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A Sensitive and Automated Approach Using Large Volume Injections Coupled with LC/TQ to Analyze Perfluorinated Compounds in Environmental Samples

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Introduction

Perfluorinated compounds (PFCs) are widely used in diverse industrial applications and consumer products due to their stability and surfactant properties. They have also been widely used in the past as a protective coating for materials such as carpets, textiles and leather, as well as in various household and industrial cleaning products. In the EU, the manufacture and use of perfluorooctane sulfonate (PFOS) is prohibited under Directive 2006/122/EC that came into force in June 2008. Perfluorooctanoic acid (PFOA) is still manufactured and is mainly used in the production of fluoropolymers, which are used in electronics, textiles and non-stick cookware. However, PFCs such as PFOS and PFOA do not decompose easily in the natural environment and can bio-accumulate or build up in certain living organisms. An automated LC/TQ method for the analysis of a mixture of PFCs comprised of 19 perfluorinated compounds has been developed using an Agilent 6495 triple quadrupole mass spectrometer. This automated method employs large volume injections to provide a faster, more sensitive, robust, and accurate solution for the analysis of PFCs without sample pre-concentration.

Experimental

Method

A eclipse plus C18 column packed with 1.8 μm particles was used to achieve uHPLC analysis with symmetric peak shapes and a poroshell EC C18 trapping column to reduce background. Environmental samples were analyzed by direct large volume injection for quantification of multi-PFCs analysis.

Figure 1. Agilent 1290 II and 6495 LC/TQ

Experimental

Instrumental

A gradient elution and dMRM acquisition were employed for simultaneous identification and quantitation (optimal peak shapes and acquisition of requisite data points). The Agilent dual-needle option provides two flow paths within one autosampler by doubling the needle, the sample loops (500 μL and 20 μL), and the needle-seats, along with an additional valve, it shows in Figure 2

Figure 2. Agilent 1290 II multisampler dual needle

LC system	Agilent 1290 II
Column	Analytical: Agilent Eclipse plus C18 3.0x100 mm, 1.8 um Trap: Poroshell EC C18 3x50 mm, 2.7um
Injection volume	400 µL
Mobile phase	A: 10 mM ammonium acetate in H2O B: MeOH
Column Temp	40 C
Gradient	B: 2 5 50 100 100 Time:0 4 5 18 22
Flow rate:	0.4 mL/min
Post time	3 min
Mass system	Agilent 6495 Triple Quadrupole
Dry Gas Temp.	290°C
Dry Gas Flow	18 L/min
Nebulizer	35 psi
Sheath Gas Temp	400°C
Sheath Gas Flow	12 L/min
Nozzle Voltage	0 (negative)
Capillary Voltage	4000 V (negative)
Delta EMV	400-600 (negative)
Low pressure funnel	RF: 60V (negative), V drop: 100 (negative), DC V: 15V
High pressure funnel	RF: 90V (negative), V drop: 110 (negative), DC V: 15V

Results and Discussion

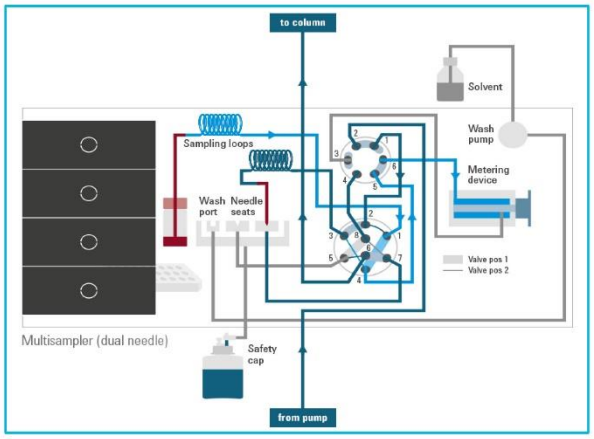

Figure 3. 1290 II multisampler dual needle valve scheme

Large-volume injection (LVI) with LC/TQ

LVI consists of the direct injection of samples with volumes ranging up to 500 µL, which is large compared to conventional injection volumes of 5–20 µL (valve scheme is shown in figure 3). LVI works on the principle of concentrating analytes onto the head of the analytical column during injection of a low-elutropic strength sample. Salts and other matrix into the stationary phase pass unretained through the column. Following analyte concentration on the analytical column, which is analogous to SPE, an increase in the elutropic strength of the mobile phase promotes elution and separation of the concentrated analytes. The major advantages of LVI include an increase in sensitivity, while maintaining accuracy and precision with minimal sample volume.

LVI was optimized and evaluated by accuracy and precision through standard addition experiments. The detection and quantification limits of the instrument and method were then determined using these optimized conditions.

Sensitivity, Linearity and Precision

The on-column sensitivity and linearity of the instrument were assessed by analyzing PFCs standards prepared in H_2O, with a calibration range of 0.1 – 1000 ng/L. A large volume injection of 400 µL was used and the linearity was evaluated using the external standard calibration approach. Excellent sensitivities were achieved through LVI. The standard mixtures for PFCs are shown in figure 4. The calibration curves for PFNA and PFOSA were generated with tap water and correlation coefficients were greater than 0.992 (shown in figure 5).

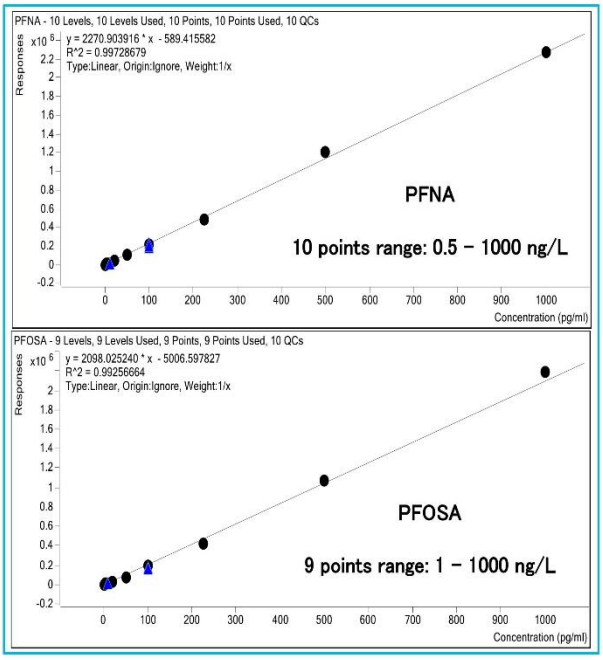

Figure 5. The calibration curves for PFNA and PFOSA

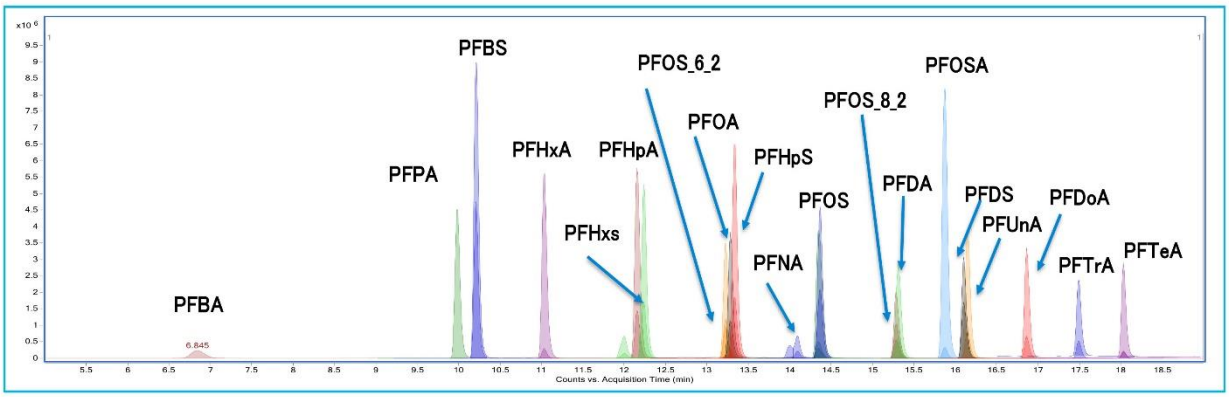

Figure 4. Standard of 19 PFCs with 100 ng/L for Large volume injection 400 uL

Results and Discussion

Compounds	Compounds Full name	Precursor Ion (charge state)	Product Ion m/z (Collision energy)	RT (min)	Limit of detection (ng/L)	Linear range (ng/L)	Calibration Curve y = ax ± b	r^2
PFOS_6_2	perfluorooctane sulfonate_6:2	427(−1)	407(25), 81(45), 80(49)	13.2	0.2	0.2 – 1000	y = 513.7* x +3757.9	0.9984
PFOS_8_2	perfluorooctane sulfonate_8:2	527(−1)	507(29), 81(29), 80(33)	15.3	0.2	0.2– 1000	y = 432.2 * x – 363.6	0.9951
PFBA	perfluorobutanoate	213(−1)	169(8)	6.80	10	25 – 1000	y = 1647.8 * x + 87659.6	0.9982
PFBS	perfluorobutane sulfonate	299(−2)	99(33), 80(40)	10.2	0.1	0.1 – 1000	y=1.41e5x-1.91e4	0.9950
PFDA	perfluorodecanoate	513(−1)	469(9), 269(17)	15.3	0.2	0.2 – 1000	y = 1380.5 * x – 238.7	0.9955
PFDoA	perfluorododecanoate	613(−1)	569(90, 319(21)	16.8	0.5	1 – 1000	y = 1137.1 * x – 5751.8	0.9921
PFDS	perfluorodecane sulfonate	599(−1)	99(50), 80(50)	16.1	0.1	0.2 – 1000	y = 561.0 * x – 587.8	0.9902
PFHpA	perfluoroheptanoate	363(−1)	319(7), 169(17)	12.1	0.1	0.2 – 1000	y = 1865.1 * x + 6317.7	0.9968
PFHpS	perfluorohexane sulfonic acid	449(−1)	99(41), 80(57)	13.3	0.1	0.1 – 1000	y= 1270.9 * x – 1044.4	0.9967
PFHxA	perfluorohexanoate	313(−1)	269(5), 119(17)	11.0	0.1	0.1 – 1000	y = 1552.8 * x + 365.0	0.9934
PFHxS	perfluorohexane sulfonate	399(−1)	99(37), 80(41)	12.3	0.1	0.1 – 1000	y = 981.3 * x – 746.0	0.9962
PFNA	perfluorononanoate	463(−1)	419(5), 219(17), 169(21)	14.3	0.25	0.5 – 1000	y = 2270.9 * x – 589.4	0.9973
PFOA	perfluorooctanoate	413(−1)	369(9), 169(15)	13.2	0.05	0.1 – 1000	y = 1648.4 * x + 2535.3	0.9972
PFOS	perfluorooctane sulfonate	499(−1)	99(53), 80(50)	14.4	0.05	0.1 – 1000	y = 898.5 * x – 171.8	0.9926
PFOSA	perfluorooctane sulfonamidoacetic acid	498(−1)	169(30), 78(45)	15.8	0.5	1 – 1000	y = 2098.0 * x – 5006.5	0.9926
PFPA	perfluoropentanoate	263(−1)	219(5), 197(8), 69(40)	10.0	1	2 – 1000	y = 1318.7 * x – 5211.1	0.9961
PFTeA	perfluorotetradecanoate	713(−1)	669(9), 269(25), 169(30)	18.0	25	25 – 1000	y = 1581.1 * x – 51796.7	0.9911
PFTrA	perfluorotridecanoate	663(−1)	619(9), 169(29)	17.5	25	25 – 1000	y = 1744.2 * x – 52794.3	0.9961
PFUnA	perfluoroundecanoate	563(−1)	519(9), 269(16)	16.2	0.5	1 – 1000	y = 1734.7* x – 3886.0	0.9918

Table 1. MRM parameters , linearity range, calibration curve and retention time information

Background reducing

The trapping column was installed in place of the JetWeaver. It was positioned after the mixing point to minimize delay volume increase and its purpose was to trap PFCs traces originating from the solvent system. Owing to this design, the trapping column was regenerated from run to run to avoid possible breakthrough of the trapped compounds over time. The introduced elution time delay between the interfering (higher RT) and target (lower RT) compounds allowed for the accurate determination of the target compounds. Tap water sample shows no carry over after injection of the QC sample. (shows in figure 6)

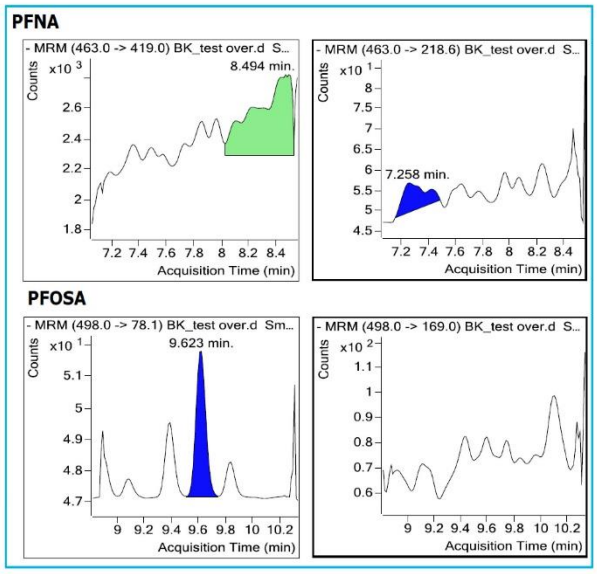

Figure 6. Tap water sample for PFNA and PFOSA

Conclusions

- Recoveries were found to be in the range of 80—120% using fortified tap water standards.
- The limit of detection (LOD) was below 0.05 ng/L for multi-PFCs analytes with standard calibration for quantitative analysis (except PFTrA and PFTeA).
- This automation method uses large volume injections and provides a faster, more sensitive, robust, and accurate solution for the analysis of PFCs without sample pre-concentration.

References

1.Trace Level Determination of PFOS, PFOA and HBCD in Drinking Water by Direct Aqueous Injection on the Agilent 6495 LC/MS/MS. Agilent 5991-5669EN.

2. TRACE LEVEL DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs) IN WATER USING THE AGILENT 6460 LC/MS/MS. Agilent 5991-5532EN.

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