AUTOMATED ENRICHMENT AND CLEAN UP OF WATER SAMPLES FOR ANALYSIS OF PFAS

APPLICATION NOTE AS-300

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Abstract

Perfluorinated alkyl substances (PFAS) have attracted significant attention due to their persistence in the environment. Water authorities are increasing their monitoring of these compounds in order to assure safe drinking water.

This application note describes an automated method for online solid phase extraction followed by LC-MS/MS to clean up and enrich water samples to allow low to sub ng/L detection. Due to the sample enrichment gained using solid phase extraction of samples, many of the issues of background contamination are overcome.

INTRODUCTION

Perfluorinated alkyl substances (PFAS) are a class of chemicals that consist of a fluorinated alkyl chain with a variety of functional groups. PFAS have a number of applications including non-stick coating, stain repellents, paints, polishes, seals and firefighting foams.

PFAS are a concern as they are highly chemically stable and undergo very little degradation, as such, they have been branded 'forever chemicals'. They are therefore classified as persistent (P), many of them also have the ability to bioaccumulate (B) due to the lipophilic alkyl long chain and some have been linked to toxic (T) effects. Due to this PBT status, Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA) manufacture in the EU is prohibited under Directive (2006/122/EC). Regulators are also considering threshold limits for drinking water which are likely to be at the low ng/L level.

Sophisticated LC-MS/MS systems are capable of detecting low ng/L PFAS concentration in drinking water, however come with a relatively large price tag, and without sample pre-treatment, analytical column lifetime will significantly reduce and the requirements for detector maintenance will increase, due to contamination by the sample matrix. This application note describes an automated procedure to enrich and clean up water samples using Instrument Top Sample Preparation (ITSP) solid phase extraction, to minimise the need for column replacement and allow analysis on less sophisticated, less expensive, LC-MS/MS systems.

EXPERIMENTAL

Instrumentation

GERSTEL Multi-purpose sampler (MPS) with dual head Robotic/Robotic pro.SmartSPE®

Agilent technologies 1260 HPLC with 6470 MS/MS.

METHOD

Bottled spring water (medium-hardness), was used as a blank matrix for preparation of matrix matched standards. All waters were buffered with 2 g/L ammonium acetate and spiked with internal standards prior to being pipetted into 10 mL vials and loaded onto the MPS. Blank waters were spiked with PFAS to make calibration standards, the MPS then carried out the automated solid phase extraction by ITSP, the procedure is shown in Figure 2.

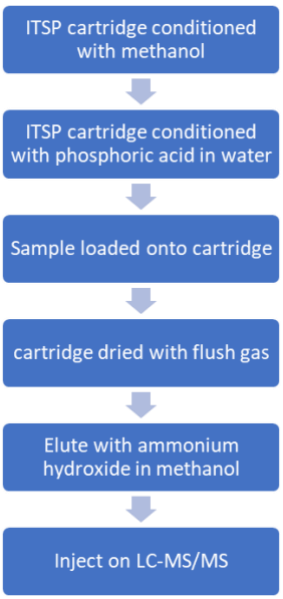

Figure 2: *Automated procedure for sample extraction and analysis.*

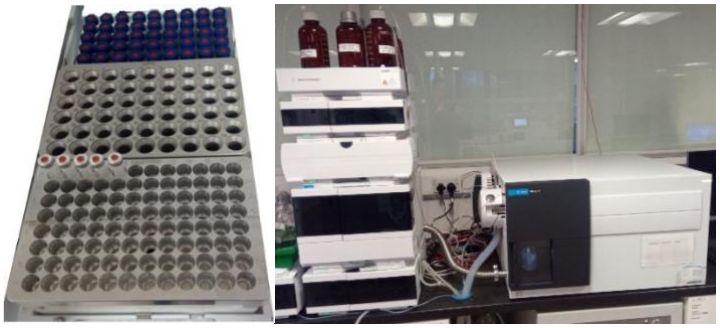

Figure 1: ITSP setup and Agilent 1200 LC with 6470 MS/MS

LC-MS/MS analysis

Analysis was carried out on an Agilent 1260 HPLC fitted with Agilent PFAS conversion kit, coupled to a 6470 MS/MS using a 10 µL sample extract injection. The conversion kit removes replaces components the on the standard setup would contain fluorinated materials, hence reducing the background contamination. Chromatographic separation was carried out using gradient elution with a Halo 90Å PFAS 2.7 µm 2.1 x 100 mm column, and a Halo 160Å 2.7 µm 3 x 50 mm delay column. The run time was 20 minutes. The delay column is used to shift contamination from sources prior to the injection port, such as solvents and tubing and shift their retention away from the target peaks retention time. The detector used the Agilent jet stream source, optimised using the Source Optimiser software. The MS/MS operated in multiple reaction monitoring (MRM) mode. Full details of conditions are available on request. A typical extracted ion chromatogram can be seen in Figure 3.

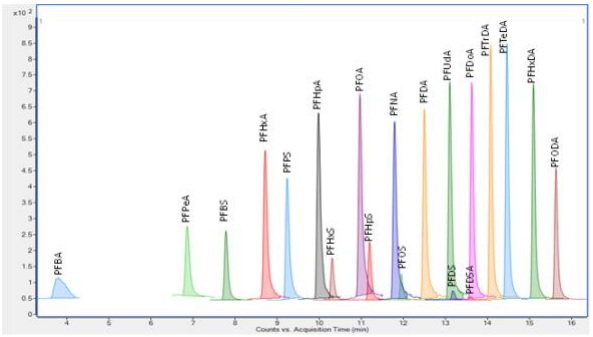

Figure 3: Typical extracted ion chromatogram of a spiked bottled water extract.

RESULTS

The results are shown here

To assess the performance of the method, evaluations of linearity, limits of detection and bias were undertaken.

Linearity assessment was carried out on Buxton water, which was spiked with PFAS at 0, 0.5, 1, 2.5, 5, 10, 25, 50, 100 and 200 ng/L and with internal standard at 10 ng/L. These were taken through the full ITSP procedure as previously described. All analytes were fitted to a linear calibration and gave r^2 of 0.994 or greater as can be seen in Table 1.

Table 1: Linearity of target analytes.

Analyte	r^2	Analyte	r^2
PFBA	1.000	PFNA	0.997
PFPeA	1.000	Br-PFOS	0.996
L-PFBS	1.000	9Cl-PF3ONS	0.997
FBSA	0.999	8:2FTS	0.997
4:2FTS	0.996	PFDA	0.996
PFHxA	1.000	L-PFNS	0.996
L-PFPeS	0.999	L-PFDS	0.995
HFPO-DA GenX	1.000	Br-NMeFOSAA	0.998
PFHpA	1.000	PFUdA	0.995
Br-PFHxSK	0.999	FOSA	0.997
11Cl-PF3OUdS	0.994	Br-NEtFOSAA	0.995
6:2FTS	0.996	ADONA	0.995
PFOA	0.999	PFDoA	0.994
L-PFHxSK	1.000	PFTrDA	0.997
FHxSA	1.000	PFTeDA	0.996

Recovery and reproducibility were evaluated in three sample matrices; bottled, hard tap and ground water at 20 and 80 ng/L of each analyte. This data can be seen in Figures 4 and 5 for 20 and 80 ng/L spike levels respectively. Spikes showed good reproducibility at both concentrations with %rsd between 0.2 and 11.7 %. Recoveries in the 80 ng/L spiked samples were greater than 80% for all analytes. Recoveries of the 20 ng/L spike were greater than 70 %, with the more hydrophobic PFAS species showing the lowest recoveries. These greater losses are believed to be due to analyte adsorption to the sample vessel. A longer chain internal standard should better correct for these losses. The addition of 10 % methanol in the samples was also investigated to determine if this could reduce losses to sample vessels. This gave around a 10 % increase in recovery of the hydrophobic analytes but as this required an additional step and a dilution in the sample by 10 %, this was not routinely used.

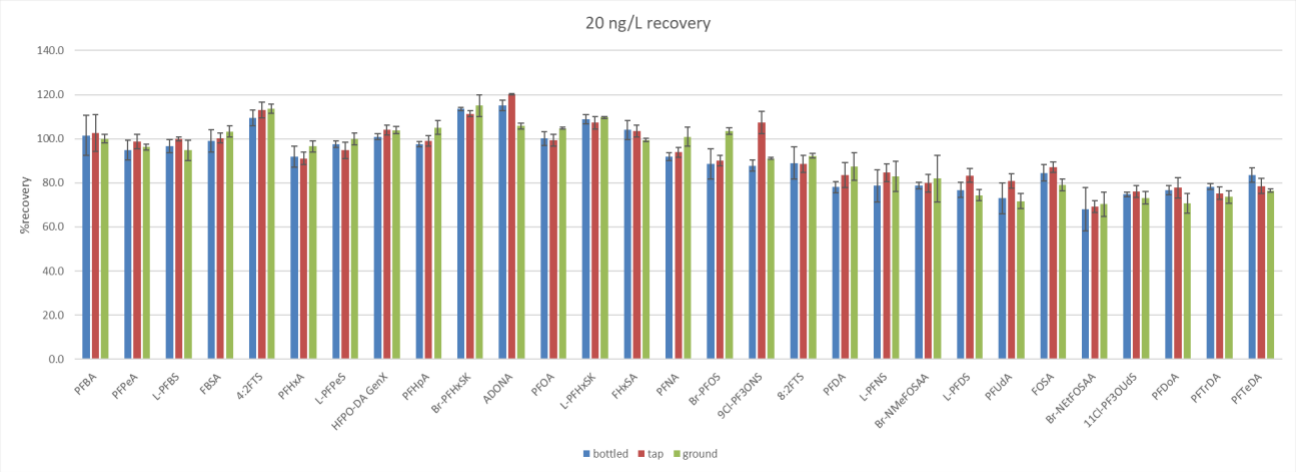

Figure 4: Recovery of samples spiked at 20 ng/L

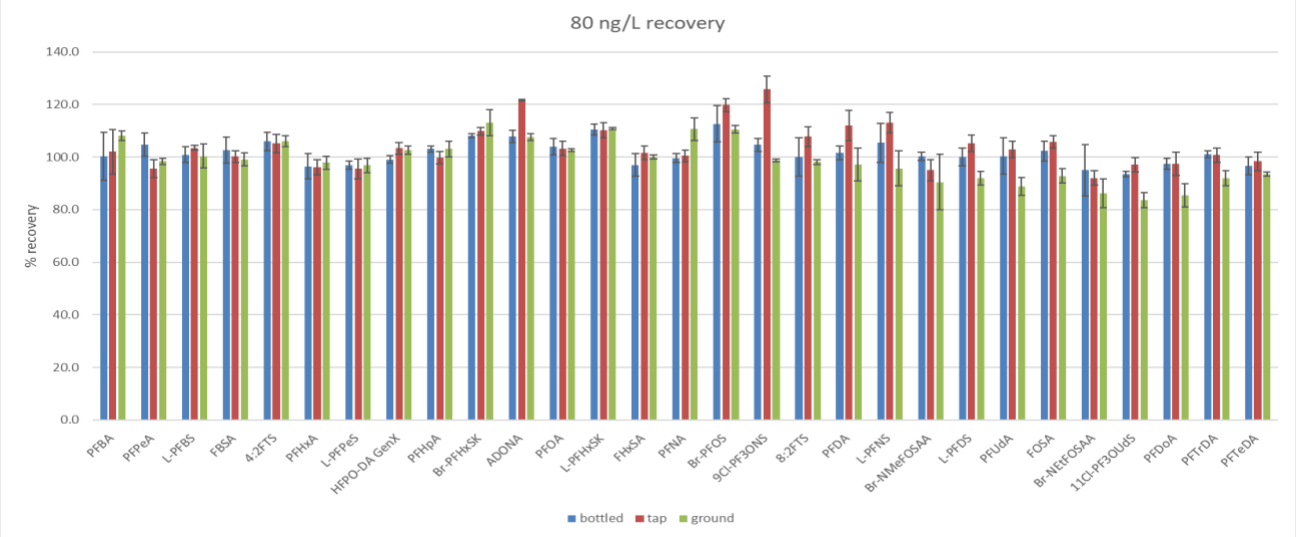

Figure 5: Recovery of samples spiked at 80 ng/L

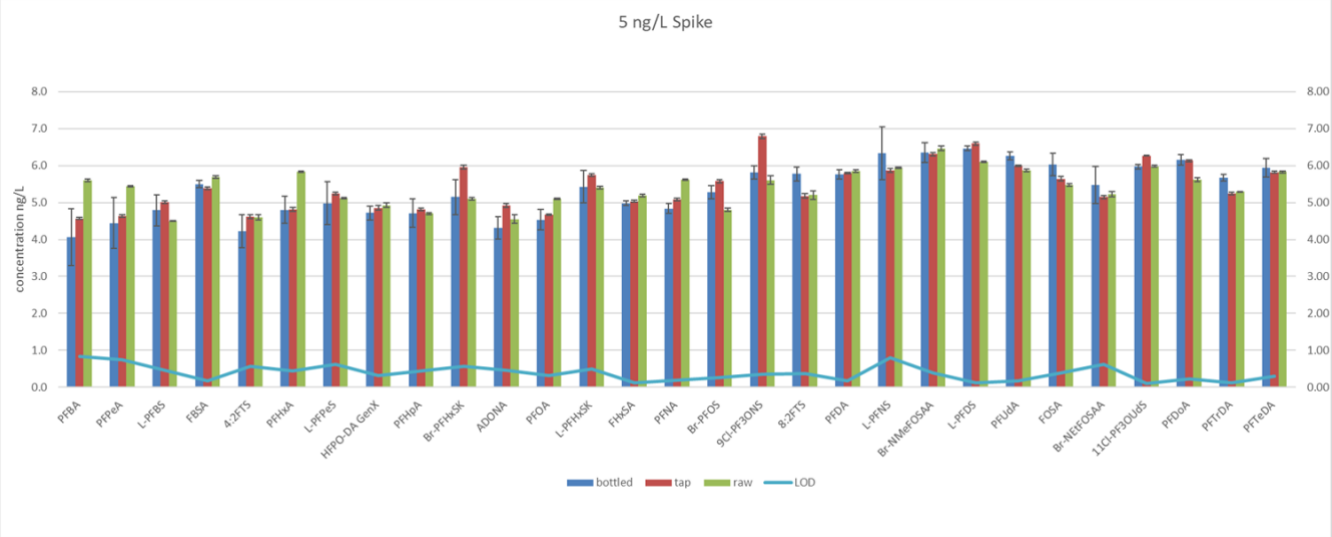

Figure 6: measured concentration of 5 ng/L spiked waters and limits of detection

To assess limit of detection, matrices were spiked to a level of 5 ng/L, and calculated from the 3 times standard deviation (n=3). The results can be seen in Figure 6. Due to the SPE enrichment process, samples demonstrated good signal to noise at this level, as is demonstrated in Figure 7 for PFOS. This enrichment in sample concentration elevates signals further away from background levels, than that possible to achieve with direct injection.

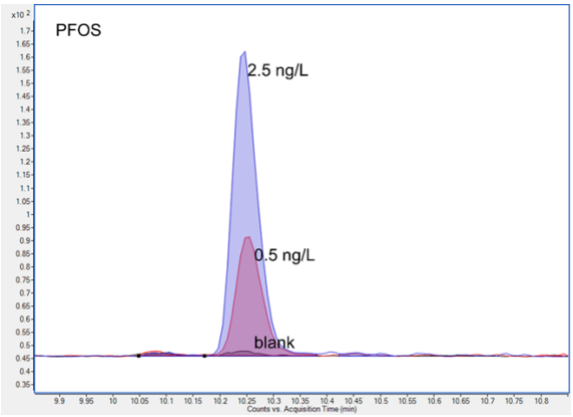

Figure 7: Chromatogram of a blank and water spiked at 0.5 and 2.5 ng/L taken through the full extraction procedure

CONCLUSION

PFAS analysis has a number of difficulties to overcome, the major issues are losses to sample containers and sources of contamination. The use of non-fluorinated plastics such as polypropylene for sample storage can reduce the losses to sample vessels. However, this does not completely eliminate the issue, so the addition of internal standards as early in the analysis as possible is recommended to account for these losses. A small amount of methanol added to the sample was shown to reduce the losses to sample.

Any fluorinated material in the sample extraction and analysis pathway can result in contamination, and wherever possible these should be avoided. Some of the potential sources are vial caps which are frequently Teflon coated. SPE cartridges, specific fluorinated species free ITSP cartridges were used for this analysis. Solvents can be contaminated and need to be checked prior to use. The HPLC systems also have a number of sources of contamination such as the solvent lines and valves. This work utilised an Agilent HPLC PFAS free conversion kit to eliminate these sources. A delay column was also used to shift the retention time of any contamination from solvent away from the peaks of interest. The use of the automated ITSP methods helps to mitigate some of the effect of contamination by enriching the sample and hence shifting the calibration to higher concentrations making the background comparatively smaller, and as such a distinct benefit over direct injection.

The method developed showed good linearity over the evaluated range of 0.5 to 200 ng/L for all analytes. Recoveries of spiked samples were greater than 70 % for all analytes in the evaluated matrices. Reproducibility were in the range of 0.2 and 11.7 %rsd. Limits of detection were all sub 1 ng/L.