Simultaneous LC/MS Analysis of Ultra-Short Through Long Chain PFAS Compounds (C1-C10) in Industrial and Ground Water

Zijie Beryl Xia[1], Alexander Schrum[2],Tanya Napolitano[2], Ronald Benson[2]
[1]Claros Technologies, Minneapolis, MN
[2]Resonac America/Shodex, New York, NY

Contact us at **support@shodexHPLC.com**
For more information visit **www.shodexHPLC.com**

Introduction

Shodex collaborated with Claros Technologies using HILICpak™ VT-50 2D Shodex column to study PFAS in industrial and ground water samples. Per and polyfluoroalkyl substances (PFAS) have been in industrial use since the 1960's and are commonly found in the environment. However, PFAS compounds have been linked to multiple health concerns, including cancer, birth defects, and many other life-threatening health conditions. As a result, the Environmental Protection Agency (EPA) has put global PFAS advisories in place to drive the development of PFAS monitoring. Like long chain PFAS compounds, short-chain PFAS compounds, do not easily break down in the environment and have high mobility in water and soil, leading to an increased focused on detecting ultra-short through long chain PFAS. The current challenges to overcome are ultra short chain and long chain PFAS cannot be simultaneously retained on a C18 column, shown in the EPA methods 533 and 537.1. A validated method was developed for screening short to long chain PFAS in industrial and ground water, using direct injection with no sample preparation. This method uses multimode chromatography coupled with mass spectrometry for increased sensitivity and detection of ultra-short chain to long length PFAS compounds.
Shodex™, founded in 1973, is best known for innovative polymer-based LC columns including Size-Exclusion, HILIC, and Ion Chromatography columns. Claros Technologies Inc. is an advanced materials company that strives to lead the industry towards a holistic approach in material design and innovation to develop more efficient, safe, and sustainable products with zero toxic waste.

Shodex HILICpak™ VT-50 Series Columns

Features

- Retains anions without the use of ion-pair reagents
- Operates under HILIC and Anion Exchange mode under high organic solvent conditions

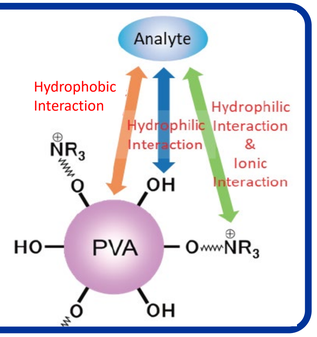
Product name	Column size (mm) I.D. x Length
HILICpak VT-50 2D	2.0 x 150
HILICpak VT-50G 2A	2.0 x 10 (Guard)

*PEEK housing

Specifications

- Base Material: Spherical porous particles of polyvinyl alcohol modified with Quat. Ammonium functional group
- Particle Size: 5 µm
- Pore Size: 100 Å
- Column Housing: PEEK
- Usable pH: 2 - 13
- Usable temperature: 4 – 60 °C
- Applicable solvents: Mixture of water and acetonitrile or water and methanol of any ratio. Up to 100 % water, acetonitrile, or methanol.

Workable in alkaline conditions



PFAS Calibration Standards

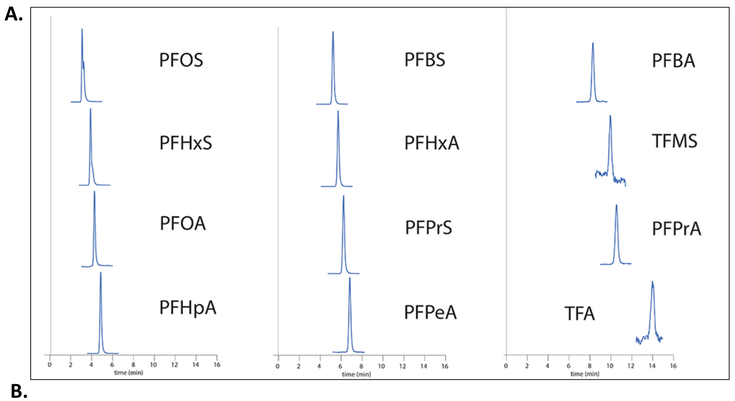


Figure 1 A. Legacy PFAS MS analysis at 1ppb.
B. Next generation PFAS MS analysis at 1ppb.

Table 1 .PFAS standards MS analysis of serial dilutions results.

Compound	R^2	LOD (ppb)	Dynamic Range (ppb)	Internal Standard
TFA	0.9995	0.25	0.25 - 100	C2TFA
PFPrA	0.9999	0.05	0.05 - 100	C3PFPrA
PFBA	0.9999	0.05	0.05 - 100	C5PFHxA
PFPeA	0.9999	0.05	0.05 - 100	C5PFHxA
PFPrS	0.9993	0.05	0.05 - 100	C3PFPrA
PFBS	0.9985	0.1	0.1 -100	C5PFHxA
PFHxA	0.9999	0.05	0.05 - 100	C5PFHxA
PFHxS	0.9995	0.05	0.05 - 100	C8PFOS
PFHpA	0.9999	0.05	0.05 - 100	C8PFOA
PFOA	0.9999	0.05	0.05 - 100	C8PFOA
PFOS	0.9998	0.05	0.05 - 100	C8PFOS
6:2 FTS	0.9994	0.05	0.05 - 10	C2-6:2FTS
HFPO-DA	0.9995	0.05	0.05 - 100	C5PFHxA
Bis - TFSI	0.9998	0.05	0.05 - 100	C2TFA
TFMS	0.9942	0.5	0.5 - 200	C2TFA
444 - TFBA	0.9986	0.05	0.05 - 100	C2TFA

Internal standards are used for the calibration and quantitation. All samples contain 10 ppb of each internal standard. The corresponding internal standard or surrogate for each analyte is labeled in Table 1.

Method Conditions

Instrument	Waters TQ-Absolute coupled with Acquity Premier UPLC
Column	Shodex HILICpak VT-50 2D (2.0 mm I.D. x 150 mm)
Solvent A (26%)	50 mM Ammonium Acetate (pH 6.8)
Solvent B (74%)	Acetonitrile
Flow rate	0.2 mL/min
Detector	ESI-MS MRM(-)
Column Temperature	40°C
Injection volumn	5 µL
ESI voltage	0.5 kV
Cone voltage	Compound dependent
CE	Compound dependent
Source temperature	150 °C
Desolvation temperature	500 °C
Cone gas (L/Hr)	150
Desolvation gas (L/Hr)	1000
Nebulizer gas (L/Hr)	300

No Ion pair reagent needed!

Discussion

Industrial and ground water samples from clients were studied for matrix effects on the analysis of ultra short through long PFAS compounds by LC/MS. This method utilizes multimode chromatography with HILIC and anion exchange retention characteristics. For calibration standards in deionized water (Figure 1A &B), most compounds reported an LOD of 0.05 ppb and with a R^2 of 0.999, apart from TFA and TFMS (Table 1). Using direct injection, without sample preparation, sub ppb to ppt concentration levels for several PFAS species were found to be indigenous to the industrial and ground water samples (Table 2 & 3). The highest concentration PFAS compound found in industrial water was PFHxA (0.33 ppb) while in ground water it was TFA (0.529 ppb). For accuracy evaluation, recoveries of 1 ppb spiked standards were under 10% in both matrices, apart from TFMS and 444-TFBA in ground water (~15%) likely due to an increase in interference from organic compounds. Across the spiked calibration range of 0.05 ppb to 100 ppb, the R^2 recovery was found to be at least 0.99 in both samples (Figure 2B & D).

Conclusions

The Shodex™ HILICpak™ VT-50 series, polymer-based quaternary ammonium type HILIC columns, demonstrated highly selective and sensitive LC/ESI-MS measurements in industrial and ground water without sample preparation. The simple isocratic mixture of 50 mM aqueous ammonium acetate solution and acetonitrile using multimode separation allows for the analysis of ultra short through long chain PFAS in real world samples, which cannot be simultaneously retained using reversed phase methods.

Industrial Water

Ground Water

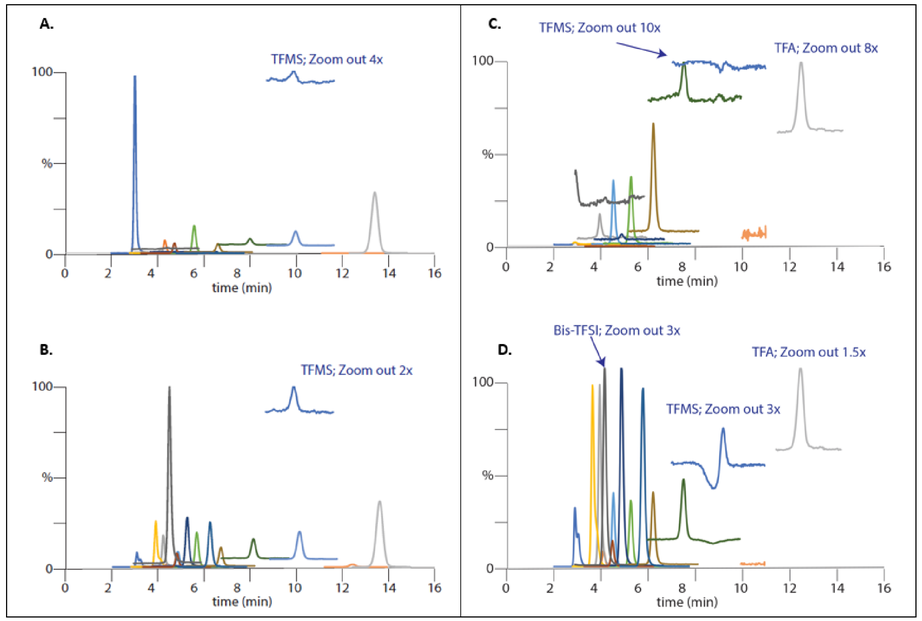


Figure 2. A. Direct injection MS analysis of industrial water. **B.** Industrial water MS analysis with 1ppb calibrant spiked. **C.** Direct injection MS analysis of ground water. **D.** Ground water MS analysis with 1ppb calibrant spiked.

Table 2. PFAS quantification in industrial water.

Compound	Matrix concentration (ppb)	% recovery at Cal 5 (1 ppb)	R^2
TFA	0.116	2.9	0.9999
PFPrA	0.123	-3.4	0.9998
PFBA	0.049	-7.6	0.9997
PFPeA	0.08	-3	0.9999
PFPrS	<0.05	-5.7	0.9997
PFBS	<0.05	3.4	0.9996
PFHxA	0.33	-9.7	0.9997
PFHxS	<0.05	1.2	0.9997
PFHpA	<0.05	2.4	0.9998
PFOA	0.05	-4.2	0.9999
PFOS	<0.05	-5.1	0.9995
6:2 FTS	<0.05	2.2	0.9983
HFPO-DA	0.123	-12	0.998
Bis - TFSI	<0.05	-5.4	0.9989
TFMS	~0.1	1	0.9993
444 - TFBA	0.071	-5.6	0.9982

Table 3. PFAS quantification in ground water.

Compound	Matrix concentration (ppb)	% recovery at Cal 5 (1 ppb)	R^2
TFA	0.529	0.1	0.999
PFPrA	<0.5	1.4	0.9998
PFBA	~0.08	6.4	0.9997
PFPeA	0.11	3.4	0.9998
PFPrS	<0.05	2.4	0.9991
PFBS	<0.05	6.8	0.9984
PFHxA	0.066	2.5	0.9999
PFHxS	<0.05	2.7	0.9974
PFHpA	~0.05	1.7	0.9994
PFOA	<0.25	5.6	0.9992
PFOS	<0.05	6.8	0.9985
6:2 FTS	<0.05	7.2	0.9986
HFPO-DA	<0.05	5.4	0.9992
Bis - TFSI	<0.05	1	0.9994
TFMS	<0.05	-15.8	0.9949
444 - TFBA	<0.05	-12	0.9983