Electronic and Optical Characterization of the Active Capillary Plasma Ionization Source

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Ambient ionization coupled with mass spectrometry has generated significant interest because it opens new ways for direct, fast and sensitive mass spectrometric detection of organic molecules. However, there are also limitations: the ionization takes place in an open environment, it is difficult to separate sample desorption from the ionization stel, and ion transport efficiency to the mass spectrometer is limited. Additionally, there are only few fundamental studies on plasma-based ionization. In our lab, we developed an active capillary plasma ionization source, which is directly connected to the MS. It provides an enclosed ionization volume, precisely controllable gas-phase conditions and a 100% transport efficiency of the ions to the MS.

In this work, this active capillary plasma ionization source, which is based on a dielectric barrier discharge, was characterized using optical emission spectroscopy and electrical current measurements of the discharge events. The source consists of a stainless steel capillary inserted into a glass capillary, working as one electrode, and a copper ring surrounding the glass capillary functioning as the counter-electrode. A cold plasma is generated by applying a sine or square modulated high voltage to the electrode, in nitrogen or air as discharge gas. All optical measurements were performed using UV-VIS spectrometry in the range of 200-850 nm facing the plasma source from the front.

We studied the influence of the applied wave form on the discharge. Square and sine waves were compared by measuring the current in the plasma. The sine wave produced more uniformely distrbuted discharge events than the square wave. However, the charge (integration of the current) over one period was the same for both wave forms, therefore the square-wave generated a higher charge carrier density. Additionally, the poperties of the filaments were studied by monitoring transitions of NO ($A^2\sum$ --> $^2\pi$) and N_2 (2^{nd} positive system and Meinel band) using optical emission spectroscopy. The intensity of the N_2 transition ($C^3\pi_u$ --> $X^1\sum_g$) could be modified by increasing the applied voltage, since the excited N_2 state $C^3\pi_u$ is mainly formed through a reaction of ground-state N_2 ($X^1\sum_g$) with electrons.

In conclusion, characterization of the plasma not only helps to improve the understanding of the ionization mechanism but also allows to optimize the performance of the plasma source when coupled with the mass spectrometer.