Environmental

Comprehensive screening of per- and polyfluoroalkyl substances (PFAS) in textiles: Utilizing combustion ion chromatography for total organic fluorine (TOF) analysis

Authors

Jingli Hu, Neil Rumachik

Thermo Fisher Scientific,
Sunnyvale, CA, USA

Keywords

AB 1817, organofluorine compounds, Dionex AS24 column, waterproof

Goal

To develop a method to measure total organic fluorine (TOF) in textiles using combustion ion chromatography

Introduction

Per- and polyfluoroalkyl substances (PFAS) are used globally across various industries and comprise thousands of individual compounds. These amphipathic substances are extensively incorporated into textile-based products, such as clothing, carpets, and other household items to provide waterproofing, oil, dirt, and heat protection, as well as increased durability. PFAS can be released from functional textiles according to an outdoor aging study.[1] The Department of Toxic Substances Control (DTSC) has found that treated textiles and leathers are major sources of PFAS exposure for people and the environment, particularly through inhalation when using these products. PFAS also contribute to widespread environmental contamination, similar to other consumer products like food packaging and cosmetics.[2]

In recent years, many U.S. states have proposed or introduced regulations to restrict the use of PFAS in various matrices, including textiles. One of the most notable restrictions is from California Assembly Bill 1817 (AB 1817), which prohibits the manufacturing, selling, and distributing of textiles containing total organic fluorine (TOF) exceeding 100 parts per million (ppm) starting in January 2025, with a further reduction to 50 ppm by January 2027.[3] Similarly, PFAS use in textiles is of elevated concern in Europe, as textiles have been identified as one of the primary sources of PFAS pollution there. As an example, Denmark's Ministry of the Environment has announced plans to ban PFAS in clothing, shoes, and waterproofing agents intended for consumers starting on July 1st, 2026.[4] This ban is anticipated to be a precursor to a broader EU-wide regulation expected to take effect in 2027.

Traditionally, PFAS testing has been conducted using liquid chromatography coupled with triple quadrupole mass spectrometry (LC-QQQ). While LC-QQQ is a targeted analytical technique, its results are limited to compounds for which standards are available. Consequently, these targeted studies do not necessarily provide a comprehensive measurement of the total PFAS in samples. Recently, laboratories have focused on developing and validating lower-cost alternatives that offer a more comprehensive measure of total PFAS content. This has led to the development of several methods for measuring total fluorine (TF) as a proxy for total PFAS contamination in textiles. Technologies employed in these methods include combustion ion chromatography (CIC)[5] and particle-induced γ-ray emission spectroscopy (PIGE).[6] However, measuring only TF is not a reliable proxy for PFAS, as it includes both organic and inorganic fluorine, the latter of which is not considered PFAS. Using TF as a measure of PFAS may result in overestimating the amount of PFAS in samples.

California AB 1817 introduces a new methodology for testing PFAS contamination or intentional use of PFAS in fabrics based on the amount of TOF in the sample. This is a significant change from previous approaches, employing a non-specific untargeted method to PFAS detection and quantification. In this study, we developed a method to determine TOF in textiles using CIC. CIC offers excellent sensitivity and versatility, independent of sample thickness, and the capability for direct ion chromatography (IC) analysis to determine inorganic fluorine (IF).

Experimental

Equipment

- A Thermo Scientific™ Dionex™ Integrion™ HPIC™ System (P/N 22153-60306) including:
  - Eluent generator
  - Pump
  - Degasser
  - Conductivity detector
  - Column oven temperature control
  - Detector-suppressor compartment temperature control
- Nittoseiko Automatic Combustion Unit Model AQF–2100H system* including:
  - Automatic Sample Changer ASC-270LS
  - Horizontal Furnace Model HF-210
  - Gas Absorption Unit GA-211
  - External Solution Selector ES-210

*Any combustion oven with equivalent performance will work.

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Version 7.3 1 with DDK driver to control the combustion system

Consumables

- Thermo Scientific™ Dionex™ IonPac™ AG24 Guard Column, 2 × 50 mm (P/N 064151)
- Thermo Scientific™ Dionex™ IonPac™ AS24 Analytical Column, 2 × 250 mm (P/N 064153)
- Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor, 2 mm (P/N 088667)
- Fisherbrand™ Narrow-Mouth field sample bottles, high density polyethylene (HDPE), for storage of standards and samples, 125 mL (Fisher Scientific P/N 02-895A) and 250 mL sizes (Fisher Scientific P/N 02-895B)
- Polyethersulfone (PES) filter 0.2 µm pore size (Fisher Scientific P/N 09-740-113)
- Polypropylene centrifuge tube 15 mL (Fisher Scientific P/N 05-539-12), 50 mL (Fisher Scientific P/N 05-539-13)

Reagents and standards

- Deionized (DI) water, Type 1 reagent grade, 18 MΩ·cm resistivity or better
- Certified fluoride standard (1,000 mg/L), (Fisher Scientific P/N NC1145532)
- Certified seven-anion standard mixture (Fluoride 20 mg/L, Bromide 100 mg/L, Chloride 100 mg/L, Nitrite 100 mg/L, Nitrate 100 mg/L, Sulfate 100 mg/L, Phosphate 200 mg/L) (Fisher Scientific P/N NC1145568)
- Perfluorooctanesulfonamide (Sigma-Aldrich P/N CDS010729)
- Methanol, UHPLC-MS grade, Thermo Scientific™ (P/N A4581-1)

Preparation of solutions and reagents

Calibration standard

An 8-point calibration curve was prepared over a concentration range of 1 to 200 mg/L by diluting a certified 1,000 mg/L fluoride standard solution with DI water.

Perfluorooctanesulfonamide

A standard solution of perfluorooctanesulfonamide with a concentration of 1 mg/mL in methanol was prepared for direct combustion and sample spike recovery analysis. The solution was prepared by dissolving 25 mg of perfluorooctanesulfonamide in 25 mL of methanol.

Samples

Textile samples were purchased from an online store. Six samples, consisting of different fabric types that claimed to have waterproof or stain resistant properties, were analyzed. The fabric types include polyester, polyurethane laminate, nylon, and canvas.

Sample preparation

Textiles were cut into pieces using scissors that had been cleaned with methanol. Samples intended for the determination of inorganic fluorine were finely ground using a Freezer/Mill model 6770 (SPEX SamplePrep LLC, Metuchen, NJ) and a 6751 small grinding vial set, which includes magnetic stainless steel end caps, impactor rods, and polycarbonate center cylinders. Approximately two grams of each sample were placed into a small freezer mill grinding vial and ground according to the manufacturer's instructions. After grinding, vials were removed from the instrument and allowed to sit at room temperature for 5–10 min to warm up before the removal of the magnetic stainless steel end caps.

Inorganic fluorine was extracted from the ground samples as follows: 1 g of pulverized sample was weighed in a 50 mL centrifuge tube and mixed with 20 mL of DI water. The tube was sonicated in a water bath for 10 min and centrifuged at 15,000 × g for 10 min. The supernatant was filtered with a PES filter (pore size = 0.2 µm), and the filtrate was collected in a 15 mL polypropylene vial. This extract was directly injected into the IC to determine total inorganic fluorine (TIF).

IC conditions

Table 1A. Combustion IC conditions

Parameter	Value
Columns	Dionex IonPac AG24 guard column, 2 × 50 mm Dionex IonPac AS24 analytical column, 2 × 250 mm
Eluent	8 mM KOH from 0 to 6 min 8–75 mM KOH from 6 to 9 min 75 mM KOH from 9 to 12 min 8 mM KOH from 12 to 20 min
Eluent source	Dionex EGC 500 KOH cartridge with CR-ATC 600
Flow rate	0.3 mL/min
Injection volume	25 µL in Push-Full mode
Column temperature	30 ˚C
Detection	Suppressed conductivity
Suppressor	Dionex ADRS 600 (2 mm) Suppressor, recycle mode, 56 mA current
Detection/Suppressor compartment	20 °C
Cell temperature	35 ˚C
Background conductance	<0.5 µS/cm
System backpressure	≈2,200 psi (100 psi = 689.5 kPa)
Run time	20 min

Table 1B. Combustion and adsorption conditions

Parameter	Value		
Furnace temperature	950 °C inlet, 1,000 °C outlet		
Gas	Ar: 200 mL/min; O_2: 400 mL/min		
Hydration	Water: pump scale 2, 125 µL/min / Ar: 100 mL/min		
Absorption solution	3 mL DI water		
Absorption tube size	10 mL		
Boat program	Position (mm)	Wait time (s)	Boat speed (mm/s)
	130	90	20
	160	90	0.12
	0	0	0.01
	End	300	20
	Cool	60	40
	Home	120	20

TOF by CIC

TOF was measured using a hybrid CIC system consisting of a Thermo Scientific IC system and Nittoseiko modules, although any combustion oven with equivalent performance will work.

The CIC method combines an automated Nittoseiko Analytech AQF-2100H combustion-absorption unit with a Dionex Integrion IC system. There are two modes to introduce a sample into the CIC system. One mode is combustion mode (Figure 1). In this mode, samples were placed onto a ceramic boat which was introduced into a combustion oven (HF-210, Nittoseiko) heated to 1,100 °C under an atmosphere of argon (200 mL/min) and oxygen (400 mL/min). All gaseous acidic combustion products were absorbed in 10 mL of DI water (GA-211, Nittoseiko), and an aliquot of 25 µL was injected into the IC system. In this mode, all fluorine derived from organic and inorganic compounds from solid or liquid samples is converted to and determined as fluoride by IC. The other mode is called direct injection mode. In this mode, aqueous samples were introduced directly to the IC sample loop.

Fluoride was measured using a Dionex Integrion IC system equipped with a 25 µL sample loop, Dionex ADRS 600 suppressor, and Dionex EGC 500 KOH cartridge. Fluoride was separated from other anions using a Dionex IonPac AS24 analytical column and guard column maintained at 30 °C. The detailed CIC conditions are listed in Table 1.

Figure 2 describes the overall workflow for analyzing TF and TIF using the CIC method.

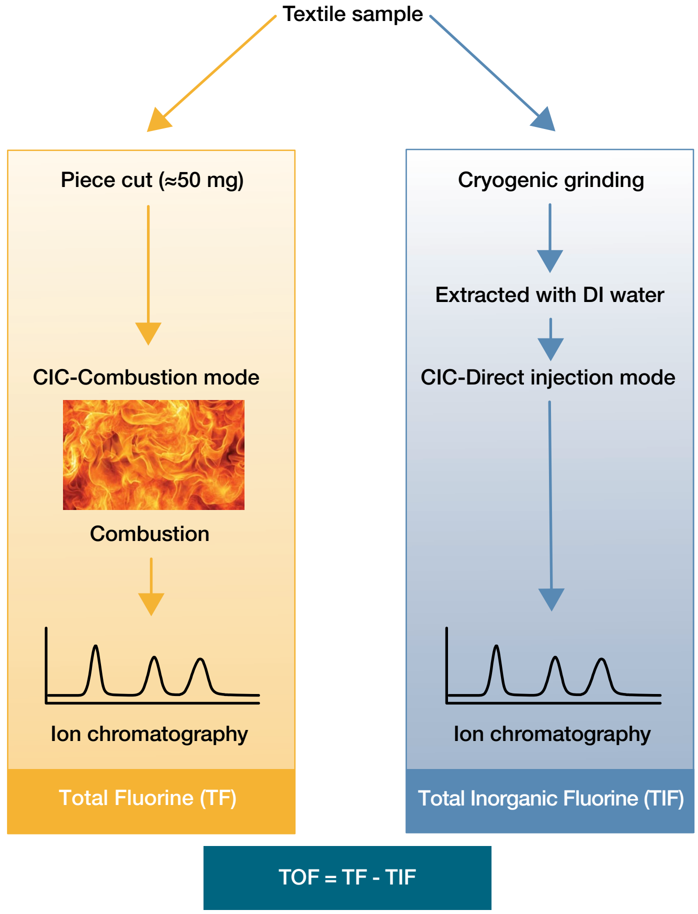

Figure 2. TOF analysis workflow

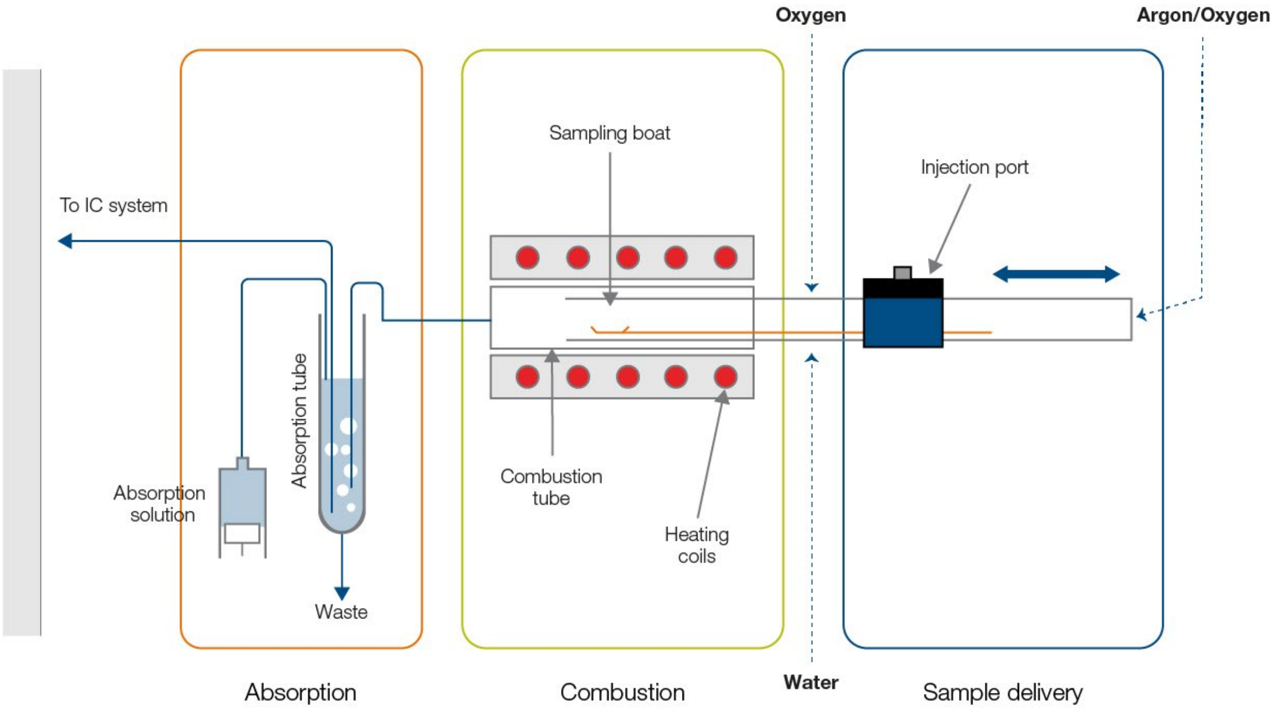

Figure 1. Diagram of a CIC system

For TF analysis, the sample amount needed may vary based on the concentration of PFAS in the samples. For the analyses described here, 50 mg of textile were cut and placed onto a pre-baked ceramic boat for analysis by CIC operated in combustion mode. To avoid carryover, two-to-three boat blanks were measured after samples with expected high fluorine content. To determine TIF, the water extract was analyzed by CIC operated in direct injection mode. TOF was calculated by subtracting TIF from TF.

Results and discussion

Separation

Establishing the appropriate eluent was essential for determining the optimal separation of fluoride from the water dip and other common anions. Carbonate and hydroxide are commonly used eluents in IC. Hydroxide eluent was chosen due to its effectiveness in separating fluoride from the water dip and its ability to yield a higher signal-to-noise (S/N) ratio after suppression compared to carbonate eluent. The use of hydroxide eluent resulted in increased overall method sensitivity.

Figure 3 illustrates the separation of seven common anions and three organic acids using combustion and direct injection modes. Only fluoride, chloride, bromide, and sulfate were detected in the chromatogram obtained from the combustion mode. Notably, fluoride was well-separated from the water dip and other anions, enabling accurate determination.

Calibration

Both combustion mode and direct injection mode can be used to build fluoride calibration curves. In this study, we choose combustion mode as recommended by the U.S. Environmental Protection Agency (EPA) Method 1621 for the determination of AOF in aqueous matrices by CIC.[7] An 8-point calibration curve was prepared over a concentration range of 1–200 mg/L by diluting a certified 1,000 mg/L fluoride standard solution with DI water. Each calibration standard was analyzed by pipetting 200 µL into clean ceramic boats. The fluoride amount was converted to nanograms (ng) for calibration, as shown in Figure 4.

The regression coefficients of the calibration curve were greater than 0.999 with a quadratic fitting. The calculated concentrations of the calibration standards were within 97–110% of the true value for all calibration levels, meeting the EPA requirements of 80–120%. The calibration was also assessed based on the relative standard error (RSE) method as listed in EPA Method 1621, and the RSE for the calibration curve was <5%, meeting the EPA requirement of 20% or less.

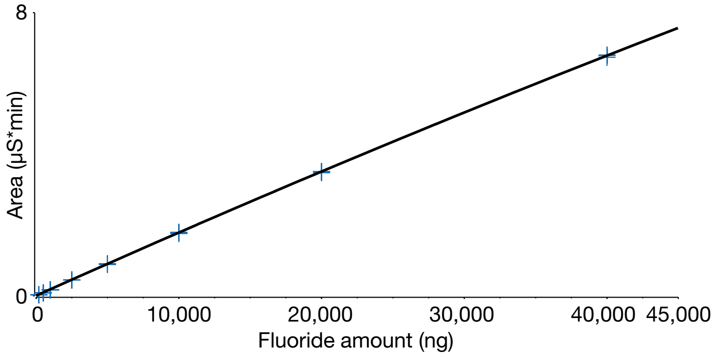

Figure 4. Fluoride calibration curve

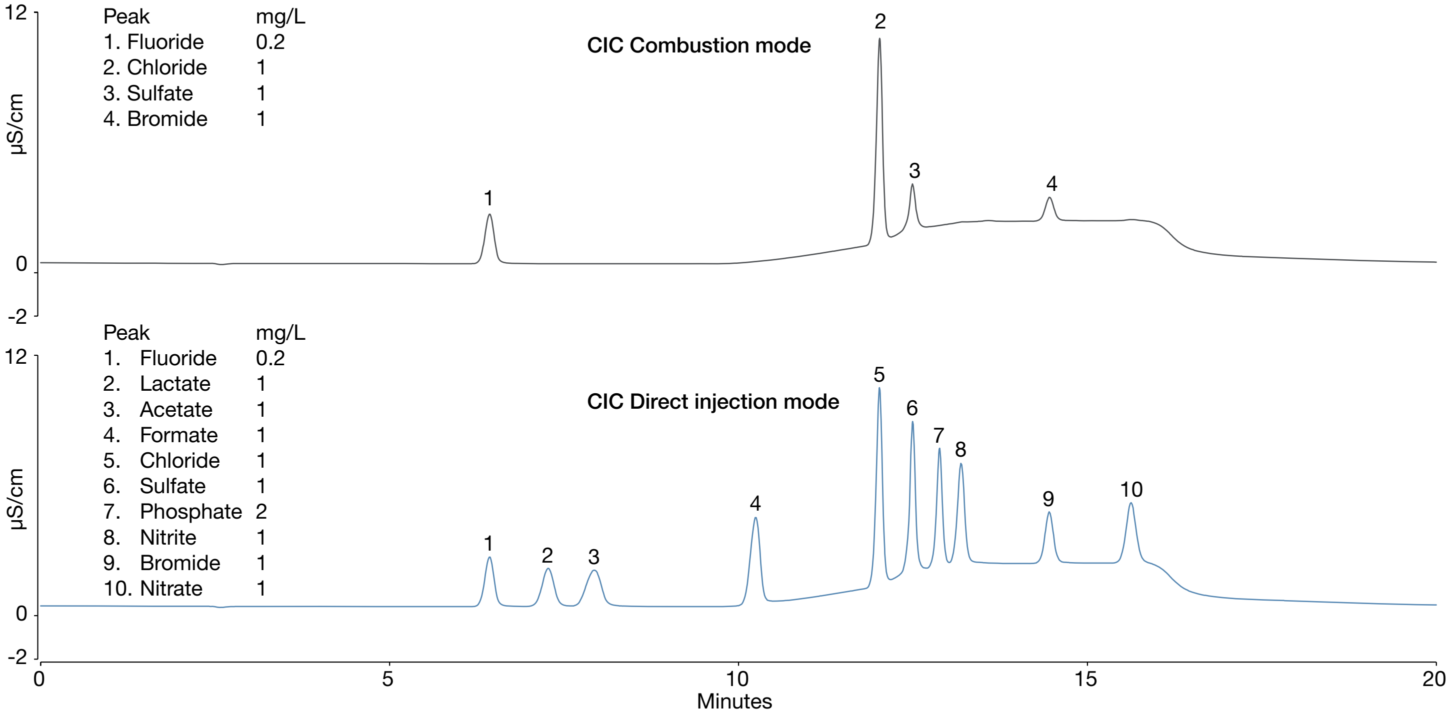

Figure 3. Separation of seven common anions and three organic acid standards (combustion mode vs. direct injection mode)

Limits of detection

The limit of detection (LOD) method for TF analysis relied on the S/N ratio. To determine the S/N ratio, peak height signals from standards with low analyte concentrations were compared to blanks, establishing minimum concentrations at which the analytes could be reliably detected. This study used a S/N ratio of 3 to estimate the LOD.

The noise was obtained from triplicate blank ceramic boat combustions, while the signal was obtained from a triplicate injection of a 0.25 mg/L fluoride standard (200 µL) on ceramic boats. Based on an assumed average sample amount of 50 mg, the LOD for TF in the sample was determined to be 0.37 µg/g. For TIF, the LOD in the samples was calculated as 37.2 ng/g, assuming an average extraction sample amount of 1 g.

Method accuracy and precision

Accuracy and precision were assessed using two approaches. First, combustion of the PFAS standard was conducted to verify the combustion efficiency of the CIC system. Second, samples were spiked with PFAS standards and subjected to the complete workflow to assess method accuracy. Sample and spiked samples were analyzed in triplicate to evaluate method precision.

To monitor for background contamination, extraction blanks were processed in every batch. Results were blank corrected by subtracting the corresponding average blank values.

A standard solution of perfluorooctanesulfonamide (1 mg/mL in methanol) was prepared for direct combustion analysis. 20 µL of this solution was added to the CIC sample boat, and the fluoride value was determined using the previously established calibration curve. A recovery of 99.3% was achieved, confirming that the combustion conditions effectively convert the fluorine in PFAS compounds to fluoride.

Method accuracy was further evaluated through recovery studies using spiked samples. To assess TF recovery in the sample, 50 µL of a 144 mg/L perfluorooctanesulfonamide standard solution was added to approximately 50 mg of sample in a CIC ceramic sample boat, resulting in a spike of approximately 93.2 µg/g of fluorine in the samples. The spiked samples were incubated at room temperature overnight to ensure absorption of PFAS into the textile matrix. The TF in the samples and spiked samples were determined using the CIC combustion mode. Recovery was assessed by first comparing the TF difference between the sample and spiked sample. The TF difference was then divided by the known amount of PFAS standard added to the spiked sample to calculate final recovery. This comparison helps determine the efficiency and accuracy of the method in recovering the added analyte from the sample matrix. Total recoveries ranging from 85% to 105% were obtained for all six samples, confirming the efficiency and completeness of the combustion as well as the accuracy of the overall workflow.

To assess TIF recovery in samples, 100 µg/L fluoride was spiked into sample water extract. As above, recovery was calculated by comparing the TIF differences between the sample and spiked samples with the known amount of fluoride that was added. Recoveries ranging from 95% to 115% were obtained for all six samples, confirming the accuracy of IC for TIF determination. The average relative standard deviation between the triplicates was less than 5%, indicating high precision.

TOF in textile samples by CIC

The TF in a sample is defined as the sum of TIF and TOF. In this study, TOF was determined by subtraction of TIF from TF. After combusting the solid sample, TF was measured using IC. High concentrations of TF (>100 ppm) were observed in five of the six samples tested (Table 2).

TIF was measured using IC after extracting the ground textile samples with DI water. The contribution of TIF to TF was found to be very small (<1 ppm), as shown in Table 2. Even after subtracting TIF, the TOF remained above 100 ppm for five of the samples. Therefore, the five samples did not meet the regulatory limit of 100 ppm TOF set by the state of California.[3]

Figure 5 shows the IC chromatograms of TF and TIF of Sample #1. Fluoride is well separated from other anions that may be present in samples, allowing for accurate determination.

Table 2. Total organic fluorine (TOF) in samples, n = 3

Sample	Sample information	TF (ppm) (RSD < 5%)	TIF (ppm) (RSD < 10%)	TOF (ppm) (TF-TIF)
S1	Polyester baby bib	334	0.21	333.8
S2	Polyurethane laminate pre-cut fabric, waterproof and breathable for cloth diapers	178	0.46	177.5
S3	Polyester waterproof and stain-resistant tablecloth	244	0.53	243.5
S4	Waterproof ripstop nylon fabric for kite, tent, flag, bag, tarp cover	4.6	0.13	4.5
S5	Waterproof canvas fabric for chair cushion furniture cover	303	0.44	302.6
S6	Waterproof canvas fabric for indoor and outdoor	178	0.19	177.8

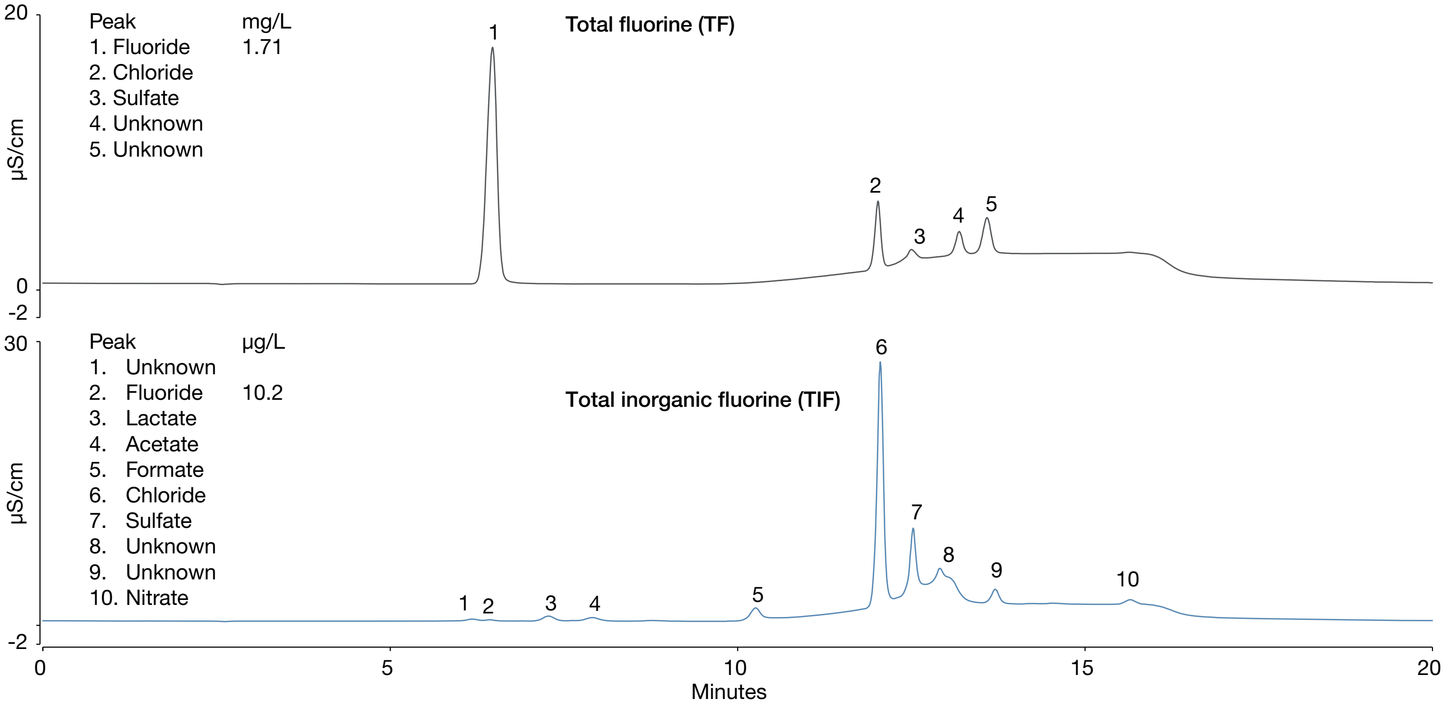

Figure 5. TF and TIF chromatogram (Sample #1)

Conclusion

We developed a sensitive and accurate method using CIC to determine TOF in textiles. The method offers a detection limit of 0.37 ppm, which is significantly lower than the regulatory threshold of 100 ppm, ensuring reliable detection of PFAS. Spiked recovery experiments show the method's accuracy falls within a range of 85–105%. This TOF method is beneficial for manufacturers who want to ensure compliance with current state regulations. Moreover, the CIC workflow provides a more comprehensive understanding of the total PFAS and fluorinated content in textiles compared to LC-MS targeted approaches, offering greater clarity about the potential PFAS contamination in textiles.

List of abbreviations

PFAS: Per-and polyfluoroalkyl substances

IC: Ion chromatography

CIC: Combustion ion chromatography

TF: Total fluorine

TOF: Total organic fluorine

TIF: Total inorganic fluorine

References

1. Schellenberger, S.; Liagkouridis, I.; Awad, R.; Khan, S.; Plassmann, M.; Peters, G.; Benskin, J.P.; Cousins, I.T. An outdoor aging study to investigate the release of per- and polyfluoroalkyl substances (PFAS) from functional textiles. *Environ. Sci. Technol.* **2022** *56*(6), 3471–3479. doi: 10.1021/acs.est.1c06812. Epub 2022 Feb 25. PMID: 35213128; PMCID: PMC8928479.
2. Department of Toxic Substances Control. https://dtsc.ca.gov/scp/treatments-with-pfass
3. AB-1817 Product safety: textile articles: perfluoroalkyl and polyfluoroalkyl substances (PFAS) https://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=202120220AB1817
4. The Danish Ministry of Environment And Gender Equality, PFAS action plan. https://mim.dk/nyheder/pressemeddelelser/2024/april/pfas-handlingsplan-regeringen-vil-indfoere-dansk-forbud-mod-pfas-i-toej-og-sko
5. Skedung, L.; Savvidou, E.; Schellenberger, S.; Reimann, A.; Cousins, I.T.; Benskin, J.P. Identification and quantification of fluorinated polymers in consumer products by combustion ion chromatography and pyrolysis-gas chromatography-mass spectrometry. *Environ. Sci. Process. Impacts.* **2024** Jan 24, *26*(1), 82–93. doi: 10.1039/d3em00438d. PMID: 38099738.
6. Per- and polyfluoroalkyl substances in North American school uniforms. Xia, C.; Diamond, M.L.; Peaslee, G.F. et al. *Environ. Sci. Technol.* **2022** *56*(19), 13845–13857 doi: 10.1021/acs.est.2c02111
7. U.S. EPA (2024) Method 1621, Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC) - (EPA 821-R-24-002) https://www.epa.gov/system/files/documents/2024-01/method-1621-for-web-posting.pdf [accessed on May 08, 2024]

Learn more at **thermofisher.com/combustionic**