

The PFAS conundrum: Mass spectrometry solutions for addressing it.

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1. Introduction

The increasing interest regarding the occurrence of Per- and Polyfluoroalkyl Substances (PFAS) in the environment since the general public become aware of the results from the Unregulated Contaminant Monitoring Rule 3 and the quantitation of GenX in drinking water has resulted in an acceleration of activities by stakeholders involved in addressing this issue. Multiple Federal and State Agencies (e.g. EPA, DOD, DEQs and DEPs) in the United States as well as international organizations (e.g. ASTM) are quickly publishing new analytical methodologies for PFAS monitoring and establishing more stringent limits. However, these rapid changes in monitoring requirements pose a challenge for environmental laboratories.

Liquid Chromatography with Mass Spectrometry-based detection is established as the most suitable technology for meeting the requirements from official methods released up to date for monitoring PFAS. These methods require sample preconcentration by Solid Phase Extraction using different sorbents or allow for direct sample injection. In the work presented here, samples were prepared and analyzed following the requirements from current EPA and ASTM methods (EPA 537, EPA 537.1, ASTM D7979). Various mass spectrometry platforms (LC/MS/MS, LC/QTOF) presenting different technical specifications were employed for this purpose.

A comparison of instruments' performance was conducted in this work. The ultimate goal was to create a guidance tools for selecting the most appropriate platform for the analysis of PFAS based on end-user' objective.

2. Experimental approach

Linearity, repeatability, precision, accuracy and method detection limits were determined with reagent water and selected environmental samples for the purpose of comparing instruments' performance for up to 30 individual PFAS included in either EPA or ASTM methods. Quantitation of selected samples for assessing repeatability, precision and accuracy was performed with the three same instruments for developing instrument's selection guidelines.

A summary of analytical methods evaluated, list of target compounds monitored and instrumentation employed in this work are included in Table 1.

Table 1. Methods, target compounds and instruments evaluated

Compound	Method				
	ASTM 7979	EPA 537	EPA 537	EPA 537.1	EPA 537.1
PFBS	√	√	√	√	√
PFHxA	√	√	√	√	√
PFHpA	√	√	√	√	√
PFHxS	√	√	√	√	√
PFOA	√	√	√	√	√
PFNA	√	√	√	√	√
PFOS	√	√	√	√	√
PFDA	√	√	√	√	√
N-MeFOSAA	√	√	√	√	√
N-EtFOSAA	√	√	√	√	√
PFUnA	√	√	√	√	√
PFDoA	√	√	√	√	√
PFTriA	√	√	√	√	√
PFTreA	√	√	√	√	√
PFBA	√			√	√
PFPeA	√			√	√
4-2 FTS	√			√	√
FHUEA	√			√	√
FHEA	√				
PFPeS	√				
6-2 FTS	√				
FhpPA	√				
FOEA	√				
FOUEA	√				
8-2 FTS	√				
PFHpS	√				
FDEA	√				
PFNS	√				
FOSA	√				
PFDS	√				
HFPO-DA				√	√
ADONA				√	√
9Cl-PF3ONS				√	√
11Cl-PF3OUdS				√	√

Triple Quad LCMS-8060 Triple Quad LCMS-8060 Triple Quad LCMS-8045 Triple Quad LCMS-8045 QTOF LCMS-9030

Instrument

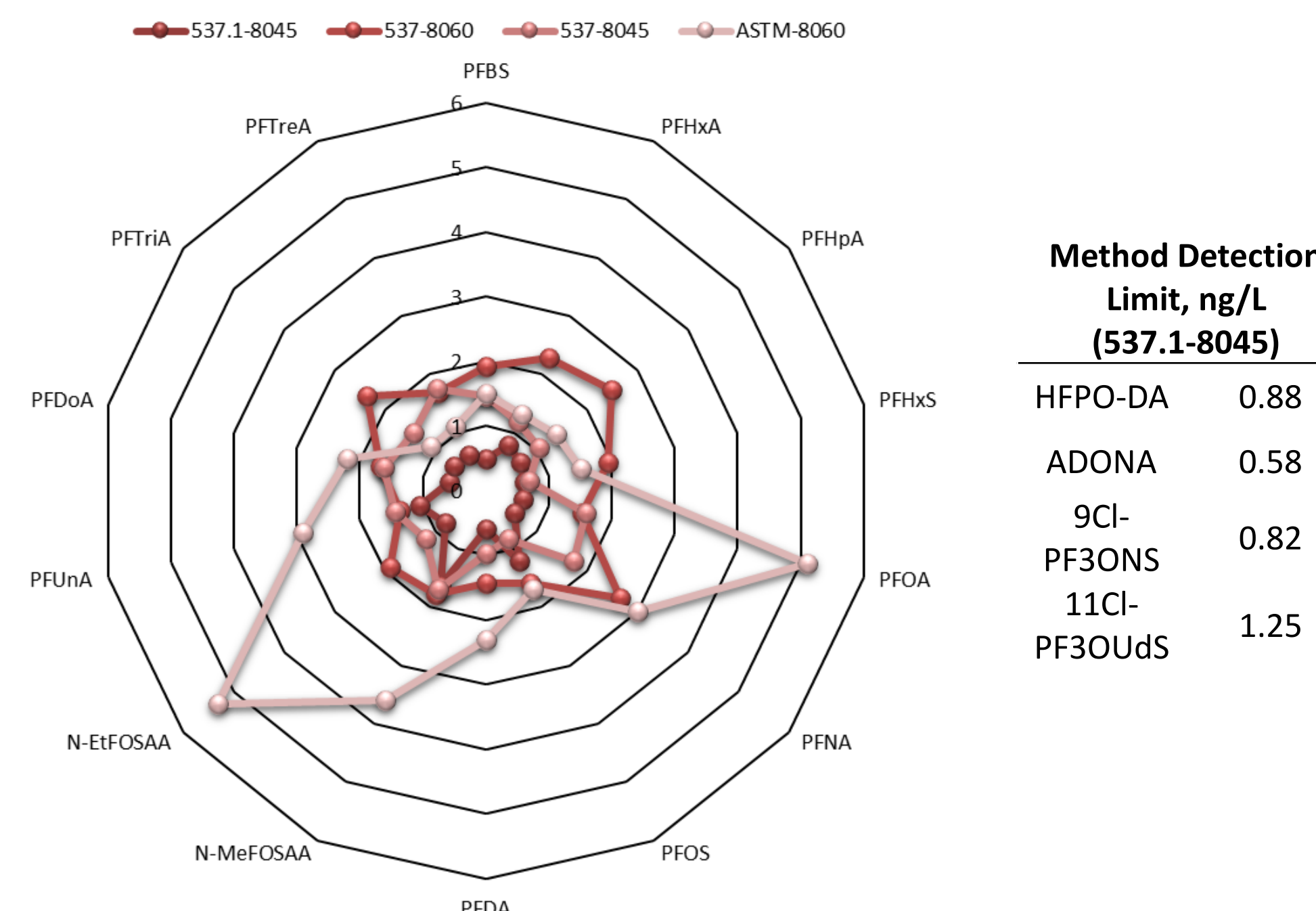


Figure 1. Methods Detection Limits of common targets from methods evaluated

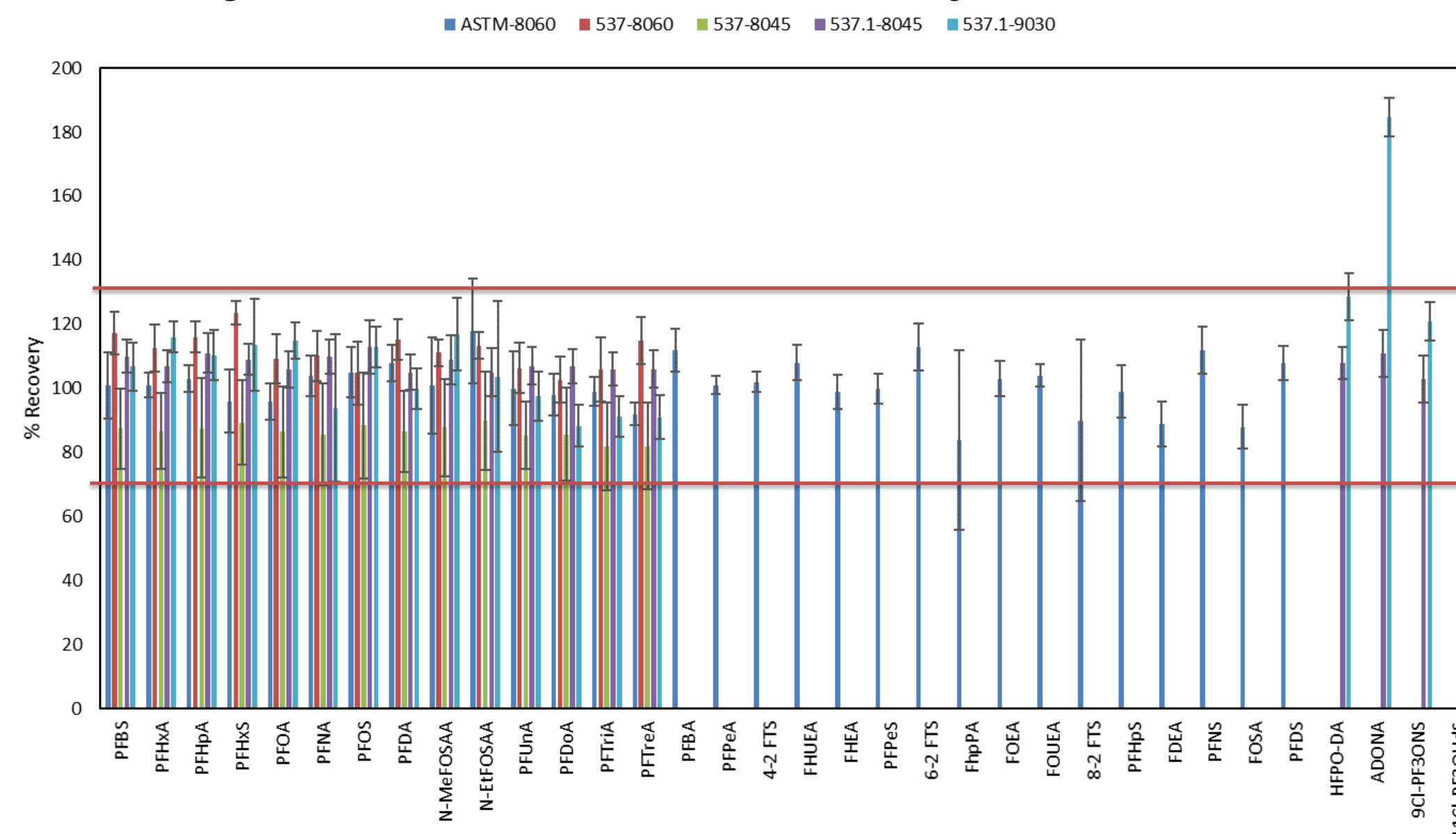


Figure 2. % recoveries with %RSD from Precision and Accuracy studies

3. Results

Calibration curves ranging between 5 ng/L and 400 ng/L (based on the 250x concentration factor established in the EPA methods) presented acceptable linearity ($R^2 > 0.99$). Method Detection Limits (MDLs) calculated based on the results from three instruments of different technical specifications ranged between 0.6 ng/L and 5.4 ng/L. Individual MDLs from common compounds in the three methods studied are reported in Figure 1. Precision and Accuracy results are included in Figure 2 as % recoveries and %RSD.

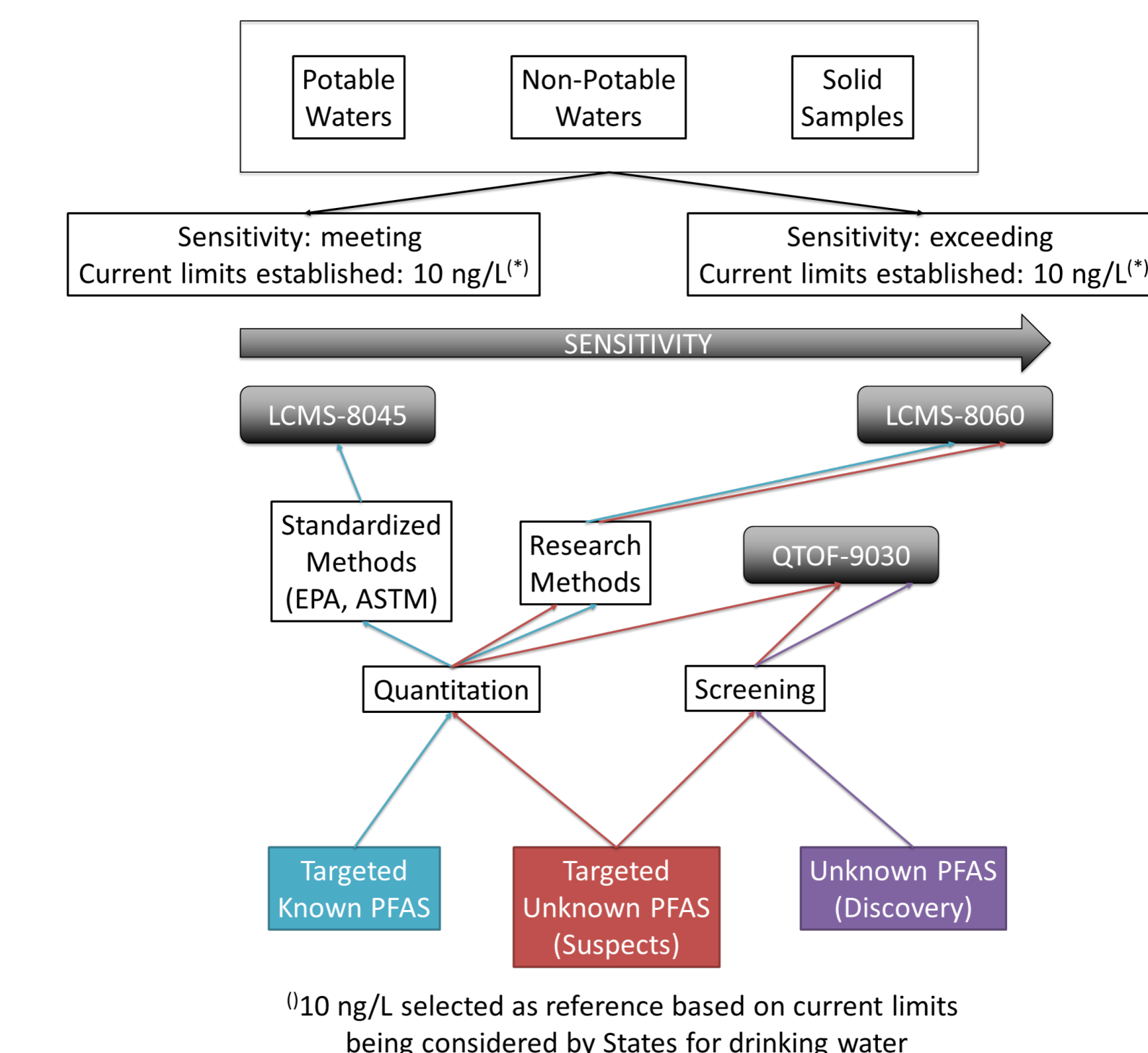


Figure 3. Guidance Tool

4. Conclusions

Performance of three instruments (two LC/MS/MS – Triple Quad LCMS-8045 and LCMS-8060; one LC/QTOF – QTOF-9030) was similar for the quantitation of selected target PFAS. The MDLs were comparable, independently from the sample preparation approach. Precision and accuracy did not differ between the methods and instruments. A guidance tool to help selecting the most appropriate instrumentation for this application is included in Figure 3.