# New strategies to improve the analytical performance of pulsed glow discharge time of flight mass spectrometry

**Lara Lobo, Rocío Muñiz, Rosario Pereiro, Alfredo Sanz-Medel**

Department of Physical and Analytical Chemistry, Faculty of Chemistry, Julián Clavería 8, 33006

## Introduction

Glow discharges (GDs) either with optical emission or mass spectrometric detection are well recognized atomization/excitation/ionization sources for the analysis of solid materials with depth resolution capabilities in the nanometric range and limits of detection at the ppb-low ppm level. During the last years, the combination of a pulsed GD (PGD) source with a time-of-flight mass spectrometer (TOFMS) has received much attention and recent developments are opening new fields of application due to its particular features.

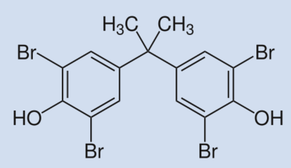
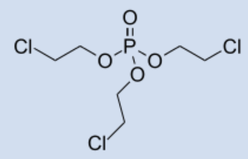
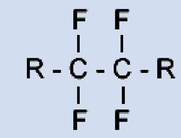
Typically, GDs are run in an Ar discharge and **positive ions** are traditionally detected. However, the determination of certain elements can be hindered due to the lower first ionization potential of Ar (compared to e.g. halogens) or because the concentration is below the limits of detection.

In this presentation, some experiments will be shown, including **detection of negative ions** for the determination of halogens in polymeric materials and the **use of alternative discharge gases** (Ar + He and Ar + $O_2$) to improve the limits of detection.

## PP-ToFMS instrument

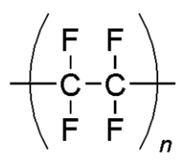

## Sample preparation

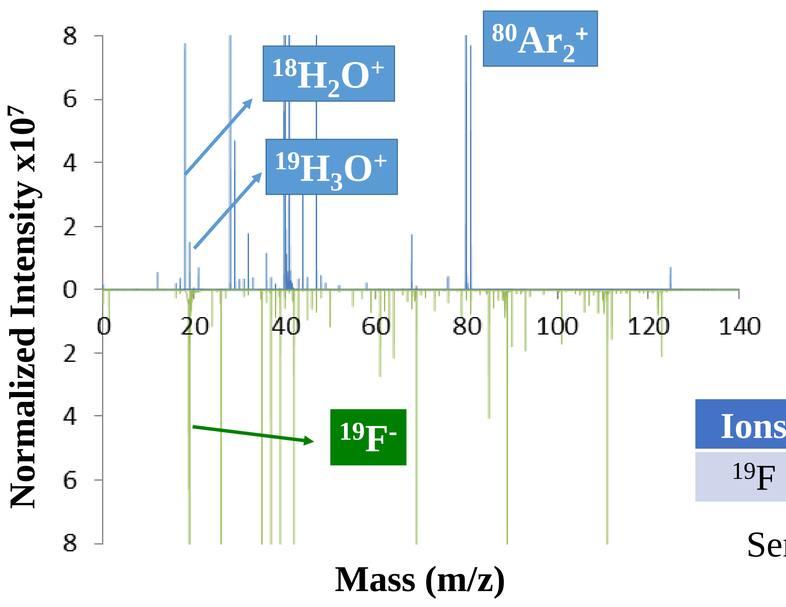
Samples were prepared dissolving methylene diphenyl diisocyanate (MDI), bisphenol A, phloroglucinol and the analyte in 4 ml tetrahydrofuran resulting in a polyurethane matrix and deposited on silicon wafers.

| TBBPA | TCEP | PTFE |
|---|---|---|
|  |  |  |
| Tetrabromobisphenol A | Tris(2-(chloroethyl) phosphate | Polytetrafluoroethylene |

## Positive vs negative detection

110 Pa 15 W
1 ms pulse
25% duty cycle



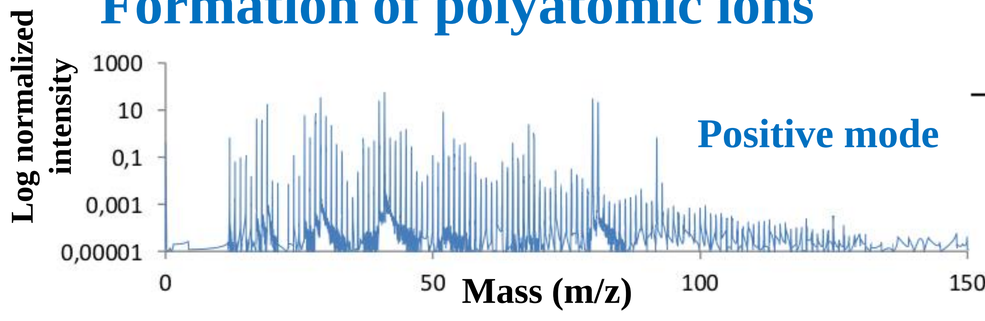



| Ions | Positive | Negative |
|---|---|---|
| $^{19}F$ | - | 0.1998 |

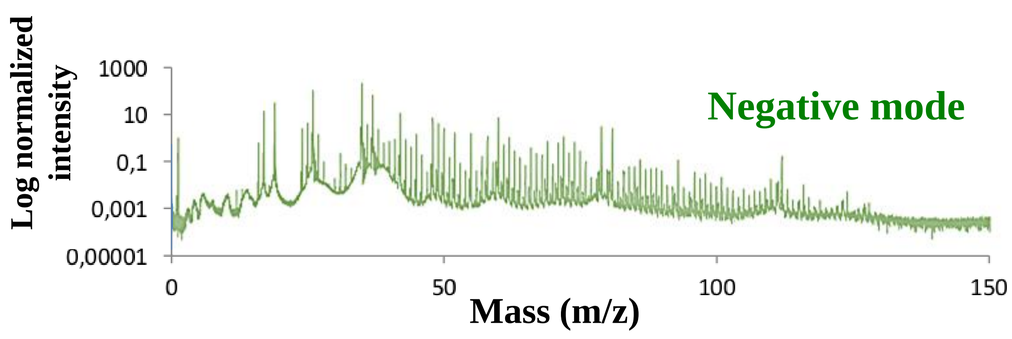
Sensitivity = cps/ TIC

*Positive ion mode: $^{19}F$ is not observed.*

## Formation of polyatomic ions



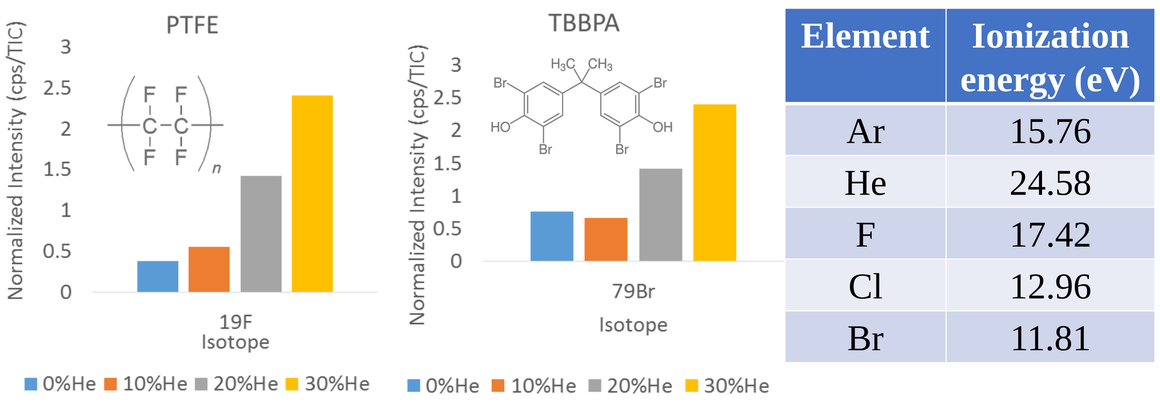

*Higher number of polyatomics and less background.*




*Higher sensitivity for elements with high ionization potential.*

## Ar+He

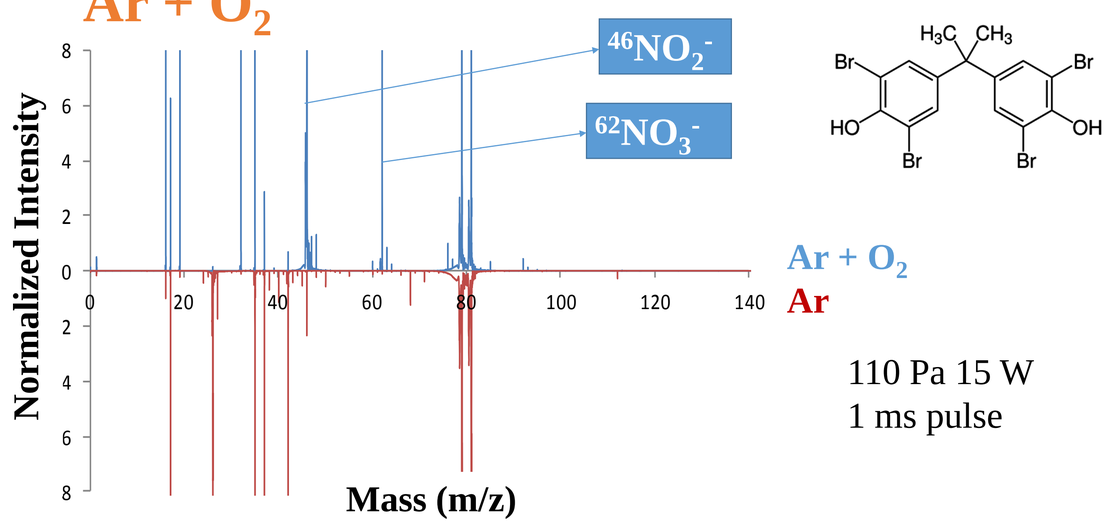
110Pa 25W 1ms pulse




| Element | Ionization energy (eV) |
|---|---|
| Ar | 15.76 |
| He | 24.58 |
| F | 17.42 |
| Cl | 12.96 |
| Br | 11.81 |

- *He ionizes more efficiently F, Cl, Br heteroatoms.*
- *Negative ion mode detection increases sensitivity and also there is less risk of polyatomic interferences as the spectra are less complex.*

## Ar + $O_2$




110 Pa 15 W
1 ms pulse

- *Polyatomic ions of similar mass but with different composition are formed in presence of oxygen (e.g. $NO_2^-$ and $NO_3^-$).*
- *The presence of $O_2$ in the discharge also increases the sputtering rate at about 10 times compared to pure Ar.*

## Conclusions

- *The comparison between positive and negative detection shows that the sensitivity of halogens increases considerably in the negative mode.*
- *With the addition of He, the sputtering rate decreases meanwhile the analytical signals increase. This means that despite less material is being sputtered, the analytes could be more efficiently transported / ionized.*
- *By adding $O_2$ to the discharge gas, the sensitivity of some specific ions increases but also the recombinations with oxygen.*