Analysis of Fullerene Clusters using the Hyphenation of Asymmetrical Flow Field-Flow Fractionation with Orbitrap High Resolution Mass Spectrometry

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Introduction

Fullerenes are an important class of chemicals used in the production process of solar cells. Furthermore, fullerenes can be formed during combustion processes. As a consequence it can be expected that fullerenes can appear in the environment. Once present in the environment, these molecules about one nanometer in size have the tendency to form water stable aggregates or clusters with different sizes depending on the water matrix and temperature. Information on these clusters is crucial as the size of clusters strongly affects their behavior in the environment (adsorption, diffusion, degradability) and their toxicology. So far, Field-Flow Fractionation techniques have often been used to separate these clusters. However, identification of the cluster components using high resolution mass spectrometry was only possible offline until now. The here outlined setup allows the online coupling of an Asymmetrical Flow FFF system to an Orbitrap HRMS [1].

Toluene Dopant Device and FFF Connection

For optimal ionization of fullerenes in an APPI chamber, the introduction of toluene is necessary. As the addition of toluene to the water phase is not possible due to immiscibility a dopant device needs to be built to add the toluene to the auxiliary gas. The auxiliary gas tube must be connected to a HPLC pump carrying the toluene using a "T"-junction. By doing this the toluene is transported to the ionisation chamber with the auxiliary gas stream. The outlet stream of the FFF is connected directly to the inlet port of the APPI probe.

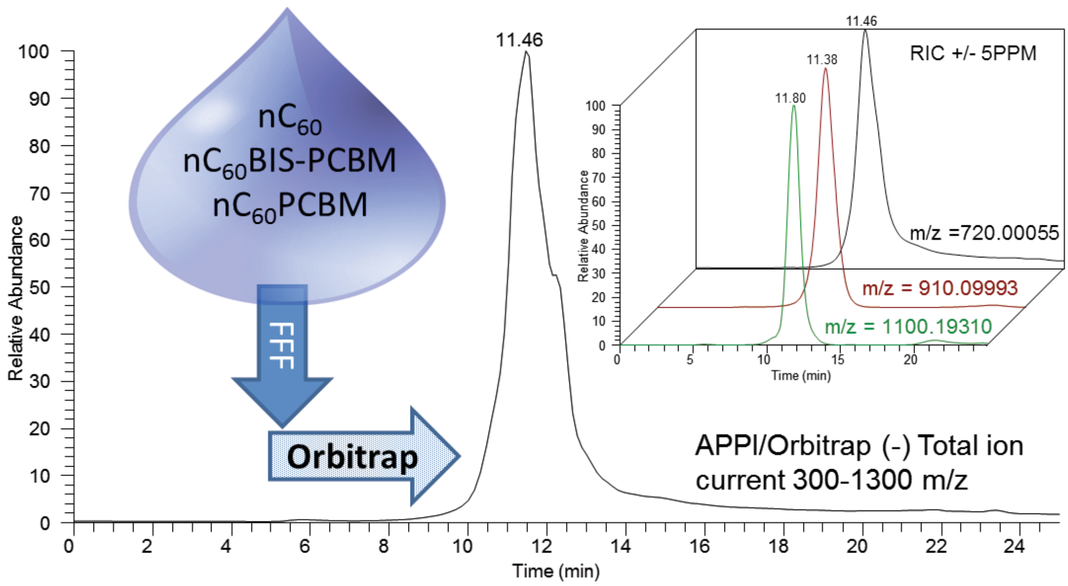

Figure 1: Graphical illustration of the FFF-MS principle. The fractograms are obtained from an actual measurement by Herrero et al..[1]

System Setup

- Postnova Analytics AF2000 Asymmetric Flow FFF System
- Thermo Scientific Orbitrap HRMS
- Thermo Scientific APPI interface
- HPLC pump for the toluene

Asymmetrical Flow FFF Settings

• Membrane:	Regenerated cellulose 10 kDa
• Carrier liquid:	Milli-Q water
• Spacer thickness:	250 µm
• Detector flow:	0.1 mL/min
• Split flow:	0.5 mL/min
• Cross flow:	1.2 mL/min (0-12 min) 1.2-0 mL/min (12-15 min, exp. 0.2) 0 mL/min (15-20 min)
• Injection time:	5 min
• Injection volume:	100 µL
• Injection flow:	0.2 mL/min
• Focusing flow:	1.2 mL/min

Obitrap MS Settings

• Interface:	(-)APPI
• Probe position:	C, 0, 0.75 µm
• Capillary temperature:	350 °C
• Vaporiser temperature:	500 °C
• Sheath gas:	20 AU
• Auxiliary gas:	10 AU
• Sweep gas:	0 AU
• Dopant:	Toluene
• Dopant flow:	0.1 mL/min
• Capillary voltage:	-20 V
• Tube lens:	-200 V
• Resolution:	30000 (FWHM m/z 400)

Conclusion

The work shows that it is possible to couple Flow FFF online to an Orbitrap HRMS with an APPI chamber. This setup facilitates the identification of fullerene clusters in aqueous matrices directly after separation of the particles with Asymmetrical Flow FFF. This enables both to characterize those clusters with non-destructive analytical techniques such as UV-Vis or MALS in the first place and to subsequently identify the mass of the compounds present in the clusters. So far, this had to be done by collecting separate fractions.

References

[1] P. Herrero, P.S. Bäuerlein, E. Emke, E. Pocurull, P. Voogt, Journal of Chromatography A, 2014, 1356, 277-282.