Application Note : 2410C

Automated extraction and fast analysis of PFAS in drinking water:

Analysis of PFAS at 10 seconds per sample using LDTD-MS/MS.

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Keywords: High-Throughput, Drinking Water, LDTD-MS/MS, PFAS

Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of chemicals made by humans. Since the 1950s, PFASs have been used in many consumer products and industrial processes. They have properties that resist heat, grease, and water. There are thousands of types of PFAS. The most common types and final products of degradation are PFOA (perfluorooctanoic acid) and PFOS (perfluorooctanoic sulfonic acid). They were widely detected in different environmental media (Mahiba Shoeib et al. 2005)[1] and human blood (Perez et al. 2013)[2].

The goal of this application note is to develop an automated sample preparation of drinking water samples and a rapid analytical method to analyze PFAS using LDTD-MS/MS.

Luxon Ionization Source

The Luxon Ion Source® (**Figure 1**) is the second-generation sample introduction and ionization source based on the LDTD® technology for mass spectrometry. Luxon Ion Source® uses Fiber-Coupled Laser Diode (**Figure 2**) to obtain unmatchable thermal uniformity giving more precision, accuracy and speed. The process begins with dry samples which are rapidly evaporated using indirect heat. The thermally desorbed neutral molecules are carried into a corona discharge region. High efficiency protonation and strong resistance to ionic suppression characterize this type of ionization and is the result of the absence of solvent and mobile phase. This thermal desorption process yields high intensity molecular ion signal in less than 1 second sample to sample and allows working with very small volumes.

Figure 1 - Luxon Ion Source®

Figure 2 - Schematic of the Luxon Ionization Source

Sample Preparation Method

Automated Sample Extraction.

Two milliliters of drinking water samples are transferred to a borosilicate tube (12X75 mm) then inserted in the Azeo extraction system (**Figure 3**). The automated extraction process is as follows:

- Add 20 µL of internal standard solution.
    - Vortex (1100 rpm/30 s).
- Add 30 µL of HCl (4N).
    - Vortex (1100 rpm/30 s).
- Add 700 µL of extraction solution (MTBE).
    - Vortex (1100 rpm/120 s).
    - Phase separation by gravity.
- In a sample holder of 96 glass tubes (6X31 mm), add 50 µL ammonium formate (20 mM in methanol).
- Transfer 200 µL of the upper layer into the 6X31 mm glass tube.
    - Vortex (1100 rpm/60 s).
    - Evaporate until dryness (40°C, 10 minutes, air flow 10 LPM).
- Add 60 µL of reconstitution solution.
    - Vortex (1100 rpm/30 s).
- Spot 5 µL of mixture on a LazWell™96 plate.
    - Dry 5 minutes at 40°C.

Figure 3 - Automated extraction system

LDTD®-MS/MS Parameters

LDTD

Model: Luxon T-960 NG, Phytronix
Carrier gas: 9 L/min (Nitrogen) + 7.5 µL/min TFA solution (0.05% in water)
Laser pattern:

- 6-second ramp to 100% power
- 4-second hold at 100% power

MS/MS

MS model: TSQ Altis plus, Thermo Scientific
IonSpray Voltage: -3800 V
Scan Time: 5 msec
Analysis Method: Negative MRM mode

Table 1 - MRM transitions for LDTD-MS/MS

	Transition	CE (V)
PFBA	327.0 → 169.0	20
PFBA-M3	330.0 → 172.0	20
HFPO-DA	443.0 → 169.0	20
HFPO-DA-M3	446.0 → 172.0	20
PFBS	451.0 → 299.0	20
PFBS-M4	455.0 → 303.0	20
PFHxA	427.0 → 269.0	20
PFHxA-M6	433.0 → 274.0	20
PFHxS	551.0 → 399.0	20
PFHxS-M6	557.0 → 405.0	20
PFOA	527.0 → 412.8	8
PFOA-M8	538.0 → 420.8	8
6:2 FTS	579.0 → 427.0	24
6:2 FTS-M6	585.0 → 433.0	24
PFNA	577.0 → 463.0	8
PFNA-M6	583.0 → 469.0	8
PFOS	651.0 → 499.0	20
PFOS-M8	659.0 → 507.0	20

Results and Discussion

Linearity

Calibration curve is prepared in HPLC water. PFAS concentration between 20 to 200 ng/L are used to evaluate the method linearity and 100 to 10 000 ng/L for PFBA. The peak area against the internal standard (IS) ratio was used to normalize the signal. Replicate extractions are deposited on a LazWell™ plate and dried before analysis. **Figure 4** and **Figure 5** shows a typical calibration curve for PFOA and PFOS. Similar results were obtained for the other PFAS.

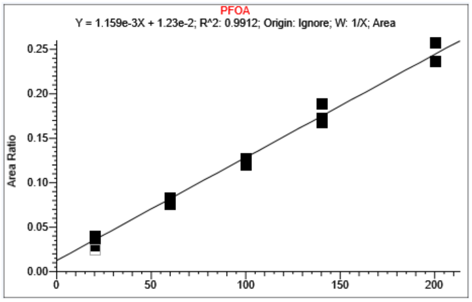

Figure 4 – Typical calibration curve for PFOA

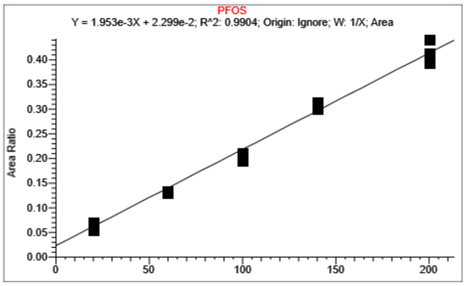

Figure 5 – Typical calibration curve for PFOS

Precision / Accuracy

Spiked samples solutions are used to validate the precision and accuracy of the method.

The following acceptance criteria were used:

- Each concentration must not exceed <20%CV.
- Each concentration must be within ±20%Bias.

For the intra-run precision/accuracy experiment, each fortified sample set is analyzed in sextuplicate in the same runs. **Table 2** shows the intra-run precision and accuracy results for PFOA. %CV was below 20% and the accuracy within 20%. Similar results were obtained for the other PFAS.

Table 2 – Intra-Run Precision for PFOA

PFOA	Cal-1	Cal-2	Cal-3	Cal-4	Cal-5
Conc (ng/L)	20	60	100	140	200
N	3	3	3	3	3
Mean (ng/L)	18.2	68.7	85.6	154.5	195.4
%CV	16.6	5.9	10.7	11.0	2.9
%Nom	91.2	114.5	85.6	110.3	97.7

For the inter-run precision experiment, each fortified sample set is analyzed in triplicate on three different runs. **Table 3** shows the inter-run precision and accuracy results for PFOA. %CV was below 20% and the accuracy within 20%. Similar results were obtained for the other PFAS.

Table 3 - Inter-Run Precision for PFOA

PFOA	Cal-1	Cal-2	Cal-3	Cal-4	Cal-5
Conc (ng/L)	20	60	100	140	200
N	9	9	9	9	9
Mean (ng/L)	18.0	65.6	91.7	148.6	198.6
%CV	19.3	9.6	9.3	9.4	3.5
%Nom	90.0	109.4	91.7	106.2	99.3

Recovery

Blank samples were extracted and then spiked at the middle calibration level after the automated extraction process. The middle standard was compared to the recovery sample to determine the recovery percentage of PFAS. **Table 4** shows the recovery results.

Table 4 – Recovery results

PFAS	Recovery
PFBA	72.3
HFPO-DA	71.4
PFBS	42.7
PFHxA	77.1
PFHxS	78.1
PFOA	78.8
6:2 FTS	72.6
PFNA	81.8
PFOS	87.0

Multi-matrix analysis

Drinking water was collected from different sites. Samples are analyzed to verify the presence of each PFAS. PFAS are spiked at 100 ng/L (500 ng/L for PFBA) and analyzed as unknown to verify the method performance. Results are report in **Table 5**.

Table 5 – Drinking water sample results

Sample	PFOA Conc. (ng/L)	PFOS Conc. (ng/L)	PFNA Conc. (ng/L)	PFHxS Conc. (ng/L)	PFHxA Conc. (ng/L)	PFBS Conc. (ng/L)	PFBA Conc. (ng/L)	HFPO-DA Conc. (ng/L)	6:2-FTS Conc. (ng/L)
DW-1	<20	<20	33.6	<20	<20	<20	<100	<20	<20
DW-1-100	118.2	108.9	143.6	110.3	122.1	124.7	514.6	99.4	130.4
DW-2	<20	<20	<20	<20	28.4	<20	<100	<20	<20
DW-2-100	115.4	105.3	113.6	105.5	120.1	108.1	548.6	98.4	102.7
DW-3	<20	<20	<20	<20	<20	21.2	<100	<20	<20
DW-3-100	97.0	99.1	112.6	103.6	105.3	123.0	492.2	88.5	107.3
DW-4	<20	<20	<20	<20	<20	26.8	<100	<20	<20
DW-4-100	101.4	102.9	106.7	103.1	112.4	111.2	547.9	109.5	116.7
DW-5	<20	<20	<20	<20	<20	28.1	<100	<20	<20
DW-5-100	95.5	101.8	108.9	102.7	117.1	118.0	512.7	117.4	116.4
DW-6	<20	<20	20	<20	35.0	26.5	<100	<20	27.7
DW-6-100	112.0	101.3	121.6	102.3	133.2	117.8	501.9	112.6	125.1

Conclusion

Luxon Ion Source® combined with a Thermo Scientific TSQ Altis Plus mass spectrometer system allows ultra-fast (**10 seconds per sample**) analysis of a PFAS panel in drinking water using a simple and automated sample preparation method.

References

1. Shoeib and al., Environ. Sci. Technol. 2005, 39, 6599-6606
2. Perez et al., Environ Int 2013 Sep:59:354-62.