Analysis of PFAS in juice using Head-Space Solid Phase Microextraction-Gas Chromatography/Mass Spectrometry (HS-SPME GCMS)

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1. Introduction

PFAS contaminate water and food through packaging that can leach volatile PFAS from plastics and inks or coatings. This work developed a headspace SPME GCMS method to analyze six volatile PFAS classes in juices. The United States Food and Drug Administration has tested for PFAS in a broad range of foods and beverages as part of its Total Diet Study. Juice matrices differ in flavor, sugar, as well as manufacturing practices, and packaging, with the latter two potentially introducing PFAS contamination. The former differences between products can impact PFAS detection.

Fig. 1 GCMS-QP2050

2. Materials and Methods

The target list consists of thirteen PFAS in the following chemical classes: PFIs, FTIs, FTACs, FTMACs, FTOHs and FASAs. Internal standards were FTOHs, FASAs, FTMA and FTAC mass-labelled compounds. A stock solution of each analyte was prepared at 1000 mg/L in methanol, which was further diluted to make an intermediate stock at 10 mg/L. These standards were 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. Sodium Chloride (NaCl) was added to each vial to achieve a final salinity concentration of 2% NaCl (w/v).

The SPME method used in this study is based on a method published by Bach et.al. (2016). An HS-SPME method is used to improve method performance when analyzing complex aqueous samples over direct immersion. The optimized parameters of the instrument method for the targeted PFAS are listed in table 1.

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 um
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
Acquisition mode	Acquisition mode: MRM, Loop time: 0.5 sec.
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

Table. 1 Analytical conditions

Prior to analyzing the samples, an ICV was performed to verify the accuracy of the calibration curve and a CCV to ensure the curve was maintained and no major drift was observed. 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.

In this study, a calibration curve for all analytes was constructed over a range of 1 to 2000 ng/L.

3. Results

The calibration curve results demonstrated a strong linear relationship for all compounds, with a coefficient of determination (R^2) ≥ 0.993. ICV recoveries for all compounds fell within the 70-130% range. CCV standards were run to assess the stability of the calibration curve, recoveries for all compounds were also within the 70-130% range.

For the LCS the mean percent recovery and the percent relative standard deviation (%RSD) were then determined based on calculated concentration 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. The mean percent recovery was within the 70-130 range, and the % RSD was less than 10 for all compounds.

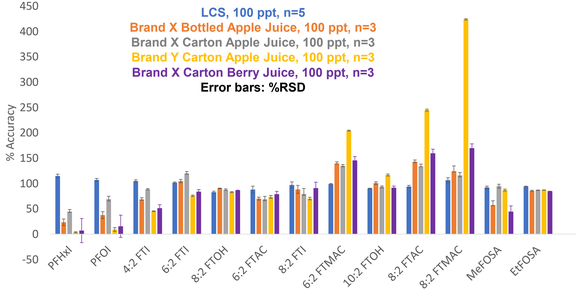

Fig 2 Recovery analysis determined without isotope dilution

Matrix effects related to method performance were evaluated through a precision and accuracy experiment. Initial analysis of the juices using a non-isotope dilution approach revealed that the target compounds experienced matrix effects. In this approach only three classes of internal standards were used for the six classes of targeted compounds. In the plastic-bottled juice, MeFOSA ion intensities were suppressed compared to the juice packaged in plastic boxes from the same brand.

ETFOSA highlighted the need for isotope dilution as the peak area was at least 24% higher in a carton apple juice compared to the LCS sample. This isotopic dilution method resulted in most compounds achieving mean percent recovery within the 60-140% range, with %RSD < 15 for all compounds. With isotope dilution, compounds such as 6:2 FTMAC, 8:2 FTAC, and 8:2 FTMAC had mean percent recoveries fell within the 75-115% range.

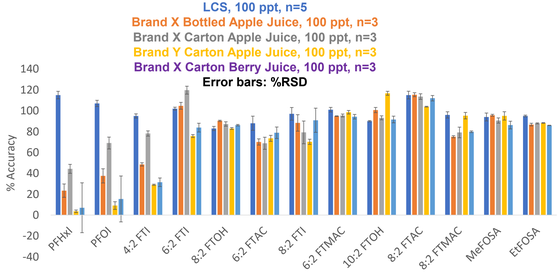

Fig. 3 Recovery analysis determine by with isotope dilution

4. Conclusion

The Shimadzu GCMS-TQ8040 NX triple quadrupole instrument, configured with an AOC-6000 Plus SPME unit, was used to measure PFAS in different juice samples. Without isotope dilution, matrix effects caused recoveries to fall outside of acceptable criteria. Method blanks showed no detectable PFAS, and calibration demonstrated excellent linearity (R^2 ≥ 0.993).

This HS-SPME GCMS-TQ8040 NX method demonstrated quantitative capability for analyzing nanogram-per-liter PFAS compounds in complex juice matrices. This application highlights a simple, fast, robust, precise, and accurate workflow for measuring volatile PFAS in challenging matrices.