

Comparing the established ionisation techniques, radioactive ⁶³Ni ionisation and UV photoionisation with a new plasma ionisation source on a GC-FAIMS system using two different methods of chemical gas standard generation

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Introduction

The ionisation section in an IMS is a critical part. It defines whether an injected substance is ionised and therefore can be detected or not. A well-established technique is the radioactive ⁶³Ni ionisation. In general this technique ionises more compounds than the other established technique, which is UV-photoionisation, but with a smaller dynamical range. The Nickel underlies restrictions according to radioactive radiation. The UV bulb does not, but it degenerates. Therefore it would be preferable to have an ionisation mechanism which ionises as much substances as the ⁶³Ni mechanism with a high dynamic range, no restrictions and no parts, wear down. A possible option could be plasma ionisation, especially the dielectric barrier discharge (DBD). This mechanism can form reactant ions like ⁶³Ni^[1] and depending on the design, without any degenerating parts. Another challenging part is the calibration with gas standards. Only a few ways exist to achieve a gaseous standard. Among those are the permeation principle and a new one based on a polydimethylsiloxan (PDMS) matrix^[2], which is spiked with the desired substances. The PDMS based system could be an option for fast on-site calibration. Therefore it has to be stable and reliable.

Aims

- to couple a DBD plasma ionisation unit to the GC-FAIMS system
- to optimise system parameter (flow, carrier/discharge gas, humidity, ...)
- to evaluate the performance of the DBD - FAIMS system in comparison to UV - and ⁶³Ni - FAIMS
- to test the long term stability of both gas standards (permeation tube and matrix based)
- to test the reliability of the matrix based gas standard

Results

Coupling DBD to GC-FAIMS:

Two DBD positions were tested: at the standard UV-FAIMS gas inlet and at the position of the UV bulb. Best signal intensities were obtained, when DBD is closest to the FAIMS detector. The resulting setup is shown in Figure 2. FAIMS parameter and DBD parameter were optimised regarding to maximal RIP intensity and minimal noise.

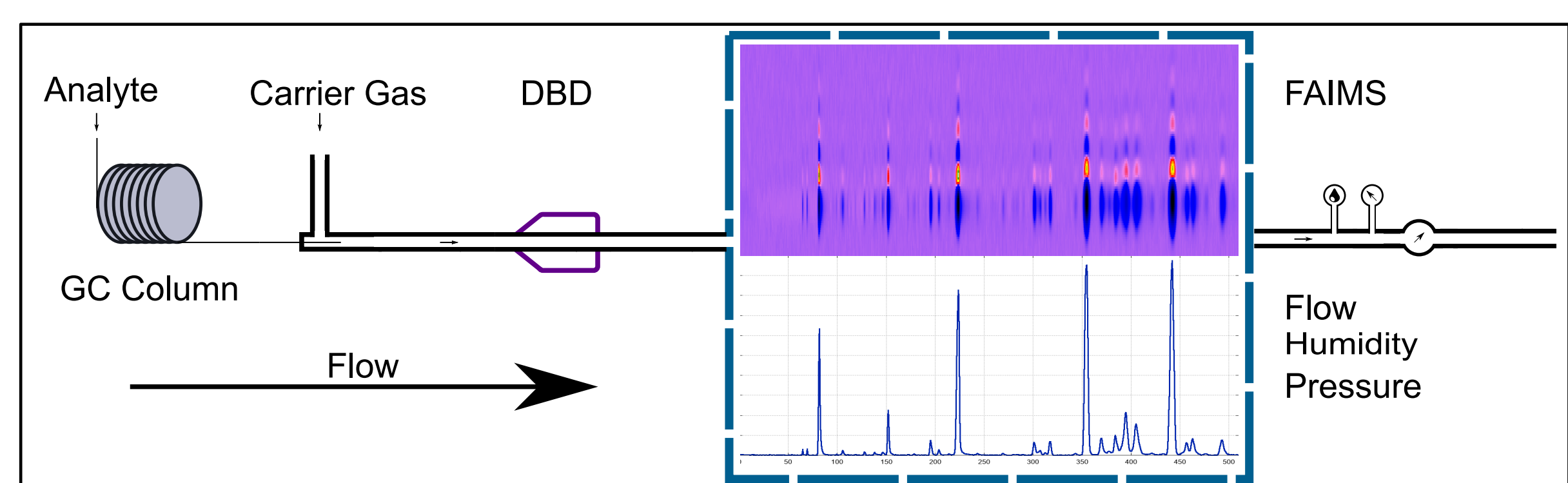


Figure 2: Schematic of the measurement setup. The analyte is injected via SPME to the GC column. The column is temperature controlled and supplied with a constant N₂ flow. The analyte passes the DBD unit and can be detected by the FAIMS system. Process parameters like gas flow, humidity and pressure are recorded.

Humidity and discharge gases:

Major influences of the received signals have the discharge gas and the humidity of the discharge gases. Two different gases were tested: cleaned air and N₂. When using N₂ as discharge gas a minimum amount of humidity is required, unless no signals were obtained. A higher amount of relative humidity reduces the signal intensities of the measured MVOC-PDMS vial. A stronger signal dependency on the humidity is obtained when cleaned air is used as discharge gas. Even though the humidity can reach a value of zero with air as discharge gas the analytes can still be detected. As an example, the humidity dependency of Isobutanol for air and N₂ as discharge gases is shown in Figure 3.

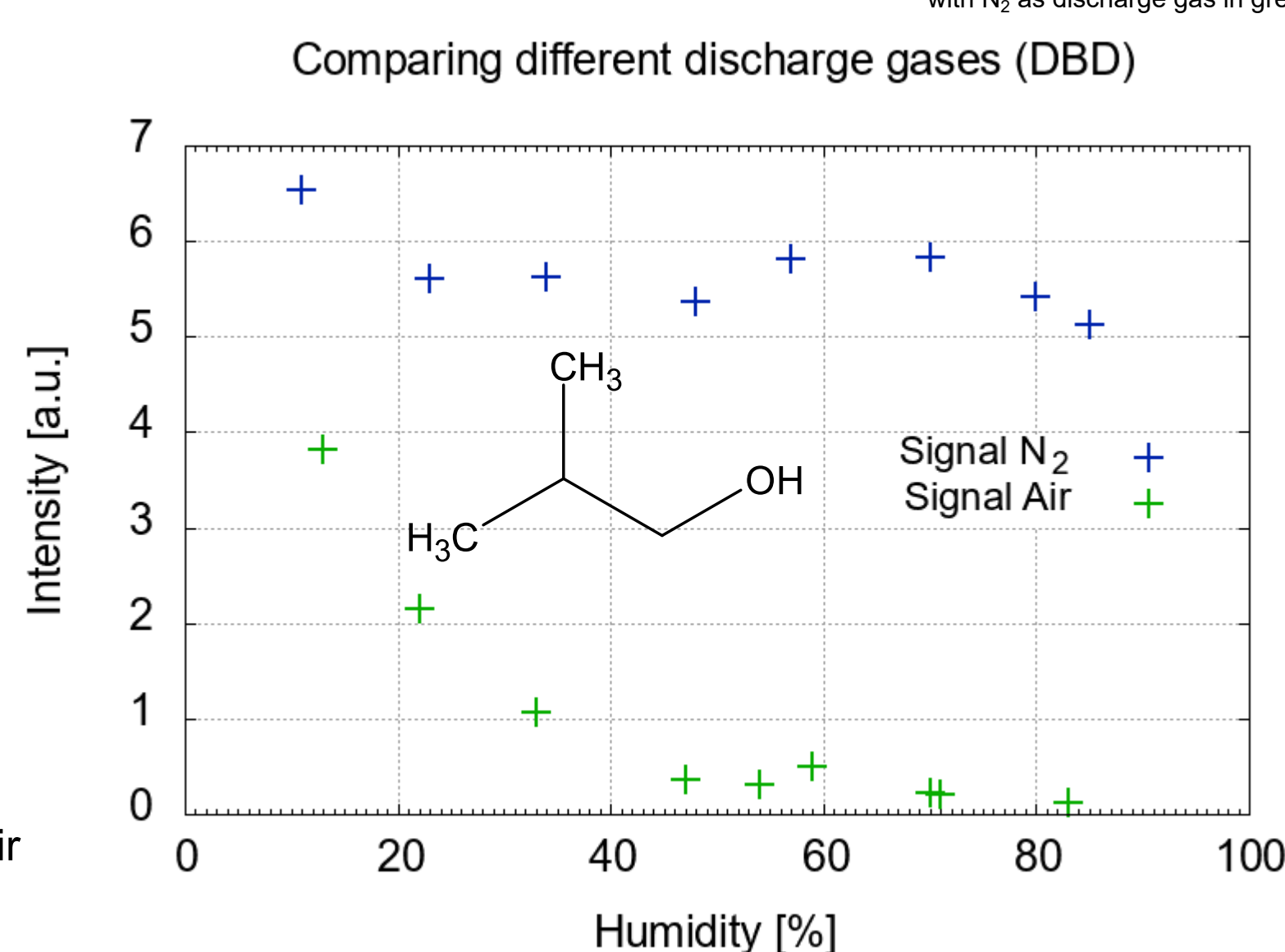


Figure 3: Intensity dependency of the Isobutanol signal on humidity when measured the MVOC PDMS vial with cleaned air and N₂ as discharge gases. The signal obtained with air as discharge gas is shown in blue. The signal obtained with N₂ as discharge gas in green.

Conclusion

- the DBD system was successfully coupled to the GC-FAIMS system
- the DBD analyte signal intensities are in the same order as for the Nickel system
- the most parameter were optimised, majorly influenced by the relative humidity and the discharge gas
- for Isobutanol the dynamic range is in the order of more than 2 magnitudes, the LOD is in the single-digit ppb_v range
- for 2-Hexanone the dynamic range starts below 1.38 ppm_v and ends above 6.6 ppm_v (measurements in progress)
- ongoing observation of the matrix based gas standard vials, obtained signals already remain constant in ranges of 10 days

Discussion & Outlook

A detailed characterisation of the ionisation mechanism in DBD plasmas should follow. The fact that the reactant ion signal is lower as for the ⁶³Ni ionisation mechanism, but the higher measurable Isobutanol concentration shows that not only the detected reactant ions are responsible for the ionisation. Additionally, the different relative peak intensities of the same probe measured in DBD with different discharge gases serve as evidence for different reactions. A better understanding of humidity influence of the plasma would help to obtain a clearer understanding of reactions in the plasma. Besides more measurements to determine the dynamical range for other groups of organic compounds are of note.

The matrix based gas standards can be a great benefit because prepared vials with substance mixtures can produce a constant gas phase concentration for each component. The actual measurements suggest that external influences exist because all components in all prepared vials show the same signal sequence. Influences might be ambient parameters like pressure or temperature, even if the vials are heated to 30 °C and held more than one hour before measurement.

Funding & Acknowledgement

References

- N. Na, M.X. Zhao, S.C. Zhang, C.D. Yang, X.R. Zhang, Development of a dielectric barrier discharge ion source for ambient mass spectrometry, J. Am. Soc. Mass Spectrom. 18 (2007) 1859–1862.
- United States Patent, Pawliszyn et al., Patent No.: US 9,625,426 B2 (2017)

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Materials

Measurement System:

- GC-FAIMS systems: GC-⁶³Ni-FAIMS, GC-UV-FAIMS, GC-DBD-FAIMS (a UV system where the bulb was exchanged)
- Calibration Gas Generator with four independent permeation chambers
- metal block heater
- Mininert™ Valve
- brown glass vial 40 mL
- FAIMS Carrier gas: filtered, dried air
- GC carrier gas: N₂ 5.0
- sample injection with Carboxen/PDMS SPME

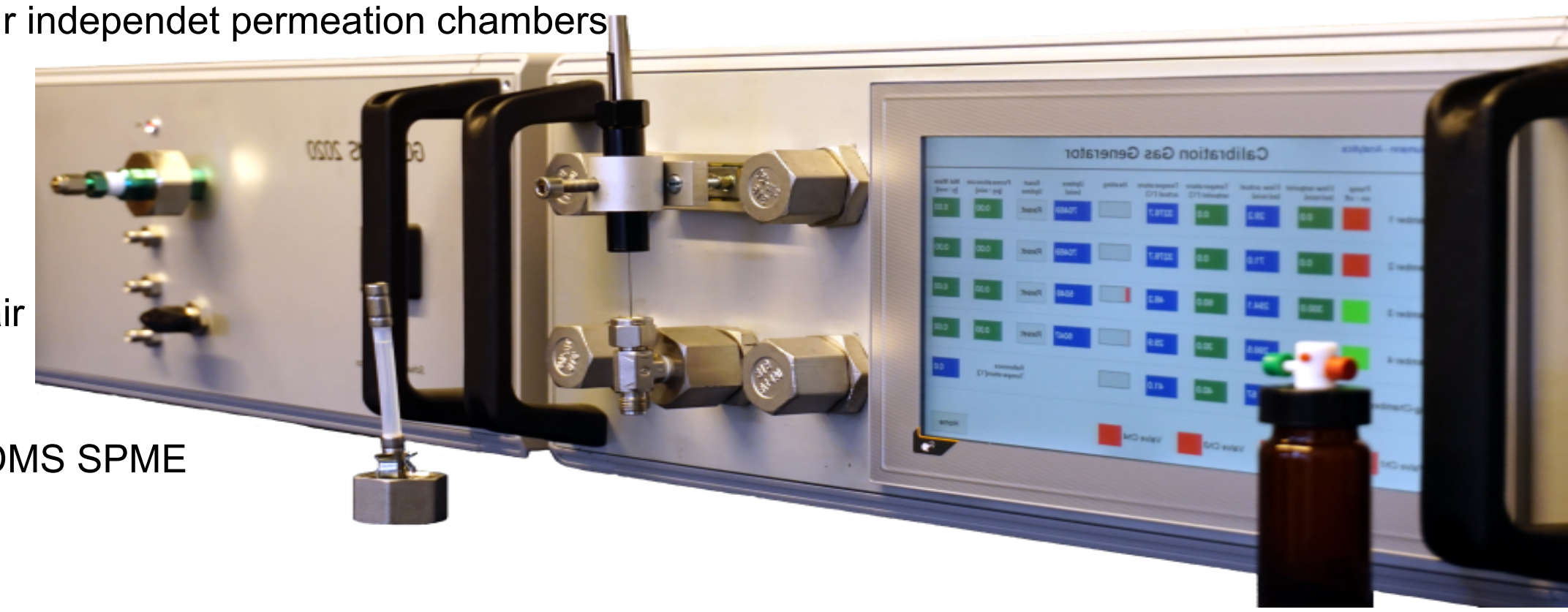


Figure 1: Image of the GC-FAIMS (left), the Calibration Gas Generator (right) with SPME port, a permeation tube (middle), a PDMS vial (right front)

DBD unit:

- max voltage approx. 2.3 kV
- frequency 10 kHz

Gas standards:

Permeation tubes:

- 2-Methyl-1-propanol 300 ng/min permeation rate
- 2-Methyl-1-propanol 600 ng/min permeation rate
- 2-Hexanone 1600 ng/min permeation rate

PDMS matrix based standard in 40 mL vial with Mininert™ Valve:

- one vial spiked with microbiological volatile organic compounds (MVOC): 2-Methylfuran, Styrene, 2-Methyl-1-propanol (Isobutanol), Dimethyldisulfid, 2-Hexanone, 2-Heptanone, 3-Octanone, 3-Methyl-1-butanol, 1-Octen-3-ol
- six vials spiked with Ethanol, Toluene, Hexanal with different amounts of matrix (1 g, 1.5 g, 2 g)

Comparing the dynamic range:

The dynamic range for Isobutanol permeation tubes was measured with all three systems in cleaned and dried air. Due to the permeation rates a concentration range of approx. 22 ppb_v to 682 ppb_v was measurable. The FAIMS with ⁶³Ni ionisation is able to detect signals lower than 22 ppb_v, but saturates at 300 ppb_v. The FAIMS with DBD ionisation does not saturate in the measured range. A linear interpolation reveals a lower limit in the single-digit ppb_v range. The dynamical range is larger than two orders of magnitude. The LOD for the UV-ionisation dynamical range lies above the producible concentration. Another measurement is currently under record for a 2-Hexanone permeation tube with cleaned air and a relative humidity of approx. 30 %. Preliminary results reveal a dynamic range for the ⁶³Ni-FAIMS and the DBD-FAIMS from lower than 1.38 ppm_v to higher than 6.6 ppm_v. The measurements with the UV-FAIMS is currently under progress.

Comparing Isobutanol dynamic range

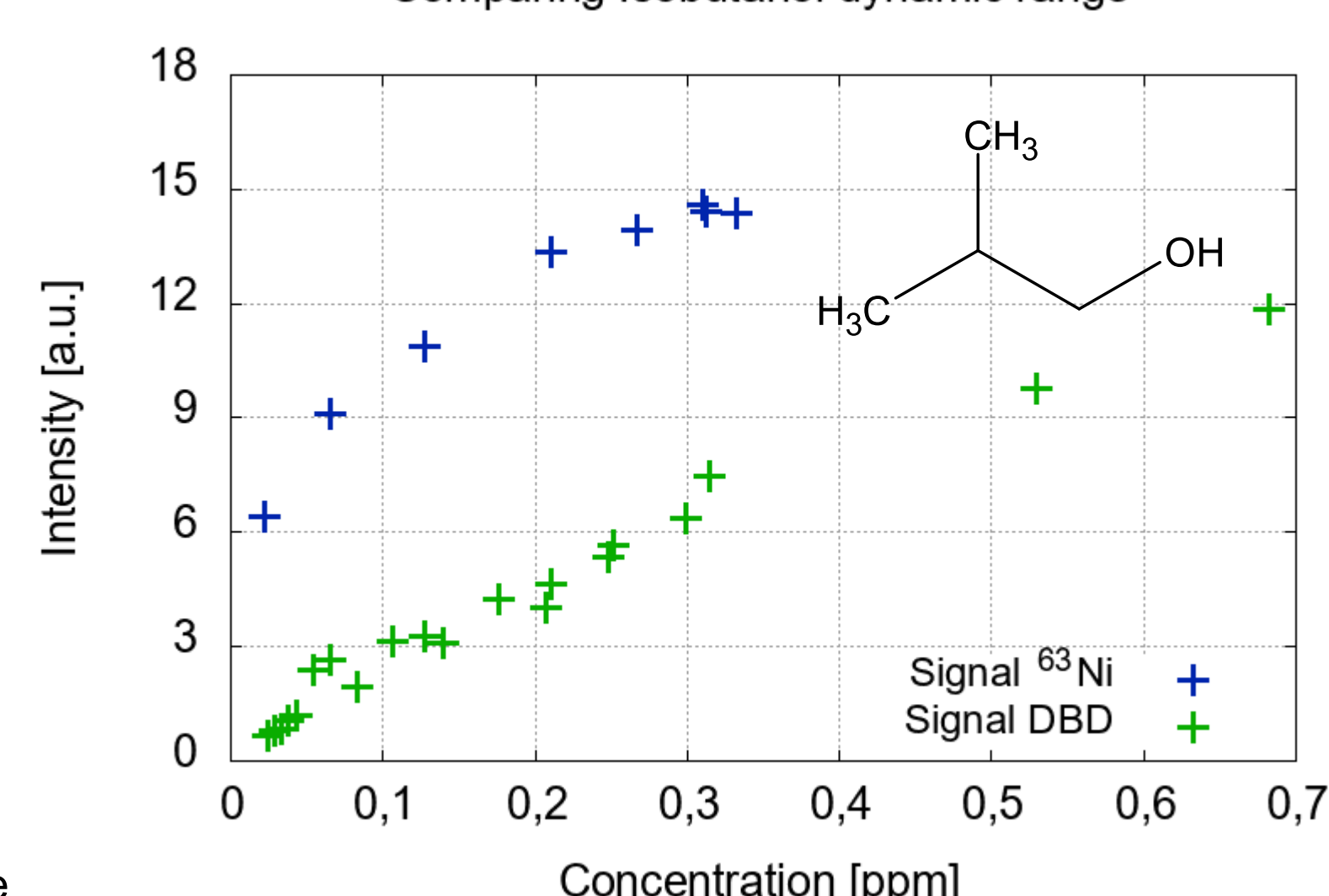


Figure 4: Comparison of the signal intensity vs concentration of an Isobutanol permeation tubes for a ⁶³Ni- (blue) and DBD-FAIMS (green)

Studying PDMS matrix based gas standard

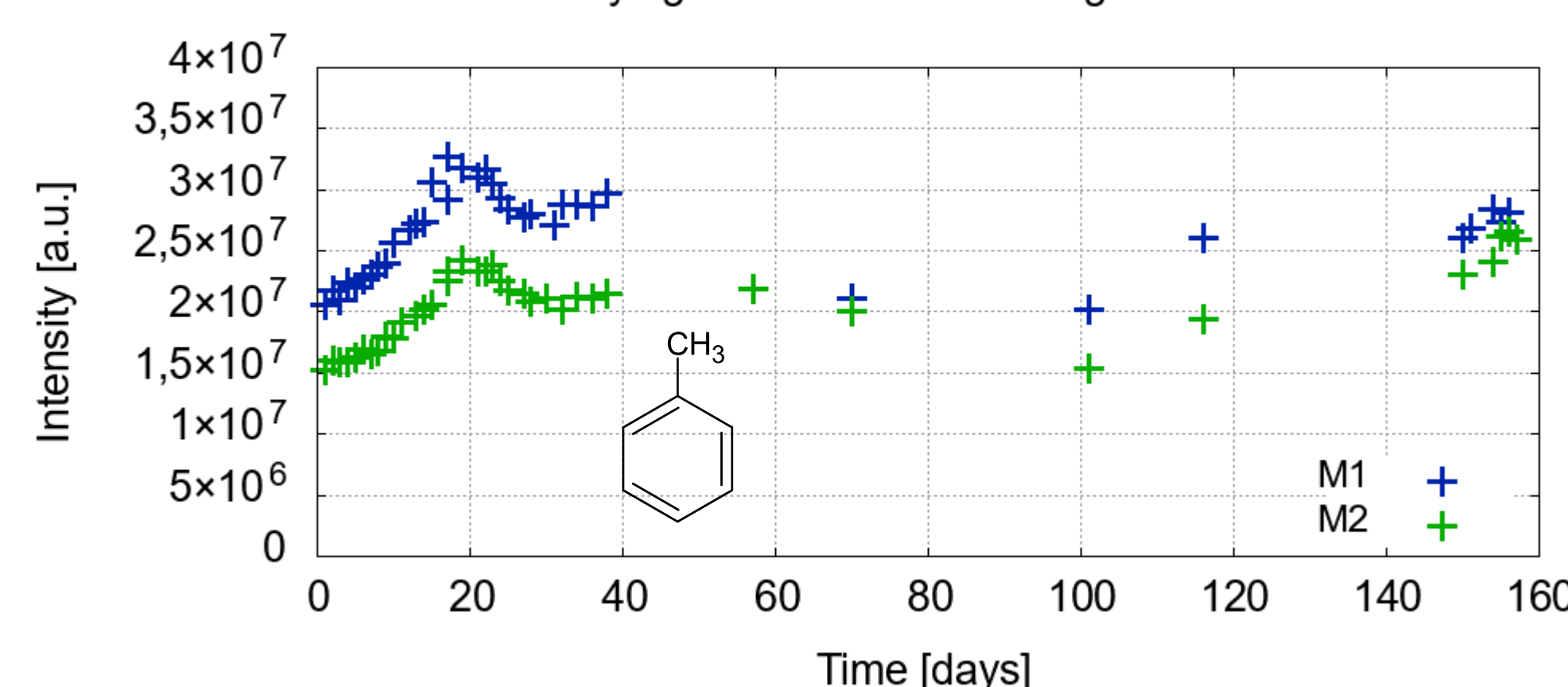


Figure 5: Signal intensities for Toluene for a period of 158 days for two vials with different amount of PDMS matrix, but the same amount of Toluene. The green corresponds to an amount of 2 g matrix, the blue corresponds to an amount of 1 g matrix.

Longterm observation of gas standards:

A set of six PDMS matrix based gas standards spiked with Ethanol, Toluene and Hexanal were observed (GC-MS) until now over a period of 158 days. The vials were held at 30 °C for a period longer than 1 h before measuring. Two measurements for the Toluene signal are exemplary shown in Figure 6. The sequence of the data points is identical for all signals and all components. Only the absolute values differ. Vials with a higher amount of matrix result in an absolute lower signal for spiked components.

Comparing the MVOC-PDMS vial with different discharge gases

Measuring the MVOC PDMS based vials with DBD plasma and cleaned air and N₂ as discharge gas reveals different peak relative intensities (see Figure 6). Especially the peak between 350 s and 400 s shows in N₂ a double peak in air only one. The substances corresponding to the retention time are 2-Heptanone and Styrene. Moreover, the relative intensity of the 2-Methylfuran signal at 98 s to the Isobutanol signal at 110 s shows a reversed behaviour when using air as discharge gas instead of N₂.

MVOC Chromatogram

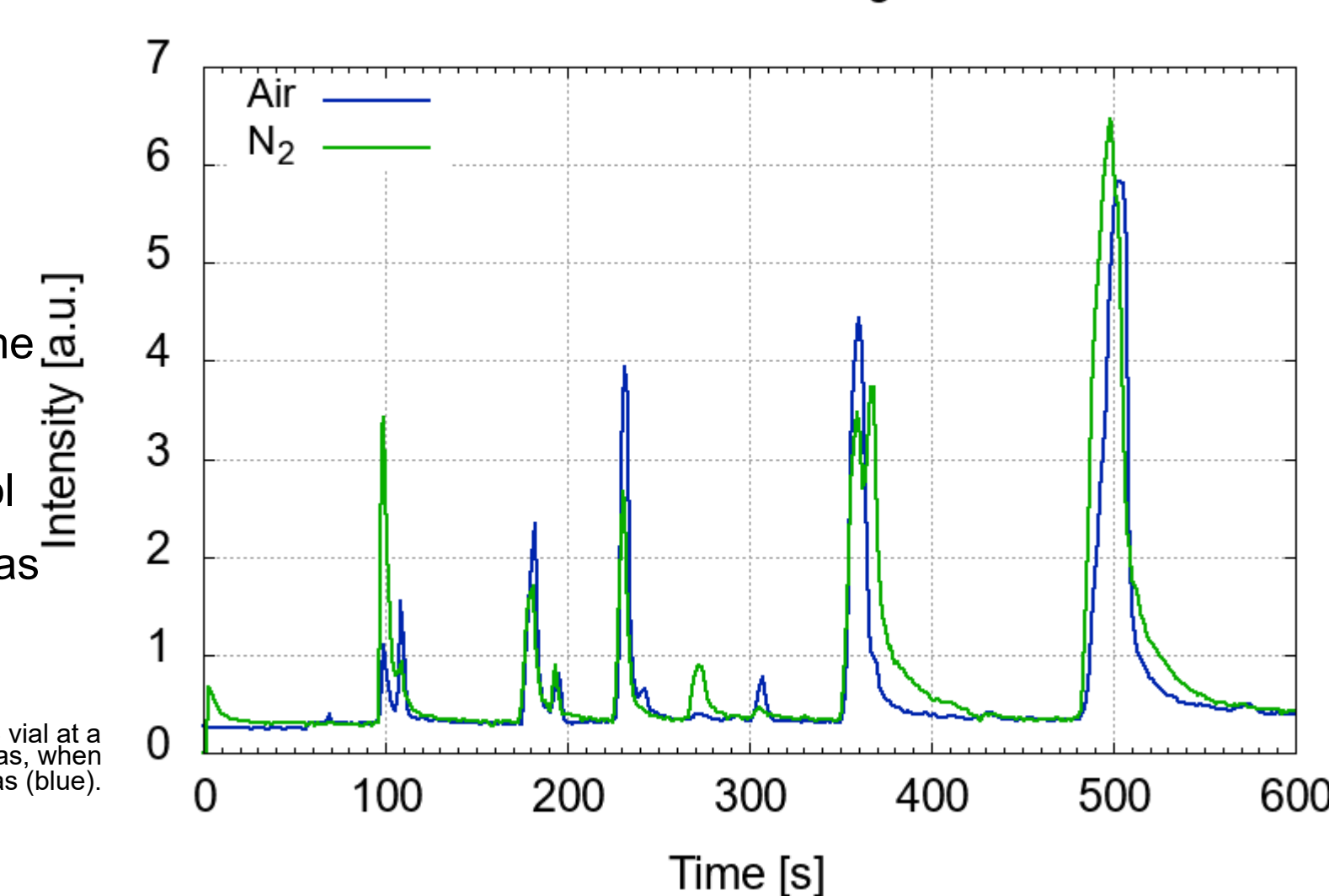
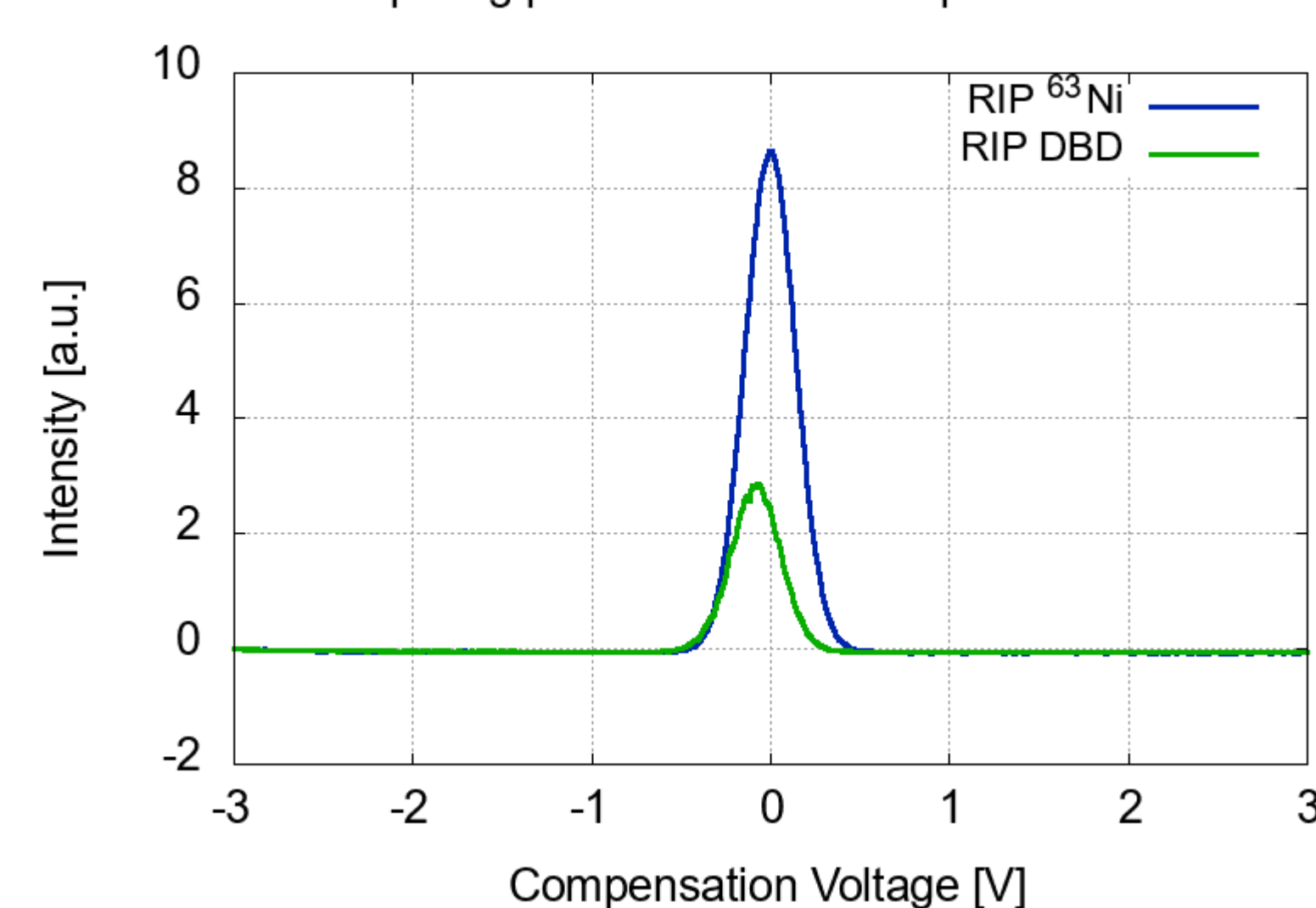


Figure 6: Chromatogram obtained from GC-DBD-FAIMS when measuring the matrix based MVOC vial at a humidity of approx. 22 %. Green: the measurement obtained, when using N₂ as discharge gas, when using air as discharge gas (blue).

Comparing positive reactant ion peak at 5% HV



Reactant ion peak:

DBD plasmas can form reactant ions. These depend strongly on the humidity and the discharge gas. Despite the fact that not only reactant ions are responsible for the ionisation in DBD a comparison is made for discussion. When comparing the reactant ion peaks obtained with the ⁶³Ni - and the DBD - FAIMS at 0 % relative humidity and 5 % high voltage of the FAIMS field, the signal received with ⁶³Ni is approx. 4 orders of magnitude higher than the DBD reactant ion signal (Figure 7).

Figure 7: Reactant ion peak for the DBD plasma ionisation (green) and for the ⁶³Ni ionisation (blue) for air as discharge / carrier gas with 0 % relative humidity.