Low-level quantification of PFAS in water samples with high sensitivity and precision

Rapid, low-level analysis using the SCIEX 7500 system

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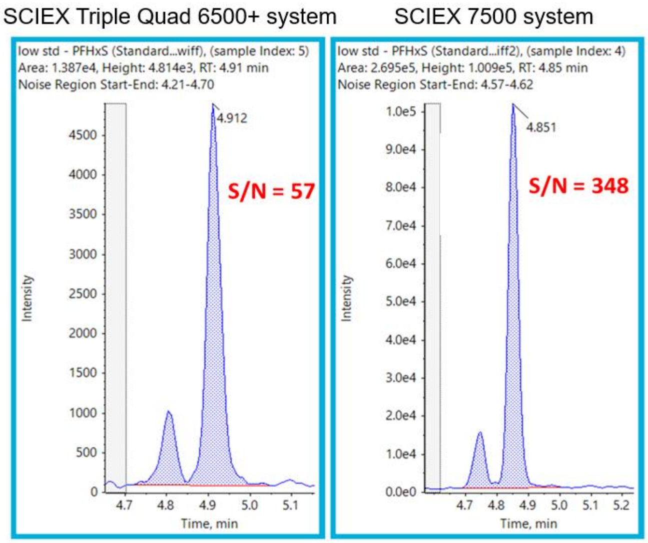
Per- and polyfluoroalkyl substances (PFAS) are synthetic chemical compounds with properties that have excellent resistance to heat, water, oil and grease. PFAS are widely used in food and other product packaging materials, as water and stain repellents, in firefighting foams and within many industrial processes.[1] There is now ample evidence that exposure to high levels of PFAS can lead to adverse health outcomes in humans.[2] Because PFAS bio-accumulate, the risk is even more profound.

Studies over the last two decades have shown that PFAS can be found in virtually every environmental matrix. Many municipal drinking water supplies within the US and around the world contain PFAS contamination. As a result, the EU has set regulations for acceptable levels of PFAS.[3] While the US Environmental Protection Agency (EPA) is still establishing maximum contaminant levels (MCLs) for PFAS, it has issued health advisories. To better evaluate the risks of PFAS to human health, it is important to monitor their levels within humans, water supplies and the environment.


SCIEX Triple Quad 6500+ system

SCIEX 7500 system

Figure 1. MRM peaks for perfluorohexanesulfonic acid (PFHxS). The SCIEX 7500 system data (right) shows a 7.1x increase in S/N compared with the SCIEX Triple Quad 6500+ system data (left). Note: gray shaded areas represent the noise region used for the S/N calculation.

In this technical note, the SCIEX 7500 system was evaluated for the quantification of a comprehensive suite of PFAS compounds in a sample of surface water. This system was designed to enable new levels of sensitivity for the quantification of previously undetectable compounds. Results from the SCIEX 7500 system were compared with results from the SCIEX Triple Quad 6500+ system, an established platform that is routinely used for low-level quantification of PFAS compounds. Figure 1 shows the comparison of a representative PFAS compound, perfluorohexanesulfonic acid (PFHxS).

Key features of the SCIEX 7500 system for PFAS quantification

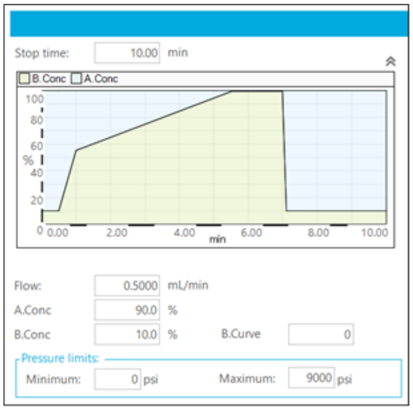
- A fast, 10-min method for quantification of PFAS provides rapid analysis with even greater sensitivity than previous platforms.
- Greater signal-to-noise (S/N) leads to the ability to quantify PFAS compounds even at trace levels.
- Excellent precision with CV of less than 10% across multiple replicate injections means higher confidence in quantified levels.
- Intuitive and user-friendly, SCIEX OS software automatically detects, quantifies, flags outliers and reports results to ease the manual workload and speed up final answers.

Methods

Sample preparation: A surface water sample and a low-level standard (50 ppt) were analyzed in this study. The standard consisted of a comprehensive suite of PFAS compounds, including perfluorinated carboxylic acids (PFCAs), fluorotelomer sulfonates (FTSs), sulfonamides and fluoroether acids (Wellington Laboratories, Guelph, ON). Table 1 contains a list of all compounds studied. The surface water sample was prepared by extraction of 500 mL of water through weak anion exchange (WAX) SPE cartridges. The eluent was reduced in volume under N_2 gas and reconstituted in an 80:20 methanol and water mixture. Five replicates of the standard and 3 replicates of the sample were analyzed.

Chromatography: An ExionLC system was plumbed with a Phenomenex Gemini C18 (5 µm, 3 x 50 mm) column between the LC pumps and the autosampler. This column temporarily retains contaminants from the mobile phases and LC system and elutes them later in the gradient.[5] A Phenomenex Gemini C18 (3 µm, 3 x 100 mm) column was used as the analytical column. An LC flow rate of 500 µL/min was used along with a 1 µL injection volume. Mobile phases were water and methanol, both amended with 10 mM ammonium acetate. The LC gradient is shown in Figure 2.

Time (min.)	% A	% B
0.0	*90.0*	*10.0*
0.5	*90.0*	*10.0*
1.00	*45.0*	*55.0*
5.50	*1.0*	*99.0*
7.00	*1.0*	*99.0*
7.10	*90.0*	*10.0*
10.00	*90.0*	*10.0*



Stop time: 10.00 min

Flow: 0.5000 mL/min

A.Conc 90.0 %

B.Conc 10.0 % B.Curve 0

Pressure limits:

Minimum: 0 psi Maximum: 9000 psi

Figure 2. Flow program for analysis of PFAS compounds.

Mass spectrometry: A SCIEX 7500 system was used with an OptiFlow Pro ion source and an electrospray ionization (ESI) probe in negative ion mode. The source and MS parameters were as follows: TEM = 400°C, GS1 = 40, GS2 = 70, ISV = -2000, CUR = 40, CAD = 14. For comparison purposes, a SCIEX Triple Quad 6500+ system was used with the IonDrive Turbo V ion source. Primary (and, in most cases, secondary) multiple reaction monitoring (MRM) transitions were monitored for each PFAS compound based upon previous studies and were identical for both instruments. Each system was optimized for maximum sensitivity.

Data processing: Data acquisition and automatic data processing were performed using SCIEX OS software and analytics in SCIEX OS software. Flagging rules were specified within the analytics module to quickly flag good and bad data.

Key innovations that improve sensitivity

The SCIEX 7500 system was designed to push sensitivity boundaries beyond those previously established with the high-end SCIEX Triple Quad 6500+ system. These sensitivity improvements are realized through several areas.[4] For example, the E Lens probe of the OptiFlow Pro ion source more efficiently breaks up droplets, releases ions and actively drives ions toward the orifice. The 4.3x increase in the area of the entrance orifice allows more ions to enter the instrument, improving ion sampling. The D Jet ion guide more efficiently captures and focuses ions from the ESI spray plume, allowing more ions to traverse the instrument to be analyzed and detected. All of these enhancements improve the total number of ions available for analysis in the system. Since the noise does not increase proportionally, the S/N ratio increases, quite dramatically for some compounds, for SCIEX 7500 system data.

Because of these changes in source and entrance optics, PFAS compounds were first evaluated using a range of source and entrance parameters to find optimum conditions. Although there were some dependencies on source temperature and ionization voltage as a function of PFAS class and chain length, conditions were found that produced good signal for all compounds. Interestingly, lower voltages were generally required using the OptiFlow Pro ion source than previous source designs due to the function of the E Lens probe.

Signal-to-noise comparison

The sensitivities of the SCIEX Triple Quad 6500+ system and the SCIEX 7500 system were evaluated by injecting the low-level standard onto each system. Table 1 lists all of the PFAS compounds contained within the low-level standard. The S/N was automatically calculated within SCIEX OS software using the “peak-to-peak” algorithm and is listed for each MRM transition. The table also shows the improvement factor in S/N for the SCIEX 7500 system versus the SCIEX Triple Quad 6500+ system. Improvements in S/N for the SCIEX 7500 system were on average around 5.5x but ranged anywhere from ~1x to more than 50x.

Table 1. S/N for each PFAS MRM transition. Each PFAS was measured (using both the SCIEX Triple Quad 6500+ system and the SCIEX 7500 system) and the S/N was calculated. The "7500/6500+" column shows the improvement factor for the SCIEX 7500 system, ranging from ~1 to >50.

		Signal to noise					Signal to noise		
#	Analyte	SCIEX Triple Quad 6500+ system	SCIEX 7500 system	7500/6500+	#	Analyte	SCIEX Triple Quad 6500+ system	SCIEX 7500 system	7500/6500+
1	PFBS	124	316	2.6	28	6:2 FTS	39	44	1.1
2	PFBS_2	38	58	1.5	29	8:2 FTS	17	18	1.0
3	PFPeS	62	318	5.1	30	10:2 FTS	29	27	0.9
4	PFPeS_2	37	87	2.3	31	PFBA	52	110	2.1
5	PFHxS	81	577	7.1	32	PFPeA	21	136	6.3
6	PFHxS_2	40	121	3.0	33	PFHxA	15	112	7.5
7	PFHpS	78	204	2.6	34.	PFHxA_2	5	45	9.6
8	PFHpS_2	40	96	2.4	35	PFHpA	32	188	6.0
9	PFOS	53	74	1.4	36	PFHpA_2	30	104	3.4
10	PFOS_2	46	99	2.2	37	PFOA	14	191	13.5
11	PFNS	67	139	2.1	38	PFOA_2	15	140	9.3
12	PFNS_2	23	47	2.1	39	PFNA	18	12	0.7
13	PFDS	64	224	3.5	40	PFNA_2	15	38	2.5
14	PFDS_2	17	93	5.3	41	PFDA	17	88	5.1
15	PFDoS	96	111	1.2	42	PFDA_2	5	27	5.4
16	PFDoS_2	39	84	2.1	43	PFUdA	12	112	9.1
17	PFOSA	132	774	5.9	44	PFUdA_2	7	31	4.4
18	MeFOSA	22	42	2.0	45	PFDoA	19	69	3.6
19	EtFOSA	8	32	3.8	46	PFDoA_2	5	42	7.7
20	N-MeFOSAA	102	789	7.7	47	PFTrDA	14	88	6.3
21	N-EtFOSAA	6	291	52.2	48	PFTrDA_2	11	28	2.4
22	9Cl-PF3ONS	62	512	8.3	49	PFTeDA	20	40	2.0
23	11Cl-PF3OUdS	39	351	9.0	50	PFTeDA_2	11	44	3.9
24	HFPO-DA	14	20	1.4	51	PFHxDA	25	201	8.0
25	DONA	86	289	3.4	52	PFHxDA_2	6	65	10.2
26	DONA_2	88	682	7.7	53	PFODA	46	216	4.7
27	4:2 FTS	40	98	2.4	54	PFODA_2	5	58	12.4

Note: most analytes have more than 1 transition, which is indicated by the "_2" appended to the end of its name.

Figure 1, Figure 3 and Figure 4 show MRM peaks obtained for 3 representative PFAS compounds on the SCIEX 7500 system compared with the SCIEX Triple Quad 6500+ system. Integrated peak areas are shaded in purple while the gray highlighted areas represent the noise used by the S/N algorithm.

For the SCIEX 7500 system data, peak areas and total peak intensities are greater while the noise is maintained at relatively low levels, resulting in increased S/N in all cases. This ultimately results in improved sensitivity and lower limits of quantification (LOQ). For example, as shown in Figure 4, the increased S/N using the SCIEX 7500 system enables quantification of important, lower-level isomers for N-ethyl perfluorooctane sulfonamide (EtFOSA).

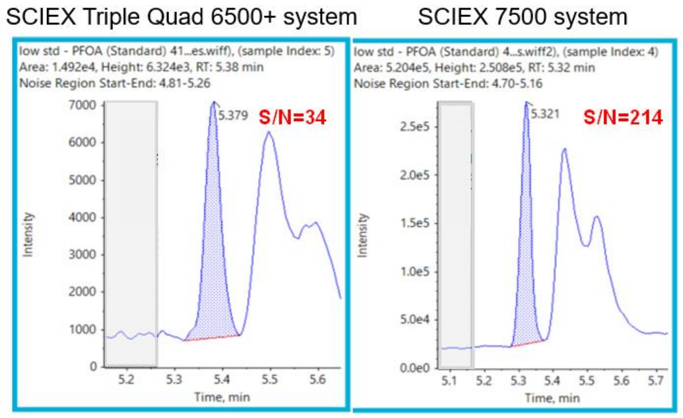


Figure 3. MRM peaks for perfluorooctanoic acid (PFOA). The SCIEX 7500 system data (right) shows a 13.5x increased S/N compared with the SCIEX Triple Quad 6500+ system data (left). Note: gray shaded areas represent the noise region used for the S/N algorithm.

Precision comparison

Five replicate injections were made for the low-level standard and %CVs were calculated. As shown in Figure 5, precision was excellent with CVs of less than 10% for the SCIEX 7500 system data.

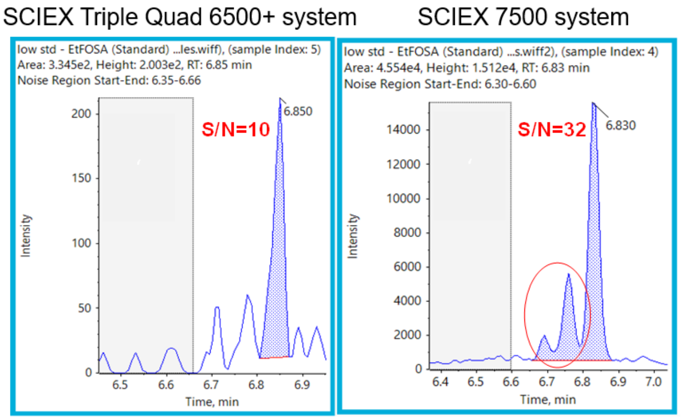


Figure 4. MRM peaks for N-ethyl perfluorooctane sulfonamide (EtFOSA). The SCIEX 7500 system data (right) shows a 3.8x increased S/N compared with the SCIEX Triple Quad 6500+ system data (left). The increased S/N enables quantification of important lower-level EtFOSA isomers (red circle) that are missed using the SCIEX Triple Quad 6500+ system. Note: gray shaded areas represent the noise region used for the S/N algorithm.

For the SCIEX Triple Quad 6500+ system data, CVs were generally less than 20%, with some outliers ranging as high as 30%. The lower %CV of the SCIEX 7500 system represents improved precision and therefore improved data quality near the lower LOQ.

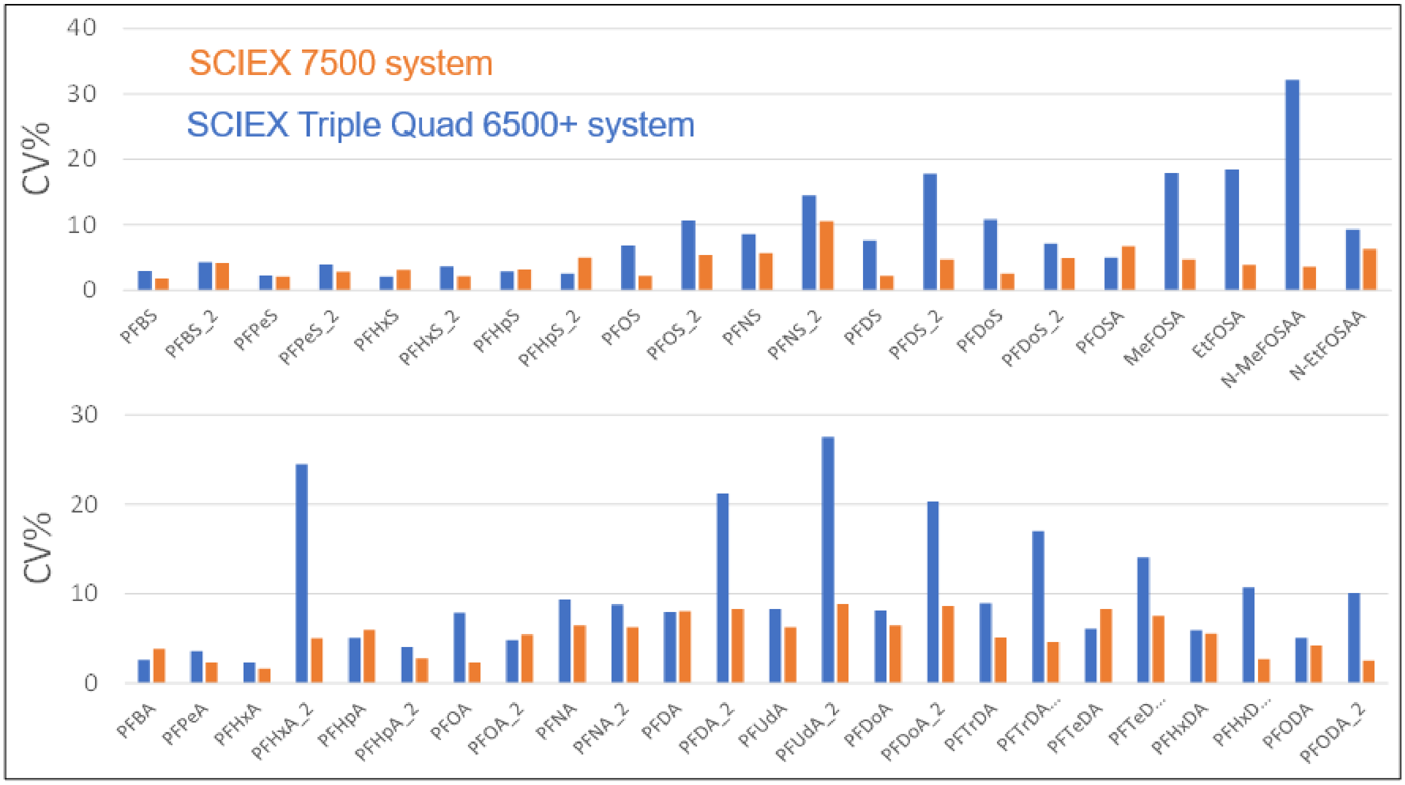


Figure 5. Precision for 5 replicate injections of the low-level standard. The SCIEX 7500 system had CVs of <10% for all PFAS transitions (orange bars) while the CVs for the SCIEX Triple Quad 6500+ system were generally under 20%, but with some outliers ranging up to 30% (blue bars).

Water sample evaluation

The surface water sample was analyzed in triplicate on both the SCIEX Triple Quad 6500+ system and the SCIEX 7500 system. As shown in Figure 6, Figure 7 and Figure 8, the higher sensitivity of the SCIEX 7500 system resulted in higher signals and greater S/N for all compounds, transitions and replicates.

For example, this increased sensitivity enabled the detection of low-level isomers of N-methylperfluorooctane sulfonamidoacetic acid, or MeFOSAA (Figure 7), and it increased confidence in the detection of perfluorotridecanoic acid, or PFTrA (Figure 8), a hydrophobic compound that normally would not be expected to be present in surface water.

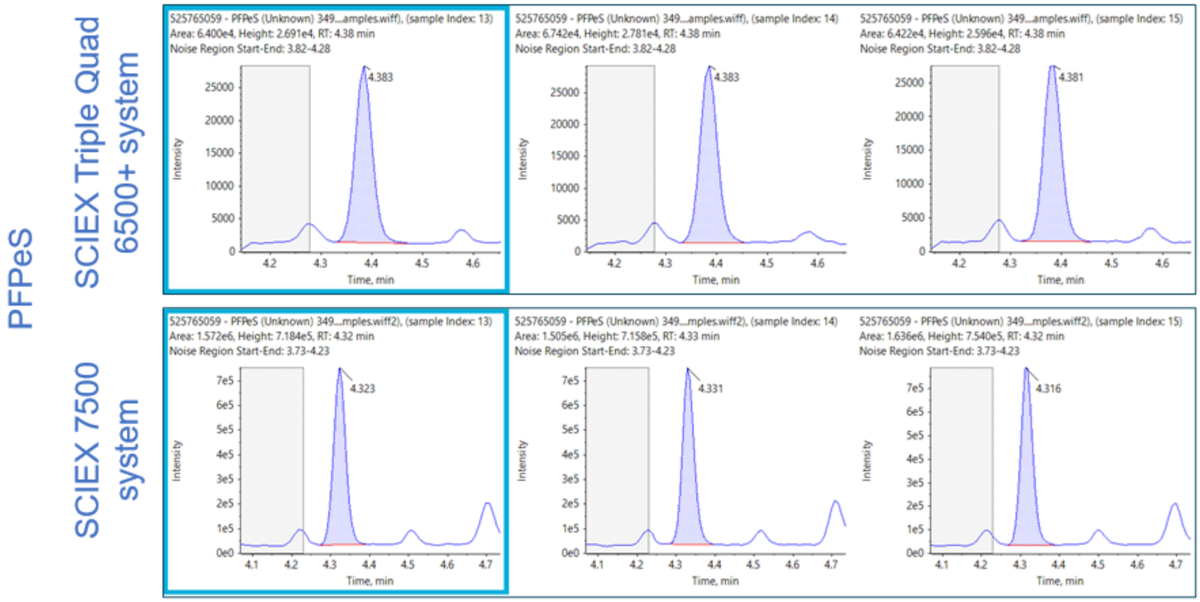


Figure 6. Quantification of perfluoropentane sulfonic acid (PFPeS) in a surface water sample. Triplicate analysis comparing the SCIEX Triple Quad 6500+ system (top) and the SCIEX 7500 system (bottom). The higher S/N observed with the SCIEX 7500 system leads to higher precision and confidence in the analysis.

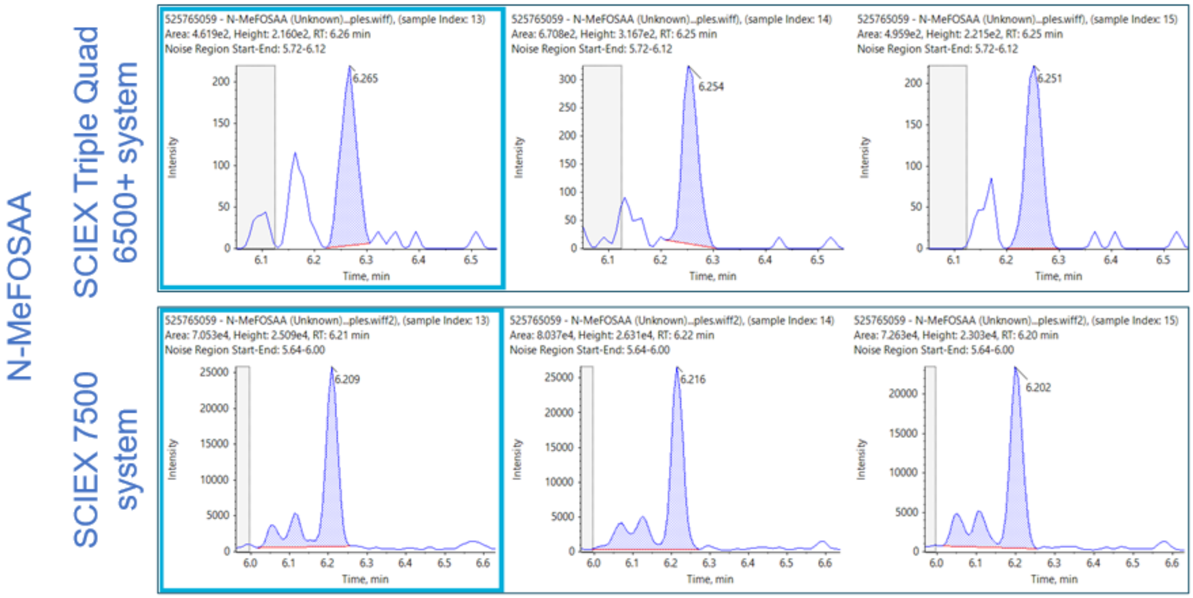


Figure 7. Quantification of N-methylperfluorooctane sulfonamidoacetic acid (MeFOSAA) in a surface water sample. Triplicate analysis comparing the SCIEX Triple Quad 6500+ system (top) and the SCIEX 7500 system (bottom). The higher S/N observed with the SCIEX 7500 system leads to the detection of low-level isomers in the analysis.

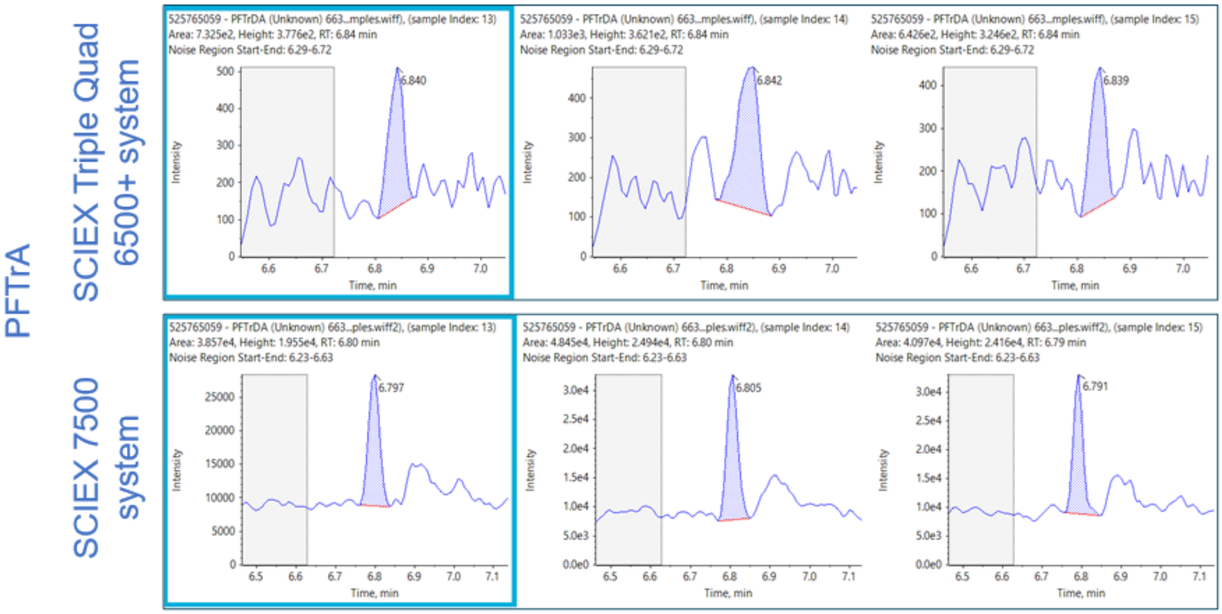


Figure 8. Quantification of perfluorotridecanoic acid (PFTrA) in a surface water sample. Triplicate analysis comparing the SCIEX Triple Quad 6500+ system (top) and the SCIEX 7500 system (bottom). The higher S/N observed with the SCIEX 7500 system leads to the detection of unexpected low-level analytes.

Conclusions

The increased sensitivity of the SCIEX 7500 system allows a new level of performance for the analysis of PFAS compounds.

- Lower-level compounds and important lower-level isomers can be detected and quantified.
- Improved S/N leads to lower limits of detection.
- Unexpected compounds that are detected can be quantified with higher certainty.
- Higher precision is achieved for replicate analyses, leading to more confidence in the quantified amounts.
- Less sample can be utilized for the analysis.
- Sample preparation strategies can be simplified.
- Intuitive and friendly SCIEX OS software handles all data acquisition and processing, streamlining the entire workflow.

References

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