

A Rapid Screening and Quantification Approach to PFAS Analysis Enabled by DART-MS

William L. Fatigante¹; Ronald V. Emmons²; Aghogho A. Olumukoro²; Emanuela Gionfriddo²; Brian D. Musselman¹

Bruker Applied Mass Spectrometry, Billerica, MA¹ Department of Chemistry and Biochemistry, University of Toledo, Toledo, OH²

Introduction

Per- and polyfluoroalkyl substances (PFAS), also known as “forever chemicals,” are an emerging class of toxic anthropogenic chemicals. Due to their wide-spread contamination in the environment and human health implications, the development of rapid analytical methods for screening and quantifying these compounds is a must. Published methods require extensive sample preparation and LC-MS/MS protocols for PFAS analysis. In this work, we investigate the potential of rapid PFAS analysis performed by DART-MS coupled to ion-exchange SPME. This was enabled by the use of an HLB-WAX/PAN extraction phase and careful tuning of DART-MS parameters through a central composite design approach.¹



Figure 1. QuickStrip™ module with JumpShot equipped DART-EVOQ-TQ

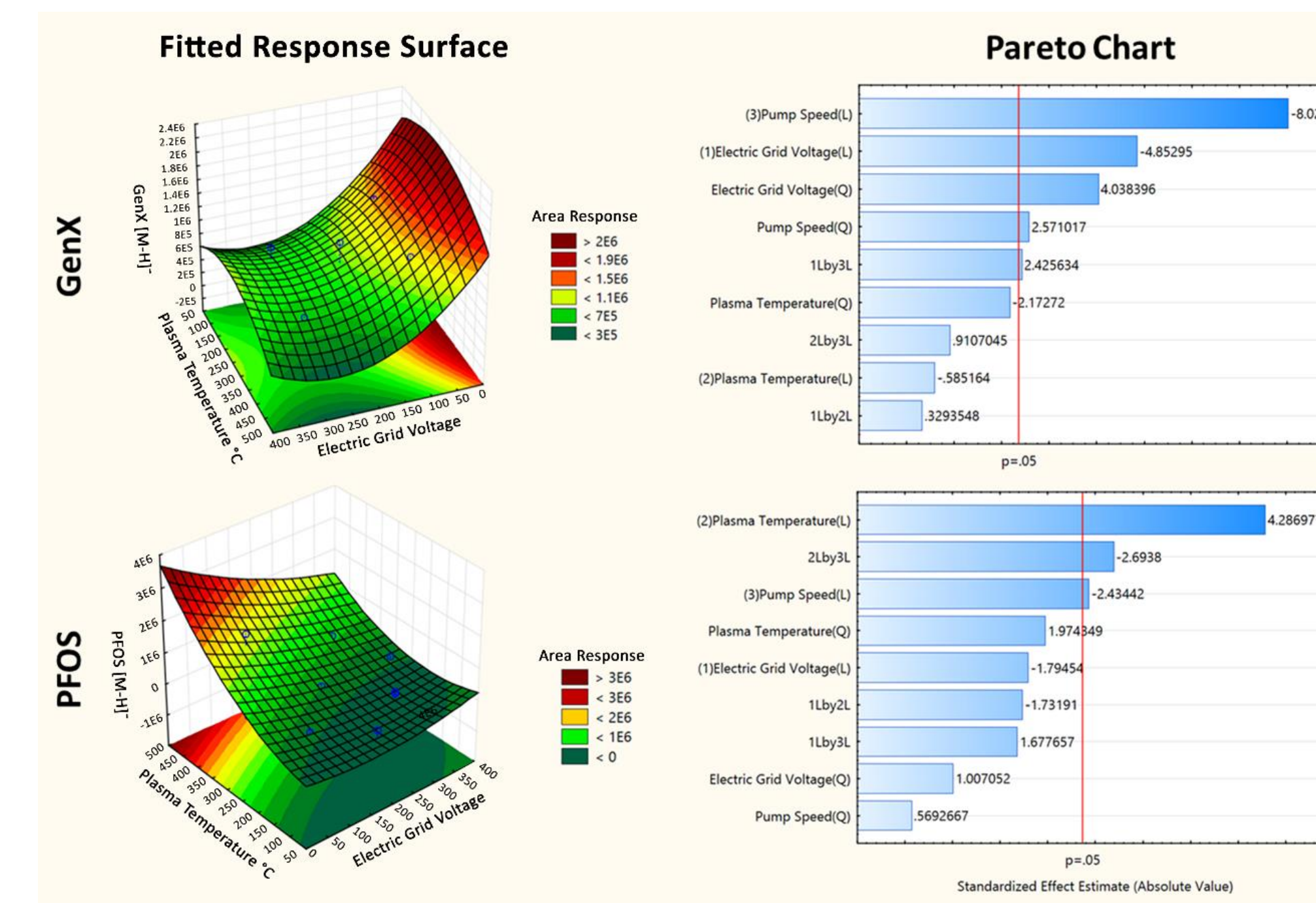
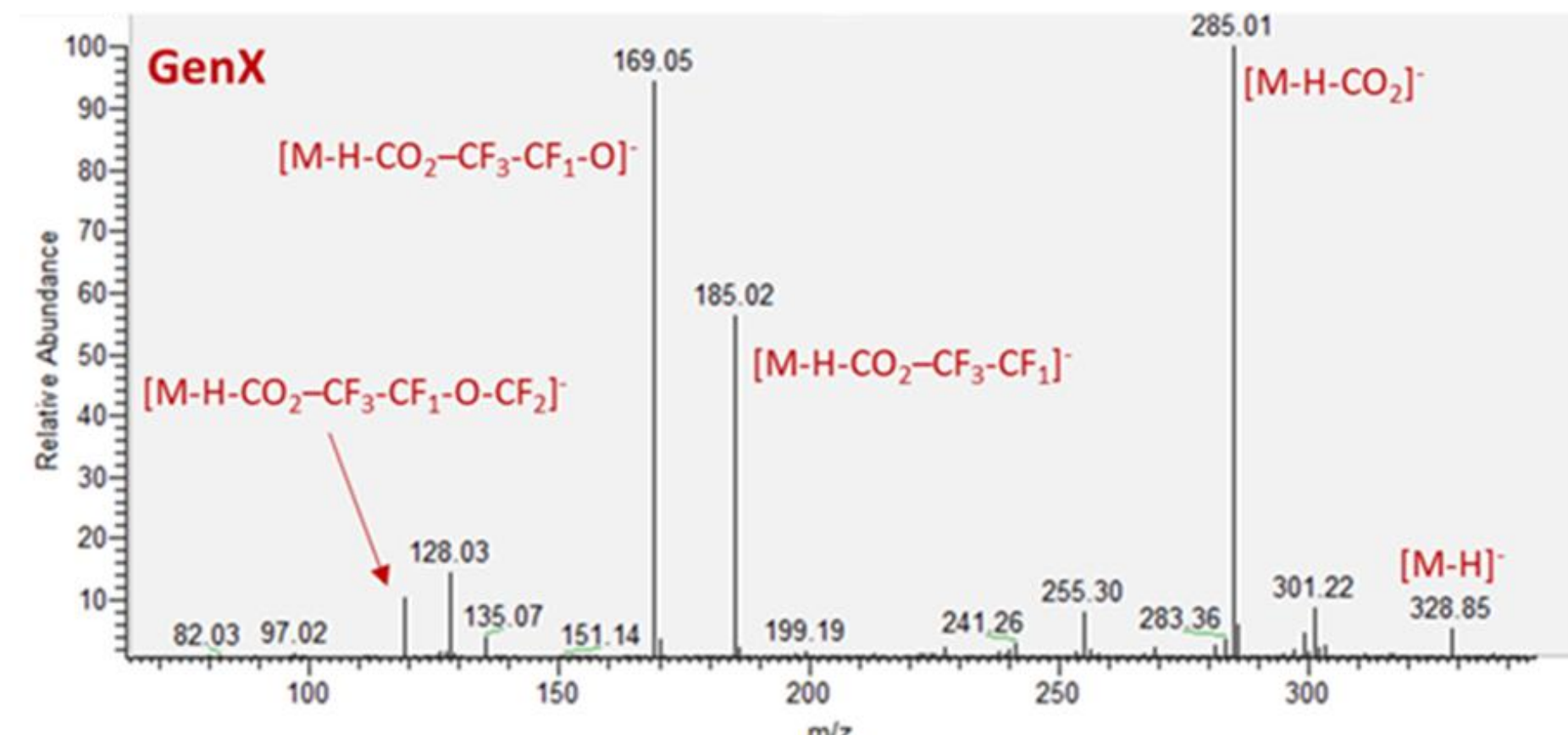
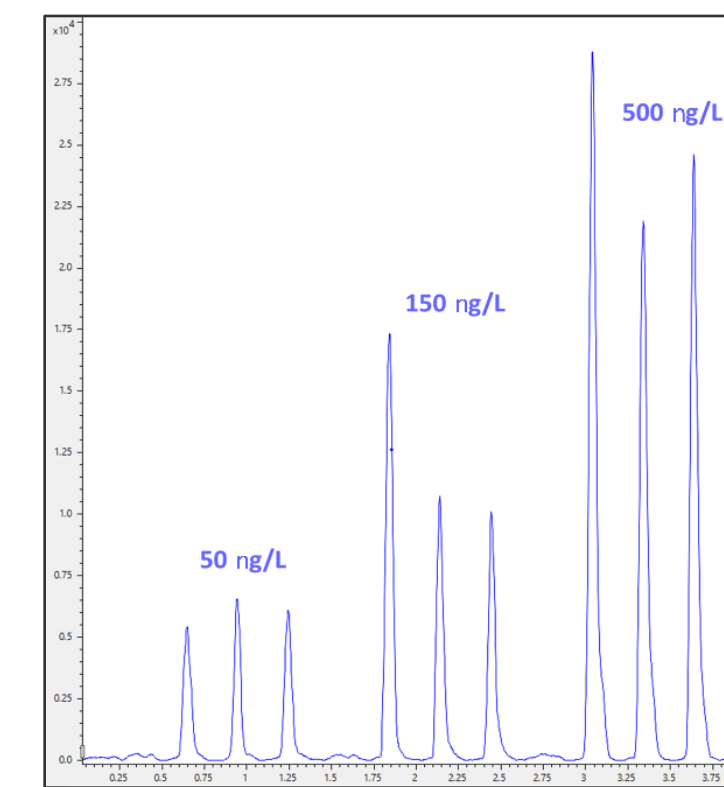
Methods

SPME devices (fiber and blade geometry) were developed as described by Olumukoro et al.^{2,3} Hydrophilic-lipophilic balance-weak anion-exchange particles embedded in polyacrylonitrile (HLB-WAX/PAN) were used as an extraction phase. PFAS standards (see below) were spiked in ultra-pure water and extracted at a range of 10 – 5000 ppt. DART parameters included negative ionization mode with helium gas, -50 V electric grid and the Vapor interface set at 897 mbar. Plasma heater temperature was set at 250 °C for PFOA and GenX and 400 °C for PFOS and PFBS. Central-composite design (CCD) experiments were performed with a Thermo LTQ XL linear ion trap MS. Calibration and quantification were performed on a Bruker EVOQ Elite TQ-MS.

- ❖ 4 PFAS compounds: Perfluorooctanoic acid (PFOA), Perfluorooctanesulfonic acid (PFOS), Perfluorobutanesulfonic acid (PFBS) and GenX
- ❖ 3 Isotopically labeled internal standards: ¹³C₈ -PFOA, ¹³C₈ -PFOS, ¹³C₃ -GenX
- ❖ Desorption solution – 80:20 (MeOH:H₂O, v:v) with 2% ammonium formate

Results

- ❖ Extracted ion chromatogram of PFOA (right) using the optimized SPME-DART-MS method
- ❖ In-source fragmentation (below) is extensive for carboxylic acid and ether moiety PFAS
- ❖ Fragmentation is plasma temperature dependent, observed with both helium and nitrogen as the plasma

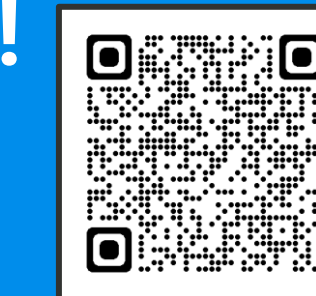


- ❖ CCD experiments were performed to investigate the different DART parameters and how they influence ionization
- ❖ When comparing GenX (top) and PFOS (bottom), it was found that carboxylic acids PFAS do not rely on plasma temperature as much as the sulfonic acid groups
- ❖ Both analytes favor a lower electric grid voltage (50V) than what is commonly used for other applications (350V)

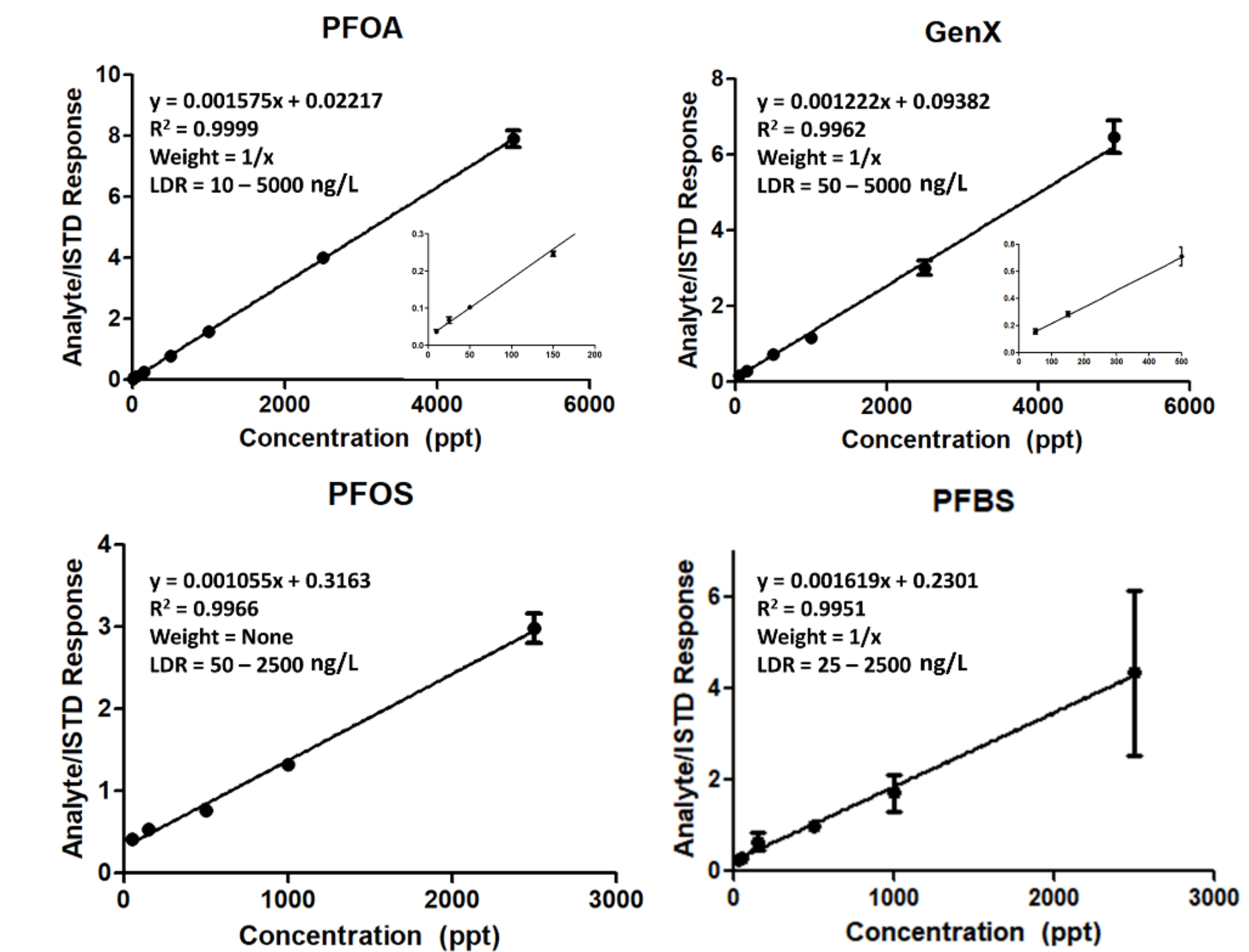
References

- Emmons, R. V.; Fatigante, W.; Olumukoro, A. A.; Musselman, B. D.; Gionfriddo, E. J. *Am. Soc. Mass Spectrom.* 2023.
 - Olumukoro, A. A.; Emmons, R. V.; Godage, N. H.; Cudjoe, E.; Gionfriddo, E. J. *Chromatogr. A.* 2021, 1651, 462335.
 - Olumukoro, A. A.; DeRosa, C.; Gionfriddo, E. *Anal. Chim. Acta.* 2023, 1260.
- Special thanks to the lab of Emanuela Gionfriddo (University of Toledo) for providing the samples and statistical analysis of results.

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- ❖ Each concentration was analyzed in triplicate. 12 samples were ionized in ~1.8 min
- ❖ Area counts of the 4 PFAS analytes were normalized against the corresponding internal standard
- ❖ PFBS, shown corrected with ¹³C₃ -GenX, was found to require a different internal standard for more robust quantification



Conclusions

- The hyphenation of ion-exchange SPME and DART-MS analysis enabled rapid quantification of PFAS
- When compared to traditional LCMS testing, using DART-MS reduces:
 - The time required for individual sample analysis
 - The cost and amount of organic consumables needed
- By adjusting DART parameters, we can promote greater ionization of different PFAS classes (i.e., carboxylic acid v. sulfonic acid groups), creating optimal DART methods for each.
- Method has potential for screening of >1000 samples per hour against large databases with reduced solvent or chromatographic materials