

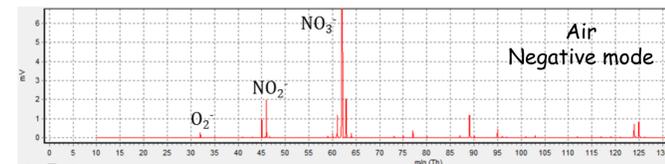
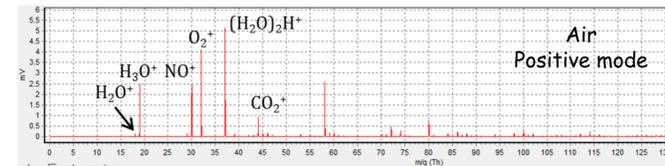
Introduction



Atmospheric pressure plasma source have been largely investigated for ambient ionization mass spectrometry [1-4]. The use of a mass spectrometer allow measurements with high sensibility and selectivity for chemical analysis. However the efficiency is influenced by the plasma properties.

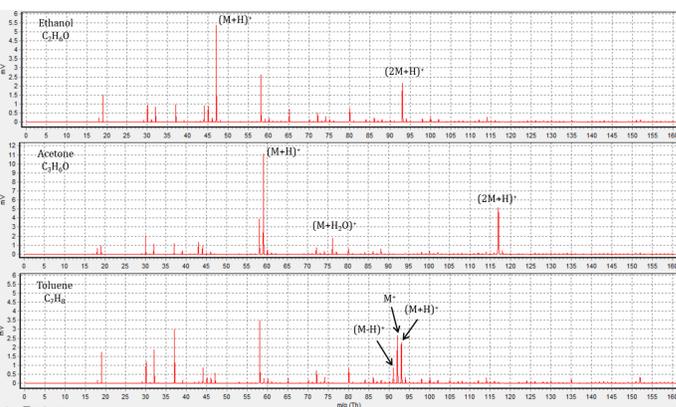
An atmospheric pressure plasma jet source based on DBD has been developed, It is coupled with a Time Of Flight Mass Spectrometer (TOF MS, CTOF-Tofwerk AG, Thun, Switzerland). The source is fed with Ne and powered by a square alternating voltage (20 kHz).

The purpose of this work is the evaluation of the source ability to ionize volatile samples such as ethanol, acetone, toluene and chloroform.



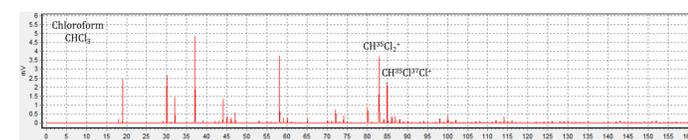
Mass spectra of different volatile samples

Positive mode

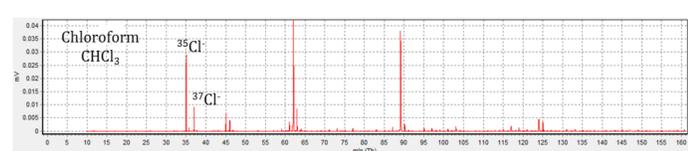


Sample	Formula	Masse (Da)	Peak	m/z (Th)	Proton affinity
Ethanol	C ₂ H ₆ O	46	(M+H) ⁺ ; (2M+H) ⁺	47; 93	776
Acetone	C ₃ H ₆ O	58	(M+H) ⁺ ; (M+H ₂ O) ⁺ ; (2M+H) ⁺	59; 76; 117	812
Toluene	C ₇ H ₈	92	(M+H) ⁺ ; M ⁺ ; (M+H) ⁻	91; 92; 93	794
Chloroform	CHCl ₃	118	CH ³⁵ Cl ₂ ⁺ ; CH ³⁵ Cl ³⁷ Cl ⁺	83; 85	660
Water	H ₂ O				694
Water cluster	(H ₂ O) ₂				831

Positive mode



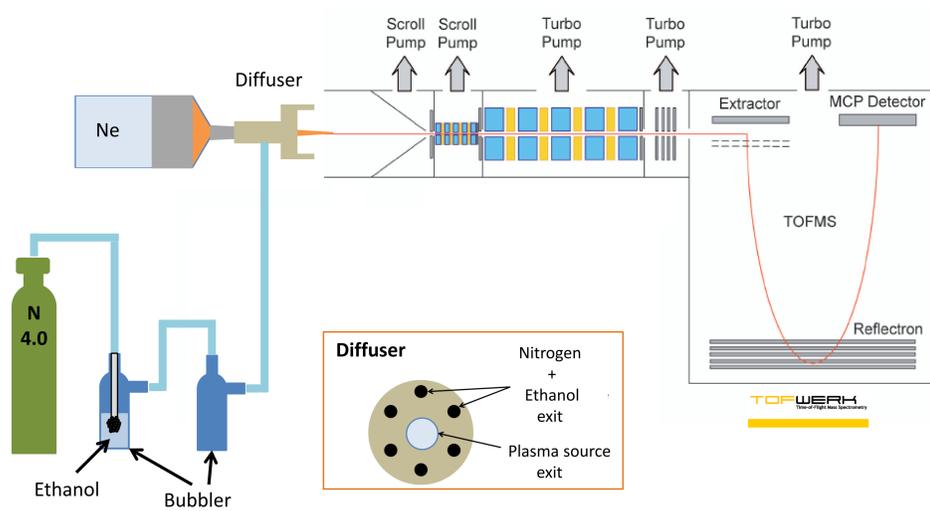
Negative mode



Two behaviors are observed: the molecules not fragmented (ethanol, acetone, toluene) and the molecule that has undergone fragmentation (chloroform). For the molecule not fragmented, we observe a peak corresponding to the protonated molecular ion at (M + H)⁺, for acetone and ethanol we also observe a peak at (2M + H)⁺ for the protonated dimer; and in the case of acetone a peak at (M + H₂O)⁺, which indicates a transfer of a water molecule to the acetone molecule. The apparition of these peaks occurs simultaneously with the decrease of the air ion peaks.

With the chloroform sample, the molecule was fragmented. In positive mode we observe two peaks corresponding to the dichloromethane ions and in negative mode two peaks corresponding to the chlorine ions.

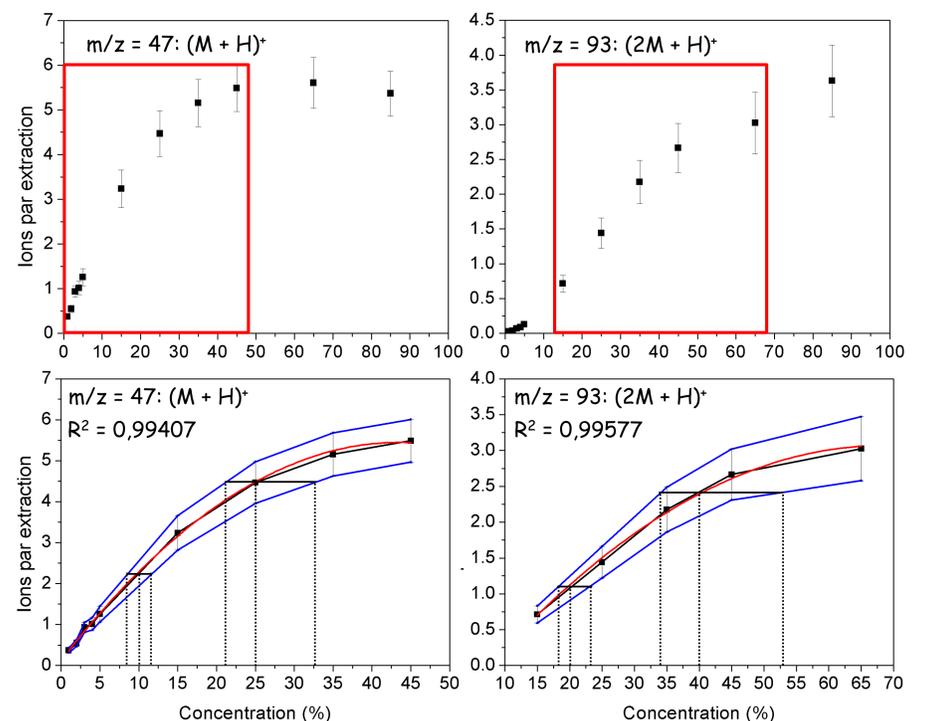
Preliminary quantitative analysis on ethanol sample



Next we tried to realize some quantitative experiments. These experiments were conducted with neon. The sample tested is ethanol (purity > 99%).

Samples of various concentrations are placed, in turn, in a nitrogen stream at 200 mL.min⁻¹. A diffuser has been designed, it allows the injection of the sample continuously around the plasma plume. Spectra are recorded during 5 minutes and the number of ions per extraction is averaged over that duration. From these results, calibration curves have been plotted for the protonated ion (m / z = 47) and the protonated dimer (m / z = 93).

Concentrations for reference samples have been deduced from these curves. For both calibration curves, the error on the concentration increase with the concentration. And for a fixed concentration, the error is bigger when the concentration is deduced from the calibration curve at 47 than when it is deduced from the calibration curve at 93.



Reference concentration (%)	Concentration deduced from the calibration curve for the peak at 47 (%)	Concentration deduced from the calibration curve for the peak at 93 (%)
20	23 ± 7	23 ± 5
30	26 ± 10	30 ± 8
50		42 ± 21

Conclusion

An atmospheric DBD plasma jet has been designed and studied with neon flow. The plasma source generated a jet extending over a few cm in open air. It has been coupled with the TOF-MS.

Ambient air characterization has been made in positive and negative modes.

Some volatile samples have been characterized by mass spectrometry in positive mode for the ethanol, acetone and toluene samples and in positive and negative modes for the chloroform sample.

A diffuser has been designed to inject the analyte through a nitrogen flow in the neon plasma plume at atmospheric pressure.

For ethanol, calibration curves were plotted for protonated ion (m/z = 47) and protonated dimer (m/z = 93). These curves have been tested with various reference concentrations.

References

- [1] J. T. Shelley and G. M. Hieftje. Ambient mass spectrometry: Approaching the chemical analysis of things as they are. *J. of Analytical Atomic Spectrometry*, 26 (2011), 2153-2159.
- [2] X. Ding, X. Zhan, X. Yuan, Z. Zhao, Y. Duan. Microfabricated Glow Discharge Plasma (MFGDP) for ambient Desorption/Ionization Mass Spectrometry. *Analytical chemistry*, 85 (2013), 9013-9020.
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