PULSED RADIOFREQUENCY GLOW DISCHARGE TIME OF FLIGHT MASS SPECTROMETRY FOR VOCs ANALYSIS: DEVELOPMENT OF A NEW INTERFACE

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INTRODUCTION

Analytical *glow discharge* plasmas can be operated in continuous or *pulsed* power mode. The pulsed mode allows the application of higher instantaneous power, enhancing the excitation and ionization efficiencies of gas species. Additionally, the pulsed GD source is a dynamic plasma that shows different ionization processes along the temporal distribution of power (e.g. pre-peak, plateau, and afterglow). Therefore, it is an interesting source to be coupled to a Time-of-Flight Mass Spectrometer (TOFMS) with a high mass spectra acquisition rate [1].

In previous works [2,3], the gas species were directly introduced at the plasma site. However, *i*n this study, an *innovative interface* has been investigated to introduce the gas sample at the *spatial afterglow region* to minimise plasma quenching and matrix effects. Different operating conditions (e.g. applied power, pressure and distance from sample inlet to plasma) have been evaluated using volatile compounds.

[1]. C. L. Lewis, G. P. Jackson, S. K. Doorn, V. Majidi and F. L. King, *Spectrochim. Acta - Part B At. Spectrosc.*, 2001, 56, 487–501.

[2]. A. Solá-Vázquez, A. Lara-Gonzalo, J. Costa-Fernández, R. Pereiro and A. Sanz-Medel. *The Analyst*, 2010, 135, 987-993.

[3]. A. Solá-Vázquez, J.Costa-Fernández, R. Pereiro and A. Sanz-Medel, *Analytical and Bioanalytical Chemistry*, 2011, 401, 2771–2777.

Experimental set-up

Pulsed-radiofrequency Glow Discharge (prf-GD)-ToFMS prototype from Horiba:

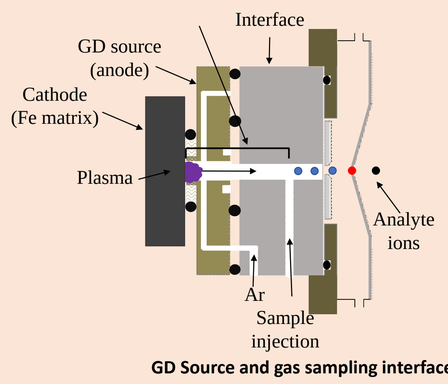
- A Grimm type GD source (GD1 with a flow-tube, and UNIOVI without flow-tube).
- An orthogonal TOFMS (Tofwerk, Switzerland).


GD1 Chamber


UNIOVI Chamber

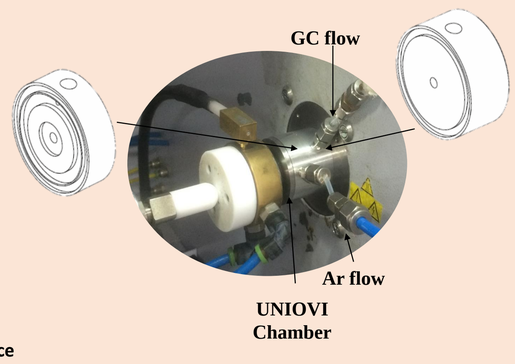
New Interfaces for gas sampling:

- Two-pieces interface (distance sample inlet to cathode ≈ 8 mm).
- Single-piece interface (distance sample inlet to cathode ≈ 4 mm).

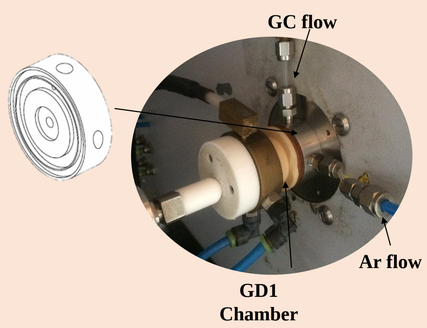


GD Source and gas sampling interface

Two-pieces interface

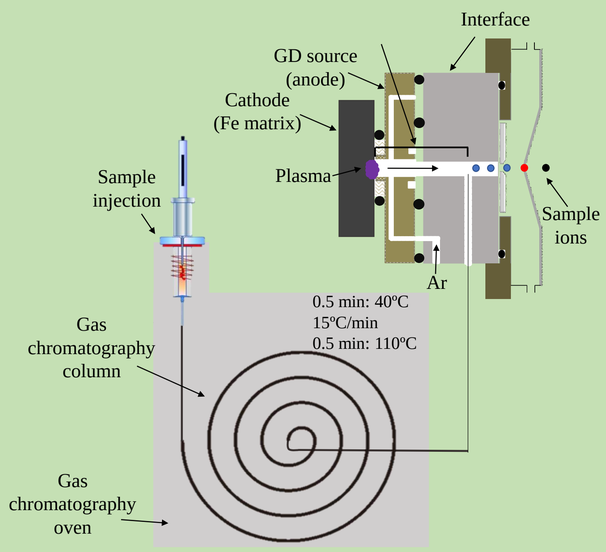


Single-piece interface

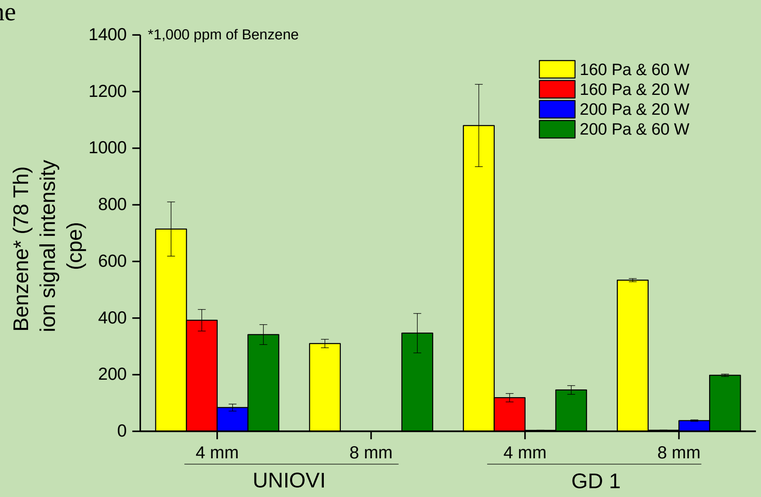


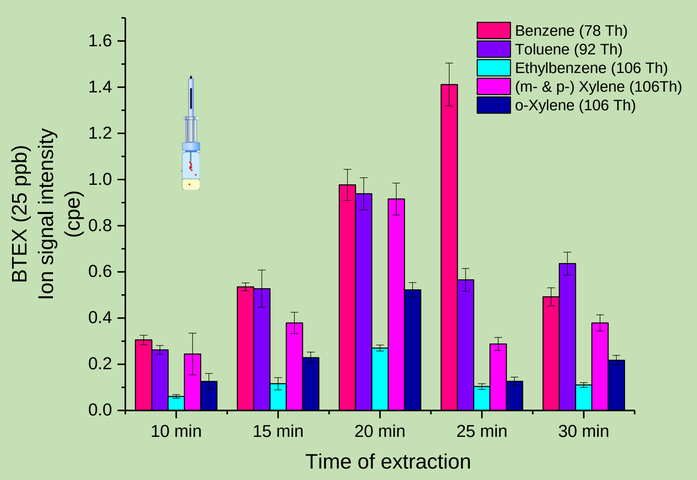
RESULTS & DISCUSSION

The ***prf-GD-ToFMS prototype*** has been coupled with a **gas chromatographer**, using a SPME fiber to pre-concentrate the analytes. BTEX (Benzene, Toluene, Ethylbenzene and Xylene) have been used as model analytes.



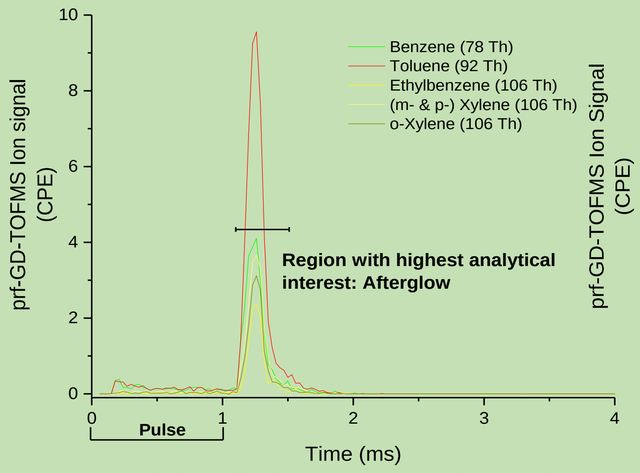
Optimization of operating conditions:



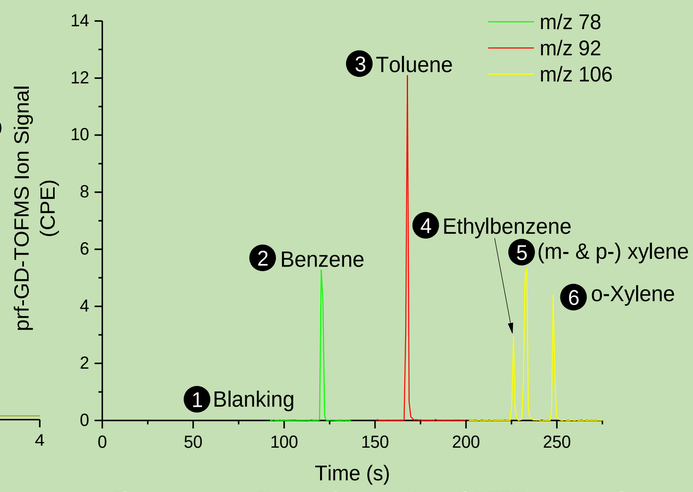


The use of GD1 source (with flow-tube), at higher powers and lower pressures provides the highest analytical sensitivity using the single-piece interface (distance sample inlet to plasma region = 4mm).

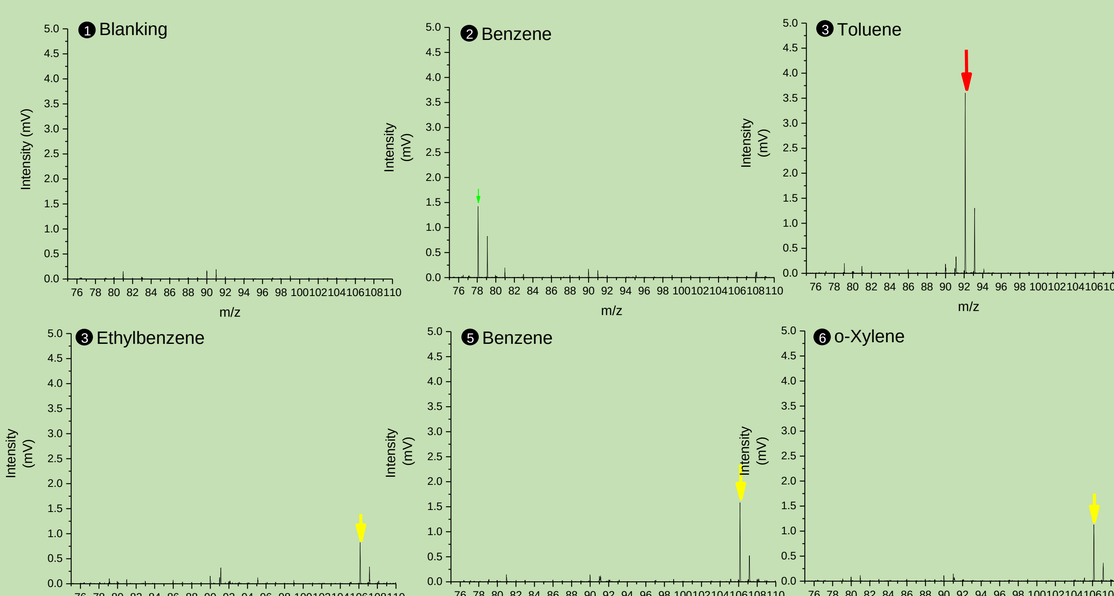
Application of GC-prf-GD-TOFMS for the analysis of BTEX:



GD pulsed profile for BTEX compounds (25 ppb). GD operating conditions: 160Pa, 60W, Pulse width: 1 ms; Period: 4 ms.



Chromatogram: Temporal separation of BTEX compounds (25 ppb): 0.5 min: 40ºC, 15ºC/min, 0.5 min: 110ºC



Mass spectra collected in the temporal afterglow region for BTEX compounds (25 ppb), where parent-ions are highlighted.

Calibration curves in the temporal afterglow region for BTEX compounds (25 ppb).

The analytical capability of the new coupling has been evaluated for VOCs analysis. Samples with different concentrations of BTEX, dissolved in distilled water, (between 1 and 50 ppb) have been analyzed. Linear calibration curves have been obtained for the investigated concentration interval with a good statistical correlation.

These calibration has been employed to analyze a known BTEX sample:

	Benzene	**Toluene**	**Ethylbenzene**	**(m- & p-) Xylene**	**o-Xylene**
Nominal concentration (ppb)	*1.85*	*1.85*	*1.85*	*1.85*	*1.85*
Calculated Concentration (ppb)	*2.14 ± 0.56*	*1.85 ± 0.51*	*2.01 ± 0.68*	*1.86 ± 0.56*	*2.06 ± 0.76*

CONCLUSIONS

- ❑ An innovative interface has been successfully tested for the analysis of gaseous compounds using a prf-GD-TOFMS
- ❑ Power, pressure, plasma - sample introduction distance and extraction time have been set at 60 W, 160 Pa, 4 mm and 20 minutes, respectively, for the GD1 chamber.
- ❑ Linear calibration curves have been obtained between 1 and 50 ppb with a good statistical correlation. These curves have been successfully validated.

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