

Supporting information  
Monitoring of n-hexane degradation in a plasma  
reactor by Chemical Ionization Mass  
Spectrometry

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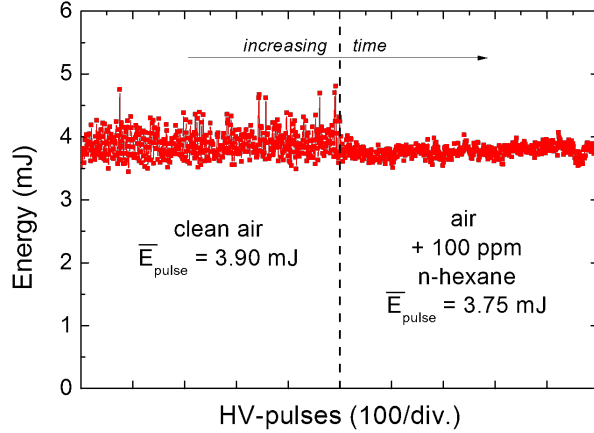


Figure 1: Energy per pulse deduced from the current and voltage waveforms, for a sample of 1000 HV-pulses, effect of n-hexane on the discharge stability.

For the same parameters values as in figure 2 in the article, plotted in this figure are the values of  $E_{pulse}$  measured for a sample of 1000 HV-pulses, the first five hundred being for air whereas the others were captured while the air was rapidly replaced by the mixture containing 100 ppm of n-hexane at the fixed flow rate of 0.5 L/mn. For clean air, the mean energy is 3.90 mJ (with a standard deviation of 0.2 mJ), whereas it is slightly lower for the mixture with n-hexane, 3.75 mJ (with a standard deviation of 0.1 mJ). However, there is a clear effect of the hydrocarbon on energy fluctuation: it is significantly lower when n-hexane is present compared to clean air. In other words, the functioning of the pulsed dielectric barrier discharge is somewhat stabilized by the hydrocarbon. At a given value of the HV-pulse repetition frequency, the amplitude of the current waveform may vary a little bit from pulse to pulse, depending on the applied voltage but above all depending on the gas mixture type, i.e. without (“clean” air) or with the presence of the hydrocarbon molecules. This current fluctuation effect induces a fluctuation of the deposited energy in the plasma from pulse to pulse, as can be seen in the figure 1.

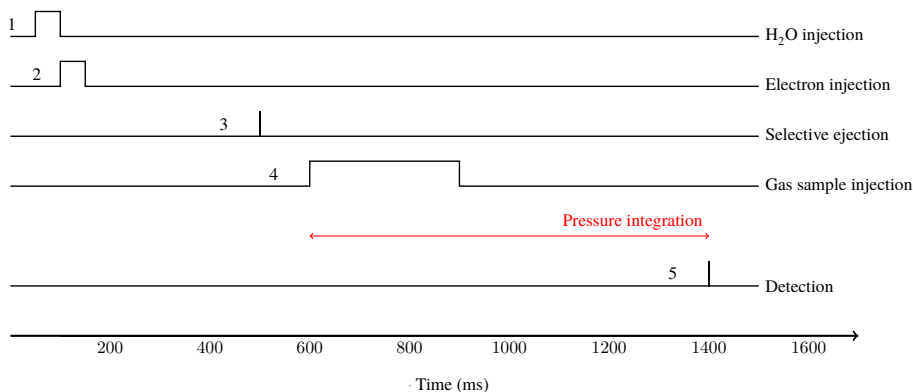


Figure 2: Timing diagram of the BTrap sequence.

Figure 2 shows the operating loop necessary for the real-time analysis of the gas stream:

1. The introduction of the precursor molecule H<sub>2</sub>O at a pressure of  $2 \cdot 10^{-6}$  Torr for 10 ms.
2. The ionization of the H<sub>2</sub>O molecule with a 70 eV electron beam  $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2\text{O}^+ + 2 \text{e}^-$ . The generated H<sub>2</sub>O<sup>+</sup> ions then need a sufficient amount of time to form the precursor ion H<sub>3</sub>O<sup>+</sup> through reactions with H<sub>2</sub>O molecules:  $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HO}$ .
3. The ejection of all ions excluding H<sub>3</sub>O<sup>+</sup>, these unwanted ions were formed alongside H<sub>3</sub>O<sup>+</sup> but are not necessary for the experiment.
4. The introduction of the gas sample, proton transfer reaction between the precursor H<sub>3</sub>O<sup>+</sup> and the gas sample *M* takes place during this phase:  $\text{H}_3\text{O}^+ + \text{M} \rightarrow \text{H}_2\text{O} + \text{MH}^+$ . A delay of about (500 ms) is needed for the complete pumping of the cell to allow the pressure to drop to around  $10^{-8}$  Torr.
5. RF excitation and detection of the signal.

Difluorobenzene is injected at very low pressure ( $10^{-7}$  torr) for a few ms at the end of the experimental sequence as a calibrant for better mass identification. The reaction with O<sub>2</sub><sup>+</sup> precursor ion gives C<sub>6</sub>H<sub>4</sub>F<sub>2</sub><sup>+</sup> ion ( $m/z$  114.028) and with H<sub>3</sub>O<sup>+</sup> ion, C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>-H<sup>+</sup> ( $m/z$  115.035).

**General quantification formula for CI-MS** In the data treatment step, we need to determine the intensity of each analyte  $A_i$ . If a single analyte  $A_i$  reacts with the precursor ion  $P^+$  and shows fragmentation:



with  $j = 1 \dots f$ , the intensities of all the fragments issued from  $A_i$  have to be summed:

$$I_{F_i^+} = \sum_j I_{F_{ij}^+} \quad (2)$$

For a complex mixture of analytes, most of the  $F_{ij}^+$  ions appearing in the mass spectrum are common to several analytes. These ions are therefore not characteristic of a single analyte  $A_i$ , and the sum of the corresponding  $I_{F_{ij}^+}$  intensities does not give  $I_{F_i^+}$ .

An alternative solution for obtaining  $I_{F_i^+}$  consists in choosing a single fragment ion  $F_{i1}^+$  characteristic of  $A_i$ , and dividing its intensity by the corresponding branching ratio  $\alpha_{i1}$ . The products and branching ratios of the CI reaction of  $A_i$  are then supposed to be known, either from literature or better from measurements under the same experimental conditions, as done in the present work.

The molecular formula of  $F_{i1}^+$  requires a very careful choice, since  $F_{i1}^+$  must originate from the analyte  $A_i$  exclusively, with the highest possible intensity in comparison with the other  $F_{ij}^+$  fragments.

The absolute ion intensities  $I_{F_i^+}$  are divided by  $I_{sum}$ , in order to obtain the relative intensities of each ion  $[F_i^+]$ , where *sum* represents the sum of the intensities of all detected ions.

The general quantification formula is based on the perfect gas law. At temperature  $T$ , it is expressed as follows,  $k_B$  being the Boltzmann constant, and  $[A_i]$  (ppm) being the mixing ratio of  $A_i$  in the gas sample:

$$[A_i] = -\frac{\ln(P^+) \cdot I_{F_i^+} \cdot k_B \cdot T \cdot 10^6}{(1-(P^+)) \cdot k_i \cdot P \cdot t} \quad (3)$$

For  $T = 298$  K and accounting for unit conversion factors, the quantification formula becomes:

$$[A_i] = -\frac{\ln(P^+) \cdot (F_i^+) \cdot 10^6}{(1-(P^+)) \cdot 3.21 \cdot k_i \cdot P \cdot t} \quad (4)$$

Where  $k_i$  ( $10^{-9} \text{ cm}^3 \cdot \text{s}^{-1}$ ) represents the rate coefficient of the CI reaction  $\text{P}^+ + \text{A}_i$ , an  $P \cdot t$  (mbar·ms) represents the sample amount introduced in a gas pulse.

The above relationship can be used either to determine analyte concentrations if the rate constants are known (case of  $\text{H}_3\text{O}^+$  precursor) or to determine rate constants and branching ratios if the sample composition is known (done with both precursors).

Fragments obtained from the reaction of the  $O_2^+$  precursor with n-hexane are presented in figure 3. This figure shows the linearity of product ion intensities as a function of n-hexane mixing ratio.

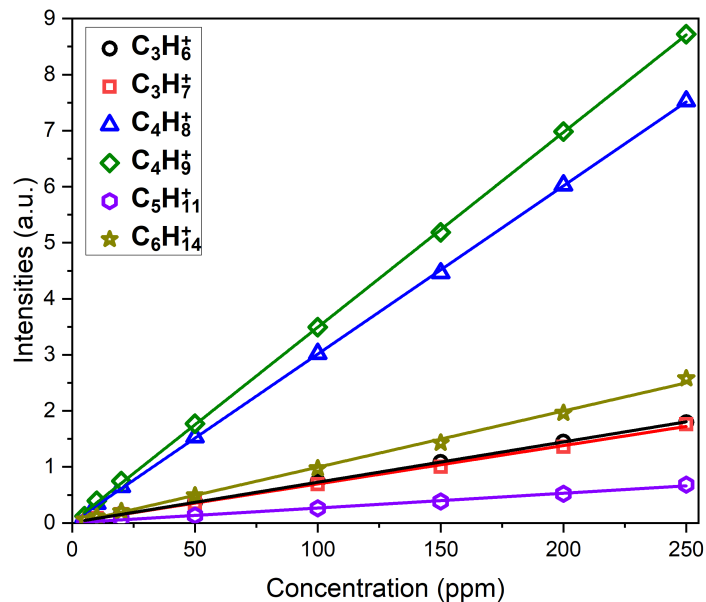
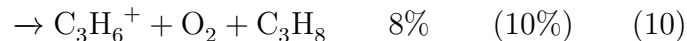
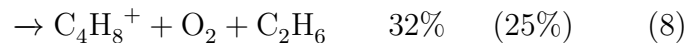
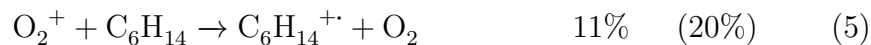


Figure 3: Intensities of the products issued from  $O_2^+$  reaction with n-hexane as a function of n-hexane mixing ratio.



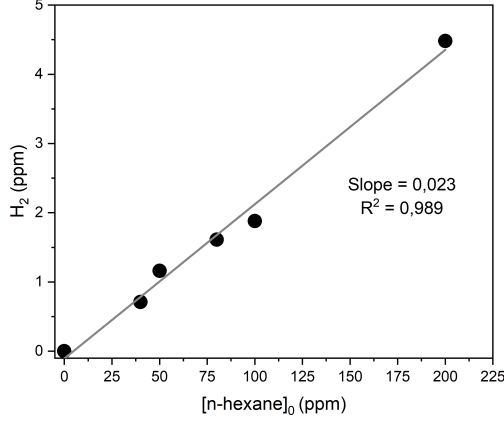
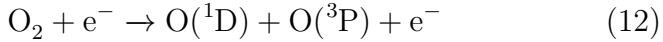
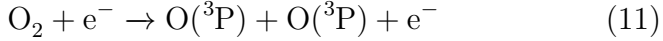


Figure 4: H<sub>2</sub> mixing ratio at the exit of the DBD for mixing ratios of n-hexane in air (SED: 225 J/L, applied voltage: 23.4 kV, HV-pulse repetition frequency: 500 Hz, gas flow rate: 0.5 L/min).

Ozone generation in a non-thermal plasma [1]–[3] can be simplified by the following reactions:

The initial step in forming O<sub>3</sub> is the electron impact dissociation of molecular O<sub>2</sub>:



The addition of a molecule in the air plasma, n-hexane in this case, leads to a decrease in the measured mixing ratio of ozone as illustrated by the results presented in figure 5. This can be explained by the consumption of atomic oxygen in oxidation reactions at the expense of ozone formation.

Since the degradation of most VOCs in air plasma is mainly initiated by atomic oxygen, measuring ozone mixing ratio in the plasma reactor is a good method to assess the capacity of the plasma to oxidize a VOC or a hydrocarbon via the formation of oxygen atom.

Exact mass (u)	Ion	Attribution	k	50 ppm	37.5 ppm	25 ppm	17.5 ppm	10 ppm	5 ppm
28.019	HCN-H <sup>+</sup>	hydrogen cyanide	3.33	0.086	0.075	0.046	0.036	0.01534	0.009
29.998	NO <sup>+</sup>	nitrogen oxyde	0.89	0.104	0.088	0.057	0.046	0.023	0.007
31.018	COH <sub>2</sub> -H <sup>+</sup>	formaldehyde	1.84	17.431	13.847	10.022	7.273	4.887	2.15536
33.034	CH <sub>4</sub> O-H <sup>+</sup>	methanol	2.3	0.146	0.095	0.043	0.033	0.006	0
43.018	C <sub>2</sub> H <sub>2</sub> O-H <sup>+</sup>	ketene	2.4	1.043	0.827	0.558	0.425	0.220	0.0976
43.055	C <sub>3</sub> H <sub>6</sub> -H <sup>+</sup>	propene	1.64	0.218	0.159	0.087	0.048	0.026	0.001
45.034	C <sub>2</sub> H <sub>4</sub> O-H <sup>+</sup>	acetaldehyde	3.09	2,003	1,324	0.672	0.374	0.090	0
45.993	NO <sub>2</sub> <sup>+</sup>	nitrogen dioxide	1.2	1,438	1,130	0.828	0.658	0.381	0.198
48.008	NO <sub>2</sub> H-H <sup>+</sup>	nitrous acid	1.81	0.089	0.091	0.068	0.048	0.034	0.015
59.05	C <sub>3</sub> H <sub>6</sub> O-H <sup>+</sup>	propanal	3.13	0.465	0.263	0.066	0.002	0	0
61.029	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> -H <sup>+</sup>	acetic acid	2.2	0.185	0.143	0.060	0.054	0.009	0
62.024	CH <sub>3</sub> NO <sub>2</sub> -H <sup>+</sup>	nitromethane	3.7	0.130	0.093	0.062	0.032	0.006	0.010
64.003	HNO <sub>3</sub> -H <sup>+</sup>	nitric acid	1.6	0.604	0.473	0.318	0.223	0.130	0.068
71.086	C <sub>5</sub> H <sub>10</sub> -H <sup>+</sup>	pentene	1.91	0.131	0.055	0.048	0.018	0	0.002
78.019	CH <sub>3</sub> NO <sub>3</sub> -H <sup>+</sup>	methyl nitrate	2.96	0.292	0.224	0.151	0.103	0.060	0.030
85.102	C <sub>6</sub> H <sub>12</sub> -H <sup>+</sup>	hexene	2.05	0.954	0.681	0.411	0.265	0.126	0.039
92.035	C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub> -H <sup>+</sup>	ethyl nitrate	3	0.109	0.082	0.047	0.024	0.017	0.004
101.097	C <sub>6</sub> H <sub>12</sub> O-H <sup>+</sup>	hexanal	4	0.190	0.138	0.032	0.001	0.010	0
122.009	C <sub>2</sub> H <sub>3</sub> NO <sub>5</sub> -H <sup>+</sup>	PAN	2.7	0.253	0.200	0.115	0.086	0.037	0.026

Table 1: Mixing ratios of the by-products detected with H<sub>3</sub>O<sup>+</sup> precursor as a function of the mixing ratio of n-hexane injected with their rate coefficients k (10<sup>-9</sup> cm<sup>3</sup>s<sup>-1</sup>) (SED: 225 J/L, applied voltage: 23.4 kV, HV-pulse repetition frequency: 500 Hz, gas flow rate: 0.5 L/min).



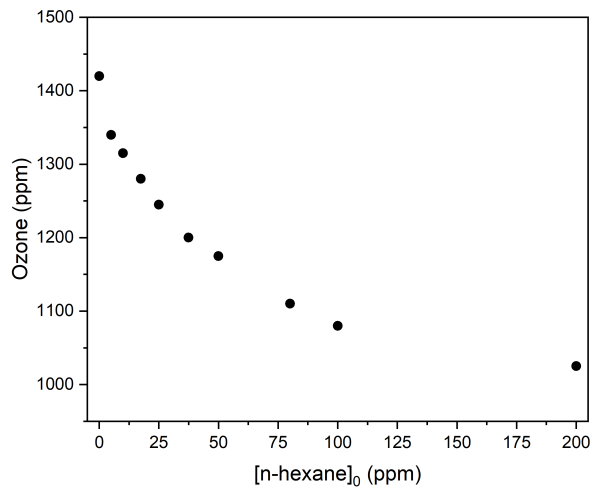


Figure 5: Measurement of ozone mixing ratio at the exit of the DBD for mixing ratios of n-hexane in air up to 200 ppm (SED: 225 J/L, applied voltage: 23.4 kV, HV-pulse repetition frequency: 500 Hz, gas flow rate: 0.5 L/min).

For the heaviest compounds, where several isomers are possible, quantification is carried out using an average value for the rate coefficient. Attributions and rate coefficients obtained from the PTR library (Pagonis, D., Sekimoto, K., & de Gouw, J. (2019)).

## References

- [1] S. Pekárek, “Non-thermal plasma ozone generation,” *Acta Polytechnica*, vol. 43, no. 6, pp. 47–51, 2003.
- [2] A. Fridman, *Plasma Chemistry I*. Jan. 2008, pp. 383–392, ISBN: 9780521847353. DOI: 10.1017/CB09780511546075.
- [3] U. Kogelschatz, B. Eliasson, and M. Hirth, “Ozone generation from oxygen and air: Discharge physics and reaction mechanisms,” *Ozone: Science & Engineering*, vol. 10, no. 4, pp. 367–377, 1988. DOI: 10.1080/01919518808552391. eprint: <https://doi.org/10.1080/01919518808552391>. [Online]. Available: <https://doi.org/10.1080/01919518808552391>.