Rapid Screening of PFAS in Contaminated Soil utilizing DART-MS/MS

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Introduction

Per- and polyfluoroalkyl substances (PFAS) have emerged as pervasive environmental contaminants, with soil serving as a significant reservoir for these persistent "forever" chemicals. One specific source of PFAS contaminations is industrial fire-fighting foams specifically used for their Aqueous Film Forming (AFFF) properties. These firefighting foams are prolific, present in very-high to extreme concentrations, and pose a risk to the environment and biological life. Areas which have historically and continue to receive heavy usage are airports and military installations globally.

This study explores the application of Direct Analysis in Real Time Mass Spectrometry (DART-MS) as an efficient and effective tool for the screening and quantitation of PFAS in soil samples. Samples were collected from various military sites where contamination is known to be present but the specific areas in need of remediation need to be determined. The 40 PFAS regulated by EPA method 1633 were the targets for our analysis.

An extraction method was optimized by a collaborator and the extracted samples were analyzed by DART-MS/MS, utilizing a helium-driven corona discharge to ionize the compounds and a Bruker DART-TQ+ for detection. This approach allowed for the rapid screening of PFAS without the need for the typical lengthy LC separation. The development of the analysis was particularly crucial due to the large number of samples that are collected to properly evaluate the sites and the extent of their contamination.

Fig. 1 Example Soil Samples

Methods

Calibrators were prepared using standards acquired from Wellington Laboratories and diluted using 80/20 MeOH/H2O. The calibration scheme was designed to cover the range outlined in EPA 1633. The samples were collected from military sites in Canada, California, Nebraska, and Oklahoma. Varied soil types (Fig. 1) were targeted to identify if the matrix affected detection of PFAS. Both the calibrators and the samples were spiked with ISTD mix also from Wellington labs according to EPA 1633.

Aliquots of 5 μL of each calibrator and sample were transferred onto a Bruker DART QuickStrip HTS-96 screen and allowed to dry. The prepared QuickStrip-HTS 96 screen was loaded onto the TQ+ (Bruker Daltonics) triple quadrupole mass spectrometer for DART-MS/MS analysis. Helium gas was pulsed for 6 seconds per acquisition. Accuracy was determined in triplicate for each analyte within the linear range of each calibration series.

Analyte Name	LOD [ng/mL]	Samples confirmed by LC-MS/MS
11Cl-PF3OUdS	80	
3-3 FTCA	10	
4-2 FTS	80	
5-3 FTCA	12.5	
6-2 FTS	80	X
7-3 FTCA	12.5	
8-2 FTS	80	X
9Cl-PF3OUdS	50	
ADONA	2	
HFPO-DA	0.8	
NEtFOSA	0.5	
NEtFOSAA	20	X
NEtFOSE	200	
NFDHA	0.4	
NMeFOSA	5	
NMeFOSAA	20	
NMeFOSE	500	
PFBA	0.8	X
PFBS	2	X
PFDA	0.2	

Analyte Name	LOD [ng/mL]	Samples confirmed by LC-MS/MS
PFDoA	2	
PFDoS	20	X
PFDS	20	X
PFEESA	4	
PFHpA	5	X
PFHpS	5	X
PFHxA	5	X
PFHxS	5	X
PFMBA	0.4	
PFMPA	0.4	
PFNA	0.5	X
PFNS	5	
PFOA	0.2	X
PFOS	5	X
PFOSA	0.5	X
PFPeA	1	X
PFPeS	5	X
PFTeDA	20	
PFTrDA	5	
PFUna	5	

Fig. 2 Analyte LODs and samples with detected PFAS contamination confirmed by LC-MS

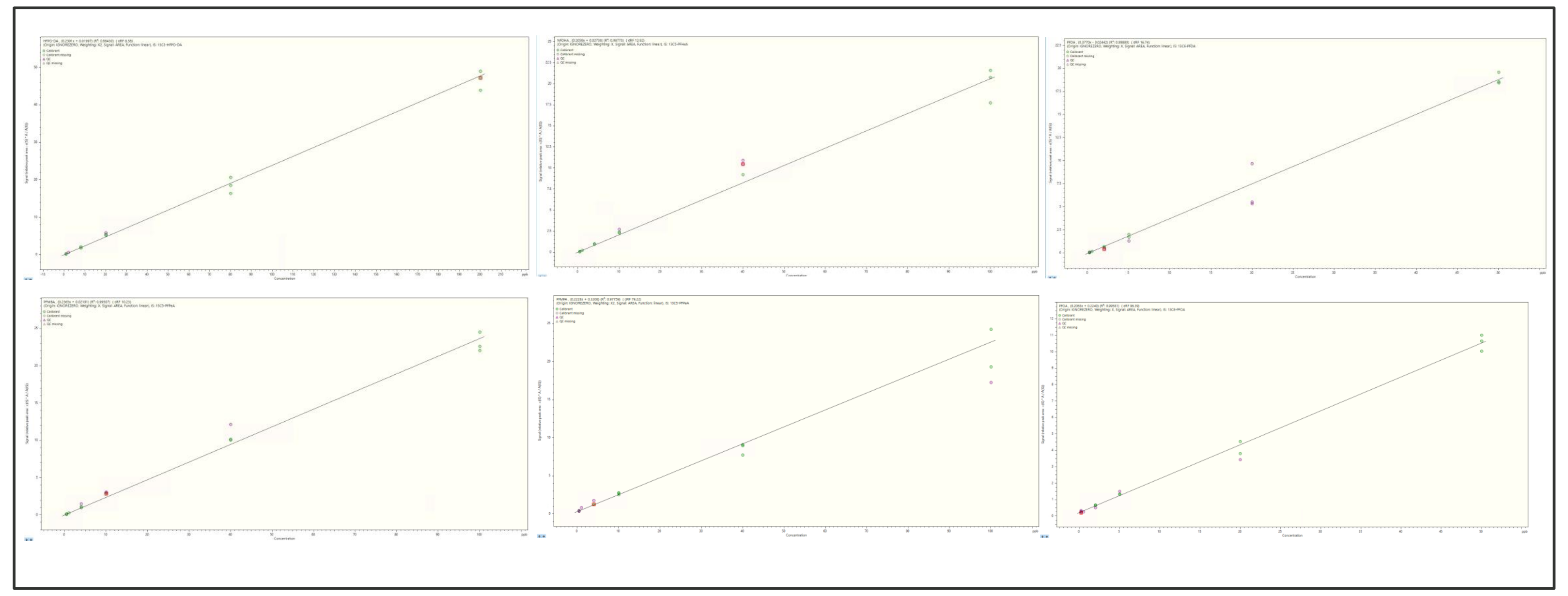
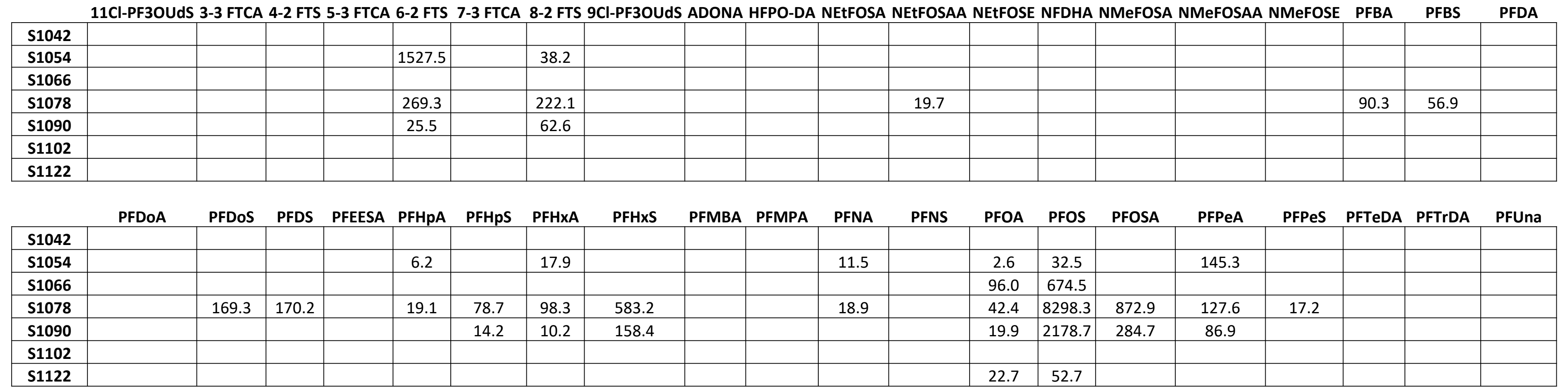


Fig. 3 Calibration Curves - HFPO-DA(GenX), NFDHA, PFDA, PFMBA, PFMPA, PFOA



	11Cl-PF3OUdS	3-3 FTCA	4-2 FTS	5-3 FTCA	6-2 FTS	7-3 FTCA	8-2 FTS	9Cl-PF3OUdS	ADONA	HFPO-DA	NEtFOSA	NEtFOSAA	NEtFOSE	NFDHA	NMeFOSA	NMeFOSAA	NMeFOSE	PFBA	PFBS	PFDA
S1042																				
S1054					1527.5		38.2													
S1066																				
S1078					269.3		222.1					19.7						90.3	56.9	
S1090					25.5		62.6													
S1102																				
S1122																				

	PFDoA	PFDoS	PFDS	PFEESA	PFHpA	PFHpS	PFHxA	PFHxS	PFMBA	PFMPA	PFNA	PFNS	PFOA	PFOS	PFOSA	PFPeA	PFPeS	PFTeDA	PFTrDA	PFUna
S1042																				
S1054					6.2		17.9				11.5		2.6	32.5		145.3				
S1066													96.0	674.5						
S1078		169.3	170.2		19.1	78.7	98.3	583.2			18.9		42.4	8298.3	872.9	127.6	17.2			
S1090						14.2	10.2	158.4					19.9	2178.7	284.7	86.9				
S1102																				
S1122													22.7	52.7						

Fig. 4 Semi-Quantitative results (ppb)

Results

- DART and TQ+ MS parameters were optimized for to maximize sensitivity, selectivity, precision, and achieve rapid analysis time.
- DART gas temperatures were set at 200°C/450 °C depending on PFAS class and grid voltage at -50 V. Unique MS/MS transitions, collision energies, and MS scan times were successfully identified for all 40 PFAS in EPA 1633.
- The varied sample origins and soil types produced no interference in detection of PFAS.
- Multiple analytes were able to match 1633 sensitivity requirements on LC-MS: HFPO-DA(GenX), NFDHA, PFDA, PFMBA, PFMPA, PFOA

Summary

The results presented herein demonstrate the suitability of the DART-MS/MS workflow as a rapid and reproducible screening method with the benefits of minimizing carryover and analysis time associated with chromatography-based confirmatory testing. This allows for large scale testing of contaminated sites to quickly ascertain which areas are in need of remediation. The sensitivity also indicates the potential for use as a quantitative tool in PFAS analyses with further development and optimization.

Conclusion

- **DART-MS/MS** provides a **chromatography-free** approach for assessing PFAS contamination in soil while eliminating solvent usage and further environmental impact
- **Maximized** throughput
- **Minimal** solvent and gas use
- **96 samples** in less than **50 minutes**

DART-TQ+