# Highly sensitive targeted and non-targeted HPLC-MS analysis of PFAS

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 technical note presents a method for identifying and quantifying PFAS 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.

*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<br>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 |

*Table 3: Substances included in the standard mixture.*

| Name | Abbreviation | Mass (Da) | *m/z* | Retention time (s) |
|---|---|---|---|---|
| Perfluorobutanoic acid | PFBA | 213.9865 | 212.9792 | 291 |
| Perfluoropentanoic acid | PFPeA | 263.9833 | 262.9760 | 359 |
| Perfluorohexanoic acid | PFHxA | 313.9801 | 312.9728 | 398 |
| Perfluoroheptanoic acid | PFHpA | 363.9769 | 362.9696 | 432 |
| Perfluorooctanoic acid | PFOA | 413.9737 | 412.9664 | 469 |
| Perfluorononanoic acid | PFNA | 463.9705 | 462.9632 | 505 |
| Perfluorodecanoic acid | PFDA | 513.9673 | 512.9600 | 538 |
| Perfluorobutanesulfonic acid | PFBS | 299.9503 | 298.9430 | 366 |
| Perfluorohexanesulfonic acid | PFHxS | 399.9439 | 398.9366 | 435 |
| Perfluorooctanesulfonic acid | PFOS | 499.9375 | 498.9302 | 503 |
| 6:2 Fluorotelomer sulfonic acid | FTSA | 427.9752 | 426.9679 | 467 |

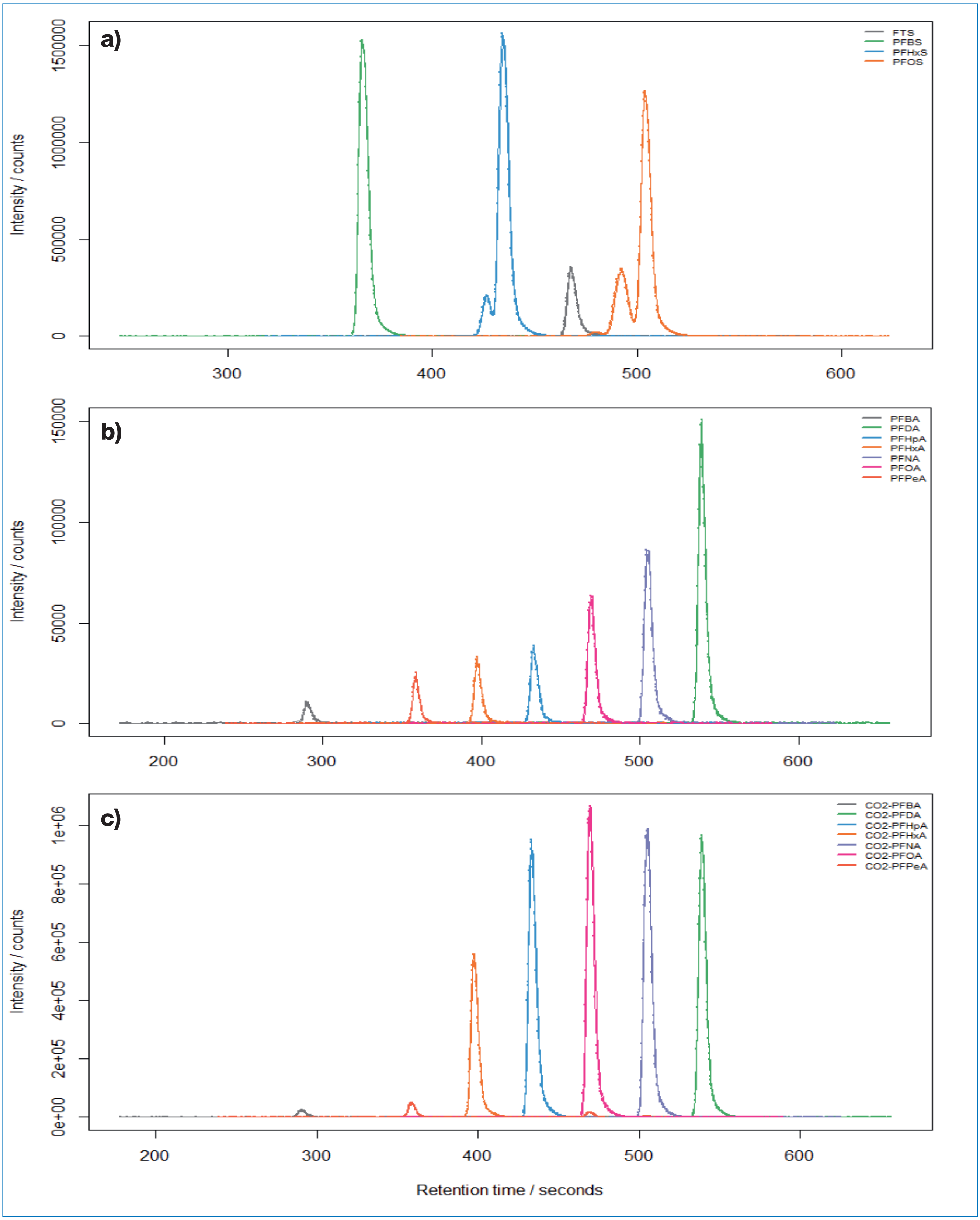

*Figure 1: Extracted ion chromatograms of (a) perfluoroalkyl sulfonic acids (PFSAs), (b) perfluoroalkyl carboxylic acids (PFCAs) and (c) perfluoroalkyl carboxylic acids (PFCAs) with loss of $CO_2$ during ionisation obtained with +/-120 seconds and +/-15 ppm at a concentration of 75 ng/ml each.*

PFAS standards (Table 3) were analysed at concentrations ranging from 5–100 ng/mL. The standards could be well resolved by the YMC-Triart column (Figure 1). Notably, partial separation of PFOS and PFHxS isomers within 10 seconds facilitated fragmentation pattern analysis for structural elucidation.

For perfluoroalkyl carboxylic acids (PFCAs), higher peak intensities were observed for longer carbon chains as expected (Figure 1b). Additionally, $CO_2$-loss ions exhibited remarkably higher intensities than the primary molecular ions (Figure 1c). Calibration curves (Figure 2) demonstrated a linear quantification range, and carry-over tests confirmed no residual analytes after injections of 100 ng/mL. These results highlight the YMC-Triart C18 column's suitability for robust PFAS analysis.

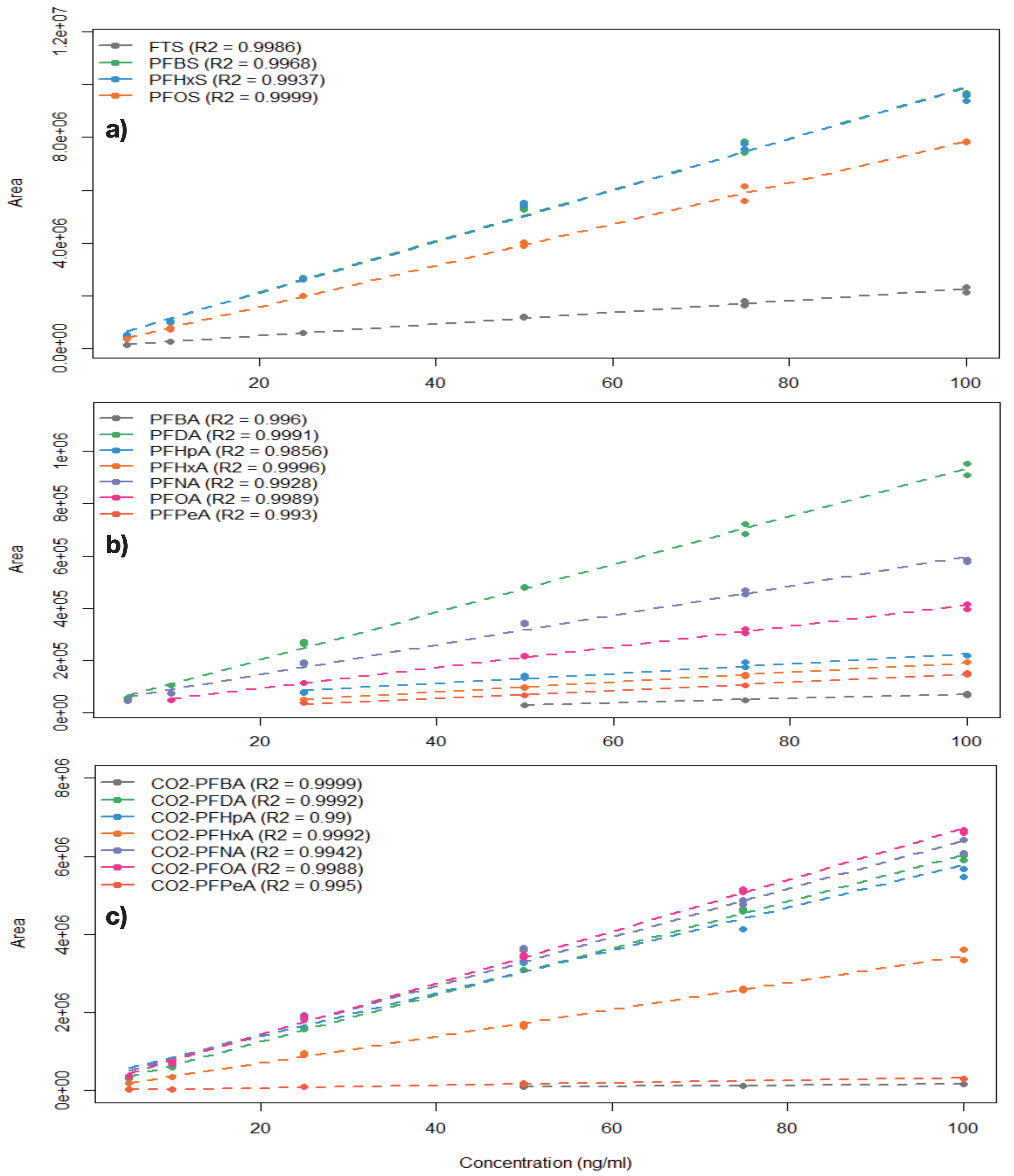

*Figure 2: Calibration curves of (a) perfluoroalkyl sulfonic acids (PFSAs), (b) perfluorinated carboxylic acids (PFCAs) and (c) perfluorinated carboxylic acids (PFCAs) with loss of $CO_2$ during ionisation at concentrations of 5-100 ng/mL.*

## Non-targeted analysis in a soil extract

To evaluate performance in complex matrices, 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 3) revealed consistent profiles, despite the high matrix complexity. Table 4 lists pre-identified PFAS clusters detected in the analysis (originally identified in Zweigle et al. [1] and shared by courtesy).

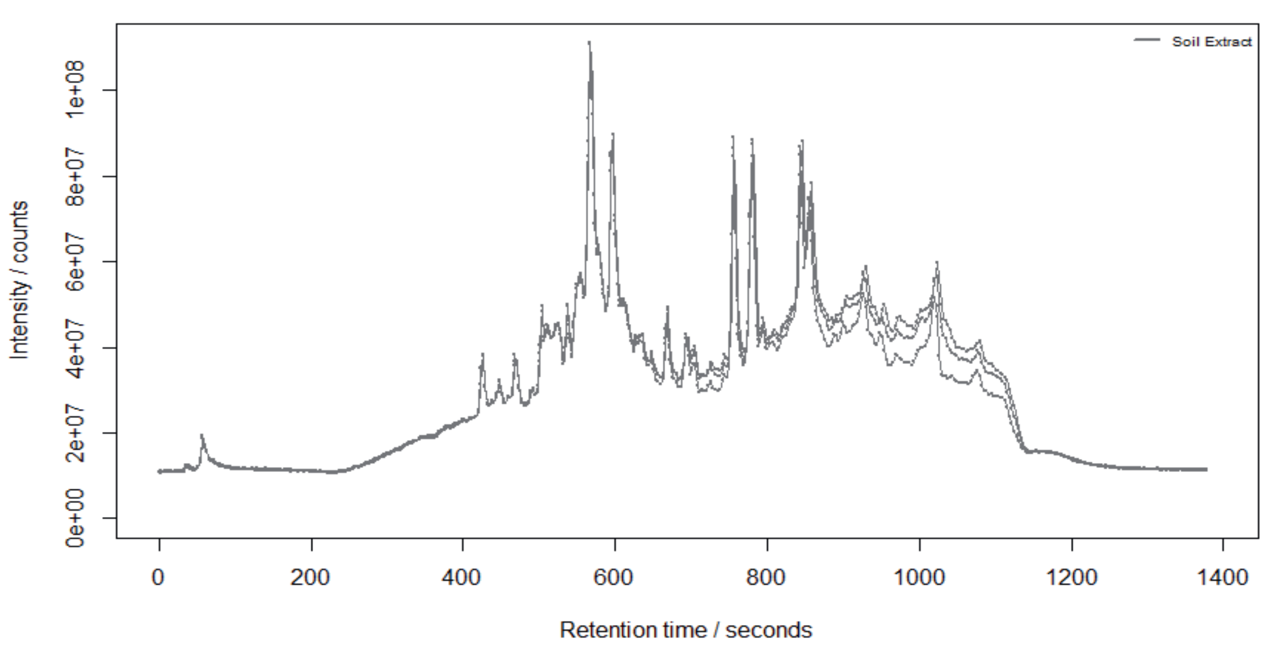

*Figure 3: Total ion chromatograms (TIC) of the soil sample measured in triplicate.*

*Table 4: 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 | |

## Improved separation of isomers

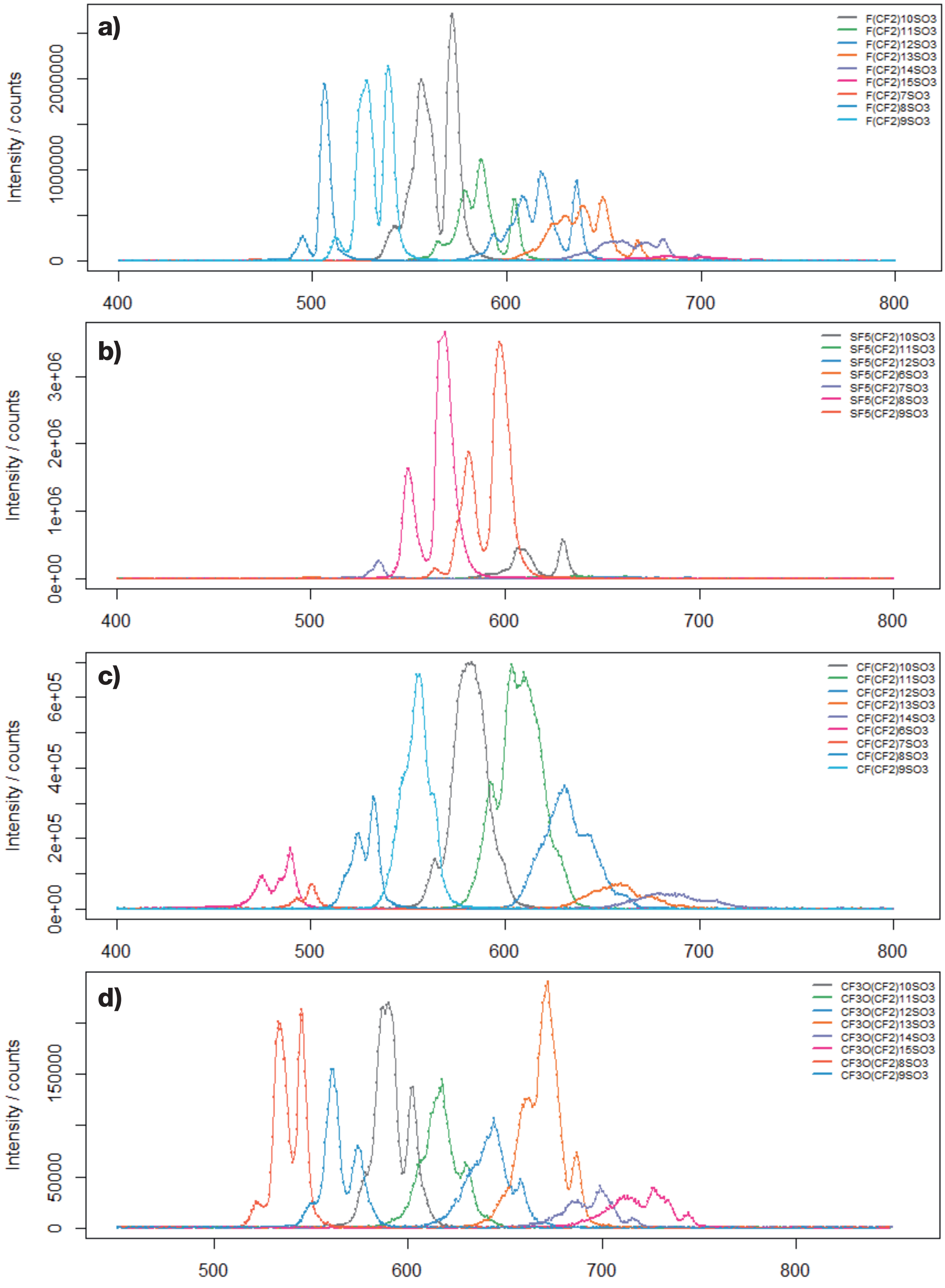

*Figure 4: Extracted ion chromatograms of (a) PFAS group* $F(CF_2)_nSO_3$*, (b) PFAS group* $SF_5(CF_2)_nSO_3$*, (c) PFAS group* $CF(CF_2)_nSO_3$*, (d) PFAS group* $CF_3O(CF_2)_nSO_3$*, (e) PFAS group* $CF_3OC_2F_2(CF_2)_nSO_3$ *and (f) PFAS group* $FC_2F_2C_2F_2(CF_2)_nSO_3$*.*

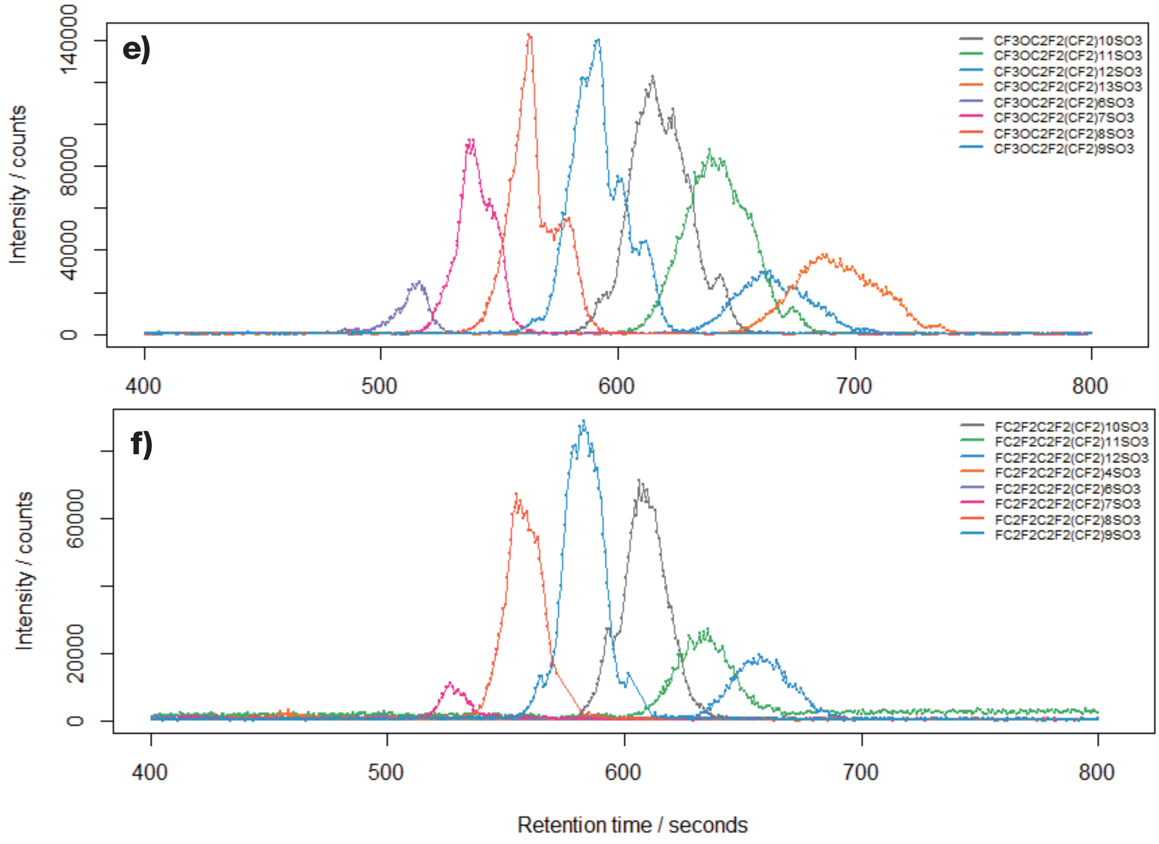

*Figure 4: Extracted ion chromatograms of (a) PFAS group $F(CF_2)_nSO_3$, (b) PFAS group $SF_5(CF_2)_nSO_3$, (c) PFAS group $CF(CF_2)_nSO_3$, (d) PFAS group $CF_3O(CF_2)_nSO_3$, (e) PFAS group $CF_3OC_2F_2(CF_2)_nSO_3$ and (f) PFAS group $FC_2F_2C_2F_2(CF_2)_nSO_3$ continued.*

The YMC-Triart C18 column achieved effective separation of PFAS (Figure 4), including improved partial resolution of isomers compared to Zweigle et al. [1]. For instance, $SF_5(CF_2)_9SO_3$ isomers were separated (Figure 5), enabling the acquisition of distinct fragmentation spectra (Figure 6). Ion traces at 575 s and 600 s revealed differences in fragmentation patterns, indicating structural variations. Identifiable fragments are listed in Table 5. The larger fragments in longer retention indicate an exclusively linear isomer. Specifically, the shorter retention time and the smaller fragments suggest a branched isomer or a differently positioned $SF_5$-group.

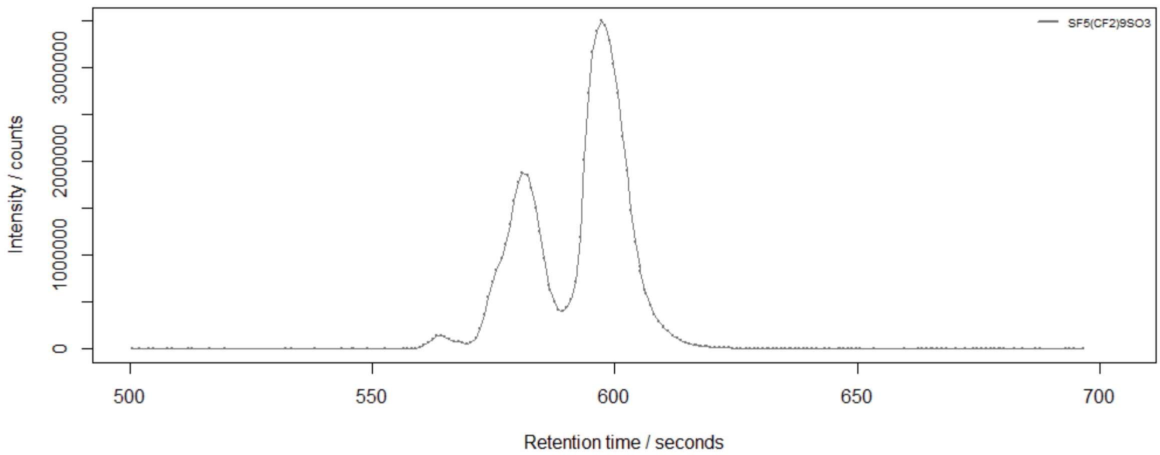

*Figure 5: Ion trace correspondent to $SF_5(CF_2)_9SO_3^-$ with m/z 656.8927 +/-20 ppm.*

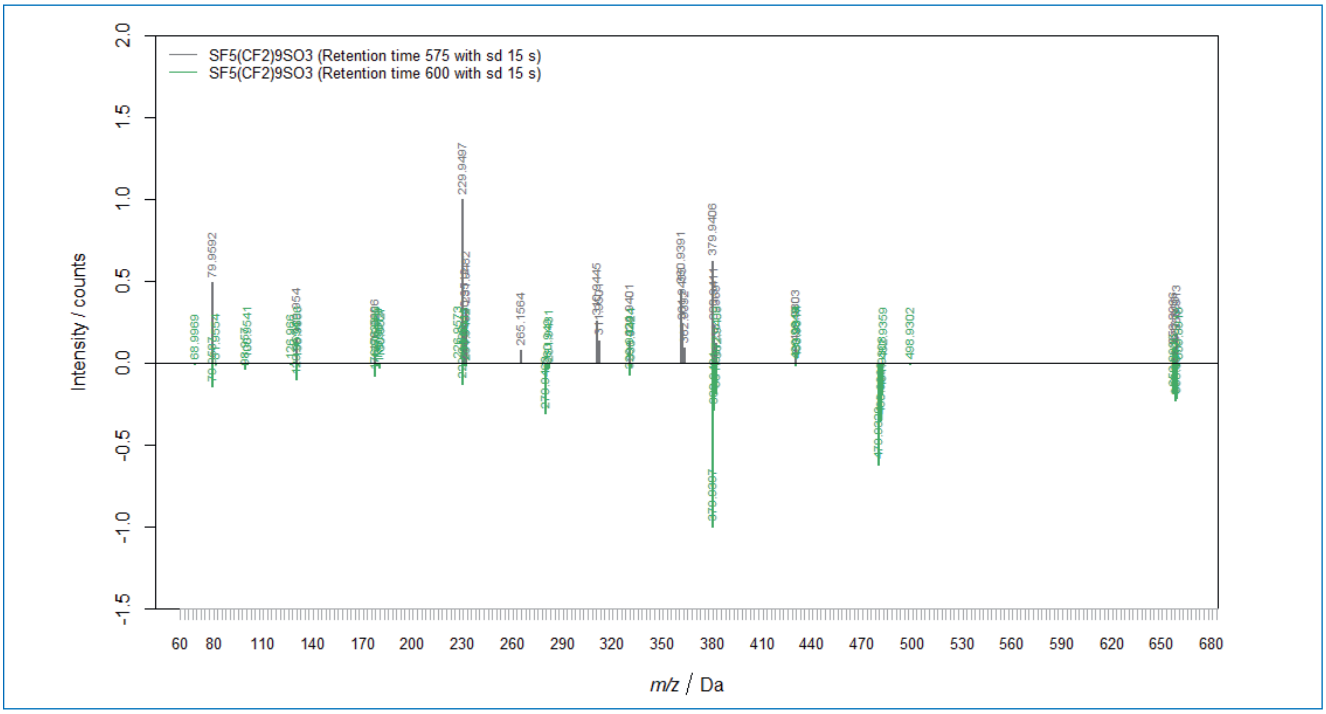

*Figure 6: Comparison of the averaged fragmentation patterns of the ion trace $SF_5(CF_2)_9SO_3^-$ at 575 +/-15 seconds (grey) and at 600 +/-15 seconds (green).*

*Table 5: Identifiable fragments of the averaged fragmentation patterns of the ion trace $SF_5(CF_2)_9SO_3^-$ at 575 and 600 seconds.*

| 575 s | | 600 s | |
|---|---|---|---|
| Fragment | *m/z* | Fragment | *m/z* |
| $SF_5^-$ | 79.9592 Da | $(CF_2)_4SO_3^-$ | 279.9440 Da |
| $(CF_2)_3SO_3^-$ | 229.9472 Da | $(CF_2)_6SO_3^-$ | 379.9377 Da |
| $(CF_2)_6SO_3^-$ | 379.9377 Da | $(CF_2)_8SO_3^-$ | 479.9313 Da |

## Conclusion

The YMC-Triart C18 column demonstrates robust performance for PFAS analysis. It delivers:

- **Efficient separation** of key PFAS standards with linear quantification.
- **Reproducible results** in complex matrices, such as soil extracts.
- **Improved isomer separation**, enabling structural elucidation through distinct fragmentation patterns.

The column provides a reliable and enhanced approach to targeted and non-targeted PFAS analysis, supporting environmental monitoring and regulatory compliance.

** 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.*