Water analysis

Monitoring PFAS

Per- and polyfluorinated alkyl substances, or PFAS in short, are ever present and persistent in water. Some members of this huge substance class fall under the Drinking Water Directive. The analysis only requires a single milliliter of water and very little solvent - when online SPE is used.

By Thomas Brandsch, Ph.D.

Per- and polyfluorinated alkyl substances (PFAS) form a family of highly fluorinated organic chemicals, in part based on carboxylic and sulfonic acids with a chain length of four to 18 carbon atoms. Examples are fluorinated alkyl sulfonates, with perfluorooctane sulfonate (PFOS) as the best-known unpleasant representative, and fluorinated carboxylic acids, the most notorious representative of which is perfluorooctanoic acid (PFOA). Fluoroplastics such as Teflon are also counted among PFAS. Tailored PFAS are found in our everyday consumer products from food packaging and cookware to carpets and clothing. They are added to cleaning agents and fire-fighting foams and are widely used industrially, for example in seals, surface coatings and lubricants. When synthesizing such PFAS, hydrogen atoms of organic compounds are replaced with fluorine atoms. This means that the PFAS carbon chain tail is hydrophobic, and the functional head group is hydrophilic. The resulting amphiphilic character explains the use of some PFAS as surfactants. Unlike classic surfactants, these PFAS are lipophobic. This means that they repel water as well as oil and grease. Additional advantages for technical applications include their excellent durability when exposed to heat and aggressive chemicals.

Clear and present danger to our drinking water

PFAS are extremely stable under natural environmental conditions. Since they are not affected by degradation processes, they spread in the environment and PFAS that are present in ionic form can accumulate in water. All PFAS can accumulate in

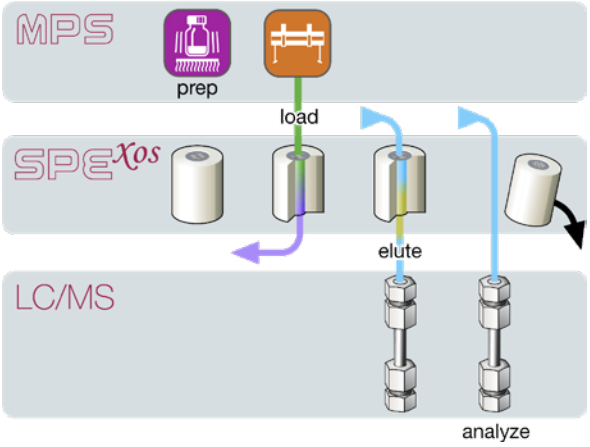

Figure 1: Schematic diagram of the online SPE process with automated cartridge exchange (©GERSTEL)

repositories adjacent to surface water and groundwater, i.e. in and near our most important drinking water reservoirs. The PFAS group of substances includes thousands of substances, 20 of which currently fall under the EU Directive 2020/2184 on the quality of water for human consumption. These 20 substances of particular concern are suspected of causing liver damage, cancer, thyroid disease, obesity, and fertility problems.

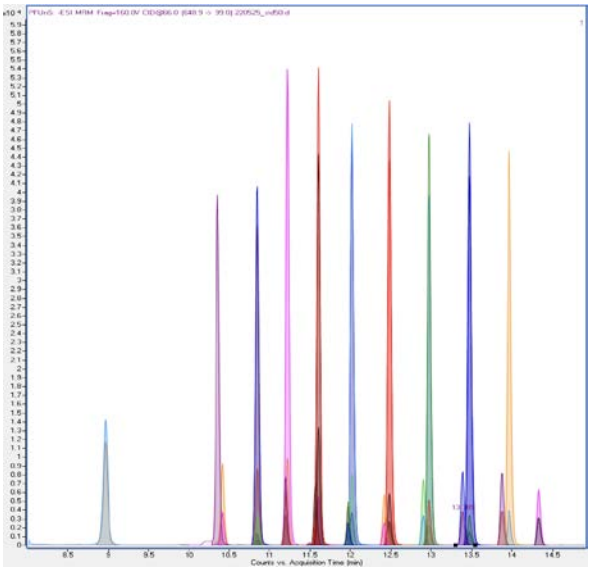

Figure 2: Example chromatogram for a standard solution (50 ng/L) in water with all recorded MRMs. (©GERSTEL)

To minimize the risk of adverse health effects from potentially contaminated drinking water, EU Directive 2020/2184 defines a total limit value of 0.5 micrograms per liter for all PFAS. For the sum of the 20 substances listed in the directive, the maximum limit is 0.1 micrograms per liter. Reliable analysis requires a detection limit of 30 nanograms per liter for the sum of the 20 listed PFAS and 1.5 nanograms per liter for individual compounds.

Analysis based on just one mL of sample

The German standard method for water, wastewater and sludge testing, DIN 38407-42, specifies solid phase extraction (SPE) with subsequent HPLC-MS/MS determination as the method of choice. How efficiently the SPE, and thus the analysis, proceeds depends in no small measure on the solid phase extraction technology used.
Compared to the conventional SPE, which is described in DIN 38407-42, online SPE with GERSTEL SPE^{xos} is based on smaller cartridges. The SPE

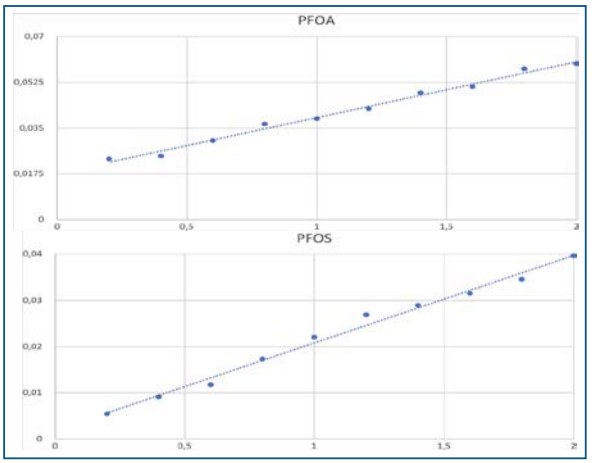

Figure 3: Example calibration curves in the range 0.2 – 2.0 ng/L with (PFOA) and without (PFOS) significant blank. (©GERSTEL)

eluate can be transferred directly and quantitatively to the HPLC column without intermediate. This leads to better limits of detection and -quantification even when a much reduced sample volume is used. Indeed, instead of several hundreds of milliliters, only one mL is required, in turn also reducing the amount of solvent used along with the associated cost and occupational hygiene and environmental impacts.

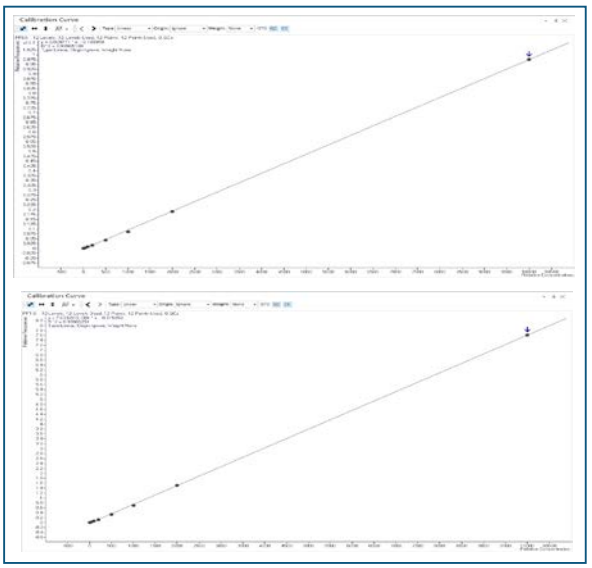

Figure 4: Example calibration curves in the range 1 – 10000 ng/L for the first and the last analyte in the chromatogram.

The use of online SPE in conjunction with a powerful autosampler such as the MultiPurpose Sampler from GERSTEL makes PFAS analysis efficient and convenient. The SPE^{xos} system performs all pre-analysis steps associated with standard SPE sample preparation – from conditioning, loading, rinsing and elution to replacing the cartridges. The MultiPurpose Sampler rinses, and flushes longer chain surface-adsorbed analytes from, the flow path and from the vial walls onto the cartridge. In this way, memory effects can be reduced

to an absolute minimum and excellent recovery of all PFAS compounds is ensured. All this is performed without intervention by laboratory staff. Following analyte elution, SPE^{xos} removes the cartridge from the mobile phase flow path and prepares the system for the next analysis. All the while, HPLC-MS/MS analysis is ongoing. The overlapping sample preparation and analysis runs increase system efficiency and sample throughput without extending the overall analysis time. Parallel processing is controlled by the MAESTRO software and all steps as well as the total analysis time are displayed in the MAESTRO Scheduler for best possible throughput and planning.

Validation round robin test delivers proof of method feasibility

Directly coupling SPE^{xos} with the MultiPurpose Sampler and an HPLC-MS/MS system has proven successful in determining the 20 PFAS listed in EU Directive 2020/2184 as part of a validation trial for the validation of the EN 17892. The new standard EN 17892 describes the LC-MS analysis of PFAS in water using direct injection or solid phase extraction (SPE), which can be performed also as online-SPE. The evaluation of the validation trial was done separately for the different methods, with comparable results for the performance data. GERSTEL participated in the direct injection and online-SPE parts, and all achieved results were consistent with the assigned values.

More detailed information on the online SPE-LC-MS/MS method used by GERSTEL for PFAS water analysis is available in a separate application note (AppNote 237). In it, the applicability of the method and the accuracy of the determination are demonstrated by spiking different water types and performing replicate analyses. According to DIN 32645 the limits of quantification were determined from calibration curves in the range 0.2 to 2 ng/L and were below 1 ng/L for all compounds.

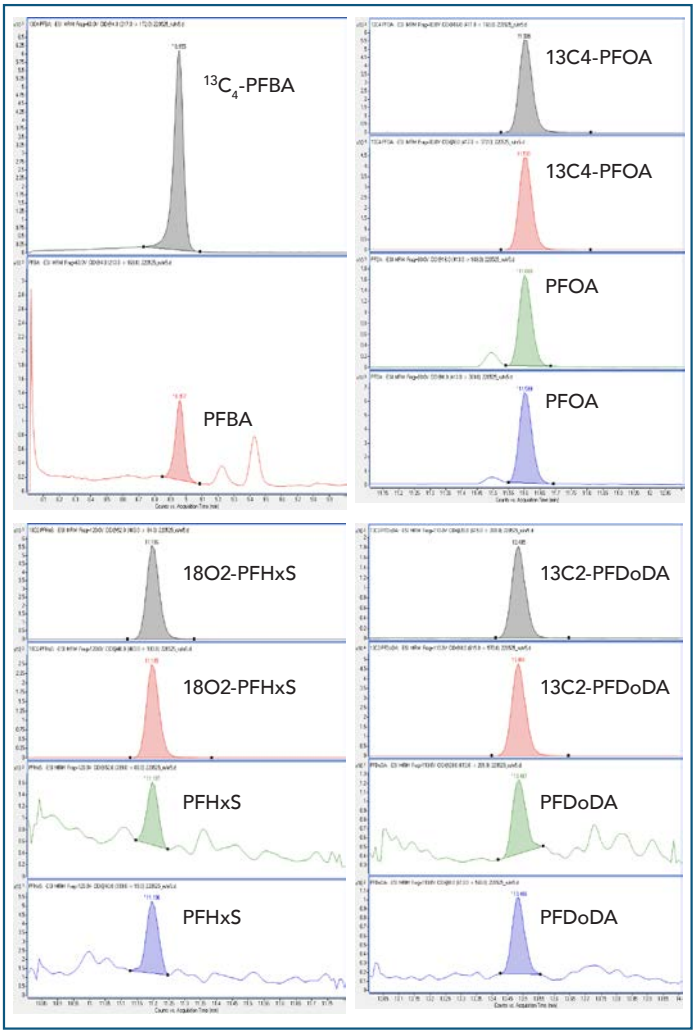

Figure 5: Example chromatograms for selected analytes and internal standards in river water, PFBA and PFOA above, PFHxS and PFDoDA below quantification limit.

More information:

- GERSTEL AppNote 237: Determination of PFAS in Water according to EU 2020/2184 and DIN 38407-42 using online-SPE-LC-MS/MS
- GERSTEL Solutions Worldwide Magazine Nr. 19, 2023, pp. 6-9.
- GERSTEL AppNote 247: Determination of PFAS in Food of Animal Origin using online SPE Cleanup and LC-MS/MS