Concept study for a sensitive and versatile chemical ionization time of flight instrument

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Overview

A sensitive and versatile chemical ionization (CI) time-of-flight (TOF) instrument using a dielectric barrier discharge (DBD) ion source and a high-transmission transfer stage featuring two ion funnels has been set-up and characterized.

Introduction

Chemical ionization mass spectrometry (CIMS) provides sensitivity for ultra sensitive trace gas measurements. The presented instrument is prototype for an airborne instrument to be deployed on a high-flying aircraft (12-20km). Stratospheric measurements at ambient pressures lower than 100 hPa require improved sensitivity. A new concept of including the ion molecule reaction (IMR) zone inside the first ion funnel is applied. This ion funnel works at 10x higher pressure compared to standard ion funnels.

Methods

A dielectric barrier discharge (DBD) ion source is used to effectively generate and ionize the reactant for negative CI. The DBD is separated from the IMR to reduce chemical noise. A transfer stage, as shown in Fig. 7, employing two ion funnels and two quadrupoles provides high transmission. The first ion funnel operates at 50 hPa and is employed as IMR region since it allows ion molecule reactions of approximately 30 ms reaction time, which is sufficient for most ion molecule reactions to reach completion. In order to provide sufficient resolution a Tofwerk HTOF was used, which allowed to acquire mass spectra on short time scales, which is an important improvement when compared to previous quadrupole analyzer instruments.

Instruments used:

- DBD plasma ion source custom built
  - ▷ Gas flow 400 - 1400 sccm N_2, Discharge gap 1.0 mm, Transfer capillary ID 0.8 - 2 mm
  - ▷ Driving circuit: Minipuls 2.1, GBS Elektronik GmbH, Germany
- Transfer stage
  - ▷ Ion funnel custom built and operated at 40 hPa (IMR)
  - ▷ Ion funnel custom built and operated at 5 hPa
  - ▷ Quadrupole custom built and operated at 10^{-2} hPa
  - ▷ Quadrupole or DC lenses at 10^{-5} hPa
- Mass analyzer: HTOF, Tofwerk Ag, Switzerland
  - ▷ Mass resolution 2500 in V-mode, Data acquisition at 20 kHz

Direct barrier discharge ion source

- Design of the ion source

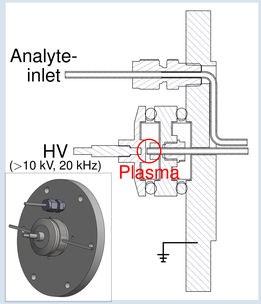

Figure 1: A cut through the DBD ion source and a drawing of the DBD setup (box lower left).

- Stability of the ion source

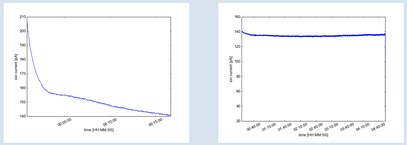

Figure 2: Measured negative ion current of the DBD ion source running for a few hours.

Fig. 3 and 4 show the measured characteristics of the ion molecule reaction zone. The dashed red and black lines in Fig. 3 indicate a plasma mode transition occurring below 150 hPa and generating much improved ion output. The ion output to the IMR depends on:

- the primary ion production in the DBD source, which depends on pressure, type of gas, and mass flow
- the transmission of the transfer capillary for given gas flow

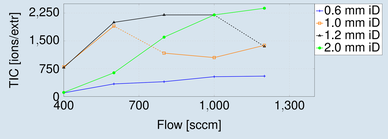

Figure 3: The measured TIC as a function of gas flow and transfer capillaries with different inner diameter (iD) and a length of 80 mm.

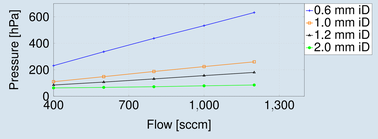

Figure 4: The measured pressure in the plasma region of the ion source using the defined gas flow of synthetic air and transfer capillaries with different inner diameter (iD) and a length of 80 mm.

- Generation of reactant ions

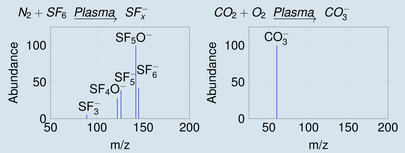

Figure 5: Generation of different reactant ions and measured mass spectra.

- Brilliance of the ion source

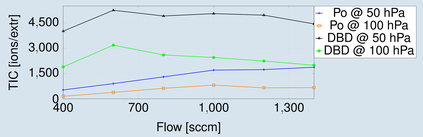

Figure 6: Comparison of a 10 mCi Po ion source with the DBD ion source (12 kV, 20 kHz, transfer capillary: ID 1,2 mm, 69 mm length). The nitrogen gas flow was mixed with 0.4 sccm SF_6.

Transfer stage

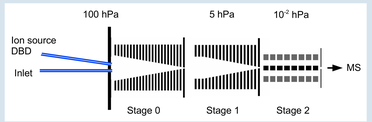

Figure 7: Schematic of the transfer stage custom built but without the last transfer element.

Stage	0	1	2	TOF
Gas flow in [sccm]	500 - 2000	500	50	0.01
Pressure [hPa]	25 - 60	5	10^{-2}	10^{-6}
Ion transmission	0.2 - 0.8	0.5	0.5	?

Ion transmission of the transfer stage: 10 %

- Ion funnel used as ion molecule reaction zone
- Lower collision induced energy at higher pressure
- Efficient ion transfer

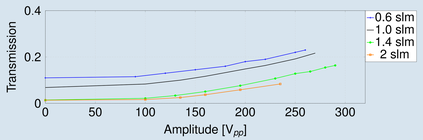

Figure 8: Transmission of ion funnel at 50 hPa using different voltage amplitudes and gas flows.

- Limit of the ion funnel

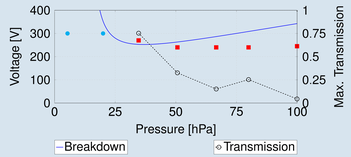

Figure 9: The electrical breakdown limit and transmission of the Stage 0 ion funnel having 0.25 mm electrode distance measured at different voltage amplitudes (@ 10 MHz). The blue line shows the calculated breakdown voltage in nitrogen for 0.25 mm electrode distance [1]. The red squares show the breakdown voltage limit in the experiment, the cyan dots have been reached without the ignition of a plasma. The black dashed line shows the maximum transmission measured before the ignition of a plasma using a gas flow of 1 slm.

An instrument with comparably low detection limit

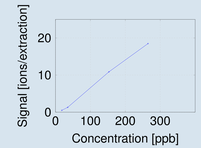

Figure 10: Calibration of the the instrument for SO_2 using CO_3^- reactant ions.

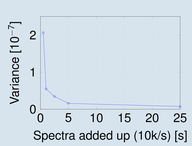

Figure 11: Variance of the SO_2 measurements.

Measured detection limit for SO_2:
< 10 pptV (1 s; 3σ)
Literature detection limits for SO_2:
- 40 pptV (60 s; 2σ) [2]
- 20 pptV (3 s; 1σ) [3]

Results and Conclusions

- Design of a brilliant and versatile DBD ion source
  ⇒ The DBD produces up to 5x more ions than a 10 mCi Po ion source
- Ion molecule reaction zone combined with an 100 hPa ion funnel for high ion transmission
- A sensitive and versatile CI-TOF prototype is available

Outlook

- Optimization of reactant analyte chemistry
- Determine detection limits for other species
- Online calibration for analytes of interest
- Construct an automated airborne instrument

Literature

K. T. A. L. Burm. "Calculation of the Townsend Discharge Coefficients and the Paschen Curve Coefficients". In: *Contributions to Plasma Physics* 47.3 (2007), pp. 177–182.

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