Towards a DART-MS Technique with SPME that Provides a Rapid Screening Approach to PFAS Analysis

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Overview:

Polyfluoroalkyl substances (PFAS), also known as "forever chemicals," have become of major interest due to their presence in the environment as well as potential health implications. These fabricated compounds are widely used in industrial settings in addition to consumer products. The increased awareness of PFAS has led to a considerable need in analytical analysis. As the published methods require significant extraction and LC/MSMS we are investigating the potential for direct analysis of SPME devices after and following up those screens with DART-MSMS in order to confirm the identity of the various PFAS and PFOS that might be detected in the screen. Coated glass capillary (CGC) devices as developed by Cody and Makenia (*RCMS* **2019**)[1] were initially use to for extraction and analysis. As the range of POP's increases the use of more robust extraction devices with higher capacity was enabled using HLB-WAX phases.
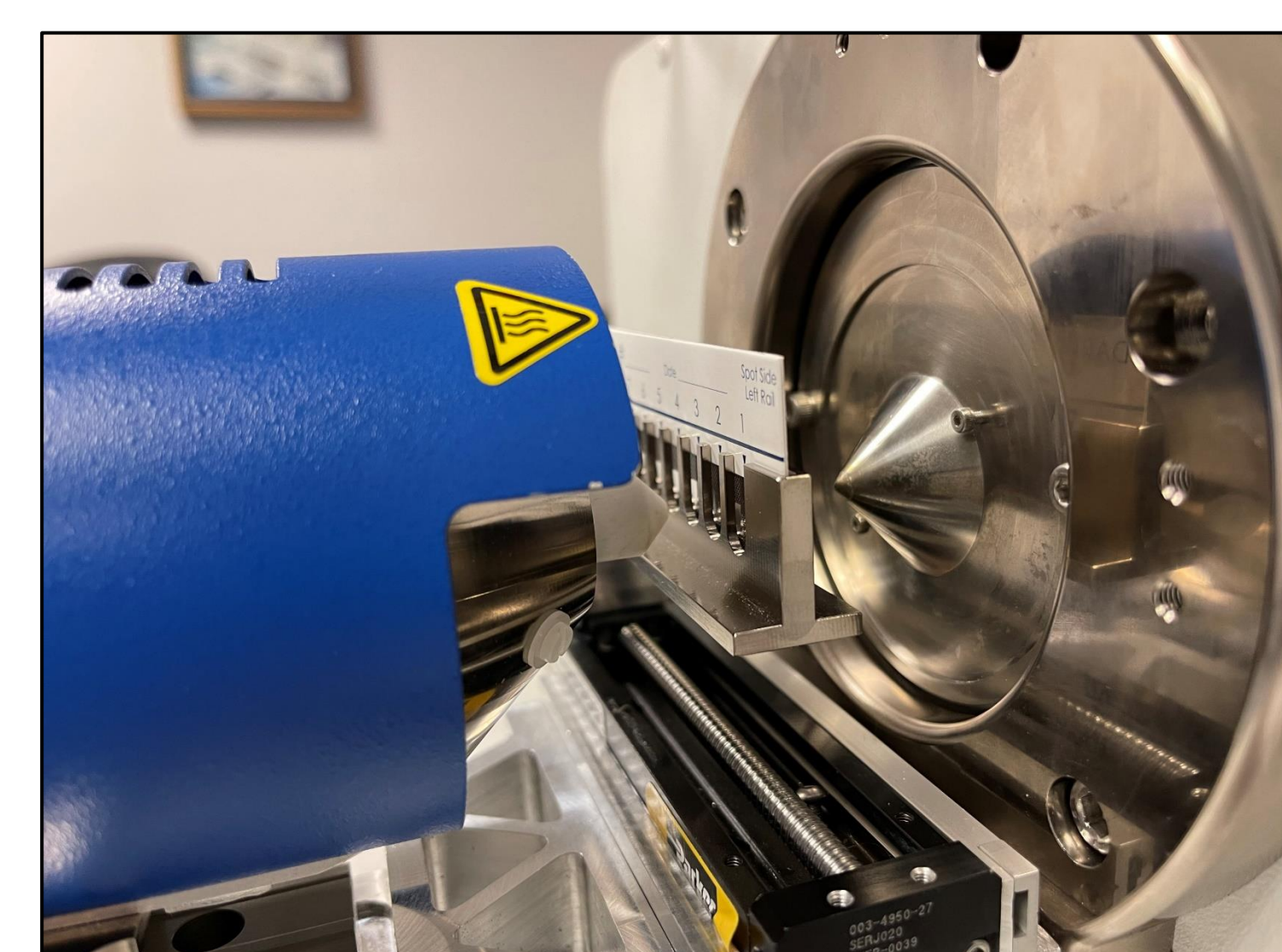

**Figure 1: QuickStrip™ module on automated presentation robotics with JumpShot equipped DART-MS**

Methods:

The SPME devices were coated with hydrophilic-lipophilic balance-weak anion-exchange/polyacrylonitrile (HLB-WAX/PAN) (*J. Chromatogr. A* **2021**)[2]. PFAS standards (see below) were extracted and diluted to a range of 25ppb – 200ppt. For analysis of extracted samples, a DART ionization source was interfaced to a JEOL AccuTOF-MS. DART parameters were: negative ionization mode, 325°C, and 2 sec Helium gas pulses per sample. Data processing was completed using MSAXEL. The extraction of PFAS samples was demonstrated to be efficient and comprehensive. DART and central-composite design (CCD) experiments were performed with a LTQ XL linear ion trap MS (Thermo Scientific, San Jose, CA).

- 4 PFAS compounds: Perfluorooctanoic acid (PFOA), Perfluorooctanesulfonic acid (PFOS), Perfluorobutanesulfonic acid (PFBS) and GenX at 200 ppt, 1 ppb, 10 ppb and 25 ppb
- 3 Isotopically labeled internal standards: $^{13}C_8$ -PFOA, $^{13}C_8$ -PFOS, $^{13}C_3$ -GenX at 2.5 ppb
- Extraction and desorption time - 20 min
- Desorption solution – 80:20 (MeOH:H_2O, v:v) with 0.05% NH_4OH

(1) Cody, R.; Maleknia, S. D. *Rapid Commun. Mass Spectrom.* **2020**, 34 (23).
(2) Olomukoro, A. A.; Emmons, R. V.; Godage, N. H.; Cudjoe, E.; Gionfriddo, E. *J. Chromatogr A* **2021**, 1651, 462335.

Experimental:

- DART-AccuTOF EIC of extracted PFOA (left) and PFOS (right) with ^{13}C-labeled internal standards (IS) underneath.
- 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 IS.
- The carboxylic acid analytes (PFOA and GenX) ionized more efficiently and displayed stronger linearity when compared to the sulfonic acid analytes (PFOS and PFBS).
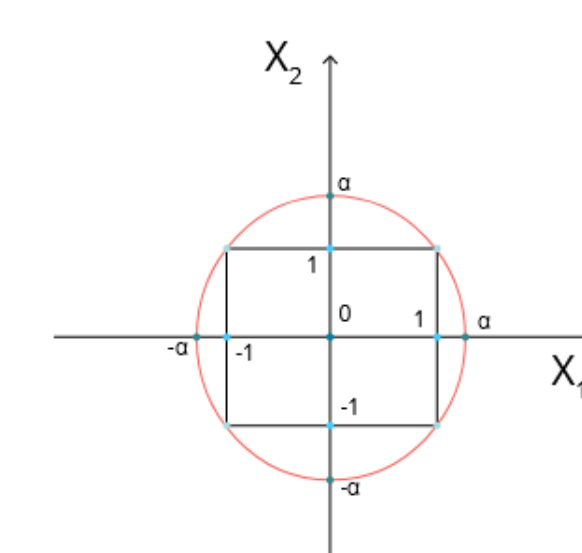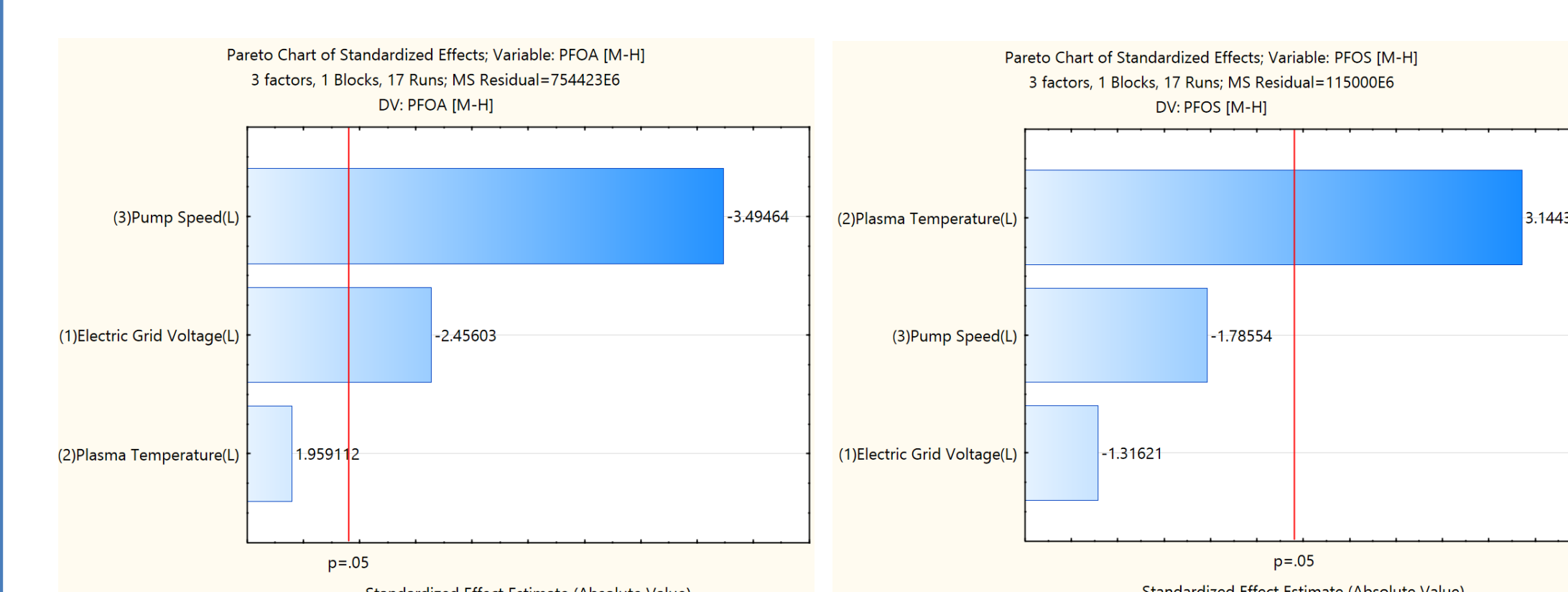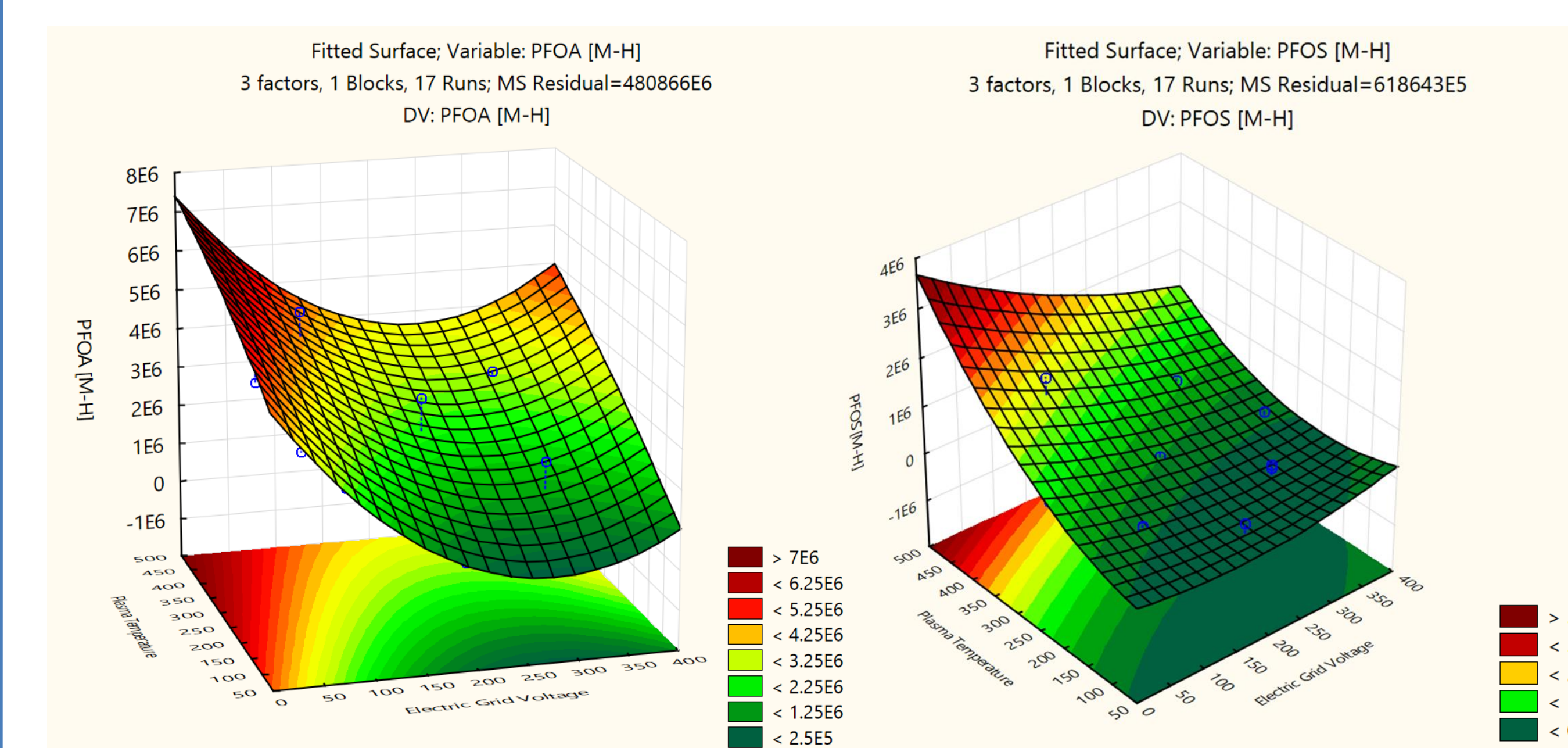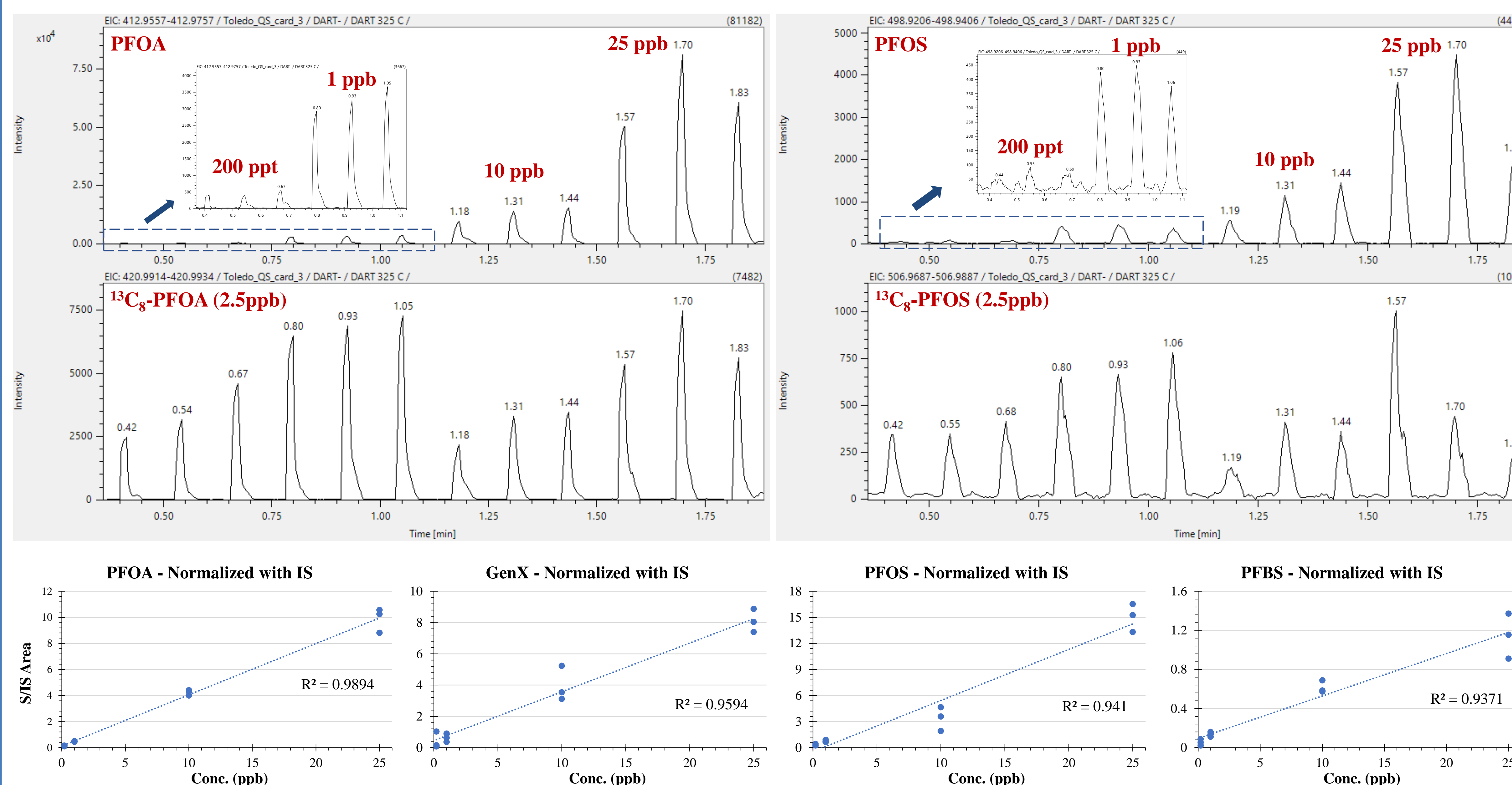
- CCD experiments were performed to investigate the different DART parameters and how they influence ionization.
- When comparing PFOA (left) and PFOS (right), the carboxylic acid (PFOA) does not rely on plasma temperature as much as the sulfonic acid (PFOS).
- Both analytes seem to favor a lower electric grid voltage.
- Using this information, DART method settings can be used to promote more efficient ionization to PFAS analyte groups based on chemical properties.

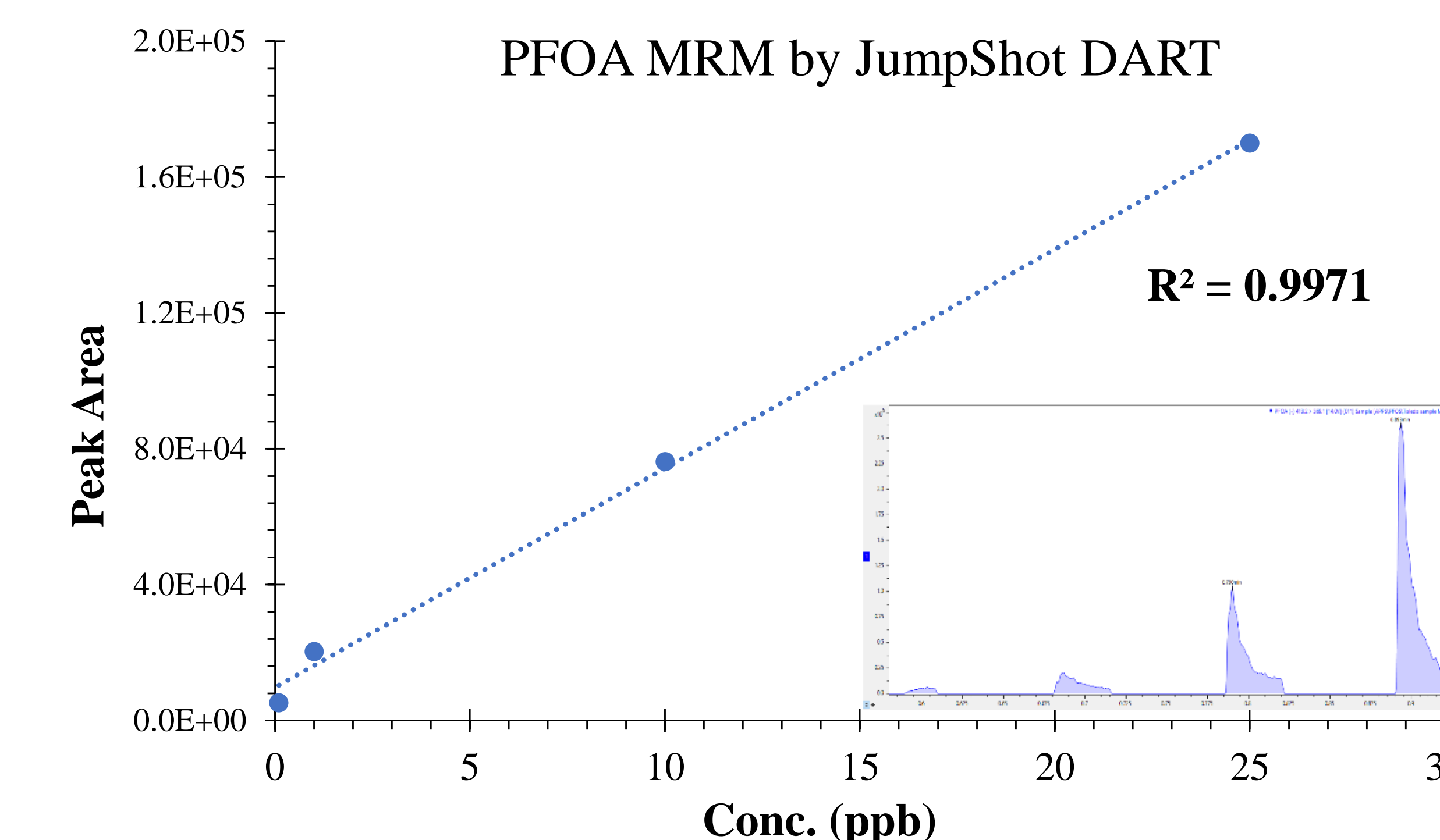| Variable	Code	Low (-)	Central (0)	High (+)	-α	+α
			Level		**Star Points (α = 1.68)**	
Electric Grid	X_1	100	200	300	33	367
Plasma Temperature	X_2	175	275	375	100 (107)	450 (442)
Pump Setting	X_3	-4	0	4	-6.7	6.7

Conclusions:

- The QuickStrip module with DART-MS analysis permits rapid screening of various PFAS analytes.
- Samples extracted using HLB-WAX phases can be immediately ionized after desorption.
- 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 no solvent or chromatographic materials

On-Going Work:

- The coupling of DART and a triple quadrupole MS, such as the Bruker EVOQ Elite, can aid in the high throughput screening and identifying various PFAS and PFOS with its high MRM speed.
- As proof-of-principal, a quick calibration curve (100ppt – 25ppb) was collected in under one minute using the MRM transition: 413.2 > 369.1 (see below)

Acknowledgement: