SHIMADZU RJ Lee Group

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Development of a Standard PFAS Method for the Evaluation of PFAS in Food Contact Materials

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS), often referred to as "forever chemicals," have gained significant attention due to their persistence in the environment, bioaccumulation potential, and adverse health effects. PFAS was manufactured for desirable water resistant, oil resistant, and heat resistant properties. Since the 1940's industries have integrated PFAS in products such as food packaging, textiles, and household products due to these properties. In response to growing concerns regarding consumer exposure to PFAS, many states have initiated bans of PFAS uses in various consumer products and food packaging. This led to a need for analytical testing to determine the amount of PFAS in these products. The lack of standardized methods presents challenges in ensuring reliability and reproducibility between labs. This application further advances the collaborative efforts between Shimadzu Scientific Instruments and RJ Lee Inc., to develop methodology for monitoring PFAS in diverse matrices. This newly developed method is specifically designed to detect and quantify PFAS in various food packaging materials. Various packaging samples were analyzed on a Shimadzu triple quadrupole mass spectrometer LCMS-8060NX (**Figure 1**) in accordance with ASTM guidelines.[1]

Figure 1. Shimadzu LCMS-8060NX

2. Methods

Stock standard solutions containing native analytes and labeled isotopes (surrogates) were diluted from commercially available mixed or single stock standards using a 95:5 methanol:water mixture. A9-point calibration curve was prepared in 50:50 (vol:vol) methanol:water with 0.1% acetic acid.

A total of seventeen food packaging materials, including hard plastics, soft plastics, and paper products, were purchased from a local grocery store to represent a broad range of products. **Table 1** summarizes the purchased matrices.

Table 1. Food packaging materials in each representative category of matrix

Food Packaging Material Matrices		
Hard Plastic	**Soft Plastic**	**Paper**
Lettuce clamshell	TetraPak milk container	Freezer paper
Potato chip snack container	Squeezable baby food	Baking cup liners
Single serve coffee pod	Microwavable rice bags	Coffee filters
Herb container		Raisin containers
Chocolate container		Paper plates
Baby food container		Snack cracker bags
		Microwavable noodle cups
		Aluminum Foil

To prepare the samples each item was cut into representative 0.5 g sub-samples using either scissors or a razor blade that were cleaned with acetonitrile and methanol rinses in between each excision. Cleaning was necessary to prevent any possible PFAS contamination from the matrix.

Each material purchased was processed following the sample preparation procedure outlined in **Figure 2** and analyzed with conditions in **Table 2.**

Figure 2. Sample preparation procedure for concrete samples

Table 2. Analytical conditions for food packaging materials PFAS assay

[LC] Nexera	
Mobile Phase (LCMS Grade)	A: 2 mmol/L Ammonium Acetate in H_2O/ Acetonitrile = 95/5 B: Acetonitrile
Delay Column	Shimadzu Nexcol PFAS Delay 50 mm x 3.0 mm, 5 µm (P/N: 220-91394-09)
Analytical Column	Shim-pack Scepter C18-120 2.1 mm x 100 mm, 3 µm (P/N: 227-31014-05)
Gradient (%B)	10% (0.5 min) ⇒22% (2.3-3.0 min) ⇒45% (6.0 min) ⇒ 75% (12.0 min) ⇒95% (12.1-14.0 min) ⇒10% (14.1-17.0 min)
Column Oven Temp.	45 ℃
Flow rate	0.45 mL/min
Multiple draw injection program	Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O → Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O
Autosampler Rinsing	60/40 Acetonitrile/2-propanol, Before/After Aspiration 5 seconds
[MS] LCMS-8060NX	
Interface Temp.	170℃
Probe position	+3 mm
Nebulizer gas flow	3 L/min
Heating gas flow	15 L/min
Interface Voltage	-0.5 kV (same value for all compounds)
DL Temp.	200 ℃
Heatblock Temp.	300 ℃
Drying gas flow	8 L/min

3. Results

Linear calibration curves were generated for each native and surrogate compound. **Table 3** shows the in-vial calibration range for each compound/surrogate, the passing calibration criteria, and the final reporting range in the packaging product.

Table 3. Summary of calibration data for native analytes

Compound	Calibration Range In-Vial (ng/L)	Calibration Curve Criteria	Reporting Range (ng/kg)
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFNA, PFOA, PFHpA, PFHxA, PFDS, PFNS, PFOS, PFHpS, PFHxS, PFPeS, PFBS, PFOSA, 8:2FTS, 6:2FTS, 4:2FTS, NEtFOSAA, NMeFOSAA, PFDoS, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, NFDHA, PFEESA, PFMPA, PFMBA, 5:3 FTCA, 7:3 FTCA, FHUEA, FOUEA, HQ-115, SURROGATES	5-200	R^2 > 0.99 RSE < 30% RF RSD < 30%	100-4000
PFBA, PFPrA, 6:2-diPAP	50-1000		1000-20000
PFPeA	25-1000		500-20000
3:3 FTCA	10-200		200-4000

Example chromatogram shown in **Figure 3** was achieved with the developed method. Adequate peak shape was attained for early eluting compounds using the co-injection function. All the compounds were eluted within 11.5 minutes.

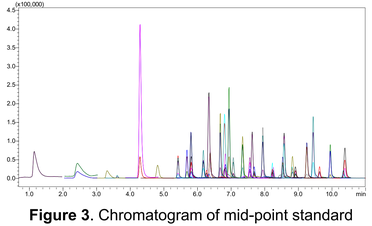

Figure 3. Chromatogram of mid-point standard

Recovery and repeatability were evaluated for the surrogates in each matrix. Example matrix was spiked with surrogate spiking solution at 1600 ng/kg in **Figure 4**, based on a 0.5g sample.

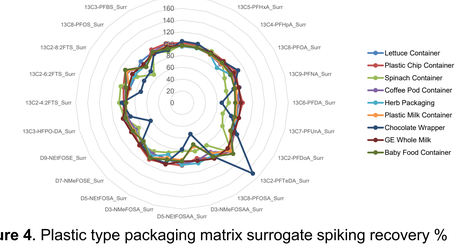

Figure 4. Plastic type packaging matrix surrogate spiking recovery %

The soft plastic type food packaging matrix was spiked with surrogate spiking solution at 1600 ng/kg in **Figure 5**, based on a 0.5g sample. **Figure 6** shows the native spiking recovery experiment for an example foil matrix.

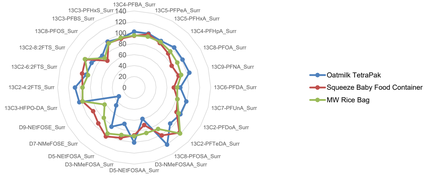

Figure 5. Plastic type packaging matrix surrogate spiking recovery %

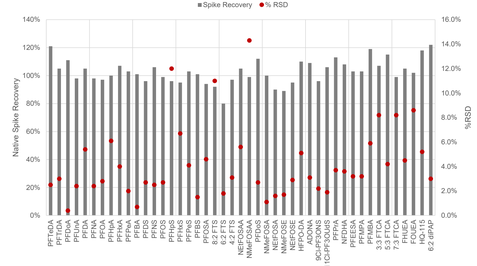

Figure 6. Foil type packaging material spiked at 1800 ng/kg with native PFAS, spike recovery and RSD % (n=3)

4. Conclusion

This work demonstrates the analysis of 45 PFAS and 25 surrogate compounds in food packaging matrices using a newly developed method employing a Shimadzu LCMS-8060NX LC-MS/MS system. The extraction procedure, chromatography, and mass spectrometry conditions were optimized to ensure optimal sensitivity for the co-solvation sample preparation procedure. These conditions resulted in a method that eliminates the need for solid phase extraction, therefore significantly reducing cost and time associated with solid-phase extraction sample preparation methodologies. Target analytes were quantitated using either an 8- or 9-point calibration curve with a resulting reporting range between 100-20,000 ng/kg (dependent on analyte, **Table 3**).

Reference

1) ASTM D8421-21