Application News

GCMS-TQ™8040 NX Triple Quadrupole Mass Spectrometer

Volatile PFAS in Complex Juice Matrices: A Simple Approach Using HS-SPME GC/MS/MS for Volatile Contaminant Analysis

Andy Sandy, Dominika Gruszecka, Ruth Marfil-Vega, Alan Owens, Evelyn Wang
Shimadzu Scientific Instruments, Inc.

User Benefits

- The highly sensitive and selective Shimadzu GCMS-TQ8040 NX triple quadrupole mass spectrometer enables low limits of quantitation for volatile PFAS with minimal matrix interferences.
- The simplified sample preparation procedure and automated SPME method using a multifunctional autosampler (AOC-6000 Plus) reduces the operation error for PFAS analysis.
- The Shimadzu HS-SPME GC/MS/MS system is capable of analyzing volatile PFAS in juice matrices with minimal sample preparation.
- HS-SPME GC/MS/MS is used as a complementary technique to LC/MS in providing a total solution for food safety.

Background

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic organic chemicals that have been widely used in products such as nail polish and food packaging.[1,2] In recent years, PFAS pollution has become a major global concern due to its link to a variety of serious health issues. Yet, many health impacts associated with PFAS remain poorly understood.[3] As a result, the true extent of PFAS contamination may be underestimated. To better address these concerns and fully assess PFAS pollution, it is crucial to detect and measure PFAS in the environment and other impacted matrices.

Juices, as one of the PFAS-contaminated matrices, have been drawing media attention. This beverage is a complex natural product matrix that consists of sugars, salts, food coloring, preservatives, vitamins, and other additives. Juice matrices vary due to diverse flavor profiles, differences in manufacturing processes, and assorted packaging that may leach various substances into the product. The United States Food and Drug Administration (FDA) has tested for PFAS in a broad range of foods, including milk as part of its Total Diet Study (TDS). However, PFAS research and standardized methods in juices remain limited. Given the widespread consumption of juices, especially by children, ensuring food safety is a top priority. Developing an effective analytical workflow for PFAS analysis in juice matrices is therefore essential. This study aims to establish an analytical method for precise and accurate quantitation of volatile PFAS in juice. Due to the variety of complex juice matrices analyzed, this method may also be applicable to other beverages, including sports drinks and vitamin water.

In this study, a Head-Space Solid Phase Microextraction-Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS) analytical method was developed to analyze PFAS in juices. GC/MS addresses volatile PFAS compounds that are impractical to analyze by LC/MS. The HS-SPME technique, with its minimal sample preparation procedure and fast workflow, offers additional benefits for volatile PFAS analysis in complex matrices. While previous PFAS HS-SPME GC/MS/MS methods have been developed for relatively simple matrices such as drinking and bottled water,[4,5,6] the more complex composition of juice matrices requires additional isotopically labeled internal standards in this study to effectively compensate for matrix effects.

Method

Instrumentation: The instrument system configuration for the application consisted of a Shimadzu GC/MS triple quadrupole mass spectrometer, model GCMS-TQ8040 NX, a multifunctional autosampler (AOC™-6000 Plus) equipped with a SPME module and a split/spitless inlet. (**Figure 1**)

Figure 1. Shimadzu GCMS-TQ™8040 NX configured with an AOC™-6000 Plus.

Standards and Reagents: The target list consists of ten PFAS in the following chemical classes: (n:2) fluorotelomer iodides (FTIs), (n:2) fluorotelomer acrylates (FTACs), (n:2) fluorotelomer methacrylates (FTMACs), (n:2) fluorotelomer alcohols (FTOHs), and perfluoroalkane sulfonamides (FASAs). Internal standards were FTOHs, FASAs, FTMAC, and FTAC mass-labelled compounds. A working solution for each analyte at 10 mg/L was prepared. This standard was stored at 4 °C. LC/MS grade water and methanol were purchased from Honeywell.

An internal calibration curve was prepared in 10 mL of water at concentrations of 2000, 1000, 500, 100, 50, 10, 2.5, and 1 ng/L. The mass labelled internal standard compounds 8:2 FTOH-$^{13}C_2$, 6:2 FTAC-d_3, 10:2 FTOH-$^{13}C_2$ and n-ethyl-d5-perfluoro-1-octanesulfobamide (N-EtFOSA-d_5) were spiked in each calibrator at 100 ng/L, while 6:2 FTMAC-d_5, 8:2 FTAC-d_3 and 8:2 FTMAC-d_5 were spiked at the concentration of 10 ng/L. n-methylperfluorooctanesulfobanide-d_3 (N-MeFOSA-d_3) was spiked at 50 ng/L.

Sodium Chloride (NaCl) was added to each vial to achieve a final salinity concentration of 2% NaCl (w/v). All samples were vortexed for 30 seconds and then placed on the AOC-6000 Plus autosampler rack for HS-SPME analysis.

HS-SPME GC/MS/MS Analysis: In this study, instead of using direct immersion SPME, an HS-SPME method was used to improve method performance when analyzing complex aqueous samples. A Multiple Reaction Monitoring (MRM) GC/MS method was used in tandem with a SPME method to enhance selective and sensitive of the targeted PFAS compounds, with risk exposure at ng/L levels. The optimized parameters of the instrument method for the targeted PFAS are listed in **table 1**. A quantifier and qualifiers for each PFAS target are listed in **table 2**. Quantitation was performed by an internal standard method. When commercially available standards were available, an isotope dilution approach was applied. The associated internal standards used for each compound are also listed in **table 2**.

Table 1. GC/MS/MS and HS-SPME operating conditions.

Gas Chromatography	**Nexis™ GC-2030**
Injection port mode	Splitless
Carrier gas	Helium
Injection port temperature (°C)	240
Column	SH-I-624Sil MS Capillary, 30 m x 0.25 mmID x 1.40 µm
Flow control mode (cm/sec)	Linear velocity: 45
Oven Temperature	40 °C (7 min.), 5 °C/min. to 190 °C (0 min.), 40 °C/min. to 300 °C (5 min.)
Mass Spectrometer	**GCMS-TQ8040 NX**
Interface Temperature (°C)	280
Ion Source Temperature (°C)	200
Detector Voltage (kV)	Relative to Tune 0.4
Threshold	0
Acquisition mode	Acquisition mode: MRM, Loop time: 0.5 sec.
Tuning mode	Normal mode
SPME analysis	**AOC-6000 Plus**
SPME Fiber	50/30 µm DVB/CAR/PDMS
Incubation time (min)	5
Extraction time (min)	30
Desorption time (min)	7
Agitation speed (rpm)	300
Extraction Temperature (°C)	50
Sample volume (mL)	10
Desorption temperature (°C)	240
Sampling salinity	2% NaCl (w/v)

Table 2. Retention time, quantifier, qualifiers, and internal standard group information for each of the targeted PFAS compounds.

	Compound	Ret. Time (min)	Quantifier (*m/z*)	CE	Qualifier #1 (*m/z*)	CE	Qualifier #2 (*m/z*)	CE	Internal standard group
Targets	6:2 FTI	19.6	473.9>326.9	12	69.0>50.0	27	473.9>263.0	21	1
	8:2 FTOH	22.4	95.0>69.0	15	127.1>77.1	15	95.0>45.1	27	1
	6:2 FTAC	23.1	418.1>99.1	15	99.1>43.1	9	99.1>57.1	12	2
	8:2 FTI	23.5	574.0>426.9	15	169.0>69.0	9	574.0>65.1	24	2
	10:2 FTOH	25.6	95.0>69.0	15	127.1>77.1	15	95.0>45.1	27	3
	6:2 FTMAC	25.6	86.1>68.1	6	432.1>113.1	12	432.1>86.1	18	5
	8:2 FTAC	26.4	518.0>99.1	15	99.1>57.1	12	99.1>71.1	6	6
	8:2 FTMAC	28.7	86.0>68.1	6	532.0>86.1	21	532.0>113.1	21	7
	MeFOSA	33.5	430.0>111.1	24	430.0>91.10	33	94.0>91.8	57	8
	EtFOSA	34.1	108.1>80.0	6	448.0>69.1	27	108.10>44.1	3	4
Internal Standards	8:2 FTOH-$^{13}C_2$	22.3	98.0>69.0	15	131.1>81.1	15	98.0>48.1	27	1
	6:2 FTAC-d_3	23.0	101.1>57.1	12	101.1>45.0	9	102.0>45.0	9	2
	10:2 FTOH-$^{13}C_2$	25.5	98.0>69.0	12	131.1>81.1	12	98.0>48.1	27	3
	EtFOSA-d_5	34.1	113.1>81.0	6	81.0>64.0	24	450.1>69.0	27	4
	6:2 FTMAC-d_5	25.5	91.1>73.1	6	437.1>118.2	12	437.1>91.1	18	5
	8:2 FTAC-d_3	26.3	521.1>102.1	15	102.1>58.1	12	102.1>74.1	6	6
	8:2 FTMAC-d_5	28.6	91.1>73.1	6	537.1>91.1	21	537.1>118.1	21	7
	N-MeFOSA-d_3	33.5	433.1>114.0	24	433.1>94.3	33	97.1>94.1	57	8

Sample Preparation: Both reagent water and four commercially available juice samples were analyzed in this study. LC/MS-grade water was used as reagent water, which served as a laboratory control sample (LCS) to assess the general performance of the method in a clean matrix. The juice samples analyzed included two brands of carton apple juice (Brands X and Y), one plastic bottled apple juice (Brand X), and a berry blend carton juice (Brand X). These juice samples were analyzed to evaluate the effect of the matrix on method performance.

Ten milliliters of reagent water and juice samples were prepared for instrument analysis. Four replicate aliquots of the laboratory control sample (LCS) were analyzed, while juice samples were analyzed in triplicate for both spiked and unspiked aliquots. The LCS and spiked juice samples were fortified with all analytes at 100 ng/L, representing the midrange concentration of the initial calibration (ICAL). Mass-labeled internal standard compounds, at varying concentrations as described in the standards and reagent section above, were also spiked into these juice samples. Unspiked samples were only fortified with mass-labeled internal standards.

Initial calibration verification (ICV) and continuing calibration verification (CCV) quality control (QC) samples were prepared for instrument analysis using 10 mL of reagent water. These QC samples were fortified with all analytes at 100 ng/L, representing the midrange concentration of the ICAL. The mass-labeled internal standards were spiked into the QC samples at varying concentrations, as outlined in the standards and reagent section.

Sodium chloride (NaCl) was added to all water and QC samples to achieve a final salinity of 2% NaCl (w/v). Each sample vial was vortexed for 30 seconds and then placed on the AOC-6000 Plus rack for HS-SPME GC/MS/MS analysis.

PFAS contamination can occur during analysis from various sources, such as consumables or solvents. In this study, all consumable, solvents, standards and reagent water were analyzed and no PFAS were detected under the method conditions.

Instrumental analysis: A demonstration of proficiency study of the instrumentation system capability to conduct PFAS analysis on juice samples was performed. Prior to the analysis of samples, the system background was evaluated by analyzing method blanks to confirm that the instrument and reagents were free of contaminants and interferences. Subsequently, an initial calibration (ICAL) was analyzed. Prior to analyzing the samples, an ICV was performed to verify the accuracy of the calibration curve. In addition, a CCV was analyzed within the batch to ensure the accuracy of the calibration curve was maintained and no major drift was observed. Both ICV and CCV data are used to validate the integrity of the calibration curve, which is used to quantitate targeted compounds in the samples. In this study, the ICV and CCV accuracy should be within 70-130 % for the calibration curve to be considered valid.

A demonstration of precision and accuracy was first performed on the LCS. After the evaluation of method performance in this clean matrix, precision and accuracy tests were carried out on the juice samples. For juice samples, the spiked samples were analyzed for accuracy and precision evaluation. It is important to evaluate the amount of target PFAS in the unspiked matrix so that accurate adjustment can be made to the expected concentration of the spiked matrix.

■ Results and Discussion

As a quality control measure, an initial demonstration of low system background was performed before developing the calibration curve and analyzing the samples. Method blanks were analyzed, confirming that the system was free of contaminants and interferences. None of the target PFAS in the method blanks were detected at quantifiable concentrations.

In this study, a calibration curve for all analytes was prepared over a range of 1 to 2000 ng/L. The calibration curve results demonstrated a strong linear relationship for all compounds, with a coefficient of determination (R^2) ≥ 0.993. The linear range and R^2 values for each target PFAS are provided in **table 3**.

An ICV standard was run prior to sample analysis. When compared to the initial calibration curve, the ICV recoveries for all compounds fell within the 70-130% range, which meets the established method criteria. A CCV standard was run after the ICV and after an average of 14 samples to assess the stability of the calibration curve and its ability to quantify the targeted compounds in the samples. The CCV recoveries for all compounds were within the 70-130% range, as compared to the initial calibration curve, satisfying the method criteria.

For the LCS, the concentration of each analyte in the replicate analyses was calculated using the initial calibration (ICAL). The mean percent recovery (mean % recovery) and the percent relative standard deviation (%RSD) were then determined for each analyte of interest. The mean percent recovery ranged from 83 to 115, while the % RSD for the analytes in these replicates ranged from 0.6 to 6.8 (**Table 4**). The LCS results met the mean % recovery and %RSD method criteria, which were established respectively at 70-130% and ≤ 20%.

Table 3. Summary of PFAS calibration range and coefficient of determination.

Compound	Calibration range (ng/L)	R^2
6:2 FTI	1.0 - 2000	0.993
8:2 FTOH	1.0 - 2000	0.999
6:2 FTAC	2.5 - 2000	0.996
8:2 FTI	1.0 - 2000	0.998
6:2 FTMAC	2.5 - 2000	0.994
10:2 FTOH	1.0 - 2000	>0.999
8:2 FTAC	2.5 - 2000	0.994
8:2 FTMAC	2.5 - 1000	0.996
MeFOSA	10.0 - 2000	>0.999
EtFOSA	2.5 - 2000	>0.999

Table 4. Precision and Accuracy (n=4) of PFAS in LCS

Compound	LCS 100ppt	
	Mean % Recovery	% RSD
6:2 FTI	102	1.4
8:2 FTOH	83	2.0
6:2 FTAC	88	6.8
8:2 FTI	97	6.1
6:2 FTMAC	101	2.2
10:2 FTOH	90	0.6
8:2 FTAC	115	3.7
8:2 FTMAC	96	3.0
MeFOSA	94	3.8
EtFOSA	95	0.8

The impact of juice matrices on method performance was evaluated through precision and accuracy experiments. Preliminary analyses revealed significant matrix effects on most targeted compounds. Moreover, compounds lacking corresponding isotopically labeled internal standards could not be quantified accurately in complex juice matrices. These initial findings highlighted the importance of using an isotopically labeled internal standard for each targeted volatile PFAS compound to ensure accurate quantitation in complex matrices. **Figure 2** illustrates the quantitation of 8:2 FTMAC across various matrices using each of the internal standards included in this method. The results indicated that an accurate quantitation of 8:2 FTMAC was achieved using its corresponding isotopically labeled internal standard, 8:2 FTMAC-d_5. Even using internal standards, 6:2 FTMAC-d_5, within the same PFAS chemical class cannot guarantee to compensate for matrix effect of this analyte. The %RSD of 8:2 FTMAC, using 8:2 FTMAC-d_5 to quantitate its recoveries, ranged from 0.8 to 5.1.

While the use of isotopically labeled internal standards is critical for reliable PFAS analysis in complex matrices, there is currently a lack of commercially available standards for many PFAS compounds as the field is emerging. As a result, some compounds in this study could not be quantified using their own isotopic internal standard. To address this, each of these targeted compounds was carefully evaluated against all internal standards included in this study to identify those exhibiting similar behavior in complex matrices. This approach enabled accurate quantification despite the absence of compound-specific internal standards. For all complex matrices that are analyzed beyond this study, it is highly recommended that in cases where isotopically labeled internal standards are unavailable for a targeted compound, alternative internal standards should be thoroughly evaluated within the specific matrix. This step is essential to ensure comparable behavior between the internal standard and the analyte, allowing for accurate quantitation.

Following the assignment of internal standards for each of the targeted compounds, juice samples were analyzed. The concentration of each targeted PFAS in the replicate analyses for both spiked and unspiked samples was calculated using the ICAL. None of the targeted PFAS were detected at quantifiable concentrations in the unspiked sample; therefore, no adjustment to the recovery concentrations was necessary.

The mean percent recovery for the targeted compounds in the brand X bottled apple juice ranged from 70 to 115, while the % RSD for these analytes ranged from 0.3 to 7.9 (**Table 5**). For brand X carton apple juice, the mean percent recovery for the targeted compounds ranged from 69 to 120, while the % RSD for these analytes ranged from 0.5 to 10.9 (**Table 5**). Brand Y carton apple juice, the mean percent recovery for the targeted compounds ranged from 70 to 117, while the % RSD for these analytes ranged from 0.3 to 4.0 (**Table 5**). The fourth juice matrix, Brand X carton berry juice, the mean percent recovery for the targeted compounds ranged from 79 to 112, while the % RSD for these analytes ranged from 0.2 to 11.6 (**Table 5**). Overall, the mean percent recovery range of 69-120% and %RSD < 12 for all compounds (**Table 5**). The overall results exceeded the method criteria.

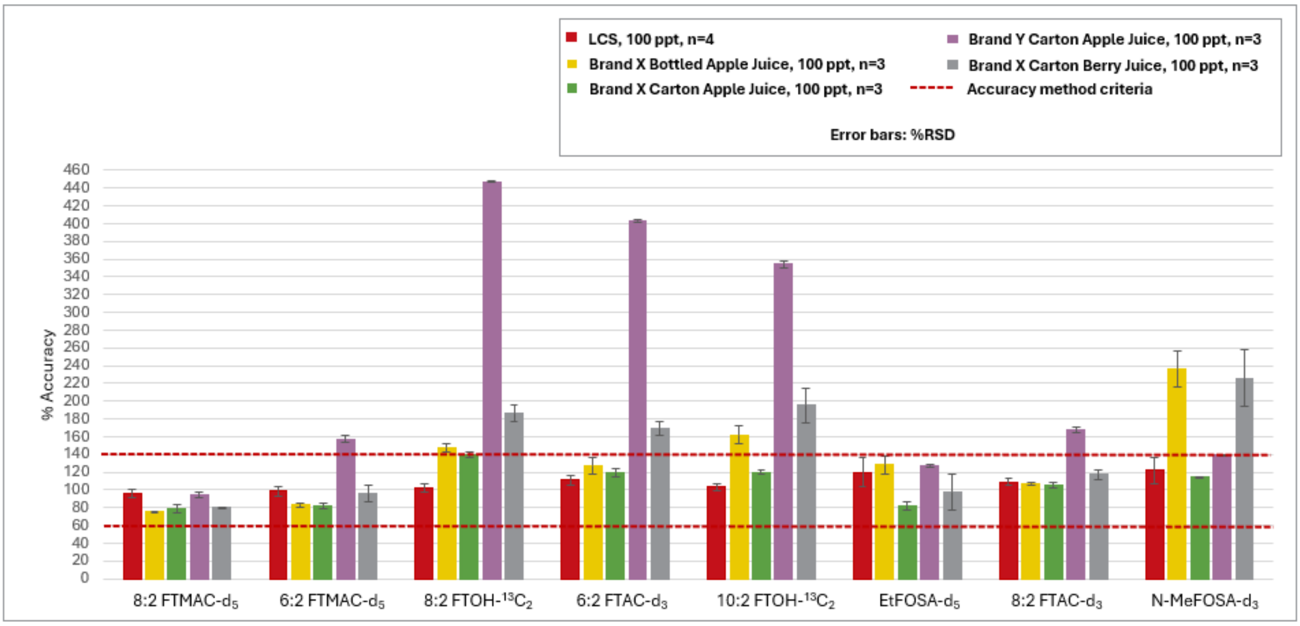

Figure 2. 8:2 FTMAC accuracy results using multiple isotopic labelled internal standards.

Table 5. Precision and Accuracy results of PFAS in juice matrices.

Compound	Brand X Bottled AJ		Brand X Carton AJ		Brand Y Carton AJ		Brand X Carton BJ	
	Mean % Recovery	%RSD	Mean % Recovery	%RSD	Mean % Recovery	%RSD	Mean % Recovery	%RSD
6:2 FTI	**105**	3.3	**120**	3.8	**76**	1.4	**84**	4.2
8:2 FTOH	**90**	0.6	**87**	2.1	**83**	0.9	**86**	0.7
6:2 FTAC	**70**	3.0	**69**	5.8	**74**	2.9	**79**	5.5
8:2 FTI	**88**	7.9	**79**	10.9	**70**	2.5	**91**	11.6
6:2 FTMAC	**95**	0.3	**95**	1.4	**99**	1.7	**94**	2.2
10:2 FTOH	**101**	2.5	**93**	1.9	**117**	1.9	**92**	3.2
8:2 FTAC	**115**	1.9	**114**	2.7	**104**	0.4	**112**	2.6
8:2 FTMAC	**75**	1.0	**79**	5.1	**95**	3.1	**80**	0.8
MeFOSA	**96**	0.9	**91**	2.5	**95**	4.0	**86**	3.7
EtFOSA	**87**	1.3	**88**	0.5	**88**	0.3	**86**	0.2

Conclusion

In this study, a Shimadzu GCMS-TQ8040 NX triple quadrupole mass spectrometer, configured with an AOC-6000 Plus solid-phase microextraction (SPME) unit, was used to develop a PFAS analysis method in complex matrices such as juice. Method blanks showed no detectable PFAS, and the calibration curve demonstrated excellent linearity ($R^2 \geq 0.993$). ICV and CCV recoveries were all within 70–130%, established as the method criteria.

For LCS precision and accuracy analyses, mean PFAS recovery was 83-115%, with %RSD ranging from 0.6 to 6.8%. LCS results met the mean % recovery and %RSD method criteria, which were established respectively at 70-130% and ≤ 20%. An isotope dilution approach was used for most compounds to achieve accurate quantitation in these complex matrices. Overall, the mean percent recovery for juice samples from two brands and two packaging materials ranged from 69-120% and %RSD < 12 for all compounds. The overall results exceeded the method criteria.

This HS-SPME GCMS-TQ8040 NX method presents an effective analytical workflow for volatile PFAS analysis in juice matrices. This application highlights a simple, robust, and accurate workflow for measuring volatile PFAS in these complex matrices.

References

1. Per-and Polyfluoroalkyl Substances (PFAS) in Cosmetics (2024, January 2024). US Food and Drug Administration. Retrieved April 15, 2024 from https://www.fda.gov/cosmetics/cosmetic-ingredients/and-polyfluoroalkyl-substances-pfas-cosmetics
2. Phelps, D. W., Parkinson, L. V., Boucher, J. M., Muncke, J., & Geueke, B. (2024). Per-and polyfluoroalkyl substances in food packaging: migration, toxicity, and management strategies. Environmental Science & Technology, 58(13), 5670-5684. https://doi.org/10.1021/acs.est.3c03702
3. Alazaiza, M. Y., Alzghoul, T. M., Ramu, M. B., Amr, S. S. A., & Abushammala, M. F. (2025). PFAS Contamination and Mitigation: A Comprehensive Analysis of Research Trends and Global Contributions. Case Studies in Chemical and Environmental Engineering, 101127. https://doi.org/10.1016/j.cscee.2025.101127
4. Shimadzu Application News. GCMS-2403. (2024, March). Volatile PFAS in water analysis using Head-Space Solid Phase Microextraction-Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS).
5. Shimadzu Application News. GCMS-2404. (2024, September). Analysis of Volatile PFAS in Drinking Water Using Head-Space Solid Phase Microextraction-Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS).
6. Shimadzu Application News. GCMS-2405. (2024, September). Analysis of Volatile PFAS in Bottled Water Using Head-Space Solid Phase Microextraction-Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS.

Consumables

Item Name	Item Description	Part Number
Capillary column	GC, SH-I-624Sil MS Capillary, 30 m x 0.25 mmID x 1.40 um	221-75962-30
SPME Inlet liner	SPME liner 0.75mm x 5.0 x 95 for Shimadzu GCs Deact., 5pk (Restek)	REST-22279
Head-Space sample vials	20ml magnetic screw-cap clear headspace vial kit	220-97331-16
Liquid injection sample vials	1.5 mL Amber glass vial w/Cap & septa	220-97331-31
Methanol	Methanol, LCMS Honeywell Chromasolv(R); 99.9%	220-91545-11
Ultra-pure water	Water, LCMS Honeywell Chromasolv(R); 99.9%	220-91545-12
SPME fiber	SPME fiber assembly (DVB/CAR/PDMS) (Millipore Sigma)	57298-U
Methylene Chloride	Methylene Chloride (GC Resolv $^{\text{TM}}$) Fisher Chemical (Fisher Scientific)	D154-4

SHIMADZU

Shimadzu Corporation
www.shimadzu.com/an/

SHIMADZU Scientific Instruments Inc.
www.ssi.shimadzu.com

02-SSI-GCMS-2501-EN

First Edition: Aug. 2025

Please fill out the survey

Related Products Some products may be updated to newer models.

GCMS-TQ™8040 NX

Triple Quadrupole Gas Chromatograph Mass Spectrome…

AOC-6000 Plus

AOC-6000 Plus Multifunctional Autosampler

Related Solutions

Food and Beverages

Food Contamination

Price Inquiry

Product Inquiry

Technical Service / Support Inquiry

Other Inquiry