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Identification and Quantification of PFAS in Food Contact Materials Using a Kinetex™ C18 Column Coupled with the MRM^{HR} Workflow on the SCIEX® X500R QTOF System

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Introduction

In comparison to other surfactants, perfluorinated alkyl substances (PFAS) have stable physiochemical structures with hydrophobic and oleophobic properties. They are widely used in industrial and consumer products like plastic packaging materials for food and as coating in non-stick pans. Due to their chemical stability and low reactivity, PFAS are highly resistant to degradation even in living organisms and can therefore be accumulated in the food chain. Human exposure to PFAS residues has been implicated in incidences of cancer, obesity, endocrine system disruption, and other adverse health effects.

With the rapid growth in the food delivery industry in China (and globally) in the past two years, one-time-use plastic packaging materials are widely used by merchants due to their low cost and high durability. One-time-use plastic packaging is made of fluorinated high-density polyethylene (HDPE). During the fluorination of HDPE containers (the process of creating the high-performance barrier designed to reduce permeation through container walls and protect against degradation) PFAS compounds may be formed and then partly leach into the products inside the containers.

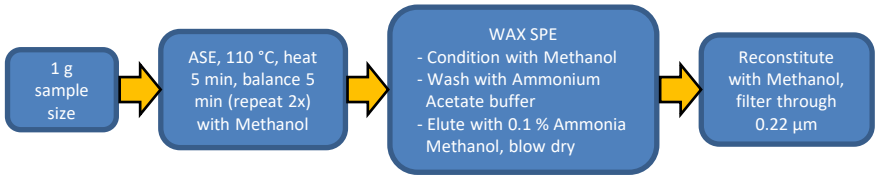
In China, the level of PFOS and PFOA in food contact materials and products is regulated according to the latest National Food Safety Standard (GB 31604.35-2016). The detection limit is set at 1.0 ng/g while the quantification limit is set at 2.0 ng/g. In 2006, the European Union (EU) has set a regulation that the level of PFOS in finished products should not exceed 0.005 % of the product mass. In this technical note, we analyzed a total of eight samples collected from different type of containers made of polyethylene, polystyrene and polytetrafluoroethylene.

For accurate PFAS analysis, the isolation of interfering ions is crucial but can be achieved through a combination of chromatographic resolution, fast scan speeds, and High-Resolution Accurate Mass systems. The Kinetex core-shell C18 column provides increased sensitivity and efficiency, yielding remarkable chromatographic resolution. The SCIEX X500R QTOF system has the industry's fastest scanning speed, allowing for the implementation of the unique MRM^{HR} acquisition mode to provide excellent quantitative performance using high-resolution MS/MS data. This approach to quantitation with LC-QTOF-MS/MS minimizes matrix interferences and the patented Turbo V ion source with curtain gas interface, twin sprayer technology, and built-in automatic calibration system help to improve and maintain instrument robustness and maintain high mass accuracy results. The high-resolution MS/MS spectra can also be used for qualitative analysis by calculating the ion ratio for confirmation, thus reducing false positives by taking advantage of the data acquired on the LC-QTOF platform.

Sample Preparation

The food packaging material to be tested is cut into small pieces. For coating sample, scrape it with a small knife. The sample preparation procedure was adapted from National Standard of China (document number GB 31604.35-2016) which was implemented on 19 April 2017.

A total of eight samples were collected as test samples which include disposable meal box, plastic bag, beverage bottle, coating of non-stick pan, etc. Packaging materials in the collected samples were mainly polyethylene, polystyrene and polytetrafluoroethylene.



LC Conditions

Column: Kinetex 2.6 µm C18
Dimensions: 100 x 2.1 mm
Part No.: 00D-4462-AN
Mobile Phase: A: 5 mM Ammonium Acetate in Water
B: 5 mM Ammonium Acetate in Methanol

Gradient:

Time (min)	%B
0	10
2.5	30
12	100
13	100
13.1	10
17	10

Flow Rate: 0.3 mL/min
Injection Volume: 5 µL
Temperature: 40 °C
LC System: SCIEX ExionLC™
Detection: MRM^{HR}
Detector: SCIEX X500R QTOF, with Turbo V™ Ion Source

MRM^{HR} Conditions

Polarity: Negative
DP: -80 V
CE: -35 V
Source Temperature: 500 °C
GS1: 50 psi
GS2: 55 psi
CUR: 30 psi
CAD: 7
ISV: -4500 V

MRM^{HR} Transitions

	Compound ID	Group Name	Precursor Ion (Da)	Fragment Ion (Da)
1	PFBA	PFBA	212.90	168.90
2	PFPeA1	PFPeA	262.90	218.90
3	PFPeA2	PFPeA	262.90	69.00
4	PFBS 1	PFBS	298.90	80.00
5	PFBS 2	PFBS	298.90	99.00
6	PFHxA1	PFHxA	312.90	268.90
7	PFHxA 2	PFHxA	312.90	119.00
8	PFHxS 1	PFHxS	362.90	318.90
9	PFHxS 2	PFHxS	362.90	168.90

Results and Discussion

Chromatogram of 17 PFAS using a Kinetex™ C18 column utilizing extracted precursor ion data from TOF-MS scan are shown (**Figure 1**).

Comparing 0.2 ppb post spiked in matrix blank, PFHpA show higher selectivity in MRM^{HR} mode as compared to TOF-MS mode for quantification (**Figure 2**). Monitoring the high-resolution fragment ion from the full scan MS/MS data collected provides greater specificity and reduced baseline, so signal-to-noise demonstrates marked improvement and method sensitivity is maximized.

The 17 monitored PFAS demonstrate good linearity and accuracy (**Figure 3**) with the correlation coefficients above 0.99. Accuracy values are within the permissible deviation range for LOD and LOQ according to the national standards.

Ion ratios can be easily calculated using the SCIEX® OS software. Ion ratio confirmation can be visually displayed in the chromatogram and result table. Depending on the requirement, the confirmation tolerance can be defined using either constant tolerance or variable tolerance as shown in **Figure 4**.

SCIEX OS software combines both qualitative and quantitative results in one single interface (**Figure 5**). The result table show the retention time, concentration, peak area, ion ratio confirmation and the mass error of 0.9 ppm for a sample tested positive with PFOA.

Among the eight samples, eight types of PFAS were detected as shown in **Table 1**. Two out of eight samples have levels which exceeded regulated level of 1 ng/g by national standard. Most of the detected PFAS are the acid derivatives of PFOA and primarily found in non-stick pan coating and disposable meal boxes. The number of actual samples collected in this test is rather small; hence statistically it does not imply that all related products are unsafe for consumers.

Figure 1. TOF-MS Extracted Ion Chromatogram of 17 PFAS using a Kinetex C18 Column.

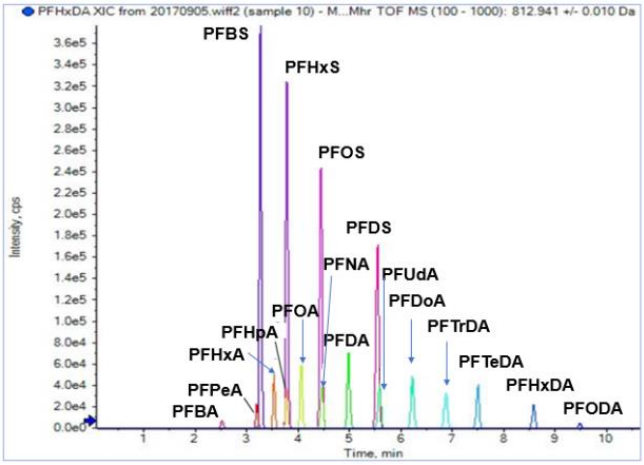


Figure 2. Signal-to Noise Comparison of PFHpA using TOF-MS and MRM^{HR} Data Using a Post Spiked 0.2 ppb Matrix Blank.

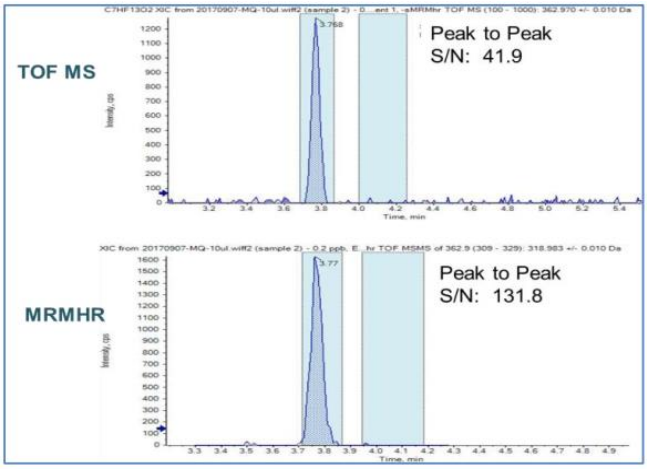


Figure 3. Calibration Curve of 17 PFAS with Acceptable Accuracy and Linear Response.

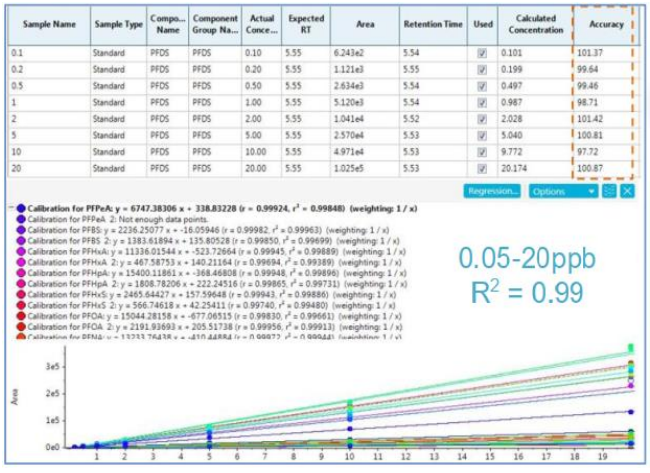


Figure 4. Setting Up Tolerance for Ion Ratios Confirmation.

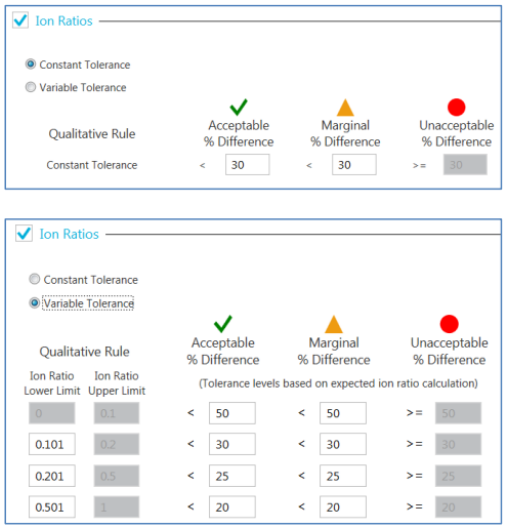


Figure 5. PFOA Results in Actual Sample.

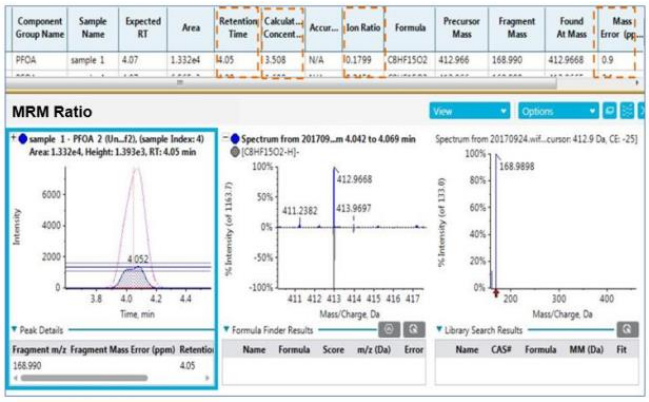


Table 1. PFAS Content in Different Food Contact Samples.

	Detected Amount (ng/g)							
	PFHxA	PFHpA	PFOA	PFDA	PFuDA	PFDoA	PFTrDA	PFTeDA
Meal box 1	0.14	0.16	3.15	-	-	-	-	-
Meal box 2	-	-	3.12	-	-	-	-	-
Plastic bag 1	-	-	-	-	-	-	-	-
Plastic bag 2	-	-	-	-	-	-	-	-
Drinking bottle 1	-	-	-	-	-	-	-	-
Drinking bottle 2	-	-	-	-	-	-	-	-
Non-stick pan 1	-	-	-	0.11	0.15	0.13	0.15	-
Non-stick pan 2	-	-	-	-	-	-	-	0.17

Conclusion

The SCIEX® X500R QTOF system and SCIEX OS software, coupled with a Kinetex™ C18 HPLC column, brings powerful performance capabilities for routine testing of PFAS. The unique MRM^{HR} quantification method enables high selectivity even in real sample with matrix interference. This improves the detection and quantification of PFAS which can meet the EU regulation and national standards in China. Although the concentration of PFAS in most of the test samples falls below the regulated level, the detection rate of PFAS is relatively high indicating that the quality of food contact/packaging materials may pose potential risks on consumer's health.

Kinetex™ Ordering Information

2.1 µm Minibore Columns (mm)						SecurityGuard™ ULTRA Cartridges‡
Phases	30 x 2.1	50 x 2.1	75 x 2.1	100 x 2.1	150 x 2.1	3/pk
EVO C18	00A-4725-AN	00B-4725-AN	—	00D-4725-AN	00F-4725-AN	AJ0-9298
PS C18	00A-4780-AN	00B-4780-AN	—	00D-4780-AN	00F-4780-AN	AJ0-8951
Polar C18	00A-4759-AN	00B-4759-AN	—	00D-4759-AN	00F-4759-AN	AJ0-9532
Biphenyl	00A-4622-AN	00B-4622-AN	—	00D-4622-AN	00F-4622-AN	AJ0-9209
XB-C18	00A-4496-AN	00B-4496-AN	00C-4496-AN	00D-4496-AN	00F-4496-AN	AJ0-8782
C18	00A-4462-AN	00B-4462-AN	00C-4462-AN	00D-4462-AN	00F-4462-AN	AJ0-8782
C8	00A-4497-AN	00B-4497-AN	00C-4497-AN	00D-4497-AN	00F-4497-AN	AJ0-8784
HILIC	00A-4461-AN	00B-4461-AN	00C-4461-AN	00D-4461-AN	00F-4461-AN	AJ0-8786
Phenyl-Hexyl	00A-4495-AN	00B-4495-AN	00C-4495-AN	00D-4495-AN	00F-4495-AN	AJ0-8788
F5	00A-4723-AN	00B-4723-AN	—	00D-4723-AN	00F-4723-AN	AJ0-9322

for 2.1 mm ID

‡SecurityGuard ULTRA Cartridges require holder, Part No.: AJ0-9000

PFAS CRM Native Standards. All analytes at the same concentration in acid form for easy calculation and dilution.

Product	Part	Volume	Concentration
EPA 533 mix	AL0-101838	1 mL	2 µg/mL in Methanol
EPA 537.1 mix	AL0-101839	1mL	2 µg/mL in Methanol
EPA 533 + 537.1 mix	AL0-101840	1 mL	2 µg/mL in Methanol

Custom CRMs available. Contact Phenomenex for details.

Other Recommended Products for Your PFAS Methods

Description	Part No.
Luna™ Omega Column 3 µm PS C18 50 x 3 mm	00B-4758-Y0
Kinetex™ EVO Column 5 µm C18 100 x 2.1 mm	00D-4633-AN
Strata™ PFAS (WAX/GCB) SPE 200 mg, /50 mg, /6mL tubes, 30/pk	CS0-9207
Strata SDB-L 500 mg/6mL tubes, 30/pk	8B-S014-HCH
Verex™ Vial, 9 mm Screw, PP, 1.7 mL, 1000/pk	AR0-39P0-13
Verex Vial, 9 mm Screw, PP, 300 µL, 1000/pk	AR0-39P2-13
Verex Vial, 9 mm Screw, PP, 700 µL, 1000/pk	AR0-39P1-13
Vial Cap Verex Cert+ Cap (one piece), 9 mm, PE w/ Starburst pre-Slit, 2mL, 1000/pk	AR0-89P6-13-C

Columns and vials available in multiple sizes. Contact Phenomenex for details.

Need a different column size or sample preparation format?

No problem! We have a majority of our available dimensions up on www.phenomenex.com, but if you can't find what you need right away, our super helpful Technical Specialists can guide you to the solution via our online chat portal www.phenomenex.com/Chat.

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