APPLICATION NOTE

Non-targeted HPLC-MS analysis of PFAS in soil

Per- and polyfluoroalkyl substances (PFAS) are persistent environmental pollutants known for their long lifetime and mobility. Their stability leads to accumulation in groundwater and soil, with proven harmful health effects. To mitigate environmental pollution, several PFAS compounds, such as perfluorooctanoic acid (PFOA), perfluorohexanesulfonic acid (PFHxS), and long-chain perfluoroalkyl carboxylic acids (C9-C14), are now regulated.

This Application Note presents a reliable method for identifying PFAS in a complex soil sample using a YMC-Triart C18 HPLC column. This column, based on a robust hybrid silica particle, offers enhanced separation of isomers and improved analytical performance when coupled with mass spectrometry. It is also highly compatible with complex matrices such as soil. This is due to its high specific surface area which is about 10% higher compared other silica-based columns.

Table 1: Chromatographic conditions.

Column:	YMC-Triart C18 (12 nm, 3 µm) 100 x 2.1 mm ID
Part No.:	TA12S03-10Q1PTH
Eluent:	A) water/methanol (95/5) + 2 mM ammonium acetate B) water/methanol (5/95) + 2 mM ammonium acetate
Gradient:	15–70 %B (0–2 min), 70–90 %B (2–5 min), 90–100 %B (5–10 min), 100 %B (10–15 min), 15 %B (15.1–22 min)
Flow rate:	0.3 mL/min
Temperature:	40 °C
Injection:	2 µL
Detection:	ESI-MS negative mode
Sample:	PFAS standards (5, 10, 25, 50, 75, 100 ng/mL) from Fluka, Sigma, Dr. Ehrenstorfer, Apollo Scientific, soil extract sample (Brilon-Scharfenberg)

Table 2: MS source parameters.

Gas Temp:	150 °C
Gas Flow:	16 L/min
Nebulizer pressure:	35 psig
Sheath gas temperature:	380 °C
Sheath gas flow:	12 L/min
Fragmentor voltage:	380 V
Capillary voltage:	3000 V
Nozzle voltage:	300 V

A soil extract from a contaminated site (Brilon-Scharfenberg, Germany; from the scientific publication of Zweigle et al. [1]) was analysed. Total ion chromatograms (TICs) from triplicate measurements (Figure 1) revealed consistent profiles, despite the high matrix complexity. Table 3 lists pre-identified PFAS clusters detected in the analysis (originally identified in Zweigle et al. [1] and shared by courtesy).

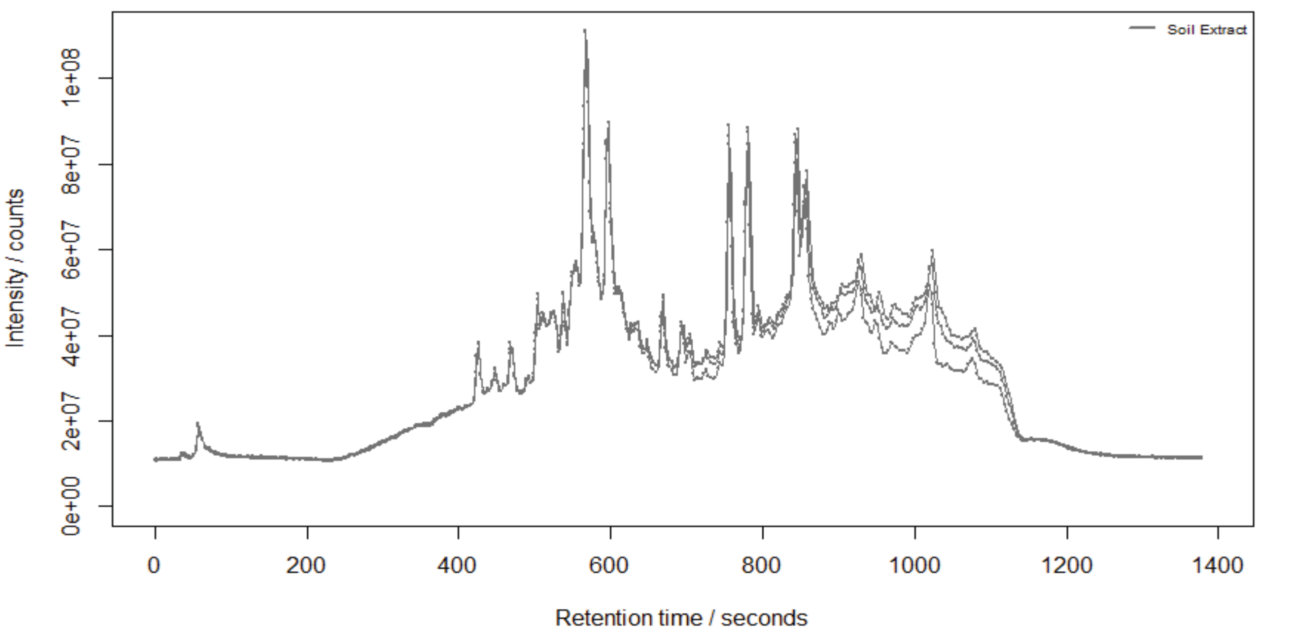

Figure 1: Total ion chromatograms (TIC) of the soil sample measured in triplicate.

Table 3: Substances identified in the soil extract by Zweigle et al. [1], using Kendrick mass defect analysis and matching of CF_2-distances in the fragmentation spectra of prioritised chromatographic peaks.

Formula	*m/z*	Cluster Group
$F(CF_2)_7SO_3$	448.93286	$F(CF_2)_nSO_3$
$F(CF_2)_8SO_3$	498.92966	
$F(CF_2)_9SO_3$	548.92647	
$F(CF_2)_{10}SO_3$	598.92328	
$F(CF_2)_{11}SO_3$	648.92008	
$F(CF_2)_{12}SO_3$	698.9168	
$F(CF_2)_{13}SO_3$	748.91369	
$F(CF_2)_{14}SO_3$	798.9105	
$F(CF_2)_{15}SO_3$	848.90731	
$SF_5(CF_2)_6SO_3$	506.901728	$SF_5(CF_2)_nSO_3$
$SF_5(CF_2)_7SO_3$	556.898528	
$SF_5(CF_2)_8SO_3$	606.895328	
$SF_5(CF_2)_9SO_3$	656.892128	
$SF_5(CF_2)_{10}SO_3$	706.888928	
$SF_5(CF_2)_{11}SO_3$	756.885728	
$SF_5(CF_2)_{12}SO_3$	806.882528	
$CF(CF_2)_6SO_3$	460.932838	$CF(CF_2)_nSO_3$
$CF(CF_2)_7SO_3$	510.929638	
$CF(CF_2)_8SO_3$	560.926438	
$CF(CF_2)_9SO_3$	610.923238	
$CF(CF_2)_{10}SO_3$	660.920038	
$CF(CF_2)_{11}SO_3$	710.916838	
$CF(CF_2)_{12}SO_3$	760.913638	
$CF(CF_2)_{13}SO_3$	810.910438	
$CF(CF_2)_{14}SO_3$	860.907238	

Formula	*m/z*	Cluster Group
$CF_3O(CF_2)_8SO_3$	564.921359	$CF_3O(CF_2)_nSO_3$
$CF_3O(CF_2)_9SO_3$	614.918159	
$CF_3O(CF_2)_{10}SO_3$	664.914959	
$CF_3O(CF_2)_{11}SO_3$	714.911759	
$CF_3O(CF_2)_{12}SO_3$	764.908559	
$CF_3O(CF_2)_{13}SO_3$	814.905359	
$CF_3O(CF_2)_{14}SO_3$	864.902159	
$CF_3O(CF_2)_{15}SO_3$	914.898959	
$CF_3OC_2F_2(CF_2)_6SO_3$	526.924553	$CF_3OC_2F_2(CF_2)_nSO_3$
$CF_3OC_2F_2(CF_2)_7SO_3$	576.921353	
$CF_3OC_2F_2(CF_2)_8SO_3$	626.918153	
$CF_3OC_2F_2(CF_2)_9SO_3$	676.914953	
$CF_3OC_2F_2(CF_2)_{10}SO_3$	726.911753	
$CF_3OC_2F_2(CF_2)_{11}SO_3$	776.908553	
$CF_3OC_2F_2(CF_2)_{12}SO_3$	826.905353	
$CF_3OC_2F_2(CF_2)_{13}SO_3$	876.902153	
$FC_2F_2C_2F_2(CF_2)_4SO_3$	422.936031	$FC_2F_2C_2F_2(CF_2)_nSO_3$
$FC_2F_2C_2F_2(CF_2)_6SO_3$	522.929631	
$FC_2F_2C_2F_2(CF_2)_7SO_3$	572.926431	
$FC_2F_2C_2F_2(CF_2)_8SO_3$	622.923231	
$FC_2F_2C_2F_2(CF_2)_9SO_3$	672.920031	
$FC_2F_2C_2F_2(CF_2)_{10}SO_3$	722.916831	
$FC_2F_2C_2F_2(CF_2)_{11}SO_3$	772.913631	
$FC_2F_2C_2F_2(CF_2)_{12}SO_3$	822.910431	

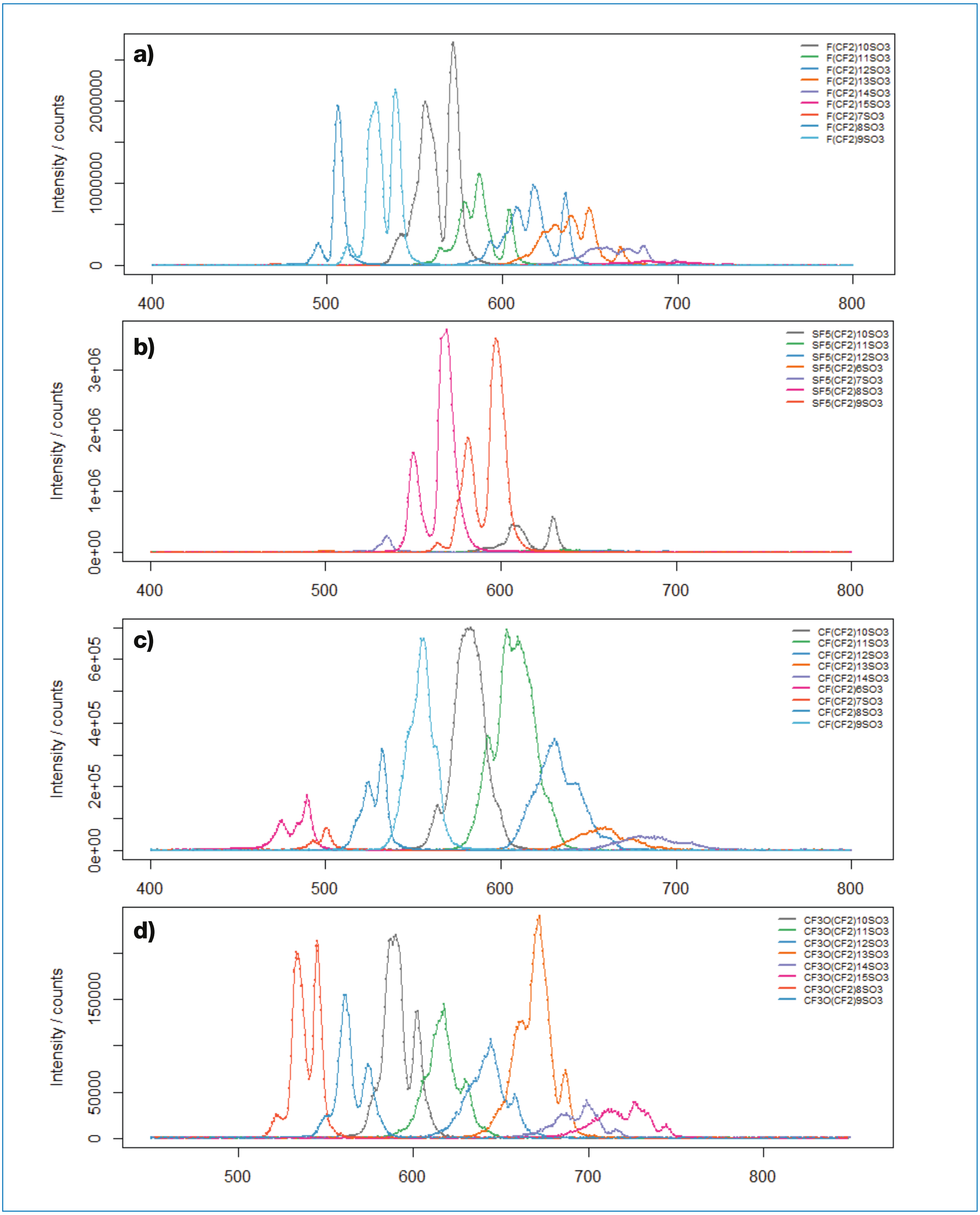

Figure 2: Extracted ion chromatograms of (a) PFAS group $F(CF_2)_nSO_3$, (b) PFAS group $SF_5(CF_2)_nSO_3$, (c) PFAS group $CF(CF_2)_nSO_3$, (d) PFAS group $CF_3O(CF_2)_nSO_3$, (e) PFAS group $CF_3OC_2F_2(CF_2)_nSO_3$ and (f) PFAS group $FC_2F_2C_2F_2(CF_2)_nSO_3$.

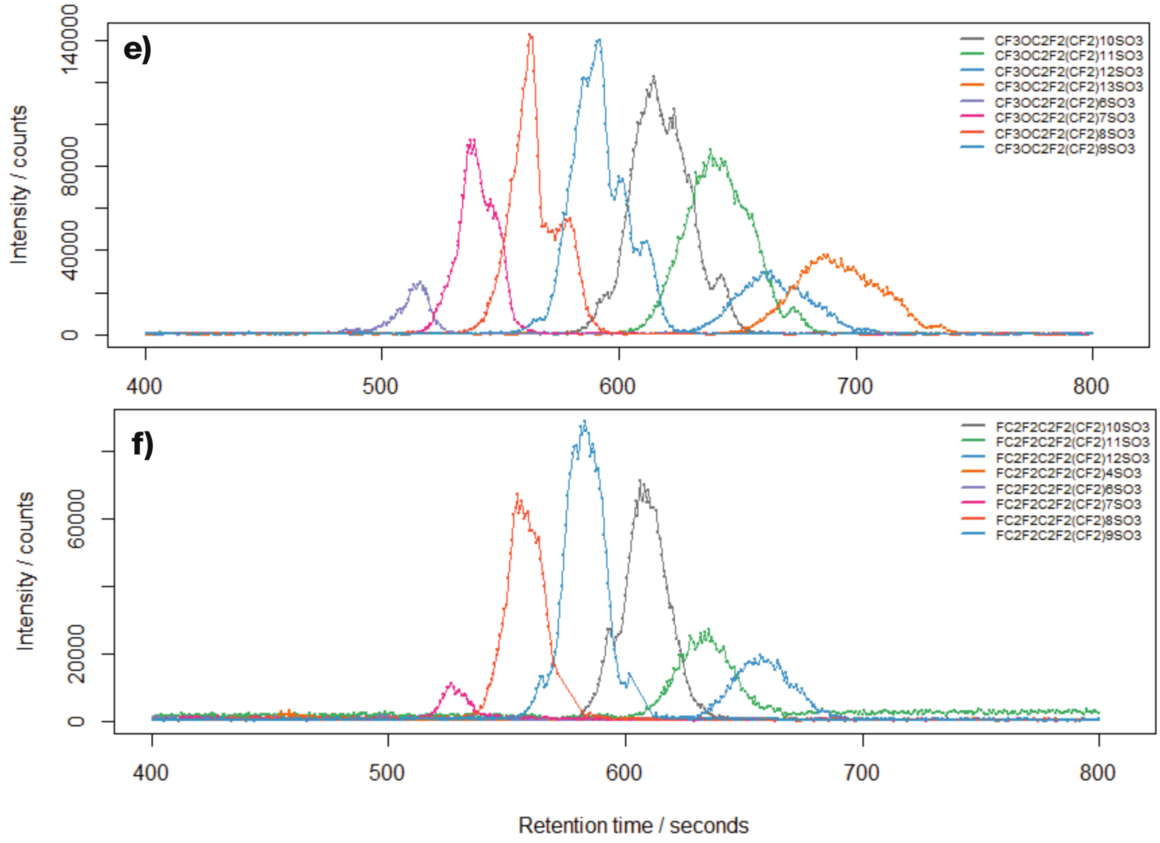

Figure 2: Extracted ion chromatograms of (a) PFAS group $F(CF_2)_nSO_3$, (b) PFAS group $SF_5(CF_2)_nSO_3$, (c) PFAS group $CF(CF_2)_nSO_3$, (d) PFAS group $CF_3O(CF_2)_nSO_3$, (e) PFAS group $CF_3OC_2F_2(CF_2)_nSO_3$ and (f) PFAS group $FC_2F_2C_2F_2(CF_2)_nSO_3$ continued.

Figure 2 shows the extracted chromatograms of the identified PFAS clusters. An effective separation was achieved, including improved partial resolution of isomers compared to Zweigle et al. [1], enabling structural elucidation through distinct fragmentation patterns.

Therefore, using the YMC-Triart C18 column provides efficient separation of several PFAS clusters, improved isomer separation, and proven superior reproducibility even for complex matrices such as soil extracts.

** Application data by courtesy of Ricardo Cunha, Institut für Umwelt & Energie, Technik & Analytik e. V. (IUTA) Duisburg, Germany, Boris Bugsel and Jonathan Zweigle.*

References:

[1] Environ. Sci. Technol. 2023, 57, 6647–6655.