

Comparing Method Performance for Testing PFAS in Aqueous Samples: EPA 537.1, EPA 533, ISO 21675

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Introduction

Extraction protocols and analytical methods utilized for detecting Per- and polyfluoroalkyl substances (PFAS) in aqueous samples have evolved rapidly over the past decade. From 2013 -2015, EPA 537 was utilized for assessment monitoring of PFAS as part of the Unregulated Contaminant Monitoring Rule (UCMR) 3 program and was updated to EPA method 537.1, shortly thereafter. In late 2019, EPA method 533 and International Organization for Standardization (ISO) Method 21675 were released, which in addition to EPA method 537.1, enable laboratories to quantify up to 37 PFAS analytes with exceptional precision and accuracy. To better improve our understanding of method performance, it is beneficial to review these top methods utilized for evaluating PFAS in aqueous samples.

Method Chemistry

Target Analytes

A total of 37 targeted PFAS analytes were quantified as prescribed in each method. Of the 37 target analytes, 13 are referenced in all three methods and therefore offer the most insight into comparing method performance. EPA method 533 references 6 unique PFAS analytes that are not found in the other methods. An additional 8 PFAS analytes are unique to ISO method 21675, which makes a full method to method comparison difficult.

Water Solubility

Figure 1 plots the number of analytes in each method based on carbon number of the analytes and its correlation to water solubility. This shows that EPA 533 has target analytes that are predominately more hydrophilic, while ISO 21675 has the widest range of analytes in terms of water solubility.



Figure 1. Water solubility (log P) as a function of carbon number for EPA 537.1, 533, & ISO analytes

Method Parameters

Sample Volumes & Matrices

Required sample volumes are referenced in each method and provided in Table 1. 250mL sample volumes were selected for this study since it is an allowable sample volume for each method. Table 2 displays the types of matrices referenced in each method. EPA methods are for analysis of drinking water while ISO 21675 is utilized for several matrices.

Method	537.1	533	ISO 21675
100mL		X	X
250mL	X	X	X
1000mL			X

Table 1. Method allowable sample volumes

Method	537.1	533	ISO 21675
DW	X	X	X
GW/SW			X
WW			X

Table 2. Method applicable sample matrices

Extraction

Sample preparation was carried out on a 20-position vacuum manifold, Biotage® VacMaster™ 20 (Figure 2). Solid phase extraction (SPE) media ISOLUTE® 101 & EVOLUTE® PFAS and were utilized according to each method requirement as well as necessary media bed masses. Detail of method steps are provided in Table 3.

Method	537.1	533	ISO 21675
Technique	SPE	SPE	SPE
Format	Tube	Tube	Tube or Disk
Media	SDVB	WAX	WAX
Biotage Media	ISOLUTE® 101	EVOLUTE® PFAS 533	EVOLUTE® PFAS
Bed Mass	500mg	200 or 500mg	50-1000mg*
Loading Rate	10-15 mL/min	5 mL/min	3-6 mL/min

Table 3. Method extraction parameters

Concentration & Analysis

Extracts were concentrated using a TurboVap® LV via nitrogen blowdown and heated bath (Figure 3). LCMSMS analysis was performed using fluoropolymer free tubing and trap column to a triple quadrupole MS system following method requirements (Table 4).

Method	537.1	533	ISO 21675
Evaporation Temperature (°C)	60 - 65	55 - 60	60
Evaporation Style	N ₂	N ₂	N ₂
Reconstitution Solvent	H ₂ O:MeOH (4:96, v/v)	H ₂ O:MeOH (20:80, v/v)	Not Prescribed
Analytical Column Size (mm)	2.1 x 150	2 x 50	Various
Analytical Column Media	C18	C18	C18
Delay Column	Not Specified	Yes	Not Specified
Quantification	ISC	ID	ISC

Table 4. Method extraction parameters. ISC = Internal Standard Correction, ID = Isotope Dilution



Figure 2. Biotage® VacMaster™ 20



Figure 3. Biotage® TurboVap® LV

Method Performance

Background Check

A minimum of seven extracted blanks were processed as prescribed in each method. Figure 4 demonstrates background levels for each method analyte is below the 1/3 MRL criteria.

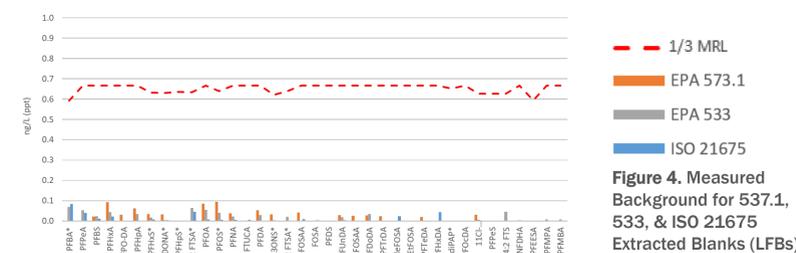


Figure 4. Measured Background for 537.1, 533, & ISO 21675 Extracted Blanks (LFBs)

Precision & Accuracy

To determine the precision and accuracy of the sample preparation process, four LFB samples were prepared at concentrations for mid level spikes at 15ppt or 20ppt. Results for each method and SPE sorbent bed mass are shown in Figures 6 & 7.

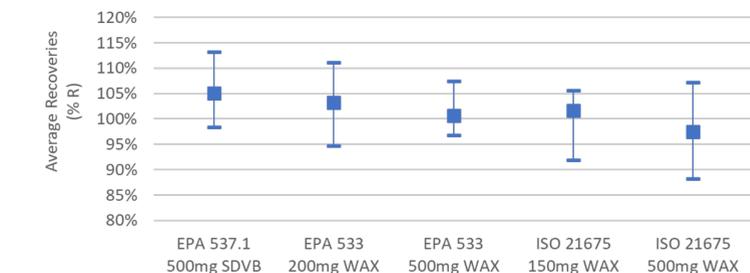


Figure 6. Average, Min and Max percent recovery for each method & SPE bed mass

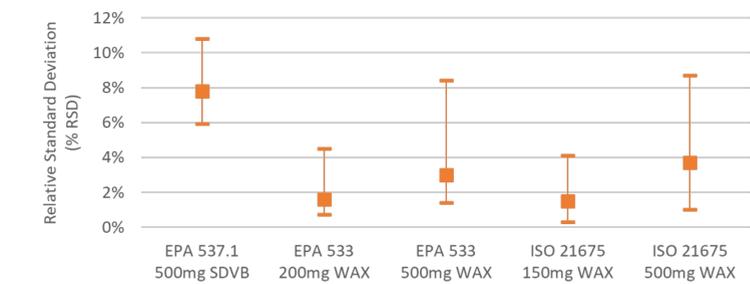


Figure 7. Average, Min and Max relative standard deviation for each method & SPE bed mass

Conclusions

This evaluation demonstrates the value obtained from comparing protocols and analytical results using current methodology for PFAS monitoring in aqueous samples. In total, EPA 537.1, EPA 533, and ISO 21675 contain 37 unique PFAS analytes, but not all targets are found in each method. The primary conclusions from this evaluation are as follows:

- » Water solubility information can help troubleshoot extraction performance
- » Biotage® VacMaster™ 20, ISOLUTE® 101, EVOLUTE® PFAS and TurboVap® LV products meet background, MDL, precision, & accuracy requirements
- » Method requirements can be achieved at 250mL sample volumes

EPA 537.1



EPA 533



ISO 21675



NEW: EPA 1633

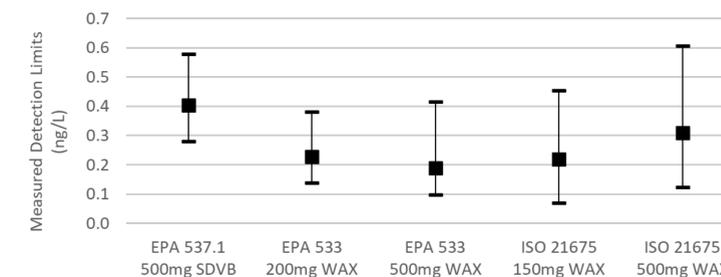


Figure 5. Average, Minimum and Maximum MDLs determined for each method & SPE bed mass