

Identification and Quantification of PFAS in Food Contact Materials using MRM^{HR} on the X500R QTOF System

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Background

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. [1]

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 [2]. One-time-use plastic has become a source of public concern and environmental pollution. Given the tremendous persistence of PFAS in the environment and the adverse effect on human health, monitoring of PFAS residue has gained traction in China and elsewhere.

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 1.0ng/g while the quantification limit is set at 2.0ng/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.



The 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

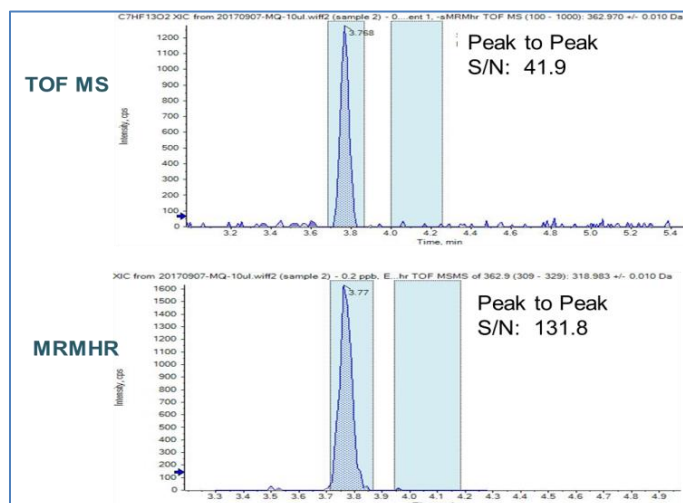


Figure 1. Signal-to-noise comparison of PFHpA using TOF-MS and MRM^{HR} data using a post spiked 0.2 ppb matrix blank. Monitoring the transition and the high resolution fragment ion results in greater specificity and reduced baseline, so signal-to-noise demonstrates marked improvement and method sensitivity is maximized.

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.

Key Workflow Advantages

- PFAS quantitation is demonstrated on the X500R QTOF system using an easily set up method and minimal method development
- 10-minute run time using a Phenomenex Kinetex® C18 column demonstrates separation of PFAS targets
- The advantage of MRM^{HR} selectivity over simply monitoring the high resolution molecular ion in TOF MS mode can be observed in the improvement in signal-to-noise results for the monitored MRM^{HR} transition
- QTOF technology can be utilized for quantitative analysis of PFAS suite without compromising method performance (excellent sensitivity, linearity demonstrated) or ion ratio reporting

Experimental Process

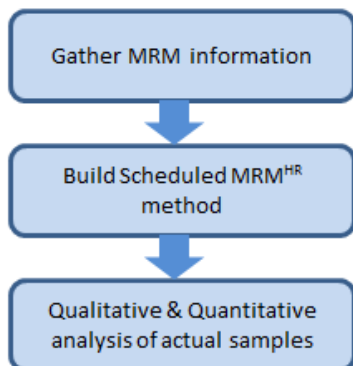


Figure 2. Setting up the acquisition method of PFAS using Scheduled MRM^{HR} Method. The Scheduled MRM^{HR} method, which monitors for selected target transitions only at the retention time at which they are expected to elute, is built using retention times (RTs) determined with the method LC and column configuration.

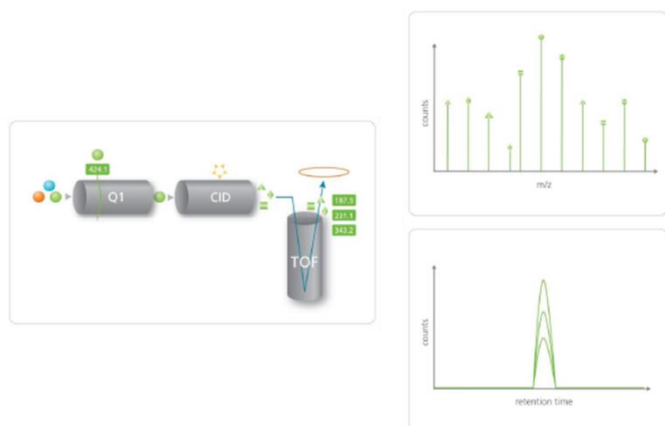


Figure 3. Schematic Diagram of MRM^{HR} scan type. In this type of data acquisition, a defined precursor mass is isolated in the quadrupole (Q1) and fragmented in the collision cell (CID). The fragment ions are separated by mass in the TOF tube and detected.

Sample Preparation

1. Sample pre-treatment

The food packaging material to be tested is cut into small pieces. For coating sample, scrape it with a small knife.

2. Extraction and clean-up

The sample preparation procedure was adapted from National Standard of China (document number GB 31604.35-2016) which is implemented on 19 April 2017 (Figure 4).

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.

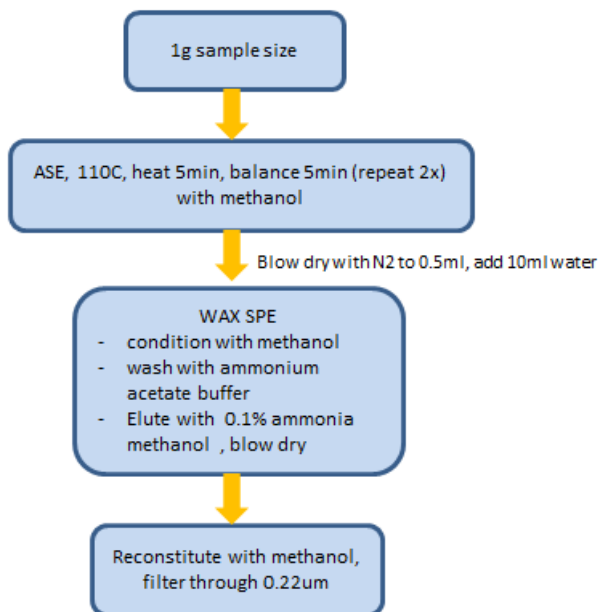


Figure 4. Extraction and Clean-up Process Flow Diagram.

LC-MS Method



LC conditions:

Chromatographic column: Phenomenex Kinetex, 2.6 μ m C18, 100 X 2.0 mm

Mobile phase A: 5mM NH₄AC; B: methanol with 5mM NH₄AC

Flow rate: 0.3mL/min; Gradient elution

Column temperature: 40C

X500R MS conditions:

Scan mode: Scheduled MRM^{HR}

ESI mode, negative

CUR: 30psi; CAD: 7; IS: -4500V; Source temperature: 500 $^{\circ}$ C;

GS1: 50psi; GS2: 55psi

Setting Up MRM^{HR} Quantitative Method

The SCIEX OS software is fully automated with a user-friendly interface. The MRM parameters can be set up easily in two

different ways. This greatly reduces the time taken to set up a new acquisition method. For compounds which are in MSMS spectral library, fragment ions can be imported easily from the library to build the MRM^{HR} list. Up to 5 fragment ions can be imported at the same time using a single click. For compounds not already found in the spectral library, spectra can be added easily to the library using TOF MS-IDA-MS/MS data acquired for standards of the desired targets.

MRM parameters like retention time, declustering potential (DP) and collision energy (CE) from an existing triple quadrupole method are fully transferrable, as shown in Figure 5. In this acquisition method, 17 derivatives of PFAS were monitored.

Mass Table								
<input checked="" type="radio"/> Apply fragment ion mass <input type="radio"/> Apply TOF start/stop mass <input checked="" type="checkbox"/> Apply scan schedule								
Compound ID	Compound name	Group name	Precursor ion (Da)	Fragment ion (Da)	Accumulation time (sec)	Declustering potential (V)	Collision energy (V)	Retention time (min)
1	PFBA	PFBA	212.90	168.9000	0.0600	-80	-35	2.55
2	PFPeA 1	PFPeA	262.90	218.9000	0.0600	-80	-35	3.22
3	PFPeA 2	PFPeA	262.90	69.0000	0.0600	-80	-35	3.22
4	PFBS 1	PFBS	298.90	80.0000	0.0600	-80	-35	3.29
5	PFBS 2	PFBS	298.90	99.0000	0.0600	-80	-35	3.29
6	PFHxA 1	PFHxA	312.90	268.9000	0.0600	-80	-35	3.55
7	PFHxA 2	PFHxA	312.90	119.0000	0.0600	-80	-35	3.55
8	PFHxS 1	PFHxS	362.90	318.9000	0.0600	-80	-35	3.79
9	PFHxS 2	PFHxS	362.90	168.9000	0.0600	-80	-35	3.79

Figure 5. Scheduled MRM^{HR} Method Setup in SCIEX OS. Unique RTs can be defined for each transition for each analyte.

Experimental Results

Chromatogram of 17 PFAS utilizing extracted precursor ion data from TOF-MS scan are shown (Figure 6).

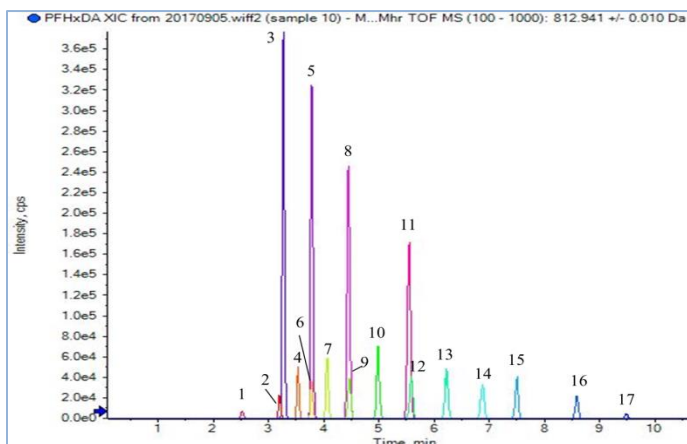


Figure 6. TOF MS Extracted Ion Chromatogram of 17 PFAS:
 1-PFBA; 2-PFPeA; 3-PFBS; 4-PFHxA; 5-PFHxS; 6-PFHxA; 7-PFOA; 8-PFOS; 9-PFNA; 10-PFDA; 11-PFDS; 12-PFUdA; 13-PFDoA; 14-PFTTrDA; 15-PFTeDA; 16- PFHxDA; 17- PFOA.

1. High selectivity data

Comparing 0.2 ppb post spiked in matrix blank, PFHxA show higher selectivity in MRM^{HR} mode as compared to TOF-MS mode for quantification (Figure 1). Monitoring the transition and the high resolution fragment ion results in greater specificity and reduced baseline, so signal-to-noise demonstrates marked improvement and method sensitivity is maximized.

2. Linearity and accuracy

The 17 monitored PFAS demonstrate good linearity and accuracy as shown in Figure 7 with the correlation coefficients above 0.99. Accuracy values are within the permissible deviation range for LOD and LOQ according to the national standard.

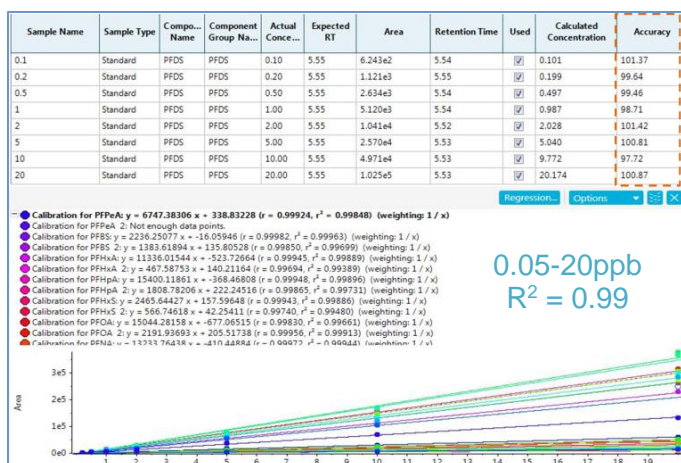


Figure 7. Calibration curve of 17 PFAS with acceptable accuracy and linear response.

3. Ion ratio Calculation

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 8.

4. Sample results

SCIEX OS software combines both qualitative and quantitative results in one single interface as shown in Figure 9. The result table show the retention time, concentration, peak area, ion ratio confirmation and the mass error of 0.9ppm 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 1ng/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

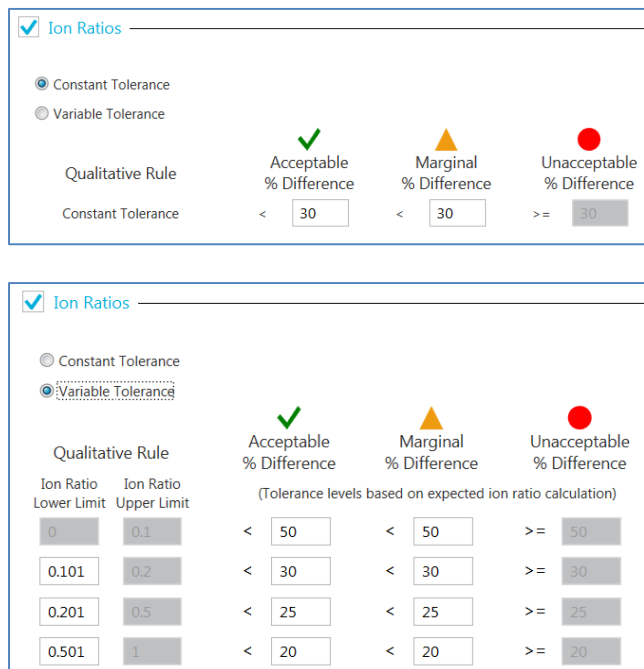


Figure 8. Setting up Tolerance for Ion Ratios Confirmation. Constant tolerance (same percent difference from measured standard ion ratio) or variable tolerance (varying percent difference dependant on concentration level) can be utilized when determining whether an unknown same meets the criteria for qualitative analyte identification by ion ratio confirmation. Different levels of percent difference can be defined by the user to be flagged as within “Acceptable,” “Marginal,” or “Unacceptable.”

rather small; hence statistically it does not imply that all related products are unsafe for consumers.

Summary

The SCIEX X500R QTOF system and SCIEX OS software 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 perfluorinated alkyl substances is relatively high indicating that the quality of food contact/packaging materials may pose potential risks on consumer’s health.

References

1. Xu R, Tan H, Yang H B, et al. Food and Fermentation Industries, 2014, 40(10): 205.
2. Kannan K, Tao L, Sinclair E, et al. Arch Environ Con Tox, 2005, 48: 559
3. GB 31604.35-2016, National Food Safety Standard - Food contact materials and products - Determination of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

Table 1. PFAS Content in Different 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	-	-	-	-	-	-	-	-
Drink bottle 1	-	-	-	-	-	-	-	-
Drink bottle 2	-	-	-	-	-	-	-	-
Non-stick pan 1	-	-	-	0.11	0.15	0.13	0.15	-
Non-stick pan 2	-	-	-	-	-	-	-	0.17

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