From Industry to Tap: Quantifying PFAS in Drinking Water

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OVERVIEW

Purpose

- Development of an automated Extraction method for PFASs analysis in drinking water.

Method

- Automated Liquid-Liquid of drinking water sample.
- Samples analyzed by LDTD-MS/MS.

Quantification

- Precision results were lower than 20%CV, accuracy results were within ±20% from the nominal value.
- Samples analyzed with a runtime of 10 seconds using LDTD-MS/MS technique.

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) and human blood (Perez et al. 2013). The goal of this presentation is to develop an automated sample preparation of drinking water sample 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. The Luxon Ion Source uses a 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

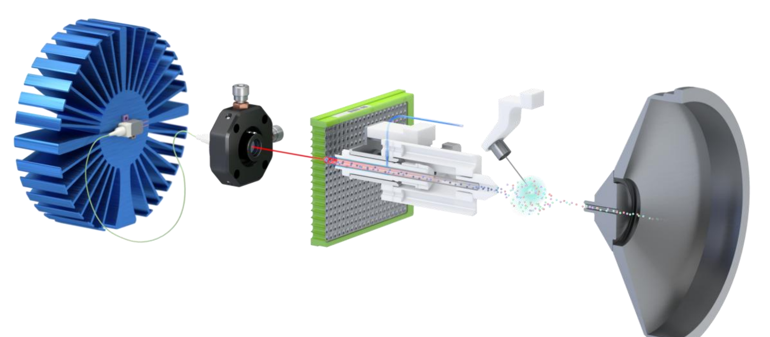

Figure 2 Schematic of the Luxon Ion Source

METHOD

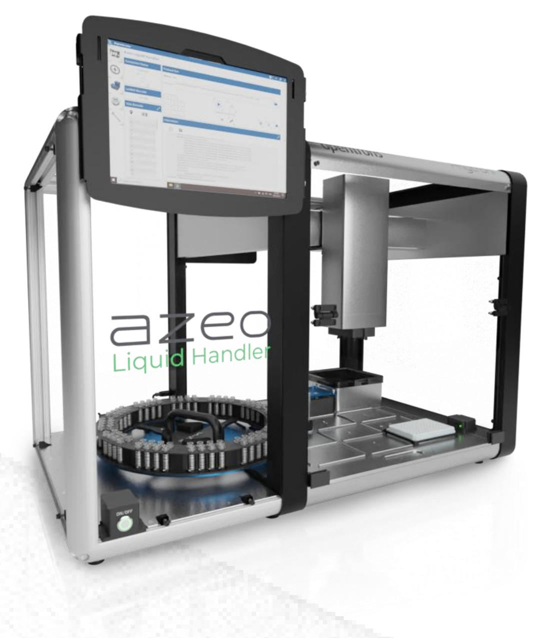

Figure 3 Azeo automated extraction system

Automated liquid-liquid extraction

- 2 mL drinking water sample were added in a borosilicate 12X75 mm tube then transferred to the Azeo automated extraction system (**Figure 3**).
- 20 µL of internal standard and 30 µL HCl (4N) are added to the water sample.
- Mixed on Lumo for 30 seconds at 1100 RPM.
- After mixing, 700 µL of MTBE are added.
- Samples are mixed on Lumo for 120 seconds at 1100 RPM.
- 200 µL of the upper layer are transferred in a 6 X 31 mm borosilicate tube having 50 µL ammonium formate (20 mM in methanol)
- Samples are evaporated to dryness at 40 °C using gentle air flow (10 LPM) for 10 minutes.
- 60 µL of a reconstitution solution are added to dry samples.
- Mixed on Lumo for 30 seconds.
- 5 µL of sample are spiked onto a Lazwell96 plate and dried.
- Samples are analyzed by LDTD-MS/MS.

Instrumentation

- Ion source:
Phytronix Luxon Ion Source T-960

- Mass spectrometer:
TSQ Altis plus, Thermo Scientific

Luxon Parameters

- Laser power pattern:
- Increase laser power to 100% in 6s.
- Hold 4 s. at 100%.
- Carrier gas flow: 9 L/min (Nitrogen) + 7.5 µL/min TFA solution (0.05% in water)

MS Parameters

- APCI (-)
- IonSpray voltage: -3800
- Time: 10 msec

Table 1 MRM transitions parameters

Drugs	Transition	CE
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

Validation

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.

Linearity

Five-point calibration curves are used to validate the method. A typical calibration curve is shown in **Figure 4**.

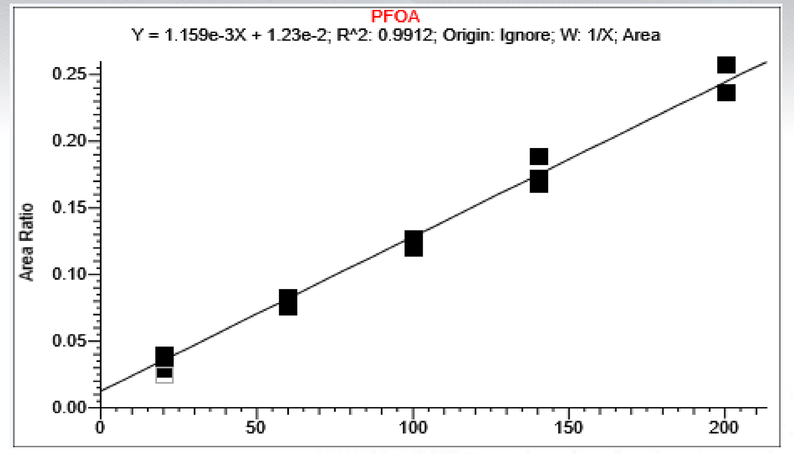

Figure 4 Calibration curve of PFOA analysis

Precision

Standards were extracted in triplicate over 3 different runs. %CV and %Nom were evaluated. **Table 2** shows the results for PFOA. Similar results were obtained for the other PFASs.

Table 2 Precision and accuracy results of PFOA.

PFOS	S1	S2	S3	S4	S5
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
%Bias	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 PFASs. **Table 3** shows the recovery results.

Table 3 Recovery results

PFASs	%
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 waters are collected from different sites. Samples are analyzed to verify the presence of each PFAS. PFASs are spiked at 100 ng/L (500 ng/L for PFBA) and analyzed as unknown to verify the method performance. Results are reported in **Table 4**.

Table 4 Multi-Matrix analysis results

	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	1178	501.9	112.6	125.1

CONCLUSION

- **Automated extraction process can be successfully used for PFASs analysis in drinking water.**
- **High-throughput analysis of PFASs using LDTD-MS/MS**
- **Precision and accuracy within the acceptance criteria.**
- **Sample-to-sample analysis of 10 seconds**

REFERENCES

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

COI Disclosure: I have a financial relationship with Phytronix Technologies as a salaried employee.