Automated Sample Preparation in Method Development and Routine

For Determination of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Water

Koepf A.[1], Wollseifen H.R.[2], Wierer S.[1]
[1]LCTech GmbH, Obertaufkirchen, Germany, 84419, koepf@lctech.de; [2]MACHEREY-NAGEL GmbH Co.KG, Dueren, Germany, 52355

Introduction and Background

Over 60 years, perfluoroalkyl and polyfluoroalkyl substances (PFAS) are used in everyday materials with non-stick coatings. They get into the environment during manufacturing process, use and disposal. Sewage plants are mostly not able to purify waste-water of PFAS, so it accumulates in sewage sludge which is often used in agriculture. The chemicals reach the groundwater and get absorbed by plants and vegetables. Humans mostly incorporate PFAS through food or contaminated drinking water.

PFAS are anthropogenic and considered non-biodegradable. Therefore, PFAS can be found globally in the environment, wildlife, human tissues and blood. The group of substances includes more than 3000 different compounds. Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride were listed in the annex B of the Convention at the fourth meeting of the Conference to the Stockholm Convention on Persistent Organic Pollutants in 2009 and is evaluating PFOA and PFHxS for listing which makes the topic of PFAS present more than ever.

The SPE step in sample preparation is applied for clean-up or concentration steps. Expected new regulations with lower TWI increase the need for concentration. Automation via FREESTYLE not only enhances the reproducibility but also the throughput due to unattended operation 24/7 and pressurized sample loading from mL up to 10 L samples.

Material and Methods

One of the key challenges in automated sample preparation for PFAS analysis is to keep the background levels of analytes as low as possible. Unfortunately, PFAS are widely spread all over the globe and are found ubiquitously, thus also in every laboratory by default. Furthermore, fluorocarbon materials are commonly used in laboratory systems due to their unique chemical non-sticking properties to avoid cross-contamination and ease rinsing steps. These are prone to a release small amounts of PFAS that may significantly increase background levels. To avoid blank levels but use the same beneficial chemical properties of material, fluorocarbon materials of the FREESTYLE SPE as well as the XANA system were consequently removed and replaced by polyethylene or polypropylene, respectively.
In order to prove the effectiveness of this measurement, PFAS background levels of neat solvents and pure water samples were compared. Table 1 shows that it is evident that any analyte concentration measured is already found in the neat solvents and does not originate from the system!
Each standard was diluted to 200 ng/mL in methanol, as working solution. After that, 500 mL of water were spiked with 25µL of each standard's working solution. Accordingly the sample has a concentration of 10 ng/L for each analyte, which is the lower application limit according to DIN 38407-42. The blanks were prepared as follows: All volumes of the solvents used were put into a vial and evaporated to dryness, with a gentle stream of nitrogen. After that, the vial was rinsed with 1 mL acetonitrile. The solution again was concentrated to dryness under a gentle stream of nitrogen and redissolved with a final volume of 1 mL with methanol/water (6:4, v/v). The same procedure was applied with the methanol/water (6:4, v/v) solution.

Reagents

Native PFAS precision and recovery standard solution (conc. 2.0 µg/mL in MeOH) and Mass-labelled PFAS standard solution/mixture (conc. 2.0 µg/mL in MeOH), both purchased from Wellington Laboratories, Canada, solvents used were of HPLC grade. Each standard was diluted to 200 ng/mL in methanol, as working solution. 500 mL of water was spiked with 25 µL of each standard's working solution.

Fig. 1: Robotiksystem FREESTYLE XANA-PFAS

Tab. 1: Recovery data of 10 selected PFAS compounds according to DIN 38407-42 and comparison of PFAS background concentrations of neat solvent and water samples processed with the FREESTYLE XANA-PFAS system

No	Component Name	Recovery [%]	STD [%]	Background FREESTYLE [ng/mL]	Background Solvent [ng/mL]
1	Polyfluorobutanoic acid (PFBA)	80	3,8	0	0
2	Polyfluoropentanoic acid (PFPeA)	106	1,1	0,09	0,06
3	Polyfluorohexanoic acid (PFHxA)	101	1,3	0,02	0,04
4	Polyfluoroheptanoic acid (PFHpA)	106	1,5	0,02	0,02
5	Polyfluorooctanoic acid (PFOA)	107	1,6	0,05	0,05
6	Polyfluorononanoic acid (PFNA)	102	1,8	0,01	0,01
7	Polyfluorodecanoic acid (PFDA)	66	2,0	0,01	0,01
8	Polyfluorobutane sulfonate (PFBS)	102	1,4	0	0
9	Polyfluorohexane sulfonate (PFHxS)	107	2,1	0	0
10	Polyfluorooctane sulfonate (PFOS)	79	1,7	0,01	0,01

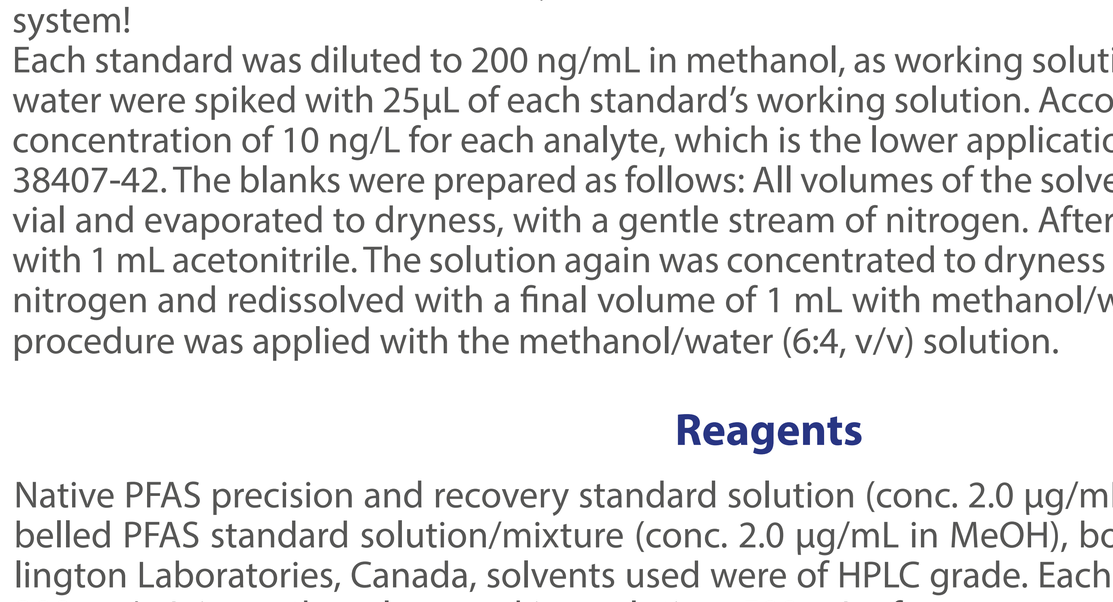

Fig. 2: Chromatogram of spiked sample over FREESTYLE XANA

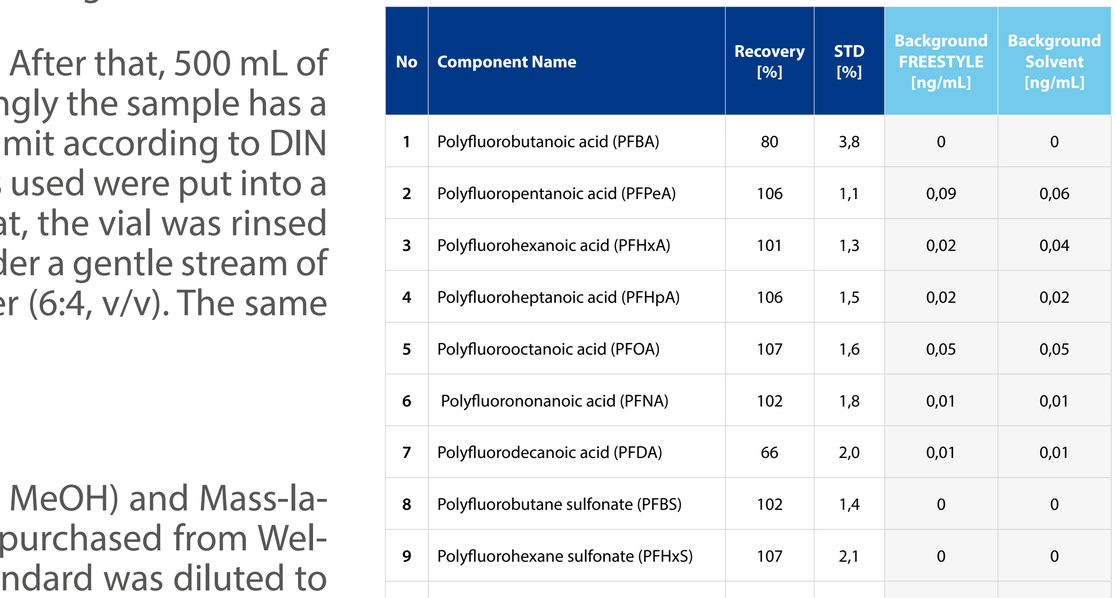

Fig. 3: Chromatogram of blank sample over FREESTYLE XANA

Results and Conclusions

The analytical targets of the applied method were found with good recoveries and very low standard variations resulting from the reliable and robust automation (see Tab. 1). Due to the specifically designed PFAS system, which is virtually free of fluorocarbon compounds, any blank values stemming from the system are minimised as shown in Fig. 3. This was shown by PFAS background measurements of the instrument that were equal to the values obtained with neat solvent (see Tab. 1). Furthermore, by the application of fully automated parallel sample preparation, multiple samples can be processed at the same time. Thus, a high sample throughput at low demand of personnel resources is obtained.