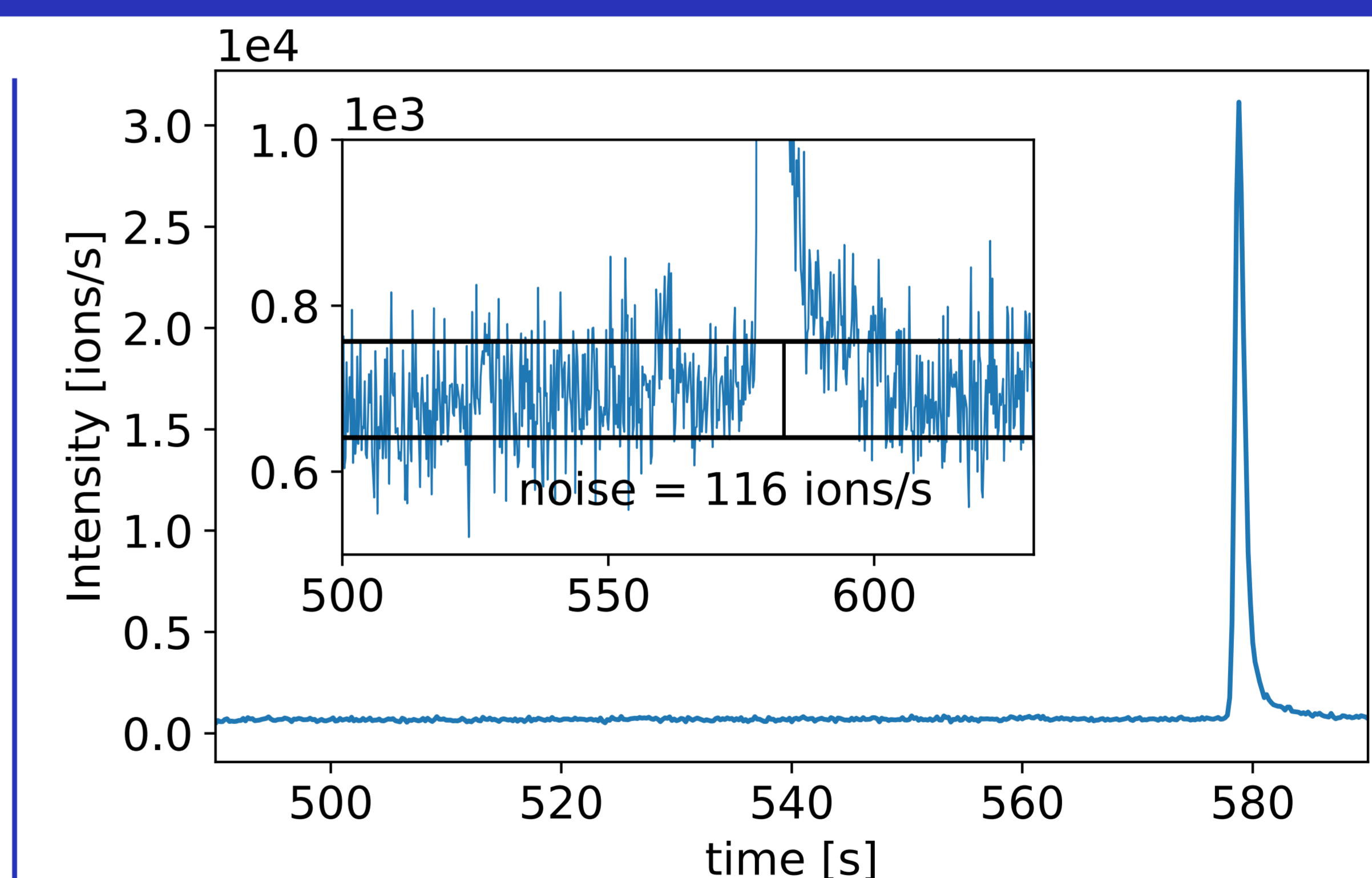

Figure 7: 100 pg Benzophenone were sampled via GC determine a signal to noise ratio of 269:1. The noise is given by the standard deviation of the background for 60 sec before the peak. The signal represents the peak hight in ions/s. The nominal mass instead of the high resolution mass was used here to determine the noise. The use of the high resolution peakfitted noise would lead to a higher S/N ratio than calculated here. The high background emerges when heating up the ion source to high temperatures. Since the ion source itself is build of gas chromatography prooven materials e.g. stainless steel, glass and graphite/Vespel, a possible reason of the higher background could be the solder or the PEEK used in the first quadropole region. Further invesitigations are required.

Conclusions

- The ion source shows an strongly improved behaviour in terms of chromatographic performance
- High boiling compounds show symmetrical peak shapes
- The driven ion-molecule chemistry is generating primarily the protonated $(M+H)^+$ signal for most compounds.
- The chromatographic performance is strongly dependents on the gas flows within the ion source region. Higher gas flows are leading to increased dilution of the sample and shorter retention times.
- Disturbance of the signal to noise ratio by the increasing background due to high ion source temperatures.

Outlook

- Decrease of background signal at high ion source temperatures to improve S/N ratio.
- Modification of RF power supply to increase ion yield.
- Useage of different CI gases for a greater diversity in protonation selectivity of reactant ions.

Literature

(1) Kroll, K; Erdogdu, D; Kutsch, T; Wissdirf, 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)**.

(2) Kroll, K; Kersten, H; Benter, T. Progress in the development of a plasma based CI-source for GC-MS, *67th ASMS Conference on Mass Spectrometry and Allied Topics*, Atlanta, GA, USA **(2019)**.

Acknowledgement