# A Rapid Screening Method for PFAS Analysis (EPA 1633a) Using DART-MS

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## Introduction

PFAS carryover in LC-MS/MS arises when residues from high-concentration samples persist in the autosampler or tubing, leading to false positives in subsequent blank or low-level samples. To mitigate this issue, a rapid screening method is necessary. This study proposes the use of DART-MS analysis, which enables screening for high PFAS concentrations with a run time of 15 seconds per sample.

## Methods

PFAS stock solutions were prepared by combining and diluting analytical standard mixtures (Wellington Laboratories, ON, CAN) in basic methanol to generate four calibration levels (L1 to L4) in accordance with Method 1633A. Five microliters of each extract were applied to the DART mesh and analyzed using DART-MS (Fig 1).

To investigate the matrix effect, samples were collected from the Charles River (MA). Briefly, 25 mL of each sample was extracted using solid-phase extraction (SPE) with a vacuum manifold. Subsequently, 100 µL of each extract was spiked with analytes and EIS. Finally, 5 µL of the resulting solution was applied to the DART mesh and analyzed using DART/MS.

DART-MS analyses were conducted using an EVOQ DART-TQ$^+$ (Bruker, Billerica, MA) triple quadrupole mass spectrometer equipped with a DART ion source and operated in negative ion mode. The DART temperature was set to 450°C (and 250°C), with a cone gas pressure of 20 psi. The cone temperature was maintained at 300°C, and the grid voltage was set to 50 V.

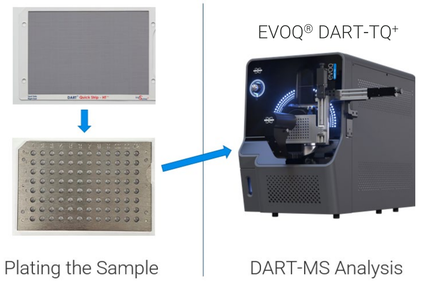


Figure 1. Spotting the samples

## Results

Table 1 presents the calibration points (L1 to L7) used for LC-MS/MS PFAS analysis according to EPA 1633a. Carryover in LC-MS/MS is theoretically observed when a sample concentration exceeds L7 (or the highest point of the calibration curve). For this method (DART-MS), new calibration points L1 to L4 were intentionally selected to encompass the region where carryover may occur. To assess reproducibility, each calibration point was analyzed five times. The results indicate that, for the 31 compounds listed in EPA 1633a, the quality controls (QCs) and relative standard deviations (RSDs) are within the acceptable range (<30%) (Fig. 2). All concentrations are reported in ng/mL. Calibration points highlighted in the table fall outside the acceptable range.

Table 1. Calibration solutions [ng/mL]

| Compound | CS1 (LOQ) | CS2 | CS3 | CS4 (CV[1]) | CS5 | CS6 | CS7[2] |
|---|---|---|---|---|---|---|---|
| **Perfluoroalkyl carboxylic acids** | | | | | | | |
| PFBA | 0.8 | 2 | 5 | 10 | 20 | 50 | 250 |
| PFPeA | 0.4 | 1 | 2.5 | 5 | 10 | 25 | 125 |
| PFHxA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFHpA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFOA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFNA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFDA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFUnA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFDoA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFTrDA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFTeDA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| **Perfluoroalkyl sulfonic acids** | | | | | | | |
| PFBS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFPeS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFHxS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFHpS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFOS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFNS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFDS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| PFDoS | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| **Fluorotelomer sulfonic acids** | | | | | | | |
| 4:2FTS | 0.8 | 2 | 5 | 10 | 20 | 50 | NA |
| 6:2FTS | 0.8 | 2 | 5 | 10 | 20 | 50 | NA |
| 8:2FTS | 0.8 | 2 | 5 | 10 | 20 | 50 | NA |
| **Perfluorooctane sulfonamides** | | | | | | | |
| PFOSA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| NMeFOSA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| NEtFOSA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| **Perfluorooctane sulfonamidoacetic acids** | | | | | | | |
| NMeFOSAA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| NEtFOSAA | 0.2 | 0.5 | 1.25 | 2.5 | 5 | 12.5 | 62.5 |
| **Perfluorooctane sulfonamide ethanols** | | | | | | | |
| NMeFOSE | 2 | 5 | 12.5 | 25 | 50 | 125 | 625 |
| NEtFOSE | 2 | 5 | 12.5 | 25 | 50 | 125 | 625 |
| **Per- and polyfluoroether carboxylic acids** | | | | | | | |
| HFPO-DA | 0.8 | 2 | 5 | 10 | 20 | 50 | 250 |
| ADONA | 0.8 | 2 | 5 | 10 | 20 | 50 | 250 |
| PFMPA | 0.4 | 1 | 2.5 | 5 | 10 | 25 | 125 |
| PFMBA | 0.4 | 1 | 2.5 | 5 | 10 | 25 | 125 |
| NFDHA | 0.4 | 1 | 2.5 | 5 | 10 | 25 | 125 |
| **Ether sulfonic acids** | | | | | | | |
| 9Cl-PF3ONS | 0.8 | 2 | 5 | 10 | 20 | 50 | 250 |
| 11Cl-PF3OUdS | 0.8 | 2 | 5 | 10 | 20 | 50 | 250 |
| PFEESA | 0.4 | 1 | 2.5 | 5 | 10 | 25 | 125 |

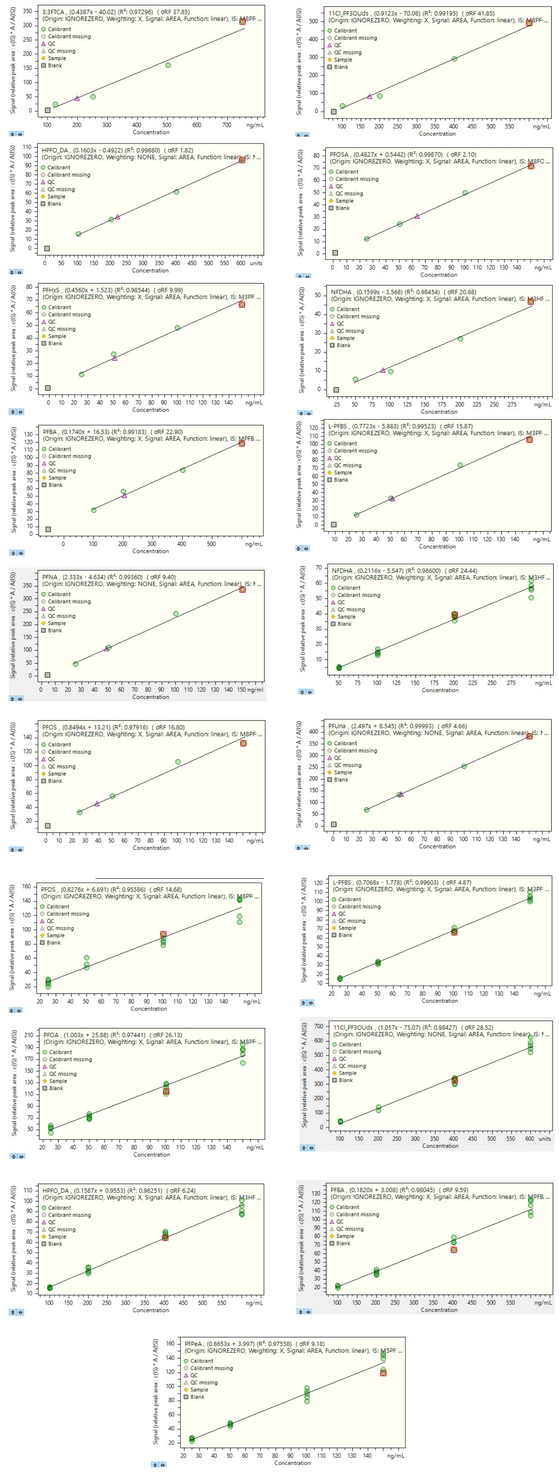

Figure 2. Calibration curve and reproducibility for selected PFAS

Table 2 presents the average percentage matrix effect (n=3) for selected PFAS compounds in the aqueous sample.

Table 2. % matrix effect (n=3)

| Compound | % Matrix effect (n=3) |
|---|---|
| 11Cl-PF3OUdS (200 ng/mL) | 99% |
| HFPO-DA (200 ng/mL) | 70% |
| PFBS (50 ng/mL) | 77% |
| PFDS (50 ng/mL) | 105% |
| PFNS (50 ng/mL) | 70% |
| PFHxS(50 ng/mL) | 80% |
| PFOSA (50 ng/mL) | 88% |

## Summary

DART/MS was implemented as a rapid screening method for samples with elevated PFAS concentrations to minimize carryover issues in LC-MS/MS. The second phase of this study is to optimize the method by using different samples (This is an ongoing project).

## Conclusion

- PFAS screening was conducted using DART-MS.
- At higher concentrations of PFAS, both linearity and reproducibility were found to be within acceptable ranges.
- Acceptable matrix effect was observed for certain PFAS compounds.

**DART-MS/PFAS**