Determination of 30 PFAS in Milk by Liquid Chromatography Triple Quadrupole Mass Spectrometry (LC-MS/MS)

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1. Introduction

PFAS have been linked to serious health effects, yet are found contaminating waters, feeds, livestock, and farmland. Accurate testing methods are needed to assess risk and prevent exposure. Testing food comes with complications, like matrix effects that can interfere with detection. Sensitive equipment and robust preparation methods are needed to detect PFAS in food. To address this, we describe a single laboratory validation study with a rapid extraction of low concentrations of 30 PFAS from high-fat milk using the QuEChERS technique followed by analysis using the Shimadzu Nexera Liquid Chromatograph coupled to the LCMS-8060NX triple quadrupole mass spectrometer (Figure 1).

In this study, we spiked samples at three concentrations in triplicate. For greater accuracy, standards were matrix-matched and extracted; spikes were quantified using isotope dilution. Recovery and precision were compared to the requirements of AOAC SMPR 2023.003. All recovery, precision, and limits of quantitation met the acceptance criteria of the SMPR.

2. Methods

Whole milk (3.7 % fat) was purchased and sampled directly from the carton. Test portions were spiked in triplicate at three different concentrations with 30 native PFAS and 16 isotopically labeled internal standards. Calibration curves were spiked with 0.05, 0.10, 0.50, 1.0, 5.0, and 10 ng of each target analyte. Quantitation was carried out on additional whole milk samples spiked in triplicate at 0.01, 0.10 & 1.0 ng/g.

Ten-gram portions were weighed, spiked with target analytes and internal standards, and 150 µL of formic acid and 10 mL of acetonitrile was added. The samples were shaken for 10 seconds, QuEChERS reagents was added followed by dispersive SPE. Details can be found in the application news of the same title. Adequate separation of all compounds was achieved in nine minutes. (Figure 2).

For this study, Shimadzu evaluated 1984 different instrument settings, and 6 different column and gradient combinations to achieve excellent peak shape and resolution between peaks, as well as to maximize the signal-to-noise ratio of PFOA, PFHxS, PFNA, and PFOS. Chromatography was adjusted to provide sufficient separation of PFOA from potential cholic acid interferences, and to provide baseline resolution of branched and linear isomers (Figure 3).

Fig. 1 Nexera™ and LCMS™-8060NX

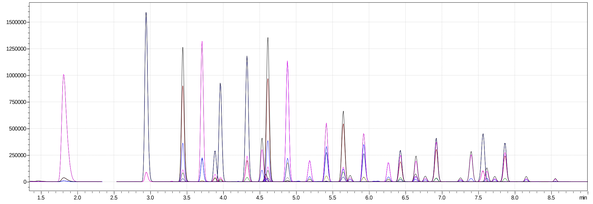

Fig. 2 Chromatogram of 0.1 ng/g PFAS in a milk matrix with separation of all peaks in nine minutes

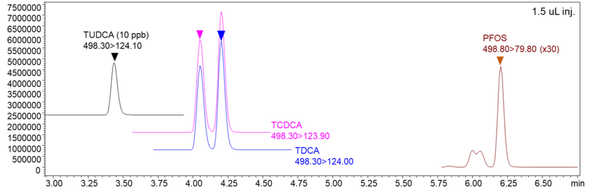

Fig. 3 Separation of PFOS from Cholic Acids and baseline resolution between PFOS branched and linear isomers

3. Results

Calibration standards were processed the same as samples. A linear model provided the best fit and best recoveries of analytes. Residuals of each point in the curve were ±25% of the expected value. Branched and linear isomers of PFHxS and PFOS were integrated together. Exact labeled analogs, where available, were used as isotope dilution standards.

Recovery and repeatability for each analyte at each concentration are given in Table 1. The LOQ for each analyte was estimated by spiking at concentrations at, or below, the required LOQs listed in SMPR 2023.003. The Limit of Quantitation (LOQ) was determined as the lowest concentration meeting requirements for accuracy, precision, ion ratio, retention time, and signal-to-noise ratio criteria of the qualifier ion.

Table. 1 Recovery and repeatability for each analyte at each spike concentration

Analyte	Spike conc. (ng/g)	Average conc. (ng/g)	%RSD	Average Recovery %
PFBA	Blank	0.000		
	0.01	0.012	7.02	116.8
	0.1	0.103	2.02	103.5
	1	0.973	0.58	97.3
PFPeA	Blank	0.000		
	0.01	0.011	2.45	107.1
	0.1	0.099	0.66	99.3
	1	0.947	0.40	94.7
PFHxA	Blank	ND		
	0.01	0.010	1.67	104.4
	0.1	0.096	0.97	96.1
	1	0.947	0.11	94.7
PFHpA	Blank	0.001		
	0.01	0.011	6.79	116.2
	0.1	0.099	0.45	99.4
	1	0.968	1.55	96.8
PFOA	Blank	ND		
	0.01	0.010	11.35	104.3
	0.1	0.098	2.93	98.5
	1	0.977	1.02	97.7
PFNA	Blank	0.000		
	0.01	0.011	0.86	112.2
	0.1	0.100	0.93	99.5
	1	0.976	0.62	97.6
PFDA	Blank	0.001		
	0.01	0.011	2.59	112.7
	0.1	0.104	0.40	104.2
	1	0.994	2.73	99.4
PFUnA	Blank	0.000		
	0.01	0.011	1.08	111.5
	0.1	0.101	0.83	100.9
	1	0.980	0.74	98.0
PFDoA	Blank	0.000		
	0.01	0.012	11.65	117.1
	0.1	0.101	1.52	101.3
	1	0.951	1.55	95.1
PFTrDA	Blank	0.000		
	0.01	0.011	2.24	106.9
	0.1	0.101	1.59	100.9
	1	0.994	0.68	99.4
PFTeDA	Blank	0.000		
	0.01	0.011	3.80	108.8
	0.1	0.098	0.68	98.2
	1	0.974	3.49	97.4
PFBS	Blank	ND		
	0.01	0.012	7.19	118.1
	0.1	0.102	1.62	101.6
	1	0.958	0.26	95.8
PFPeS	Blank	ND		
	0.01	0.010	11.41	98.7
	0.1	0.102	1.03	101.9
	1	0.953	1.70	95.3
PFHxS	Blank	0.000		
	0.01	0.010	10.76	97.6
	0.1	0.099	3.89	99.6
	1	0.956	1.42	95.6
PFHpS	Blank	ND		
	0.01	0.010	6.85	106.0
	0.1	0.105	2.17	104.4
	1	0.983	2.14	98.3
PFOS	Blank	ND		
	0.01	0.010	6.54	98.4
	0.1	0.099	2.59	99.2
	1	0.961	1.37	96.1

ND = average results less than zero

Table. 1 Continued

Analyte	Spike conc. (ppb)	Average conc. (ppb)	%RSD	Average Recovery %
PFNS	Blank	ND		
	0.01	0.010	10.20	100.4
	0.1	0.102	2.81	101.8
	1	0.992	2.60	99.2
PFDS	Blank	ND		
	0.01	0.009	3.95	94.8
	0.1	0.103	5.95	103.0
	1	1.015	1.20	101.5
PF UnDS	Blank	ND		
	0.01	0.011	2.01	109.3
	0.1	0.105	4.56	105.0
	1	0.988	3.54	98.8
PFDoS	Blank	ND		
	0.01	0.010	9.15	97.0
	0.1	0.101	2.22	100.6
	1	0.963	2.36	96.3
PFTrDS	Blank	ND		
	0.01	0.010	4.83	106.0
	0.1	0.099	3.32	99.4
	1	0.990	2.10	99.0
PFOSA	Blank	ND		
	0.01	0.011	3.36	106.8
	0.1	0.099	1.85	99.0
	1	0.950	0.58	95.0
9Cl-PF3ONS	Blank	0.000		
	0.01	0.010	4.31	102.5
	0.1	0.103	0.94	102.5
	1	0.971	3.25	97.1
11Cl-PF3OUdS	Blank	ND		
	0.01	0.009	5.61	94.8
	0.1	0.101	1.09	100.8
	1	0.992	1.23	99.2
HFPO-DA	Blank	ND		
	0.01	0.010	7.19	99.6
	0.1	0.099	2.18	99.3
	1	0.932	0.86	93.2
DONA	Blank	0.000		
	0.01	0.010	0.77	103.9
	0.1	0.099	0.42	98.9
	1	0.961	2.21	96.1
4:2 FTS	Blank	ND		
	0.01	0.011	4.63	107.5
	0.1	0.102	2.69	102.1
	1	0.989	1.29	98.9
6:2 FTS	Blank	0.001		
	0.01	0.012	10.39	114.6
	0.1	0.106	4.80	105.5
	1	0.984	1.43	98.4
8:2 FTS	Blank	0.001		
	0.01	0.012	6.86	116.7
	0.1	0.097	1.57	97.1
	1	0.888	0.26	88.8
10:2 FTS	Blank	0.000		
	0.01	0.011	10.09	108.4
	0.1	0.095	3.43	95.4
	1	0.862	1.42	86.2

4. Conclusion

The Shimadzu LCMS-8060NX Triple Quadrupole Mass Spectrometer coupled with a Shimadzu Nexera Liquid Chromatograph was used in a single laboratory study to measure 30 PFAS compounds in a high-fat milk matrix and compared to criteria set by AOAC SMPR 2023.003. Chromatography conditions and the mass spectrometer were optimized to achieve excellent separation of all analytes, baseline resolution between isomers, and a separation between PFOS and potentially interfering cholic acids in only nine minutes.

Precision and recovery and the experimentally determined LOQ are well within the requirements of the AOAC SMPR 2023.003.

Related Products Some products may be updated to newer models.

› LCMS-TQ RX Series
Triple Quadrupole LC-MS/MS

› Nexera series
Ultra High Performance Liquid Chromatograph

› LCMS-8060NX
Liquid Chromatograph Mass Spectrometer

Related Solutions

› Food Contamination

› Price Inquiry

› Product Inquiry

› Technical Service / Support Inquiry

› Other Inquiry