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Determination of Fluorotelomer Alcohols in Cookware Using Cryogen-free Direct Thermal Extraction

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Keywords

PFAS, Fluorotelomer Alcohols, Non-stick, Gas-Chromatography, Cryogen-free

Abstract

Fluorotelomer alcohols (FTOHs), a class of per- and polyfluoroalkyl substances (PFAS), are commonly used in products due to their non-stick properties, which are desirable in cookware. FTOHs are precursors to perfluoroalkyl carboxylates, both of which are harmful to human health. As a result, consumers are seeking PFAS-free alternatives to cookware, such as stainless steel. This study employs direct thermal extraction (DTE) in a cryogen-free approach to determine the concentration of FTOHs in non-stick, PFOA/PFOS-free, and stainless-steel cookware.

Introduction

Per- and polyfluoroalkyl substances (PFAS) comprise thousands of synthetic compounds that have drawn public concern due to their persistence in the environment, widespread use in consumer products, and their impact on human health. Among these, fluorotelomer alcohols (FTOHs) are a class of PFAS that degrade into more persistent PFAS, such as perfluoroalkyl carboxylates. These breakdown products are often associated with reproductive issues and carcinogenicity [1-3].

Recent studies have demonstrated that FTOHs, such as 6:2, 8:2, and 10:2, are predominantly released into the air when fluoropolymer-coated surfaces are heated, contributing to indoor air contamination and potential migration into food [4]. Teflon, a polytetrafluoroethylene (PTFE) material valued for its chemical stability and surfactant properties, is widely used in non-stick, stain-resistant, and water-repellent products. Although effective, these coatings may contribute to PFAS exposure, especially when used at high temperatures in cookware.

Despite this, literature documenting the presence and resulting concentrations of FTOHs in cookware remains limited. This gap is significant as consumers seek PFAS-free alternatives, such as stainless steel or cookware labeled as "perfluorooctanoic acid/perfluorooctane sulfonic acid (PFOA/PFOS)-free." Even if products are labeled PFOA/PFOS-free, this does not account for the numerous other forms of PFAS. Reports indicate that PFAS levels above 20 ng/mL in serum and/or plasma are associated with an increased risk of adverse health effects [5], underscoring the importance of identifying consumer product PFAS sources before such reach the bloodstream.

FTOHs are among the few classes of PFAS that can be identified using gas chromatography-mass spectrometry (GC-MS). In this study, a cryogen-free direct thermal extraction (DTE) methodology was used to extract FTOHs from coatings on cookware. DTE involves placing a milligram quantity of sample into a µ-vial within an empty thermal desorption tube. The sample is then heated in the Thermal Desorption Unit (TDU) at high temperatures and high flow rates, and the analytes are subsequently trapped in the Cooled Injection System (CIS 4). DTE enables exhaustive extraction conditions. Therefore, calibration curves can be easily generated by spiking standards onto Tenax® TA sorbent-filled tubes.

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GERSTEL AppNote 296

Experimental

Instrumentation

GERSTEL MPS LabWorks Platform on Agilent 8890/5977B GC-MSD (Figure 1).

Figure 1: GERSTEL MPS LabWorks Platform on Agilent 8890 GC and 5977B MSD.

Analysis Conditions LabWorks Platform

TDU 2	Splitless
	40 °C; 720 °C/min; 280 °C (5 min)
CIS 4	Tenax® TA-filled liner
	Solvent vent (50 mL/min), split 10:1
	10 °C; 12 °C/sec; 280 °C (3 min)

Analysis Conditions Agilent 8890 GC

Column	30 m DB-WAX (Agilent)
	d_i = 0.25 mm, d_f = 0.25 µm
Pneumatics	He, P_i = 7.0699 psi
	Constant flow 1.0 mL/min
Oven	40 °C (2 min); 10 °C/min; 170 °C (2 min);
	25 °C/min; 260 °C (5 min)

Analysis Conditions 5977B MSD

Mode	SIM/Scan
Scan	30 – 550 m/z
SIM	see Table 1
Source Temp	230 °C
Quad Temp	150 °C

Table 1: SIM Parameters for FTOH determination.

Analyte	Retention Time [min]	Quant Ion [m/z]	Qual Ion [m/z]
4:2 FTOH	6.292	131	69
6:2 FTOH	7.341	131	69
8:2 FTOH	8.531	131	95
10:2 FTOH	9.793	131	95

Standard/Sample Preparation

4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were obtained from AccuStandard (New Haven, CT). Used non-stick, PFOA/PFOS-free and stainless-steel pans were obtained from a private residence.

Standard Preparation

A 1 µL aliquot of calibration standard prepared in methanol was spiked onto a conditioned Tenax® TA-packed tube for a working calibration range of 0.0625-10.0 ng/tube. After spiking the tubes, dry nitrogen was passed through each tube at a flow rate of 50 mL/min for 3 minutes.

Sample Preparation

The coating from the non-stick pan was scraped off the center and sides of the cooking surface with a utility knife. Metal snips were used to obtain samples from the PFOA/PFOS-free and stainless-steel cookware surfaces. Approximately 5-10 mg of sample was weighed and placed in a conditioned µ-vial in an empty TDU tube. The non-stick samples were prepared in triplicate.

Sample/Standard Introduction

The samples were extracted at 280 °C for 5 minutes with a helium flow rate of 50 mL/min. Analytes were trapped in the CIS 4 inlet at 10 °C on a Tenax® TA-filled liner. An extraction temperature of 280 °C was used to stimulate high-heat cooking conditions. When desorption was complete, the analytes were transferred to the column in split (10:1) mode by rapidly heating the inlet to 280 °C for 3 minutes.

GERSTEL AppNote 296

Results and Discussion

Figure 2 shows a stacked view of two representative chromatograms of the 10 ng calibration standard on DB-5 and DB-WAX Agilent columns. The literature shows that both polar and non-polar columns are used for FTOH determination [6-7]. However, the DB-5 column showed peak tailing of the 4:2 and 6:2 FTOHs, whereas the wax column showed improved symmetry. FTOHs contain an alcohol functional group, which allows for better interaction with polar stationary phases. For these reasons, the wax column was utilized for this study.

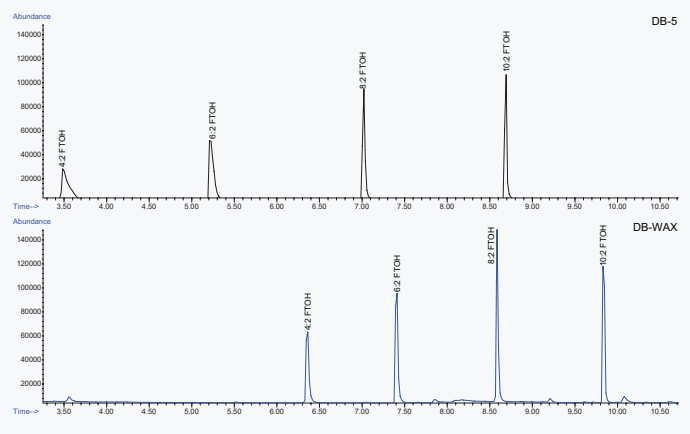

Figure 2: Stacked view of the 10 ng calibration standard obtained on a DB-5 column (top) and DB-WAX column (bottom) in SIM mode.

A six-point linear calibration curve was established for each compound as shown in Figure 3. Linearity was excellent across the calibration range of 0.0625-10.0 ng on each tube. Correlation coefficients (R^2) were greater than 0.990 for each analyte, and the limit of detection (LOD) for each analyte was below 0.0417 ng per tube, except 4:2 FTOH, as shown in Table 2. LODs were calculated based on the equation $LOD=(3S_y)/(m)$, where S_y is the standard deviation of the lowest measurable response (n=9), and m is the slope of the calibration curve. The LOD for 4:2 FTOH was calculated to be above 0.0625 ng, meaning that the instrument is incapable of reliably detecting 4:2 FTOH at the lowest calibration level. Therefore, the LOD for 4:2 FTOH could not be reliably reported in Table 2.

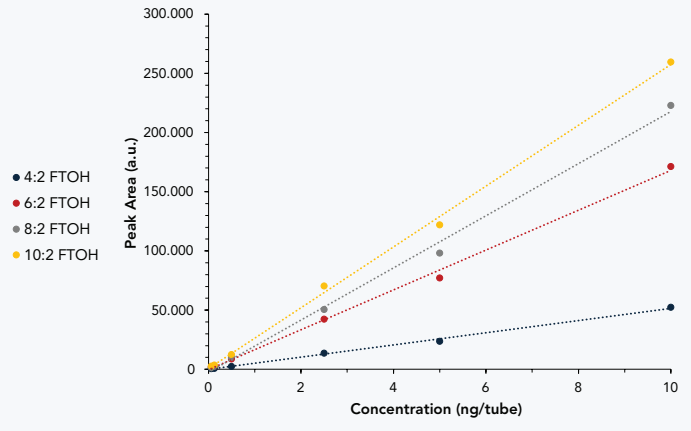

Figure 3: Calibration curves for target FTOHs with trendlines.

Table 2: Linearity and limits of detection for target FTOHs.

Analyte	R^2	LOD [ng/tube]
4:2 FTOH	0.998	N/A
6:2 FTOH	0.997	0.0330
8:2 FTOH	0.998	0.0396
10:2 FTOH	0.999	0.0417

Figure 4 shows a stacked view of SIM chromatograms extracted at the quantifier ion, 131 m/z. The top chromatogram represents 6.0 mg of non-stick cookware coating spiked with 10 ng of each FTOH. The bottom chromatogram represents the redesorption of the same sample, in which no FTOHs are detected. This indicates that the DTE method extracts FTOHs exhaustively from the cookware coating under the tested conditions.

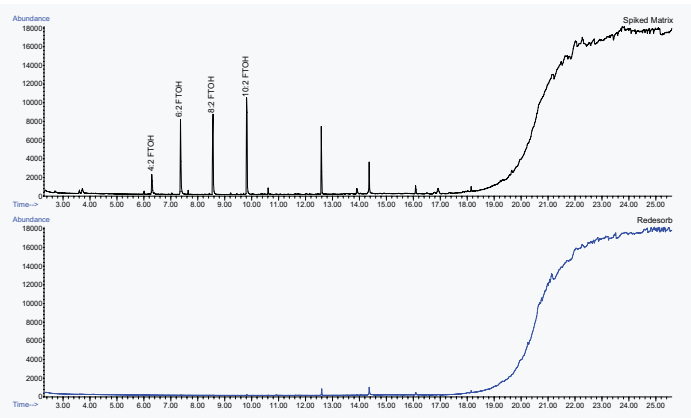

Figure 4: Overlay of SIM chromatograms for 10 ng FTOH spiked matrix (top) and redesorbed (bottom).

GERSTEL AppNote 296

After performing DTE, it was determined that only 6:2 FTOH could be extracted from and detected in the non-stick cookware. No other FTOHs were detected. After a triplicate analysis of the non-stick cookware, it was determined that an average of 0.0252 nanograms of 6:2 FTOH per milligram of non-stick cookware coating was quantified, with a relative standard deviation of less than 10.0%, as shown in Table 3.

Table 3: Concentration and reproducibility of 6:2 FTOH in the non-stick cookware.

Non-stick	6:2 FTOH [ng/mg]
Replicate 1 (6.5 mg)	0.0246
Replicate 2 (7.2 mg)	0.0280
Replicate 3 (6.8 mg)	0.0231
Average	0.0252
%RSD	9.99

Figure 5 shows a labeled total ion chromatogram of 6.5 mg of the non-stick cookware coating obtained in scan mode. Numerous peaks in Figure 5 are not attributed to FTOHs. Due to the complex matrix of used non-stick pans, SIM mode was crucial for detecting trace-level FTOHs. In addition to trace levels of 6:2 FTOH, short and long-chain fatty acids, vanillin, limonene, pyridine, furfural, and chlorinated and fluorinated alkenes and alkanes were also identified. The fatty acids were likely present because of residual oils used during cooking to enhance the non-stick effect. The terpenes, furfural, and pyridine were likely present from residual cooked foods. In contrast, the presence of chlorinated and fluorinated hydrocarbons raises further concerns about potential consumer exposure to halogenated compounds beyond FTOHs, which can occur both through airborne exposure and via food contact migration.

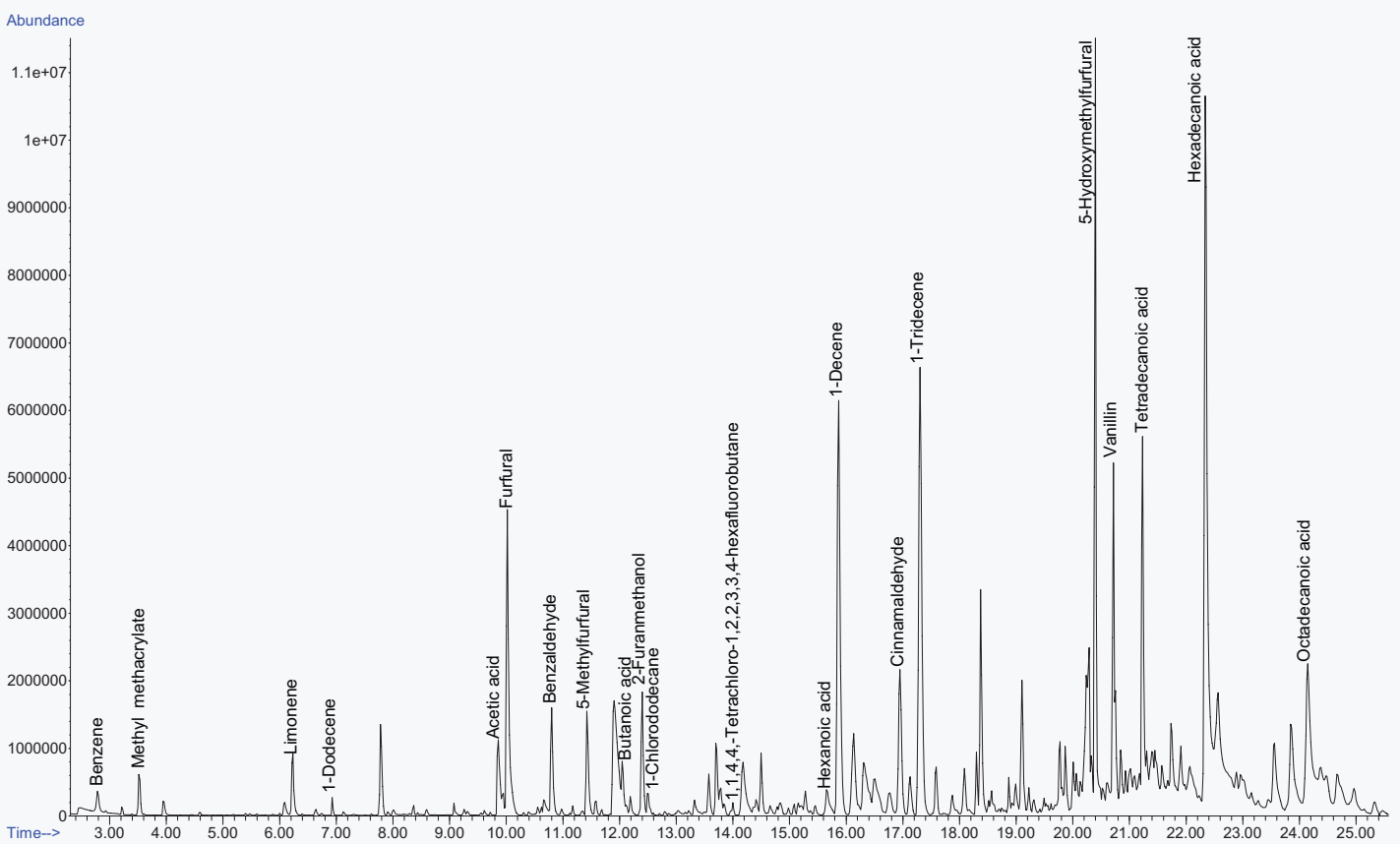

Figure 5: Total ion chromatogram of 6.5 mg of non-stick cookware obtained in scan mode.

While the toxicity of 6:2 FTOH is underreported in humans, a recent study has shown that the highest exposure level of 6:2 FTOH before adverse health effects are observed in males is 25 mg/kg/day, and 5 mg/kg/day in females [8]. It should be noted that 6:2 FTOH is present at trace levels in the non-stick pan and only accounts for a single source of PFAS exposure during an average person's daily routine. Furthermore, the presence of 6:2 FTOH in cookware raises the question of how much of it leaches into prepared foods.

DTE of PFOA/PFOS-free and stainless steel cookware did not result in a detectable level of FTOHs. However, this does not rule out the presence of numerous other classes of PFAS in the PFOA/PFOS-free pan. An alternative means of extraction to determine the presence of LC-MS-amenable PFAS would be beneficial for further investigating the non-stick and PFOA/PFOS-free cookware.

Conclusion

This study successfully demonstrates the application of DTE coupled with GC-MS in SIM mode as an efficient and cryogen-free method for extracting FTOHs. DTE provides an automated means of extracting FTOHs at very low concentrations. Among the evaluated samples, only the non-stick cookware contained detectable levels of 6:2 FTOH with good reproducibility.

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