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Capillary Dielectric Barrier Discharge: Transition from Soft Ionization to Dissociative Plasma

Felix David Klute,[†] Antje Michels,[†] Alexander Schütz,[†] Cedomil Vadla,[‡] Vlasta Horvatic,^{*,‡} and Joachim Franzke[†]

[†] ISAS—Leibniz Institut für analytische Wissenschaften, Bunsen-Kirchhoff-Str. 11, 44139 Dortmund, Germany

[‡] Institute of Physics, Bijenicka 46, 10000 Zagreb, Croatia

AUTHOR INFORMATION

*Corresponding Author

E-mail: blecic@ifs.hr

Fax: +385-1-469-8889

ABSTRACT

A capillary He dielectric barrier discharge was investigated in respect to its performance as a soft or dissociative ionization source. Spatiotemporal measurements of the plasma emission showed that in one voltage duty cycle the plasma evolved from soft to dissociative ionization source. Earliest in time the soft plasma was generated between the electrodes as well as outside the capillary forming the plasma jet. It was characterized by significant radiation arising only from He and N_2^+ , which are known to be important in the process of the soft ionization of the analyte. Later in time the plasma capable of dissociating molecules develops. It is characterized by appreciable radiation from analyte dissociation products, and is restricted to inter-electrode region in the capillary. Thus, for the soft ionization purposes, it is feasible to introduce the analyte exclusively in the plasma jet. For elemental analysis the inter-electrode plasma is appropriate.

Dielectric barrier discharges are non-equilibrium gas discharges formed between two electrodes separated by one or two dielectric barriers and powered by high alternating voltage at an appropriate high frequency. A stable operation, the possibility to operate at atmospheric pressure with different discharge gases, low power consumption, easy to set up in simple and miniaturized form and generation of various radicals and ionic species that enable molecular dissociation, excitation and ionization of the analytical targets, are the characteristics of these discharges, which made them attractive for use in a variety of analytical applications. Recent reviews that comprehensively present the principles of operation, development, applications, and future prospects of these ionization sources are available in literature.¹⁻⁵ It has been demonstrated that the plasma jets of DBDs have excellent capability for soft ionization of molecules, and therefore they have been successfully used as ionization sources in mass spectrometry⁶⁻⁸ and ion mobility spectrometry.⁹ DBDs are also able to efficiently dissociate analytes, which promoted their use as atomizers in elemental detection performed by optical emission spectroscopy.¹⁰⁻¹³

The present investigation deals with the temporal and spatial evolution of the emission intensities from the capillary DBD operated in He with CHClF_2 as analyte with the aim to explore under which operating conditions it is most appropriate for use as a soft or a dissociative ionization source. The experiment was performed in capillary DBD with two ring electrodes separated by ~ 10 mm. Due to its small plasma length (~ 1 mm) the planar geometry was not convenient for the present investigation of the spatial emission intensity distribution with adequate resolution. Based on the spatiotemporally resolved development of the emission from helium and dissociation products of CHClF_2 and H_2O , it will be shown that in time, during one half of the high voltage duty cycle, the DBD plasma evolves from soft to dissociative ionization source, and that the working regime can be altered by the proper choice of certain parameters, such as the electrode width and/or the operating voltage.

EXPERIMENTAL SECTION

Experiment. The illustration of the experimental arrangement is shown in Figure 1. The dielectric barrier discharge (DBD) was produced in a glass capillary (outer diameter: 1 mm, inner diameter: 0.5 mm) with two electrodes separated by ≈ 10 mm, which surrounded the capillary. The front high voltage (HV) electrode was suited about 1 mm from the capillary orifice. The DBD was operated in He with CHClF_2 as analyte. One line of gas supply to the DBD was pure helium, and the second one contained a prepared mixture of He/ CHClF_2 . The concentration of the prepared mixture varied from 750 ppb to 150 ppm, depending on the

measurement requirements. The overall He/CHClF₂ mixture introduced into the DBD was varied by adjusting the flows (controlled by flow-meters) in the two gas lines keeping the total flow-rate constant.

The high voltage was applied to the front electrode, while the rear electrode was grounded over the current probe of the Agilent DSO-X 2002A oscilloscope. The HV generator supplied the square-wave voltages with a rise-time within 0.01 μ s and the peak-to-peak voltages up to 4 kV. A function generator providing rectangular pulses (frequency: 20 - 40 kHz) was used to modulate the HV generator. The voltage signal on DBD electrodes was measured by a high voltage probe (Tektronix P6015).

The DBD was mounted on a micrometer stage, and the spatially resolved emission measurements were performed by translating the DBD in steps of 0.5 mm along its axis.

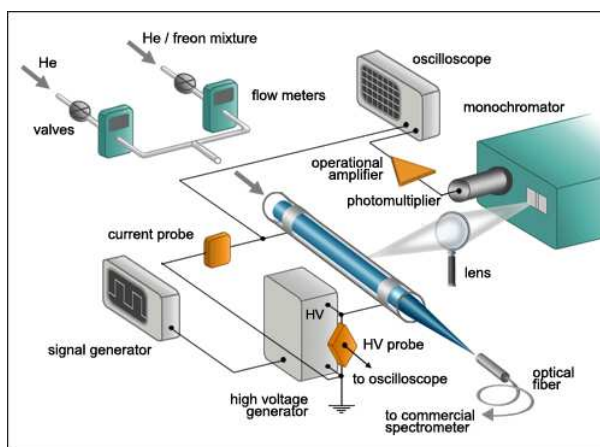


Figure 1. The illustration of the experimental arrangement.

In the spatiotemporally resolved emission of the He (706 nm), N₂⁺ (391 nm), O (777 nm) and F (739 nm) was observed side-on with respect to the discharge axis and detected by a system consisting of a 1 m McPherson monochromator (grating: 1200 grooves/mm; slit widths: 250 μ m; band pass: 0.25 nm), an EMI 9588 QB photomultiplier (rise time: 10 ns) and a home made fast amplifier (rise time: 0.8 ns). The emission light was imaged in 1:1 ratio with a lens onto the entrance slit of the monochromator.

For the determination of the limit of detection of CHClF₂ in He the plasma was observed end-on, and the emission intensities, collected by optical fiber, were measured using an Ocean Optics USB 2000 CCD spectrometer (slit width: 50 μ m, resolution: 1.5 nm).

The DBD current was measured simultaneously with the spatiotemporally resolved optical emission from the discharge by measuring the voltage over a 100 Ω metal film resistor, using a 70 MHz digital storage oscilloscope (Agilent DSO-X 2002A) triggered by the signal generator pulse.

MEASUREMENTS AND RESULTS

Measurements. At each x-position along the DBD axis the time evolution of the emission intensities of He 706, N_2^+ 391, O 777 and F 739 nm lines was recorded with the experimental arrangement shown in Figure 1. The emission intensity was simultaneously measured with the discharge current.

The acquisition time for intensity measurements was kept at $\Delta t = 25$ ns, and 2000 points were collected during one voltage duty cycle (50 μs). It was not necessary to increase the sampling rate, because with the higher time resolution (up to $\Delta t = 5$ ns) the signals showed same behavior.

Due to the statistic nature of the measurement it was necessary to average over several individual measurements. Due to the stability of the voltage supply the discharge could be operated without a noticeable drift in either the plasma current or the emission signal for several hours, allowing averaged measurements.

Results. The collection of the position and time dependent emission intensities for all investigated species enables the construction of two-dimensional x-t intensity plots in which the variation of the magnitude of the intensity is represented in different colors.

Figure 2 shows the spatiotemporal evolution of the emissions from the DBD measured in the conditions where both soft and dissociative characteristics of the discharge could be observed. The results recorded during the positive high voltage period are shown. The measurements were done in 36 ppm He/ CHClF_2 mixture with the applied voltage of 4 kV and the total gas flow-rate of 250 ml min^{-1} . The widths of the HV and ground electrodes were ≈ 0.5 mm and \approx

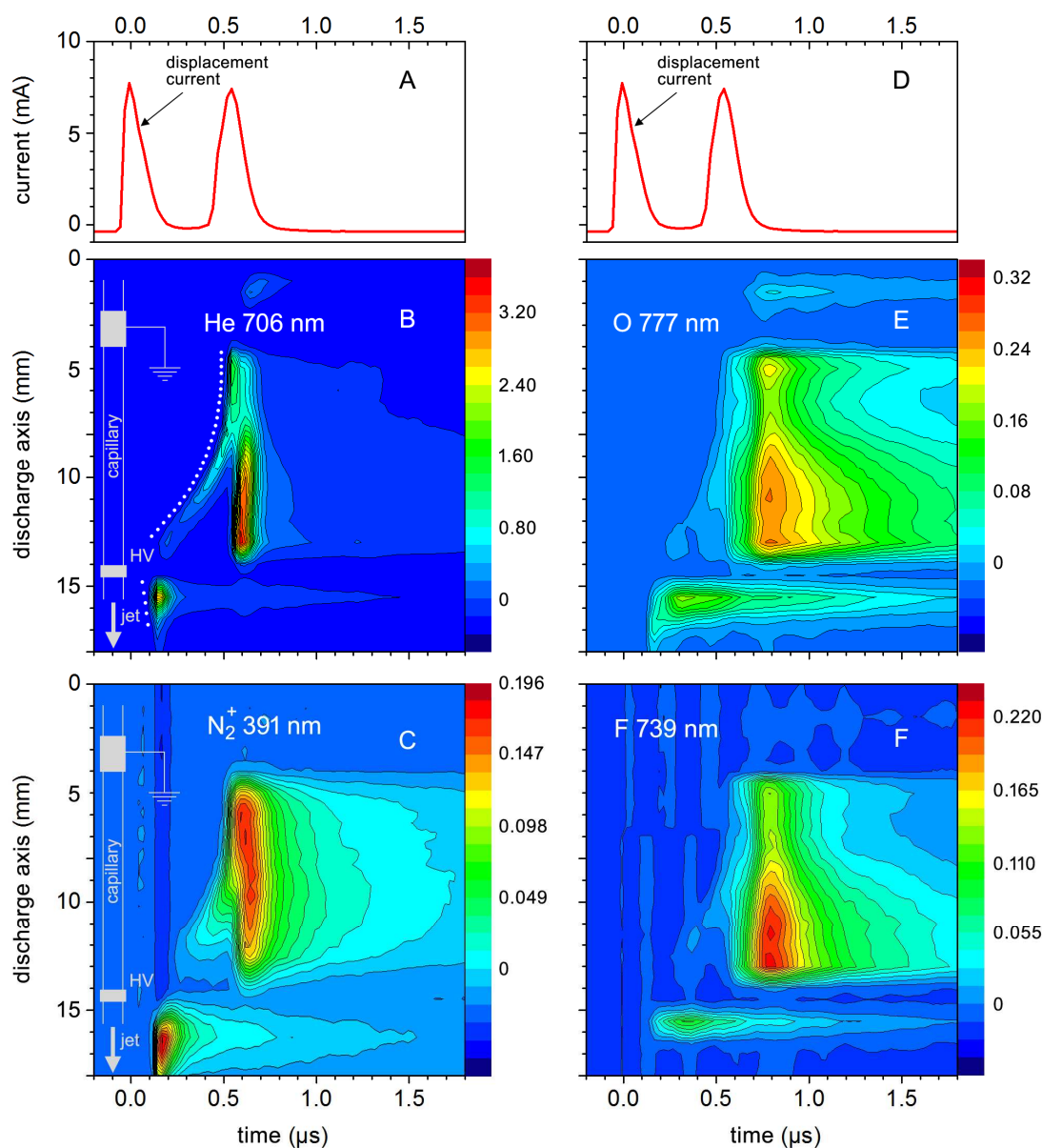


Figure 2. The spatial and temporal evolution of the emission intensities observed from DBD during the positive HV period. The HV applied and the gas flow-rate were $V = 4$ kV and 250 ml min^{-1} , respectively. (A), (D) The discharge current signal. (B), (C), (E), (F) Emissions of He 706, N_2^+ 391, O 777 and F 739 nm lines observed from a 36 ppm He/ CHClF_2 mixture, respectively. The dotted line in (B) is a guide to the eye for the early, soft plasma formation.

1.5 mm, respectively. The discharge current vs. time is displayed in Figure 2A and reproduced in Figure 2D. The time scale origin was set to coincide with the peak of the displacement current. The current corresponding to the ignition of the discharge between the electrodes in the capillary occurs at $t = 0.51 \mu\text{s}$. The spatial and temporal distribution of the intensities of the He 706 nm line and N_2^+ molecular band at 391 nm are displayed in Figures 2B and 2C, respectively. They both show the early plasma¹⁴ (indicated with dotted line in Figure 2B) formation which precedes the electrode plasma ignition in the capillary that

coincides with the discharge current. In this early stage ($t < 0.5 \mu\text{s}$) no significant emission from the dissociation products (F, Cl) of the analyte (CHClF_2) could be observed in the capillary. There were only traces of dissociation recorded in the plasma jet, and that was only due to the fact that the results presented in Figure 4 were obtained at high voltage (4 kV). At lower voltages ($V < 3.5 \text{ kV}$) no dissociation takes place in the plasma jet either, and the DBD is appropriate for the application as soft ionization plasma.

Further in time ($t > 0.51 \mu\text{s}$), after the formation of electrode plasma was completed, the dissociation of the analyte took place. This is shown in Figures 2E and 2F where the spatiotemporal evolution of the O 777 nm and F 739 nm lines is displayed. The oxygen line indicates the dissociation of H_2O (trace impurity in He), while the fluorine line is the signature of the dissociation of the analyte. In this late stage of the discharge the DBD plasma can serve as the dissociative ionization source appropriate for use in elemental spectroscopy.

By decreasing the total electrode width (anode + cathode) below $\sim 2 \text{ mm}$, and/or lowering the operating voltage to less than 3.5 kV, the dissociative capability of the DB could be suppressed nearly completely. Under these conditions the only noticeable emission that could be observed was from He and N_2^+ (see Figures 2B, 2C). The previous investigations have shown that such plasma is suitable for soft ionization of analytes.¹⁵⁻¹⁹

The observed transition from soft to dissociative character of the DBD might be explained in the following way. The early plasma visible in the helium exited species is driven primarily by electrons that are accelerated to the HV electrode by the polarization the dielectric that takes place due the fast rise of the positive voltage. The high abundance of He leads to an effective excitation and ionization of the working gas and its impurities. Probably the most prominent of these impurities is N_2 which produces N_2^+ and electrons by Penning ionization in collisions with He metastables. When the early plasma neutralizes the initial charge created by the polarization of the positive voltage, the electrons that accumulated at the HV electrode are reaccelerated by the positive space charge that is slowly formed by positive species at the grounded electrode. This reacceleration compared to the initial early plasma is very fast, and leads to a by far stronger excitation of the working gas by more energetic electrons capable of dissociating analyte molecules.

It has been observed that at the constant operating voltage and the gas flow the dissociative regime of the DBD can be easily improved by increasing the width of the electrodes. The increase of electrode width yielded two orders of magnitude bigger dissociation signals, compared to signals achieved with DBDs that have thin electrodes and are usually used for soft ionization. This is due to the increase of the power dissipated in the capillary, which will be shown in the following.

The discharge current was measured for several electrode configurations having different widths. The HV applied was 3 kV, and the total flow was 250 ml min⁻¹. The results are shown in Figure 3, and the sizes of the particular HV and ground electrode widths are given in the legend. The integrals of the current (with the contribution from the displacement current being excluded) represent the corresponding charges dissipated in the discharge, which are shown in the inset of the Figure 3 as a function of the total electrode width. It can be seen that the charge, which is proportional to the power consumed in DBD, increases linearly with the increase of the total electrode width. It has to be noted that the two capillaries with the smallest total electrode width of 4.25 mm represent a special case. Although the dissipated charge in these discharges is nearly the same, the temporal development of the discharge current is extremely different. While the plasma current of the thick HV electrode variant follows slightly under 1 μ s after the displacement current, it takes more than 8 μ s for the plasma current of the thin HV electrode variant to develop. This behavior is still under investigation and not yet fully understood.

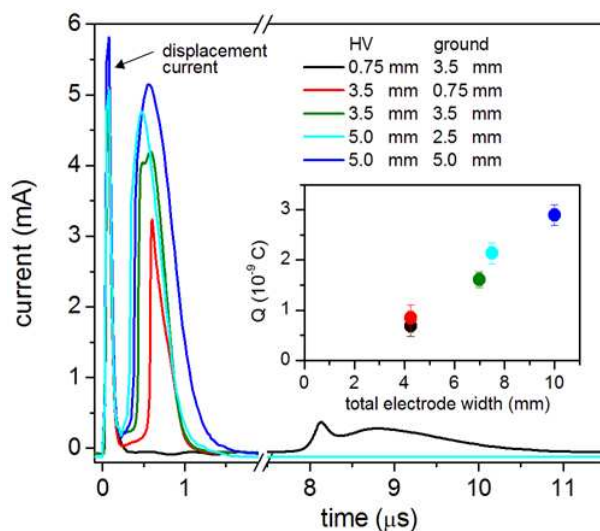


Figure 3. The discharge current recorded in the positive voltage period for DBDs having different widths of the anode and cathode. The inset shows the correlation between the charge Q dissipated in the discharge and the total (anode + cathode) electrode width.

The electrode plasma cannot only be enhanced, as described before, it is also possible to suppress this part of the plasma and thereby decreasing the effect of dissociation and making the DBDI even softer and more efficient for soft ionization. By applying a shortened high voltage pulse, while retaining the overall frequency, the development of the early plasma in the inner capillary will be interrupted before the electrode plasma can ignite. This leads to partly ignited early plasma inside the capillary and no strong dissociative processes in the discharge. Figure 4 shows the results of a first test where a plasma was operated in front of a

mass spectrometer with such a voltage, switching the electrode plasma on and off again. A mixture of Menthone ($M=154$) and Diisopropyl Methylphosphonate (DIMP) ($M=180$) was used as analyte. DIMP is known to be easily fragmented. The signal of DIMP drastically increases and has a much better S/N ratio for the switched off electrode plasma case, indicating a better efficiency of the DBDI without the electrode plasma. More investigations are still necessary in order to decide whether this behavior is representative and/or for which classes of analytes it can be observed. These investigations would go beyond the scope of this work.

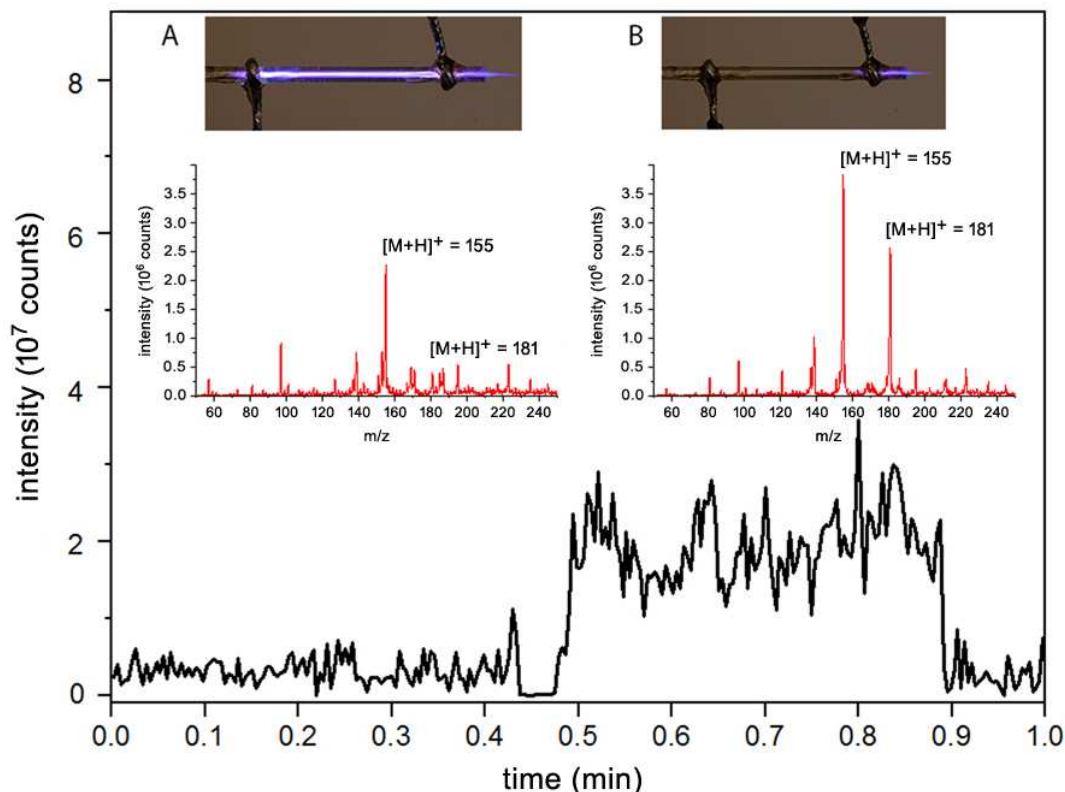


Figure 4. Time dependent development of Diisopropyl Methylphosphonate (DIMP) $[M+H]^+ = 181$ m/z for alternating plasma states. Inlet A shows the averaged mass spectrum from 0 to 0.5 min when the electrode plasma was still switched on. Inlet B shows the averaged spectrum from 0.5 to 0.9 min when the electrode plasma was switched off. DIMP: $[M+H]^+ = 181$ m/z , $[M-84+H]^+ = 97$ m/z , $[M-41+H]^+ = 137$ m/z ; Menthone: $[M+H]^+ = 155$ m/z

After improving the performance of the investigated DBD as a dissociative ionization source by optimizing discharge parameters such as electrode width, applied voltage and flow, its utility for elemental analysis was examined by measuring emission arising from dissociation products of CHClF_2 in helium. Chlorine and fluorine lines at 912 and 739 nm respectively, were measured as function of CHClF_2 concentration. The emission light from DBD was collected end-on with an optical fiber and measured using an Ocean Optics CCD spectrometer. The integration time was kept below 500 ms while measuring intensities near

the LOD and was adjusted to even smaller times when the relevant intensities increased due to high concentrations of analyte. The mixture flow-rate was 500 mL min^{-1} , the DBD electrodes were of equal widths (5 mm) and the operating voltage was 3.5 kV.

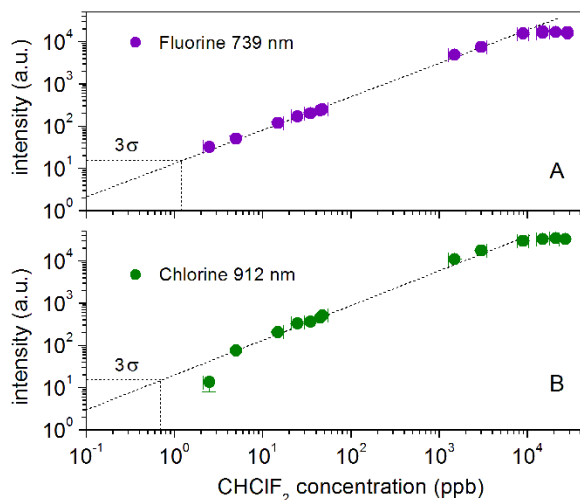


Figure 5. Calibration curve of CHClF_2 in He DBD obtained by the measurement of the emission intensities of the F 739 nm (A) and Cl 912 nm (B) lines. The 3σ LOD are indicated.

Calibration measurements of CHClF_2 in He are shown in Figure 5. The depicted Y-errors are the uncertainties of the fit that was used to determine the line intensity, while the X-error bars are estimated uncertainties for the gas mixture preparation. The dynamic range was found linear over approximately 3 orders of magnitude. The 3σ limits of detection of CHClF_2 in He, determined from signal/noise ratio, were found to be approximately 0.7 ppb and 1.2 ppb using the Cl 912 and the F 739 nm line, respectively. Given the flow of 500 mL min^{-1} for the discharge this corresponds to a detectable CHClF_2 mass flow of 22 pg/s and 39 pg/s from the Cl 912 and the F 739 nm line, respectively. The present LODs are therefore comparable to¹⁰ or better than¹¹⁻¹³ previously reported ones obtained by employing DBD-OES detection. To further emphasize these promising results, the presented DBD-OES system was coupled to a commercial GC and first tests were started. While these first measurements with halogenated liquid samples such as CHCl_3 or $\text{C}_6\text{H}_5\text{F}$ suffer from well-known problems, namely coupling the flow of the GC into the DBD-OES system, they also show comparable LODs to the previously described direct injection of the CHClF_2 in the range of some tens of picograms. This is comparable to or even better than some DBD-OES methods employed by other groups²⁰⁻²³. The DBD-OES system presented here can also be compared to established detectors like FID or BID²⁴ which can provide higher sensitivity of only a couple of tens of picograms, but have no selectivity of their own giving the DBD-OES a clear advantage for certain applications.

CONCLUSION

In summary, the present investigation has shown that within the a half-cycle of the applied voltage the capillary DBD plasma evolves in time from soft to dissociative ionization source. In early stage, prior to the main discharge between the electrodes in the capillary, the plasma and the jet are not capable of dissociating the analyte with adequate efficiency. This early plasma is appropriate to be used as a soft ionization source when coupled with the mass spectrometer. After the early discharge finishes, the ignition of the plasma in the capillary occurs. This plasma has dissociative capabilities as it has been demonstrated by the OES measurements of the dissociation products of CHClF_2 in helium. The LOD comparable with previously reported ones in DBD-OES experiments were obtained.

The soft or dissociative working regime can be simply adjusted by varying the electrode width and/or operating voltage, thus making capillary DBD appropriate for use as soft ionization source for mass spectrometry as well as dissociative ionization source for elemental analysis by optical emission spectroscopy.

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