APPNOTE

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Determination of PFAS in Water according to EU 2020/2184 and DIN 38407-42 using online-SPE-LC-MS/MS

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Keywords

EU Drinking Water Directive, LC/MS, online-SPE, SPExos, PFAS

Abstract

In the work presented here, the perfluorinated carbonic and sulfonic acids listed in the EU Drinking Water Directive (EU 2020/2184) were determined by an automated method based on solid phase extraction with weak anion exchange sorbent combined with LC-MS/MS. Limits of quantification (LOQ) were determined from calibrations in the range of 0.2 – 2.0 ng/L according to DIN 32645. These are all below 1 ng/L, allowing the monitoring of 0.1 µg/L for the sum of 20 PFAS set as limit by the EU Drinking Water Directive. The method accuracy was demonstrated based on analysis of spiked water samples from different sources. Relative standard deviations were below 10% and trueness mainly between 80 and 110%.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a family of highly fluorinated anthropogenic chemicals with special physicochemical properties that make them oil and water repellant as well as heat resistant. This makes them suited for many household and industrial applications like nonstick cookware, food packaging, carpeting, cleaning products and firefighting foams. The unique chemical properties make them useful, but also difficult to break down. The lack of environmental degradation in combination with good solubility in water leads to a global distribution. PFAS are found not only in the environment, but also in food and animal feed, in humans, and in wildlife.

PFAS are toxic and acute exposure could have detrimental health effects. Authorities worldwide are regulating their use and emissions into the environment. In addition, food and drinking water must be monitored for their presence, and the new EU Drinking Water Directive (EU 2020/2184) [1] includes maximum limits for PFAS. The limit for total PFAS is set to 0.5 µg/L and for the sum of 20 PFAS of most concern the maximum limit is 0.1 µg/L. For monitoring this value, a limit of detection (LOD) of 30 ng/L for the sum and 1.5 ng/L for individual compounds is necessary.

Given the polar nature of most PFAS, especially carbonic and sulfonic acids, the analysis is mainly done by LC/MS. The less polar carbonic chain allows reversed phase (RP) chromatography on C18-based columns. To reach low detection limits, water samples are usually extracted by means of SPE. First attempts were made with polystyrene-divinylbenzene (SDVB) cartridges (e. g. US EPA Method 537/537.1 [2]), but the need to extend the analysis spectrum to short chain acids, lead to the use of anion exchange sorbents (e. g. US EPA Method 533 [3] or DIN 38407-42 [4]). In combination with RP chromatography, this approach offers the advantage of efficient clean-up, especially if the cartridges are washed with an organic solvent prior to elution.

Since LC/MS systems have become much more sensitive over the recent years, direct injection of water samples is a competitive alternative for low level analysis of PFAS. But when following this approach, the analysis of long chain acids becomes challenging, because they tend to stick to all surfaces, leading to low (and irreproducible) recovery. To overcome this drawback, the water samples need to be diluted with methanol and filtered prior to LC/MS analysis (e. g. US EPA Method 8327 [5]).

Unlike traditional SPE, online-SPE relies on smaller cartridges inserted into the eluent flow path that can be eluted directly onto

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the HPLC column. This enables quantitative transfer of analytes to the analysis system, resulting in improved limits of detection and quantitation even when sample volumes are significantly reduced. Using this technique, the efficiency of SPE is combined with the simplicity of direct injection. Our initial attempts at performing PFAS analysis were made using RP cartridges (cf. GERSTEL AppNote 190). The work presented here is based on weak anion exchange (WAX) cartridges. Elution is performed with ammonia in methanol, which cannot be transferred directly onto the LC column. A special configuration of the online-SPE-LC/MS system is therefore needed. For the work reported here, an online SPE system (GERSTEL SPE^{xos}, figure 1) was used that performs automated cartridge exchange as well as automated rinsing of the entire sample flow path between injections to ensure that sample to sample carry over is reduced to an absolute minimum. All steps of a typical SPE workflow are performed automatically including conditioning, loading, rinsing, and eluting the cartridge. Following the elution step, the cartridge is removed from the HPLC mobile phase flow path freeing the system to prepare the next sample during the ongoing LC-MS/MS analysis. The result is fully automated sample preparation that doesn't add to the overall analysis time once the first sample has been prepared and injected into the HPLC.

Figure 1: The online SPE system GERSTEL SPE^{xos}.

Experimental

Materials and Solvents

Exactly 1 mL of water sample was filled into each conical 1.1 mL vial (GERSTEL 093640-045-00) by pipette, internal standard solution was added and the vials were sealed with screw caps (GERSTEL 093640-075-00). For the extraction online SPE cartridges for the GERSTEL SPE^{xos} (Polymer WAX, GERSTEL 018804-023-00) were used.

For chromatography methanol (hypergrade for LC-MS) and water (LC-MS grade) were used, fortified with ammonia solution 25% (for LC-MS) and/or formic acid 98-100% (for analysis, ACS, Reag. Ph Eur) all from Merck (Darmstadt, Germany). Cartridge wash was performed using a mixture of acetonitrile (gradient grade for liquid chromatography), acetone (for liquid chromatography) and formic acid 98-100% (for analysis, ACS, Reag. Ph Eur) in the ratio 50:50:1, all from Merck.

Preparation of samples and calibration standards. All standards were purchased as solutions from Wellington Laboratories (distributed by Campro Scientific, Berlin, Germany): Native perfluorinated compound mixture (2000 ng/mL for each compound), PFUnS and PFTrS as individual solutions with 50 µg/mL, and a mixture of isotopically labelled PFAS used as internal standards. All substances identified by their abbreviations are listed in Table 1. The native compounds were mixed to result in a stock solution of 1000 ng/mL, which was diluted consecutively with methanol to produce the working solutions (0.04 to 200 ng/mL) used for spiking calibration samples. The mixture of labeled compounds was diluted to 1 ng/mL. Calibration samples were prepared in the 1.1 mL vials by adding 20-50 µL of stock solution and 50 µL solution of internal standards to 1 mL LC-MS grade water.

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Table 1: List of substances.

Substance *	Abbre-viation	Molecular Formula	CAS No	Internal Standard used
Perfluorobutanoic acid	PFBA	$C_4HO_2F_7$	375-22-4	$^{13}C_4$-PFBA
Perfluoropentanoic acid	PFPeA	$C_5HO_2F_9$	2706-90-3	$^{13}C_2$-PFHxA
Perfluorohexanoic acid	PFHxA	$C_6HO_2F_{11}$	307-24-4	$^{13}C_2$-PFHxA
Perfluoroheptanoic acid	PFHpA	$C_7HO_2F^{13}$	375-85-9	$^{13}C_4$-PFOA
Perfluorooctanoic acid	PFOA	$C_8HO_2F_{15}$	335-67-1	$^{13}C_4$-PFOA
Perfluorononanoic acid	PFNA	$C_9HO_2F_{17}$	375-95-1	$^{13}C_5$-PFNA
Perfluorodecanoic acid	PFDA	$C_{10}HO_2F_{19}$	335-76-2	$^{13}C_2$-PFDA
Perfluoroundecanoic acid	PFUnDA	$C_{11}HO_2F_{21}$	2058-94-8	$^{13}C_2$-PFUnDA
Perfluorododecanoic acid	PFDoDA	$C_{12}HO_2F_{23}$	206-203-2	$^{13}C_2$-PFDoDA
Perfluorotridecanoic acid	PFTrDA	$C^{13}HO_2F_{25}$	72629-94-8	$^{13}C_2$-PFDoDA
Perfluorobutanesulfonic acid	PFBS	$C_4HO_3F_9S$	375-73-5	$^{18}O_2$-PFHxS
Perfluoropentanesulfonic acid	PFPeS	$C_5HO_3F_{11}S$	630402-22-1	$^{18}O_2$-PFHxS
Perfluorohexanesulfonic acid	PFHxS	$C_6HO_3F^{13}S$	355-46-4	$^{18}O_2$-PFHxS
Perfluoroheptanesulfonic acid	PFHpS	$C_6HO_3F_{15}S$	357-92-8	$^{13}C_4$-PFOS
Perfluorooctanesulfonic acid	PFOS	$C_8HO_3F_{17}S$	1763-23-1	$^{13}C_4$-PFOS
Perfluorononanesulfonic acid	PFNS	$C_8HO_3F_{19}S$	98789-57-2	$^{13}C_2$-PFDA
Perfluorodecanesulfonic acid	PFDS	$C_8HO_3F_{21}S$	335-77-3	$^{13}C_2$-PFUnDA
Perfluoroundecanesulfonic acid	PFUnS	$C_8HO_3F_{23}S$	749786-16-1	$^{13}C_2$-PFDoDA
Perfluorododecanesulfonic acid	PFDoS	$C_8HO_3F_{25}S$	79780-39-5	$^{13}C_2$-PFDoDA
Perfluorotridecanesulfonic acid	PFTrS	$C_8HO_3F_{27}S$	791563-89-8	$^{13}C_2$-PFDoDA

* For the sulfonic acids the corresponding Potassium (for PFBS) and Sodium salts were used for calibration and concentrations are given as such.

Different water samples were analyzed: Tap water from our laboratory, water from the river Ruhr in Mülheim an der Ruhr, Germany, groundwater from nearby, water from a mountain creek in Austria and mineral water with high salt content purchased at a local supermarket. For all water samples to be analyzed, 50 µL solution of internal standards and 50 µL of methanol were added to 1 mL sample in the vial.

Instrumentation

The automated system consists of a MultiPurpose Sampler (MPS robotic, GERSTEL) and an online SPE System (SPE^{xos}, GERSTEL) coupled to an LC-MS/MS system (Infinity II 1260 Flexible Pump and ULTIVO LC/TQ, Agilent Technologies, Waldbronn, Germany). SPE elution is performed using 0.25% ammonia in methanol delivered from an additional isocratic HPLC pump (Infinity II 1260 Iso Pump, Agilent Technologies). The eluate is merged with the starting level buffer of the binary analytical pump in a valve fitted with a special T-rotor used in the SPE^{xos} system. As analytical column a Poroshell 120 EC-C18, 4.6 x 100 mm, 2.7 µm (Agilent Technologies) was used. Between the binary pump and MPS, a delay column (Poroshell 120 EC-C18, 4.6 x 50 mm, 2.7 µm, Agilent Technologies) was installed. Injection was performed with a 2.5 mL syringe into the injection valve on the MPS, fitted with a 1 mL stainless steel sample loop.

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Analysis Workflow

The automated workflow consisted of initially conditioning the cartridge, first using 0.25% ammonia in methanol and then water. After injection of the sample into the loop, it was loaded onto the cartridge using water. The cartridge was subsequently washed with water, rinse solution (acetone/acetonitrile/formic acid), and methanol. These steps were performed by the High-Pressure Dispenser (HPD) unit of the SPE^{xos} (see figure 2).

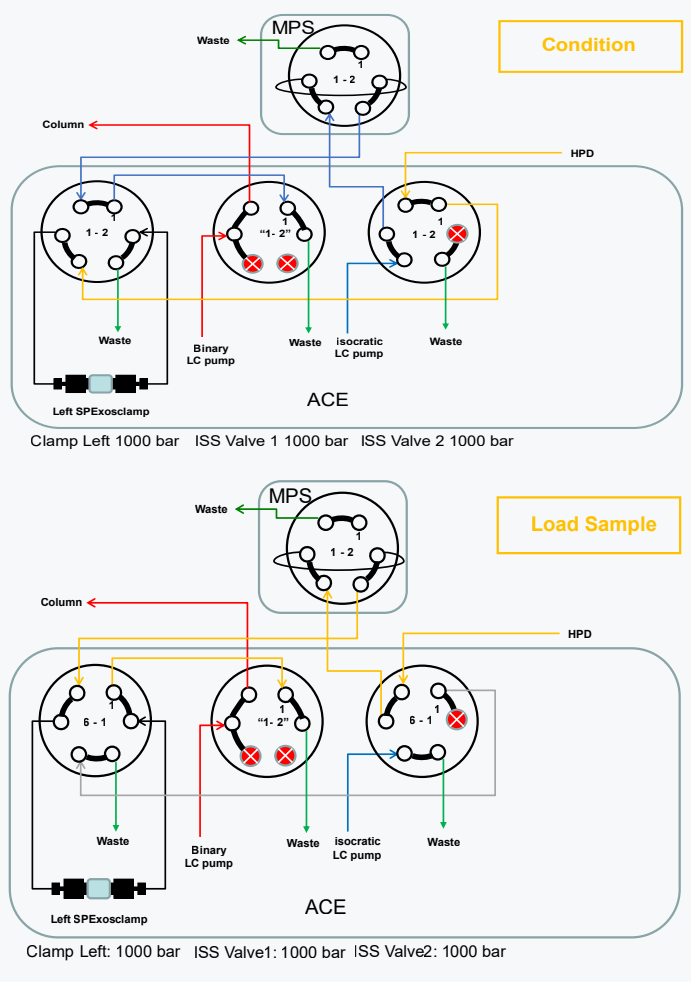

Figure 2: Flows during conditioning of the cartridge and loading the sample.

Methanol from a solvent reservoir on the MPS is added to the vial and the vial contents then aspirated and injected into the sample loop of the injection valve, before starting the pumps and switching the valves in elution position. The isocratic pump elutes the cartridge with 0.25% methanol and the binary pump delivers 0.05% formic acid in water, merged in the T-rotor valve of the SPE^{xos} (see figure 3, top). After 7.5 minutes, the elution phase is completed, and chromatography starts. Over the following 7 minutes the binary pump delivers a gradient flow of 0.6 mL/min employing water with 0.05% formic acid and methanol with 0.25% ammonia and 0.05% formic acid. During this time the SPE^{xos} system can be cleaned (see figure 3, bottom) and preparation of the next sample begins (PrepAhead Mode).

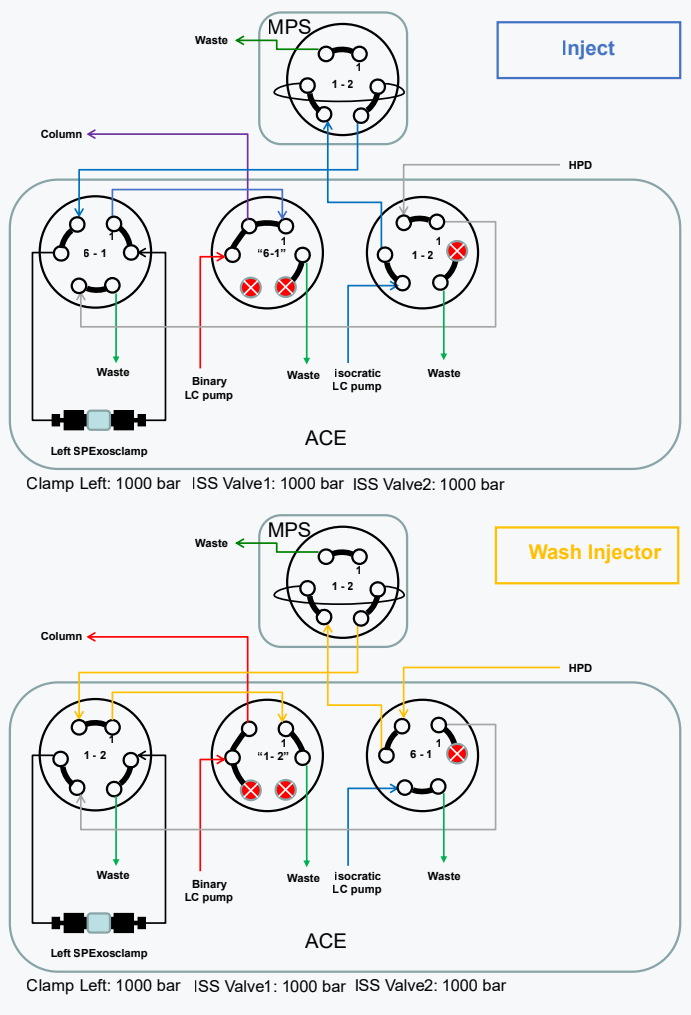

Figure 3: Flows during injection and injector wash.

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Analysis conditions LC

Isocratic pump 0.25% NH_3 in methanol

Time (min)	Flow (mL/min)
0	0.0
0.1	0.2
7.4	0.2
7.5	0.0
8.0	1.0
8.5	0.0

Binary pump A – 0.05% formic acid in water

B – 0.25% NH_3 ,0.05% formic acid in methanol

Time (min)	Flow (mL/min)	% B
0.0	0.6	0
4.0	0.6	0
7.5	0.6	70
8.0	0.6	80
14	0.6	100
15	0.6	0
20	0.6	0

Analysis conditions MS

Operation	dynamic MRM
Gas temperature	150 °C
Gas flow (N_2):	11 L/min
Nebulizer pressure:	20 psi
Sheath gas flow (N_2):	12 L/min
Sheath gas temperature:	400 °C
Capillary voltage:	4000 V
Nozzle voltage:	0 V

For each target compound and isotope labeled internal standard (ISTD) two MRM transitions were chosen, one quantifier and one qualifier (except PFBA und PFPeA, for which only one transition has sufficient intensity).

Results and Discussion

Usually in online-SPE, elution is performed using a gradient delivered by the analytical pump. However, the WAX cartridges are eluted with ammonia in methanol and this eluate cannot be transferred directly to the HPLC column. For this reason, an extra (isocratic) HPLC pump elutes the cartridge, and the eluate is subsequently merged with the starting level buffer of the binary analytical mobile phase. This takes place in the SPE^{xos} system, using a valve fitted with a special rotor. During this stage the analytes reach the analytical column under isocratic conditions of 25% methanol (with 0.25% NH_3) and 75% water with 0.05% formic acid. The short chain PFAS begin to migrate on the column, but the longer chain PFAS are trapped at the beginning of the column. Switching the valve ends the elution step and starts the gradient chromatography, during which the methanol content is increased rapidly to 80%, leading to focusing of first eluting peaks, while the later eluting peaks are separated in the second gradient stage. The result is a chromatogram with nearly equidistant peaks for the carbonic acids from C5 to C14. PFBA elutes a bit faster and in the chromatogram, the sulfonic acids elute close to the carbonic acids that have one more C atom (see figure 4).

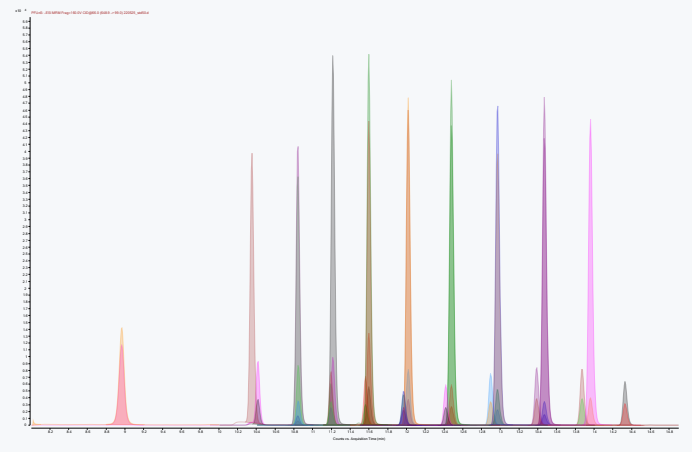

Figure 4: Example chromatogram for a standard solution (50 ng/L) in water with all recorded MRMs.

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Long chain perfluorinated acids dissolved in water are readily adsorbed on almost any type of surface. The DIN method therefore recommends solutions with at least 40% methanol to avoid loss. EPA Method 8327 starts with diluting the water sample 1:1 with methanol prior to direct injection. If samples with such high methanol content are injected to an SPE cartridge, short chain PFAS are not retained. Using the MPS as injector, the sample vial can be rinsed with methanol after the injection of the water sample. Injection of this rinse solution not only recovers analytes adsorbed on the surface of the vial, but also rinses injection syringe, sample loop, and associated tubing with the result that all adsorbed analytes were released, recovered, and transferred to the SPE cartridge. In the method described here, the transfer of the rinsing solution from the injection loop to the cartridge is done during the elution step, while the isocratic pump feeds eluent through the sample loop. This is possible because the rinsing solution only contains long chain PFAS, which are trapped during the elution step on the front of the analytical column, and no peak broadening or splitting occurs.

It is difficult to determine the absolute recovery of PFAS from water samples using this method because the absolute intensities of detector signals are highly dependent on the pH value and methanol content of the buffer when the analytes reach the MS. Injecting a small volume of standard solution directly to the column would lead to a completely different chromatogram. The peak intensities resulting from injecting a standard solution in water subjected to online-SPE were compared to the peak intensities resulting from injecting a standard solution in methanol with the same concentration directly onto the SPE cartridge using the transfer with the isocratic pump, as previously described. The results are shown in figure 5. The recovery of PFBA and some sulfonic acids is lower (which can be caused by the mentioned challenges), but there is no great discrepancy between long and short chain PFAS. The efficiency of the vial wash approach is also demonstrated by the relative recoveries achieved for standard solutions without vial wash compared to the same solutions analyzed with vial wash. While short chain PFAS (carboxylic acids up to C10 and sulfonic acids up to C8) are not affected, the long chain PFAS are recovered less than 30% without vial wash, depending also on the length of time, over which the solution stays in the vial prior to injection (see figure 6).

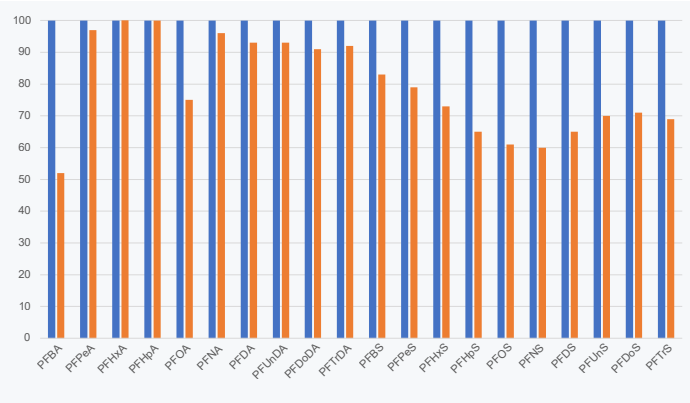

Figure 5: Recovery for a standard solution in water (1 mL, orange) compared to a standard solution in methanol (1 mL, blue) injected directly on the prepared SPE cartridge.

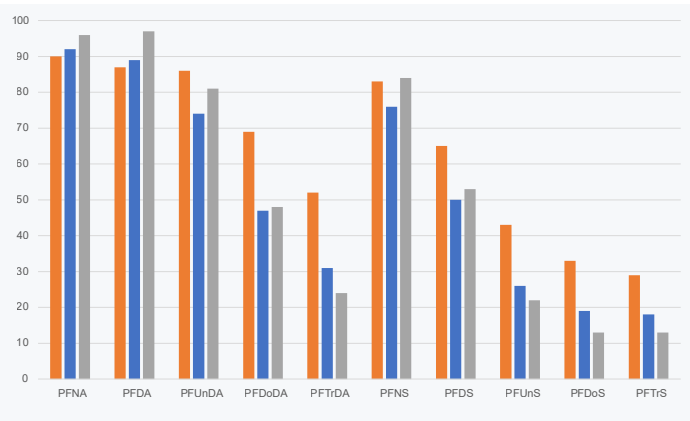

Figure 6: Recovery for selected analytes after 30 minutes (orange), 4 hours (blue) and 8 hours (grey) without washing the vial after injection.

Analyzing real water samples, we observed that the recovery of labeled PFBA was much lower than for the other internal standards used. It seems that the recovery of PFBA is negatively impacted by increased overall salt content. For the mineral water tested the salt content was 2000 mg/L and the recovery of PFBA just around 30%.

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Limits of Quantitation

Method detection limits are not determined only by the sensitivity of the instrument, but also by the unavoidable blank values at sub ng/L level. The contribution from the buffers in the binary pump can be trapped on the delay column used, but for the isocratic column this is not possible. However, the blank values were below 1 ng/L and remained consistently at the same low levels throughout, given the closed system used for online-SPE.

Limits of detection (LOD) and limits of quantitation (LOQ) were calculated from calibration lines near the expected LOQ (0.2 – 2.0 ng/L) as per the requirements of DIN 32645 [6]. Examples with and without significant blank values are given in figure 7. The calculated LOQs are all below 1 ng/L, enabling monitoring at our below the 0.1 µg/L limit for the sum of PFAS compounds as stipulated by the EU drinking water directive (table 2). In the case of high salt content in the sample, the recovery of labeled PFBA is lower and therefore the quantification limit for PFBA (and PFPeA) has to be adjusted.

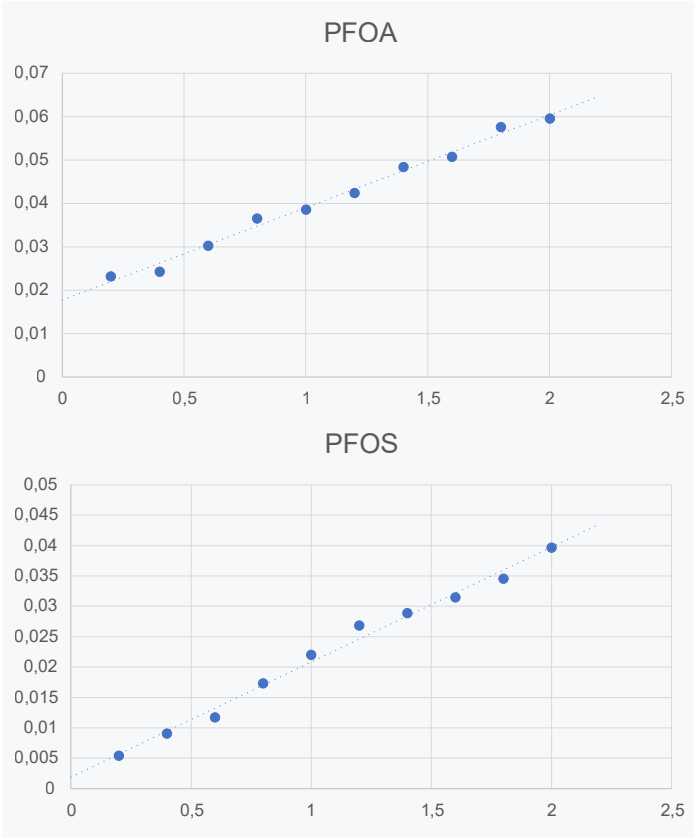

Figure 7: Example calibration curves in the range of 0.2 – 2.0 ng/L with and without significant blank.

Table 2: Limits of determination (LOD) and limits of quantitation (LOQ) obtained in accordance with DIN 32645 from 10-point calibrations in the range 0.2 - 2.0 ng/L.

Substance *	LOD [ng/L]	LOQ [ng/L]
PFBA	0.14	0.44
PFPeA	0.27	0.82
PFHxA	0.13	0.42
PFHpA	0.19	0.58
PFOA	0.22	0.68
PFNA	0.13	0.42
PFDA	0.20	0.61
PFUnDA	0.17	0.54
PFDoDA	0.04	0.13
PFTrDA	0.15	0.46
PFBS	0.20	0.63
PFPeS	0.17	0.54
PFHxS	0.18	0.57
PFHpS	0.24	0.74
PFOS	0.23	0.69
PFNS	0.27	0.83
PFDS	0.25	0.76
PFUnS	0.24	0.74
PFDoS	0.25	0.76
PFTrS	0.27	0.81

* For the sulfonic acids the corresponding Potassium (for PFBS) and Sodium salts were used for calibration and concentrations are given as such.

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Calibration

For all compounds, the linear calibration range spans up to 10 µg/L (see figure 8). After injection of higher concentration standard solutions, we observed a slight carry over of some compounds in the following chromatogram, but below 0.1%. To ensure the validity of the quantitation limits, we recommend limiting the calibration range to 1 – 1000 ng/L. For the water samples analyzed in this work, a 7-point calibration from 1 to 100 ng/L was used.

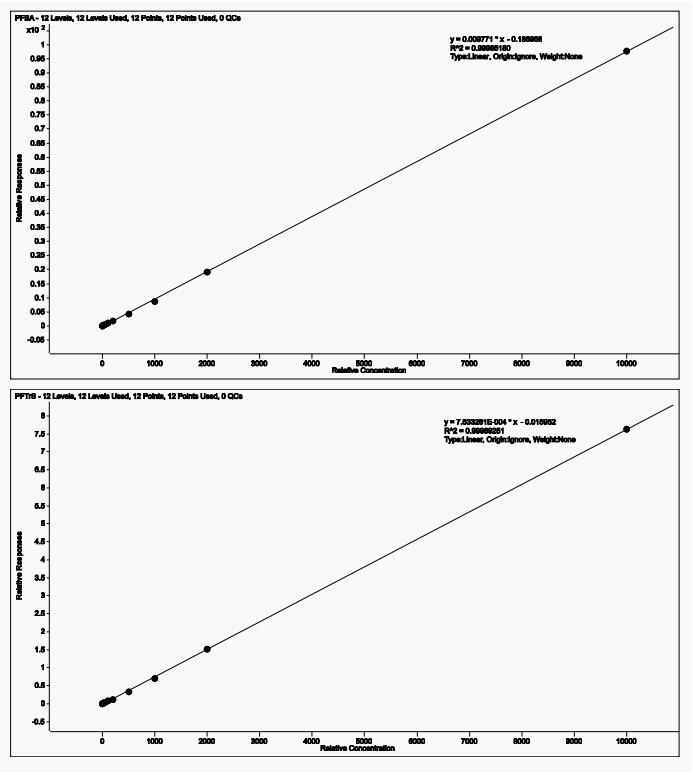

Figure 8: Example calibration curves in the range of 1 – 10000 ng/L for the first and the last analyte in the chromatogram.

Repeatability and Trueness

To show the applicability of the method and the trueness of determination, water samples from different sources were measured in replicate and spiked with two concentration levels (5 and 50 ng/L). Results from the 6-fold analyses of these samples are summarized in table 3. Only low concentrations of some PFAS were detected in tap water, river water and ground water. The highest concentration was 40 ng/L PFBA in the ground water sample analyzed. The river water contains 11 ng/L PFOA, and all other detectable concentrations were below 10 ng/L.

For the spiked tap water sample the trueness was between 74 and 117% for all compounds. The repeatability (expressed as relative standard deviation) was between 1 and 9% (average 5.9%) at low level, and between 1 and 7% (average 3.2%) at high level, respectively. As is to be expected, the deviations were moderately higher when using an internal standard that differs more from the target compound. This is the case mainly for PFPeA and some sulfonic acids.

For the spiked river water sample, the trueness was between 72 and 110% for all compounds. The repeatability was between 1 and 9% (average 4.7%) at low level and 1 and 6% (average 2.7%) at high level, respectively.

For the ground water sample the standard deviation for PFBA was somewhat higher (13% for the original sample and 18% for the low-level spiked sample) and the trueness for this compound in the low-level spiked sample couldn't be determined, because the spiked amount of 5 ng/L was far below the initial concentration. In the high-level spiked sample, the trueness was 68%. For all other compounds the trueness was between 77 and 110% and the repeatability between 2 and 9% (average 4.3%) at low level, and between 1 and 9% (average 4.0%) at high level, respectively.

As was to be expected, in the mountain creek water and mineral water no PFAS was detected. While for the mountain creek trueness (82-117%) and repeatability (2-9%, average 4.5% and 1-6%, average 2.5%), respectively, were excellent, in mineral water trueness between 79 and 136% and repeatability at low level spike between 4 and 10% (average 5.9%) were slightly less impressive. This probably was due to the high salt content of the mineral water, and the fact that under these conditions the recovery of labeled internal standards differs from that of various target compounds. At high level spike concentration, the repeatability was much better, though (1 to 6%, average 2.9%). Example chromatograms from the river water sample below and above the quantification limit are shown in figure 9.

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Table 3a: Results from 5-fold determination of PFAS in tap water, measured directly, and tap water spiked with 5 ng/L and 50 ng/L, respectively, of each compound.

	Tap water		spiked with 5 ng/L			spiked with 50 ng/L		
	Average [ng/L]	RSD [%]	Average [ng/L]	RSD [%]	Trueness [%]	Average [ng/L]	RSD [%]	Trueness [%]
PFBA	8,8	9%	14,4	7%	113%	56,2	2%	95%
PFPeA	5,6	7%	9,4	8%	74%	43,5	7%	76%
PFHxA	4,4	4%	9,1	1%	94%	50,4	3%	92%
PFHpA	1,9	6%	6,6	3%	95%	48,1	1%	92%
PFOA	<1	-	5,9	3%	117%	48,5	2%	97%
PFNA	<1	-	4,7	4%	95%	46,7	2%	93%
PFDA	<1	-	4,6	1%	92%	46,2	3%	92%
PFUnDA	<1	-	4,6	5%	92%	46,3	2%	93%
PFDoDA	<1	-	4,7	3%	94%	46,6	3%	93%
PFTrDA	<1	-	4,4	5%	87%	45,9	3%	92%
PFBS	1,8	11%	6,4	5%	92%	42,2	4%	81%
PFPeS	<1	-	4,2	7%	84%	43,8	2%	88%
PFHxS	<1	-	4,5	9%	91%	46,2	2%	92%
PFHpS	<1	-	3,9	9%	79%	45,4	3%	91%
PFOS	<1	-	4,4	6%	88%	48,4	3%	97%
PFNS	<1	-	4,7	7%	94%	52,4	7%	105%
PFDS	<1	-	5,4	9%	109%	55,1	4%	110%
PFUnDS	<1	-	4,9	8%	98%	47,4	5%	95%
PFDoDS	<1	-	4,7	7%	93%	45,2	3%	90%
PFTrS	<1	-	4,6	7%	92%	43,6	4%	87%

Table 3b: Results from 5-fold determination of PFAS in river water, measured directly, and river water spiked with 5 ng/L and 50 ng/L, respectively, of each compound.

	River water		spiked with 5 ng/L			spiked with 50 ng/L		
	Average [ng/L]	RSD [%]	Average [ng/L]	RSD [%]	Trueness [%]	Average [ng/L]	RSD [%]	Trueness [%]
PFBA	5,8	16%	10,6	8%	97%	47,5	3%	84%
PFPeA	5,3	20%	9,3	4%	80%	41,1	4%	72%
PFHxA	6,1	3%	10,3	2%	84%	51,6	2%	91%
PFHpA	3,0	3%	7,2	1%	84%	47,7	2%	89%
PFOA	11,3	2%	14,8	1%	72%	58,9	3%	95%
PFNA	<1	-	5,0	2%	100%	47,7	1%	95%
PFDA	<1	-	4,9	3%	98%	46,9	1%	94%
PFUnDA	<1	-	4,6	3%	92%	46,2	2%	92%
PFDoDA	<1	-	4,6	3%	93%	46,6	1%	93%
PFTrDA	<1	-	4,3	4%	86%	45,9	3%	92%
PFBS	3,7	9%	7,6	5%	78%	39,9	5%	72%
PFPeS	<1	-	4,5	5%	90%	45,5	3%	91%
PFHxS	<1	-	4,9	2%	98%	47,0	1%	94%
PFHpS	<1	-	4,1	8%	83%	44,0	2%	88%
PFOS	2,0	10%	7,2	6%	103%	50,5	1%	97%
PFNS	<1	-	4,4	9%	88%	50,5	6%	101%
PFDS	<1	-	5,2	9%	105%	55,0	6%	110%
PFUnDS	<1	-	5,0	7%	99%	49,9	1%	100%
PFDoDS	<1	-	4,6	6%	91%	44,8	3%	90%
PFTrDS	<1	-	4,1	8%	82%	39,2	4%	78%

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Table 3c: Results from 5-fold determination of PFAS in ground water, measured directly, and ground water spiked with 5 ng/L and 50 ng/L, respectively, of each compound.

	Ground water		spiked with 5 ng/L			spiked with 50 ng/L		
	Average [ng/L]	RSD [%]	Average [ng/L]	RSD [%]	Trueness [%]	Average [ng/L]	RSD [%]	Trueness [%]
PFBA	39,8	13%	39,4	18%	- *	73,7	5%	68%
PFPeA	<1	-	4,5	3%	89%	40,1	5%	80%
PFHxA	<1	-	4,9	2%	97%	45,0	2%	90%
PFHpA	<1	-	4,4	4%	88%	43,9	2%	88%
PFOA	3,1	6%	7,9	3%	94%	53,7	7%	101%
PFNA	<1	-	4,6	2%	92%	45,4	1%	91%
PFDA	<1	-	4,6	3%	91%	45,2	1%	90%
PFUnDA	<1	-	4,5	3%	90%	45,0	2%	90%
PFDoDA	<1	-	4,5	3%	91%	44,5	1%	89%
PFTrDA	<1	-	4,1	4%	83%	42,9	3%	86%
PFBS	<1	-	4,1	4%	82%	39,5	3%	79%
PFPeS	<1	-	4,8	5%	95%	43,8	3%	88%
PFHxS	<1	-	4,4	3%	89%	44,3	2%	89%
PFHpS	<1	-	4,1	7%	83%	43,5	2%	87%
PFOS	<1	-	4,2	5%	83%	47,7	3%	95%
PFNS	<1	-	4,4	7%	88%	50,8	6%	102%
PFDS	<1	-	5,5	4%	110%	53,5	6%	107%
PFUnDS	<1	-	5,0	6%	101%	44,4	8%	89%
PFDoDS	<1	-	4,8	3%	95%	40,9	8%	82%
PFTrDS	<1	-	4,5	9%	89%	38,4	9%	77%

* The spiked amount is far below the initial concentration.

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Table 3d: Results from 5-fold determination of PFAS in mountain creek water, measured directly, and mountain creek water spiked with 5 ng/L and 50 ng/L, respectively, of each compound.

	Mountain creek water		spiked with 5 ng/L			spiked with 50 ng/L		
	Average [ng/L]	RSD [%]	Average [ng/L]	RSD [%]	Trueness [%]	Average [ng/L]	RSD [%]	Trueness [%]
PFBA	<1	-	4,1	5%	82%	45,8	1%	92%
PFPeA	<1	-	4,7	4%	93%	46,0	3%	92%
PFHxA	<1	-	4,9	4%	98%	46,2	2%	92%
PFHpA	<1	-	4,5	5%	90%	45,5	1%	91%
PFOA	<1	-	5,1	4%	102%	47,8	2%	96%
PFNA	<1	-	4,8	5%	96%	47,5	2%	95%
PFDA	<1	-	4,7	4%	94%	46,4	2%	93%
PFUnDA	<1	-	4,7	4%	95%	46,6	1%	93%
PFDoDA	<1	-	4,7	3%	94%	46,8	2%	94%
PFTrDA	<1	-	4,4	2%	89%	46,1	2%	92%
PFBS	<1	-	4,2	5%	84%	43,7	2%	87%
PFPeS	<1	-	4,4	3%	87%	44,7	1%	89%
PFHxS	<1	-	4,8	5%	97%	46,4	2%	93%
PFHpS	<1	-	4,2	9%	84%	44,3	3%	89%
PFOS	<1	-	4,3	7%	86%	49,1	4%	98%
PFNS	<1	-	4,8	2%	96%	55,0	6%	110%
PFDS	<1	-	5,4	5%	109%	58,5	2%	117%
PFUnDS	<1	-	4,9	6%	98%	49,9	3%	100%
PFDoDS	<1	-	4,8	4%	95%	46,1	4%	92%
PFTrDS	<1	-	4,7	6%	93%	44,4	4%	89%

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Table 3e: Results from 5-fold determination of PFAS in mineral water, measured directly, and mineral water spiked with 5 ng/L and 50 ng/L, respectively, of each compound.

	Mineral water		spiked with 5 ng/L			spiked with 50 ng/L		
	Average [ng/L]	RSD [%]	Average [ng/L]	RSD [%]	Trueness [%]	Average [ng/L]	RSD [%]	Trueness [%]
PFBA	(1,7) *	10%	6,8	9%	104%	53,3	1%	103%
PFPeA	(1,8) *	3%	5,8	6%	79%	45,8	6%	88%
PFHxA	<1	-	5,6	6%	111%	50,6	2%	101%
PFHpA	<1	-	4,7	4%	94%	48,1	1%	96%
PFOA	<1	-	5,5	10%	110%	53,1	2%	106%
PFNA	<1	-	5,1	6%	102%	51,7	2%	103%
PFDA	<1	-	5,1	4%	101%	50,6	1%	101%
PFUnDA	<1	-	5,0	4%	100%	50,9	2%	102%
PFDoDA	<1	-	5,1	4%	102%	52,0	1%	104%
PFTrDA	<1	-	4,8	4%	96%	52,3	3%	105%
PFBS	<1	-	4,4	9%	88%	45,2	5%	90%
PFPeS	<1	-	4,5	5%	90%	48,5	3%	97%
PFHxS	<1	-	4,9	5%	98%	50,6	2%	101%
PFHpS	<1	-	4,2	7%	84%	48,2	3%	96%
PFOS	<1	-	4,8	7%	95%	52,2	3%	104%
PFNS	<1	-	5,7	4%	115%	55,7	6%	111%
PFDS	<1	-	6,6	5%	131%	67,8	3%	136%
PFUnDS	<1	-	6,0	8%	120%	61,9	3%	124%
PFDoDS	<1	-	5,5	6%	110%	59,2	4%	118%
PFTrDS	<1	-	5,3	7%	106%	55,6	5%	111%

* Given the low recovery of labelled PFBA used as internal standard, the quantification limit of these compounds is higher. The measured concentrations were used in calculation of trueness.

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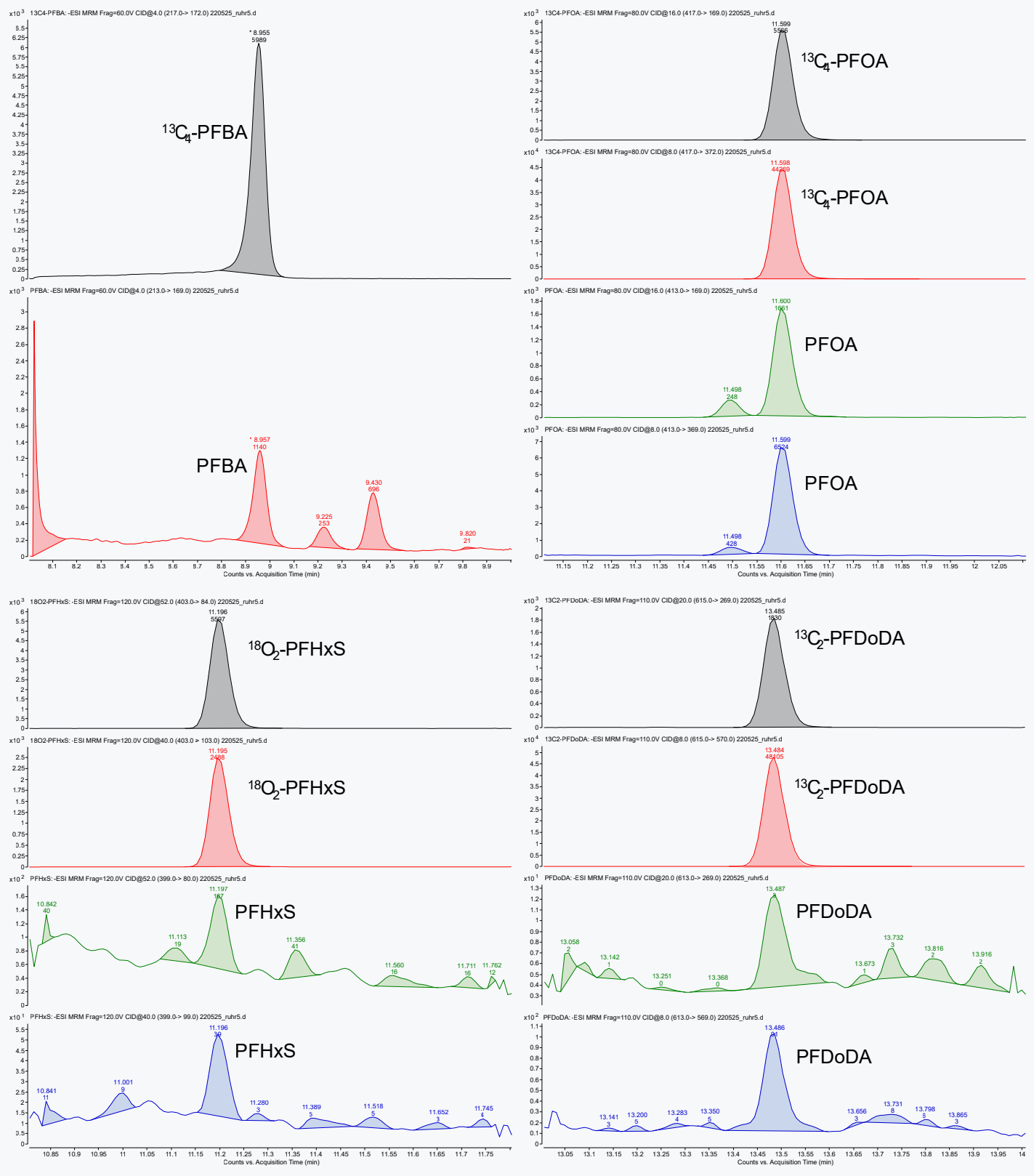

Figure 9: Example chromatograms for selected analytes in river water (upper traces are from the corresponding internal standards), PFBA and PFOA above, PFHxS and PFDoDA below quantification limit.

Conclusions

The online SPE-LC-MS/MS system combined with the presented method enables fully automated determination of PFAS compounds listed in the EU Drinking Water Directive in the low ng/L range. The main benefits are simple sample handling, very low solvent consumption and excellent reproducibility. The organic wash of the cartridges prior to elution effectively removes matrix interferences and improves the accuracy of the results.

Also, there is no need to filter water samples or dilute with methanol prior to analysis. Rinsing the vial with methanol after the sample has been injected and subsequently injecting the rinse solution to the analysis system results in the transfer of adsorbed PFAS and remaining fine sediment particles to the SPE cartridge from where they are eluted to the analysis system and included in the analysis. The method accuracy and trueness were demonstrated for water samples from different sources, resulting in relative standard deviations below 10% and trueness mainly between 80 and 110%.

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