Multiple-corona N_2/H_2 ion source for AP GC-MS coupling stages

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Introduction

The hyphenation of gas chromatography (GC) with atmospheric pressure ionization (API) mass spectrometers is gaining increasing attention. The comparably high investment costs for API instruments are partly alleviated, when the GC API stage is interchangeable with conventional LC API methods such as ESI and APCI. As EI is not feasible at atmospheric pressure we are developing a method, which is based on the generation of N_2H^+/ N_4H^+ reagent ions by a corona discharge, which in turn guarantee a wide analytical coverage, particular towards the typical GC analyte spectrum.

Challenges for the first version:

- Reproducible and constant operation of the corona discharge without sparking.
- Generation and detection of N_2H^+/ N_4H^+ as the primary reagent ions. Therefore, particular attention must be paid to the purity of the supplied gases, specifically to the partial water pressure.
- Assessing method sensitivity and chromatographic performance with first GC runs.

Methods

Instruments

- Sciex API 3200 Triple Quadrupole MS
- custom-made temperature controlled GC transfer line with sheath gas supply
- Agilent Technologies 7890A GC System
- TR-Dioxin-5MS 30 m x 025 mm D x 0.1 u GC column (Thermo Scientific)

Ionization

- multiple corona discharge in H_2, addition of N_2
- high-voltage supplied by the APCI infrastructure of the MS (8.2 kV)
- gas flows are controlled by mass flow controllers (Bronkhorst Mättig GmbH)

Chemicals

- nitrogen (liquid N_2 boil-off, Linde AG)
- hydrogen, helium (5.0, Messer Griesheim)
- aniline, methanol (Merck)

Experimental parameters

- A nitrogen flow of 750 sccm was supplied to the ion source for sustained atmospheric pressure condition.
- The dimensioning of the vacuum system essentially limits the accepted hydrogen flow by the instrument. For the presented work H_2 was supplied with 1 – 11 sccm.

Experimental Setup

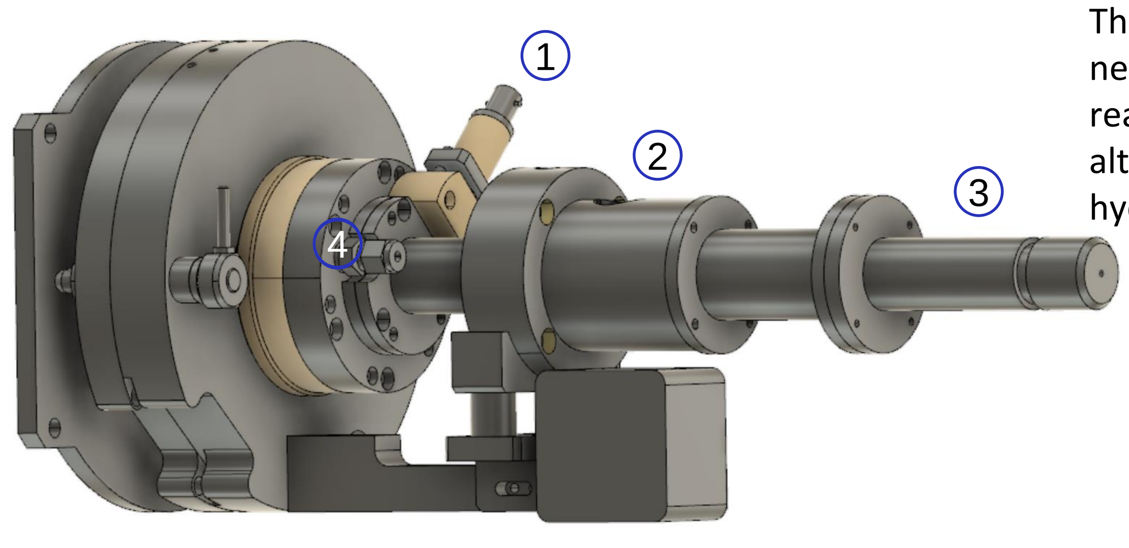

Figure 1: CAD drawing of the custom made ion source and GC transfer line.

The hydrogen flow surrounds the corona needles. The nitrogen is supplied to the reaction volume as an eluent sheath gas or, alternatively, directly mixed with the hydrogen flow.

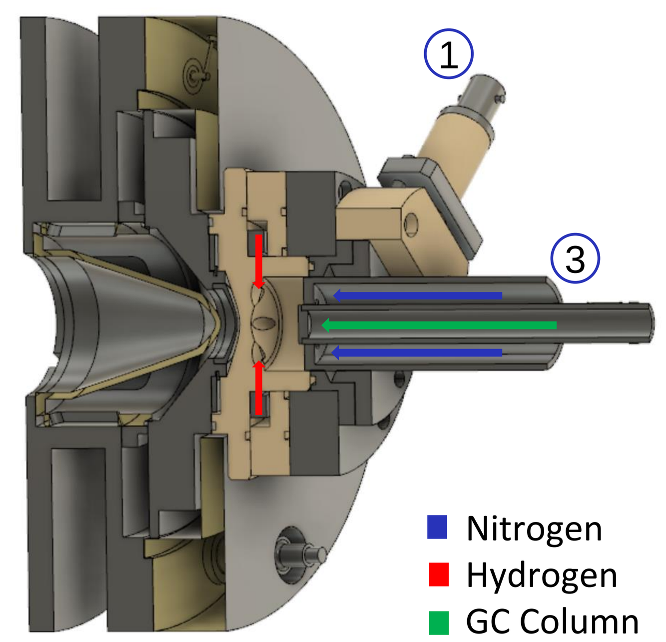

Figure 2: Cross section and gas flows of the ion source.

(1) HV connector for the corona discharge. Modified from the original APCI infrastructure of the MS.
(2) inlet for the N_2 supply
(3) temperature controlled GC transfer line
(4) inlet for the H_2 supply

Discharge characteristics

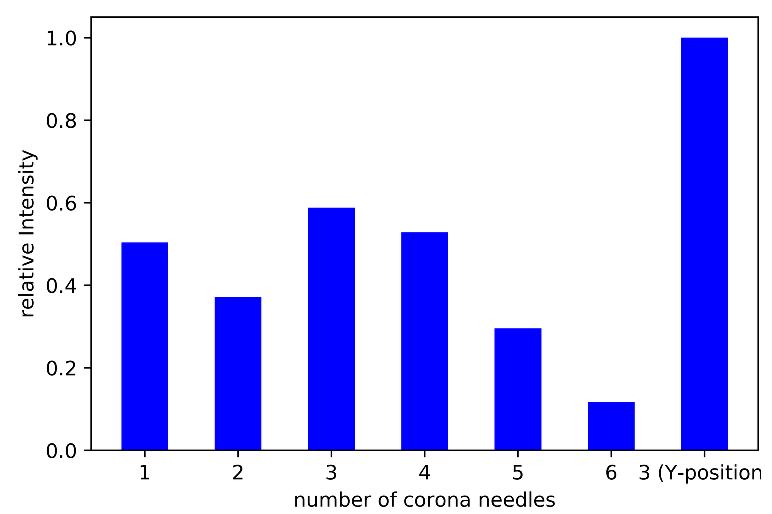

Figure 3: Relative total ion current for a different number and positions of corona needles.

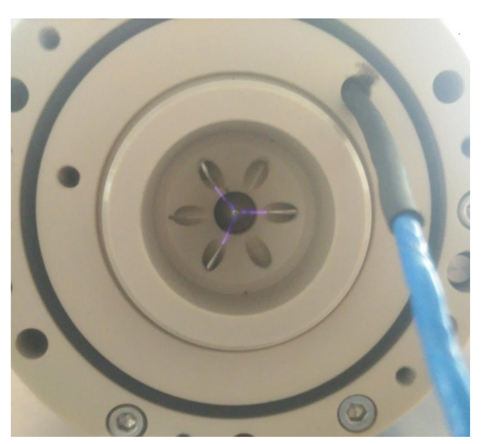

Figure 4: Picture of the corona discharge with three needles in Y-Position.

The number of installed corona needles strongly impacts the recorded TIC. Interestingly, the maximum of six needles shows least ion intensity. The best performance provided a symmetric Y- arrangement of three corona needles.

The pressure dependency of the corona discharge (convoluted with the sampling efficiency) was evaluated by means of the recorded TIC. Fig. 5 depicts a linear signal increase between 700 and 1100 mbar, levelling off at 1200 mbar. Below 700 mbar the discharge started sparking with apparent signal instabilities. Note, that the sparking event is always influenced by the position of the corona needles and the transfer line.

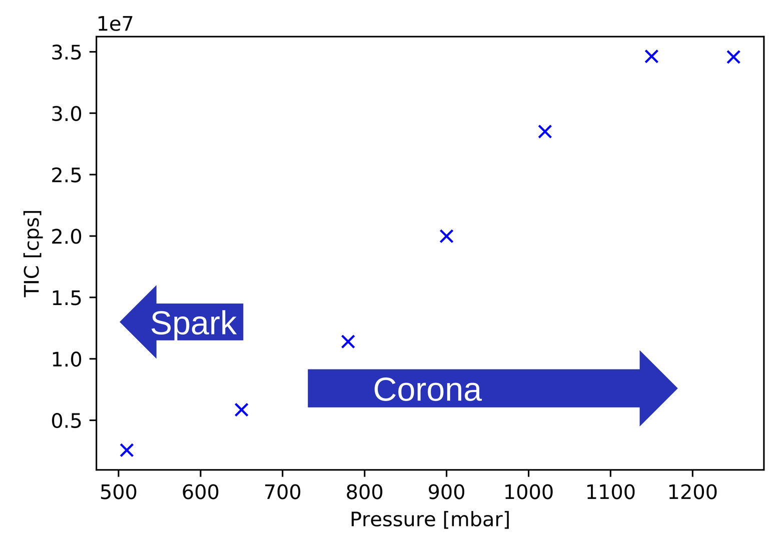

Figure 5: Impact of the operating pressure on the total ion chromatogram.

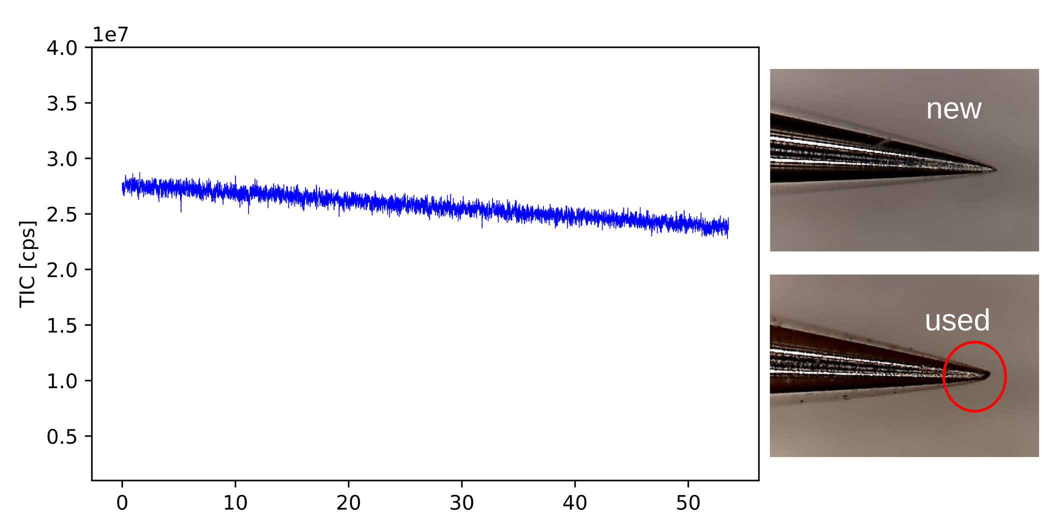

Figure 6: Stability of the TIC for a 50 min run and pictures of the corona needles before and after a few hours of operation.

Over time a slight decrease in ion intensity was observed, as exemplarily shown in fig. 6. Notable abrasion of the needles might be the cause, however, this surely requires more detailed investigation in a long-term measurement, which needs to consider the impact of the discharge on the skimmer material as well.

Theory of reactant ion formation

$$
\begin{array}{llcl}
1. & H_2 + H_2^+ & \rightarrow & H_3^+ + H \\
2. & H_3^+ + N_2 & \rightarrow & N_2H^+ \\
3. & N_2H^+ + N_2 & \rightarrow & N_4H^+ \\
4. & N_2^+ + H_2 & \rightarrow & N_2H^+ + H \\
5. & N_2H^+ + H_2O & \rightarrow & H_3O^+ + N_2 \\
6. & H_3O^+ + H_2O & \rightarrow & [(H_2O)_nH]^+
\end{array}
$$

At atmospheric pressure nearly all ionic species initially generated in a plasma of a pure hydrogen/nitrogen mixture, rapidly lead to the formation of N_2H^+ and N_4H^+ as primary reagent ions [1,4].

Table 1: Proton affinities of important substances [2][3].

Substance	Proton affinity [kJ/mol]
H_2	422.3
N_2	493.8
H_2O	691.0
$(H_2O)_2$	808.0
C_6H_7N (Anilin)	882.5

The presence of water leads to rapid formation of proton bound water clusters, which increase the proton affinity of the reagent ions and decrease the range of amenable compounds. Protonation is only possible for **PA(reagent gas) < PA(analyte molecule).**

Spectra in N_2/H_2

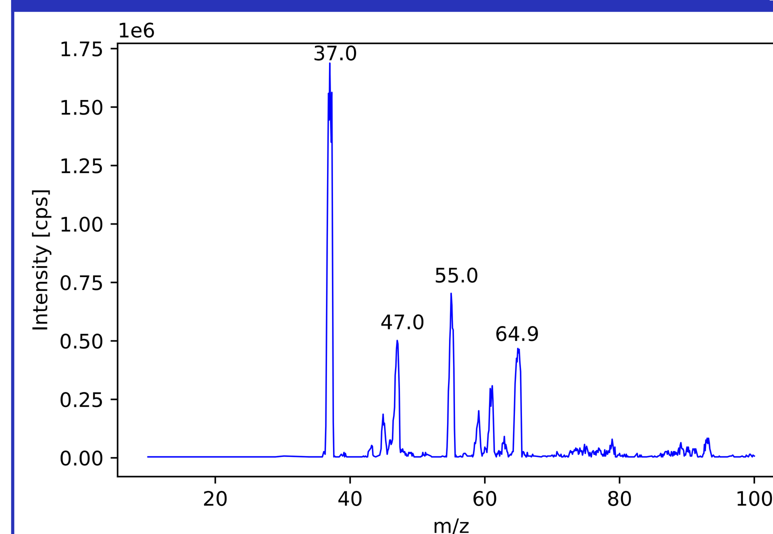

Figure 7: Corona mass spectrum in N_2/H_2 at atmospheric pressure (1 sccm H_2, 700 sccm N_2).

In particular the second and third water cluster dominate the recorded mass spectra in this first version of the GC-APCI source, when operated at elevated pressures. Lowering the pressure causes sparking with N_2H^+ N_3^+, Ar^+ and O_2^+ as the prevailing species. Both spectra indicate leaks and contamination. For APCI conditions in this setup analytes are expected to be protonated by water clusters. The next GC-API versions specifically tackles contamination issues to provide the desired reagent ions in appreciable amounts.

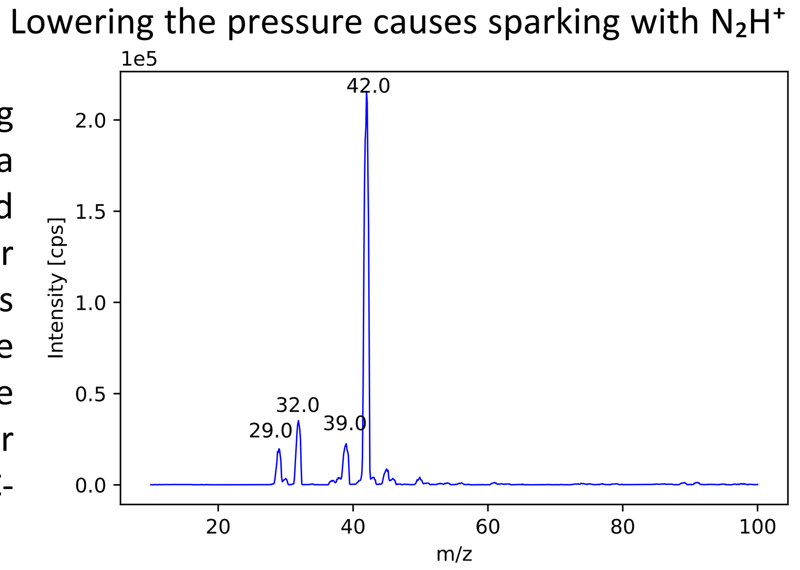

Figure 8: Spectrum in N_2/H_2 at 280 mbar (11 sccm H_2, 300 sccm N_2).

Chromatographic performance

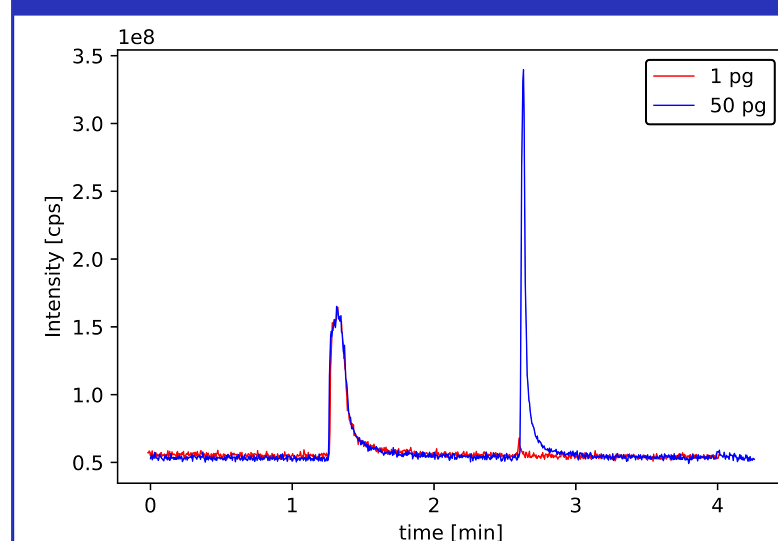

Figure 9: TIC for two GC runs of aniline in MeOH.

Samples of aniline in methanol between 0.1 and 10 ng/µl were injected with a split of 1:100. Carrier gas was helium with a flow of 1.5 sccm. The m/z range was set between 10 and 500 Da and the transfer line was maintained at 250 °C. Lowest amount of 1 pg on column was clearly visible. Appreciable linearity was observed for injection between 1 and 500 pg on column. Higher concentrations led to saturation effects.

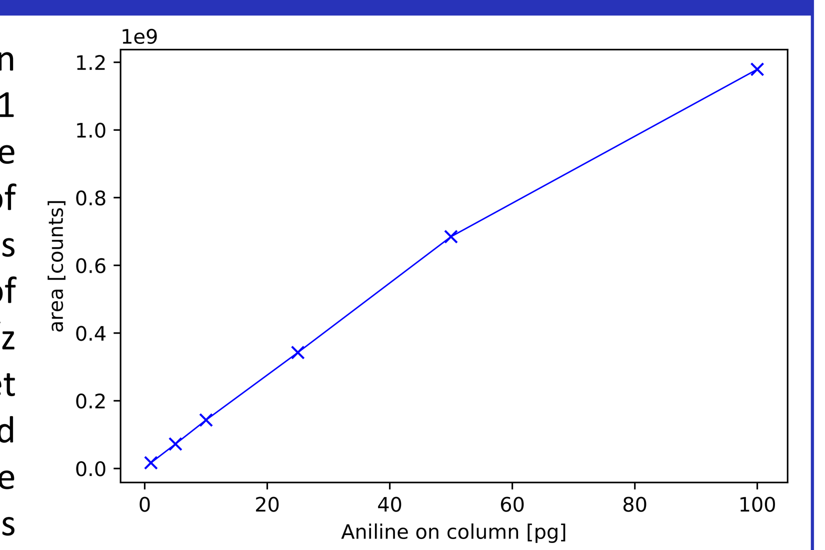

Figure 10: GC-APCI linearity measurement with aniline.

The first GC peaks showed tailing and peak width (10% definition) of > 4s, probably due to a relatively large reaction volume. Further insertion of the transfer line lowered the volume to some extend (limited by the spark breakdown between the needles and the transfer line) and peak width < 3 s were observed. Note, however, that the transfer line/needle distance effects the discharge as well.

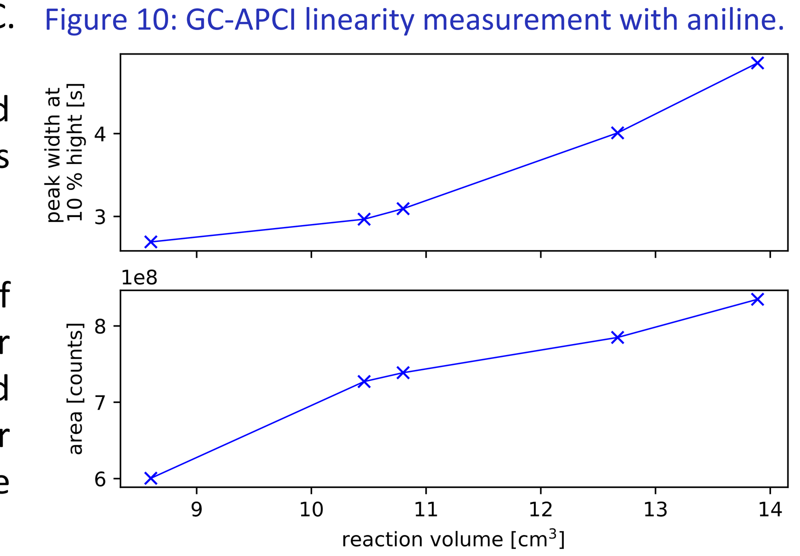

Figure 11: Impact of the reaction volume on the peak width.

Conclusions

Version 1.0 of the multiple-corona N_2/H_2 GC-APCI proved the possibility to sustain a corona discharge in a small volume for sufficient and stable primary reagent ion formation.

Preliminary GC runs showed lower pg on column sensitivity and appreciable linearity for several injected aniline solutions.

Outlook

Things to work on for version 2.0:

- Reduction of water contamination to generate mostly N_2H^+ and N_4H^+ as primary reagent ions.
- Careful reduction of the reaction volume to improve chromatographic peak shape.
- Improved needle alignment and isolation towards skimmer and transfer line. To prevent skimmer abrasion an additional protection electrode around the skimmer should be considered.

Literature

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[4] J.K. Kim, L. P. Theard, W. T. Huntress Jr. Proton Transfer reactions from H_3^+ ions to N_2, O_2 and CO molecules. *Chemical Physics Letters,* 32(3): 610-614, **1975**.

Acknowledgement

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