Enhanced screening of PFAS compounds in wastewater: Implementing U.S. EPA Method 1621 with improved combustion-ion chromatography

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Introduction

Per- and polyfluoroalkyl substances (PFAS) is the collective name for over 14,000 synthetic fluorinated compounds. A PFAS compound is defined as a compound containing a fully fluorinated methyl group or methylene on an alkane functional group (Organisation of Economic Co-operation and Development (OECD)) or as a fluorinated compound with at least two adjacent saturated carbons with one carbon fully fluorinated and the other at least partially fluorinated (U.S. Environmental Protection Agency (EPA)).[1,2] Since the 1940s, PFAS have been prevalent in many polymers, surfactants, fire-suppression chemicals, industrial products, and consumer products.[3-6] In addition to their extensive presence, PFAS compounds are persistent and bioaccumulate. Consequently, PFAS compounds are an environmental contamination concern. Toxicological studies of several PFAS compounds, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), indicate the potential for acute to chronic effects impacting reproductive health.[7-11] Fewer studies have been conducted on the thousands of other compounds grouped under the EPA PFAS classification.[2]

The U.S. EPA has defined targeted and non-targeted analysis methods for PFAS.[12-18] Combustion-ion chromatography (C-IC) was previously demonstrated as a screening method for PFAS; PFAS compounds are converted to HF, and the subsequent fluoride is analyzed by ion chromatography (IC) with suppressed conductivity detection.[19-24] This technique is incorporated into EPA Method 1621 for non-targeted determinations of PFAS as adsorbable organic fluorine (AOF).[25-28] Our results from the EPA Method 1621 multi-laboratory study are also published in the Thermo Scientific Application Note AN002748 with additional tips for successful implementation in the Thermo Scientific Technical Note TN003056.[29,30]

In the EPA Method 1621 collaboration study, we found that reduced baseline contamination and increased sensitivity, accuracy, and precision can be achieved by minimizing sources of contamination.[29,30] Another approach to reduce baseline contamination is to design the adsorption and combustion-absorption systems in a way that reduces or eliminates contamination sources. In this application, EPA Method 1621 is implemented on the offline Thermo Scientific™ Cindion™ Adsorption module, a Cindion Combustion / Absorption module with liquid and solid sample handling, and a Thermo Scientific™ Dionex™ Inuvion™ Reagent-free Ion Chromatography (RFIC™) System. The adsorption module was designed to minimize contamination by eliminating contamination sources. To increase throughput, the adsorption module is designed to semi-automatically adsorb PFAS from six water samples at a time. The Thermo Scientific™ Cindion™ Combustion-Ion Chromatography (C-IC) System was optimized for increased combustion efficiency by incorporating a Z-fold combustion tube to introduce oxygen at multiple locations. As a result, the combustion tube and furnace are shorter, and combustion times are reduced. This also results in a smaller footprint, saving crowded bench space. Data processing and system management are also more efficient because the Cindion C-IC system is controlled by a single software, the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Overall, this solution provides improved sensitivity due to increased signal-to-noise, improved recoveries of added standards, and comparable reproducibility to previous results in a smaller footprint.

Experimental

Equipment

Cindion C-IC system

- Thermo Scientific™ Cindion™ Combustion / Absorption Module (P/N B51006425) with Thermo Scientific™ Cindion™ C-IC Solids Kit (P/N B51006427)
- Thermo Scientific™ Cindion™ Solid / Liquids Autosampler (P/N B51006429)
- Thermo Scientific™ Cindion™ Adsorption Module (P/N B51006430), includes six column holders
- Thermo Scientific™ Dionex™ Inuvion™ IC System with RFIC (P/N 22185-60108)
- Optional Thermo Scientific™ Dionex™ Eluent Monitor, 4 L (P/N 22185-62708)
- Thermo Scientific™ Thermolyne™ Muffle furnace, 2 L small bench top, to clean combustion cups, recommended for EPA Method 1621 (P/N FB1415M)

Software

Chromeleon CDS software, Chromeleon 7 version 3.2, with Cindion C-IC system and eluent monitor drivers

Consumables list

IC consumables

- Thermo Scientific™ Dionex™ IonPac™ AG24 Guard and IonPac AS24 Analytical Columns, 2 mm (P/N 064151, P/N 064153)
- Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Electrolytic Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ Inuvion™ RFIC Eluent Degasser Module (P/N 106-60001)
- Thermo Scientific™ Dionex™ ADRS 600 Suppressor, 2 mm (P/N 088667)
- Thermo Scientific™ Dionex™ E/O Eluent Organizer with two 2 L HDPE eluent bottles (P/N 072057) plus one 4 L HDPE eluent bottle (P/N 063292)
- Thermo Scientific™ Dionex™ IC PEEK Viper™ Fitting Tubing Assembly Kit (P/N B51000232)
- 100 µL PEEK sample loop (P/N 042951)

C-IC consumables

- GAC removal tool (EST Analytical, P/N A16-20A-0001)
- Agilent Technologies polypropylene vials, 1 mL, (Fisher Scientific P/N NC2038456) and Thermo Scientific™ SureSTART™ Polyethylene Snap Caps, polyethylene (P/N 6ERC11PE), or Fisher Scientific™ PFAS-free vials and caps, to store open PFAS standards (P/N 03-452-581)
- Fisherbrand™ Crucible Tongs (Fisher Scientific P/N 13-820-023)
- Fisherbrand™ Nitrile Cleanroom Gloves, Class 10, ISO 4 (Fisher Scientific P/N 12892004) (A-F extra small to 2X large)
- Fisherbrand™ Elite™ Pipette, adjustable, 200 µL, and Fisherbrand™ SureOne™ Pipette Tips (Fisher Scientific P/N BE00200 and P/N 02-707-409)
- Fisherbrand™ Stainless Steel Tweezers (Fisher Scientific P/N 12-000-157)
- Hamilton™ 700 Microliter Syringes, 100 µL, metal plunger (Fisher Scientific P/N 14-813-091)
- Newtex™ ZetexPlus™ Heat Resistant Gloves, 200 series (Fisher Scientific P/N 11-392-53)
- Thermo Scientific™ Cindion™ C-IC Quartz Wool for samples containing total suspended solids (TSS > 8 mg/L) (P/N B51006451)
- Thermo Scientific™ Cindion™ C-IC Carbon Columns - Granular Activated Carbon (GAC) columns (P/N B51006452, package of 100) and column holders, used to adsorb samples using the Cindion C-IC adsorption module (P/N B1006453, each)
- Thermo Scientific™ Cindion™ C-IC Solids Sampler Kit (solid boat, solids tray, solids gripper) - reserve supplies (P/N B51006427)
- Thermo Scientific™ Cindion™ C-IC Quartz Cups (P/N B51006446)
- Thermo Scientific™ Nalgene™ HDPE, wide mouth, 125 mL bottles (P/N 02-893-5C)
- Thermo Scientific™ Nalgene™ Vacuum Polypropylene Desiccator to store clean combustion cups (P/N 08-642-5)

Reagents

- Fisher Chemical™ Ammonium hydroxide, 28–30 w/w%, Certified ACS, for cleaning containers (Fisher Scientific P/N A669S-500) (CAS 1336-21-6)
- Thermo Scientific™ Dionex™ Chloride standard, 1000 mg/L (P/N 037159)
- DI water, 18 MΩ·cm resistivity, TOC < 50 ng/mL
- Thermo Scientific Chemicals Drierite™, indicating, 500 g, 8 mesh, for storing clean combustion cups (Fisher Scientific P/N 21909-5000)
- Thermo Scientific™ Dionex™ Fluoride Standard, 1000 mg/L (P/N 037158)
- Fluoride Standard, 1000 mg/L, second source, SPEX CertiPrep™ (Fisher Scientific P/N AS-F9-5Y)
- Fisher Chemical™ Methanol, Optima™ grade for cleaning (Fisher Scientific P/N A454-4) (CAS 67-56-1)
- Thermo Scientific™ Methanol, UHPLC-MS grade, lowest PFAS-containing methanol for cleaning (P/N A458-1) (CAS 67-56-1)
- Fisher Chemical™ Sodium nitrate, ACS Certified (Fisher Scientific P/N S343-3) (CAS 7631-99-4)
- Sodium Perfluoro-1-hexanesulfonate standard, 50 µg/mL (in methanol) (Wellington Laboratories L-PFHxS), used for spike-recovery experiments (F equivalence = 64.6%; 29.26 µg/mL F) - store in PFAS-free vials and caps

Method

Sample preparation with Cindion C-IC adsorption module:	
Sample prep.	See Standard and sample preparation section
Standard prep.	See Standard and sample preparation section
Combustion with Cindion C-IC system:	
Temperatures (°C)	Furnace: 1050, 1050
	Transfer line for hydration: 175
Oxygen gas flows (mL/min)	Combustion tube entrance, Labeled as Argon line: 100
	Oxygen, primary: 200
	Oxygen, turbo: 100
2-step combustion program	3 mm/s to 75 mm, hold 60 s
	3 mm/s to 150 mm, hold 300 s
Absorption with Cindion C-IC system:	
Absorption solution	3.5 mL DI water
Injection to IC	100 µL
Analysis with Dionex Inuvion IC system with RFIC:	
Columns	Dionex IonPac AG24 guard column Dionex IonPac AS24 separation column
Eluent source	Dionex EGC-500 KOH eluent generator cartridge, Dionex CR-ATC 600 trap column, and Dionex RFIC degas module
KOH gradient	25 mM KOH (0 to 4 min) 25–75 mM (4 to 6 min) 75–25 mM (10 to 10.1 min) 25 mM (10.1–15 min)
Flow rate	0.32 mL/min
Column temp.	30 °C
Detection	Suppressed conductivity, ADRS 600, 2 mm, 60 mA, recycle mode
Typical conductance baseline	≈0.4 µS/cm
Typical system pressure	≈2000 psi with 500 psi backpressure tubing

Standard and sample preparation

Reagents

Prepare 2 M sodium nitrate and 10 mM sodium nitrate according to EPA Method 1621, Section 7.14. Prepare 1% ammonium hydroxide in methanol which is used for the initial cleaning of the Cindion adsorption module, sample bottles, and any tools. Prepare 500 mL of 10% methanol in DI water to clean the Cindion adsorption module.

Standards

Prepare 5 to 7 fluoride standards from 1 to 50 mg/L from 1000 mg/L fluoride standard stock solution. Prepare 2.5 mg/L and 12.5 mg/L fluoride calibration validation (CV) standards from the second source fluoride standard stock solution. Add 0.5 mL of 2 M sodium nitrate to each standard.

Samples

To generate the sample aliquot, add DI water for method blanks, DI water with added PFAS standard or water samples to the 125 mL wide mouth HDPE bottle until the volume reaches the bottle's neck. Add 0.5 mL of 2 M sodium nitrate to each sample. Mix. Number each bottle and cap. Record the initial weights and bottle number and the final weight after loading the sample onto the GAC material.

Preparing for combustion

Standards

To generate the calibration curve, 200 µL of each calibration standard is added directly to the combustion cups for analysis by C-IC. The CV standards are added similarly and are used to validate the calibration curve for all sequences following the calibration sequence.

To plot the calibration results, the volumes of the standards (200 µL) are first normalized to the sample volume (100 mL), resulting in a 500-fold reduced concentration (µg/L). For example, the 2.5 mg/L standard is plotted as 5 µg/L. The expected results from the 2.5 mg/L and 12.5 mg/L CV standards are 5 and 25 µg/L, respectively.

Samples

The Cindion adsorption module uses the "Load Tray" function to move the tray, making it more convenient to load samples and vials. Positions: samples without caps are loaded in the front, followed by 10 mM sodium nitrate rinse in the vials, DI water rinse in the next row of vials, 10% methanol cleaning solution, and finally DI water cleaning solution. The "Run" function processes 100 mL of the samples onto granular activated carbon (GAC) columns, rinses with 25 mL of sodium nitrate, and finally rinses with 20 mL of DI water then dries with air pumped from empty syringes. The "Clean" function cleans empty GAC holders with the first row of DI water, followed by 10% methanol, and then DI water. It is recommended that you use two clean cycles between samples.

After processing the samples through the "Run" mode, record the final weight of the sample bottles, and analyze the GAC material by C-IC.

Instrument setup and installation

Potential sources of contamination

To exploit the full potential of the trace analysis method, potential sources of contamination must be excluded in advance. A detailed discussion on achieving low contamination levels and tips for successful implementation of EPA Method 1621 are discussed in Thermo Scientific Technical Note TN003056.[30]

Install and set up the Dionex Inuvion IC system with the other Cindion C-IC system components as indicated in Figure 1, Thermo Scientific Technical Note TN003773, and the instrument manuals.[31-36]

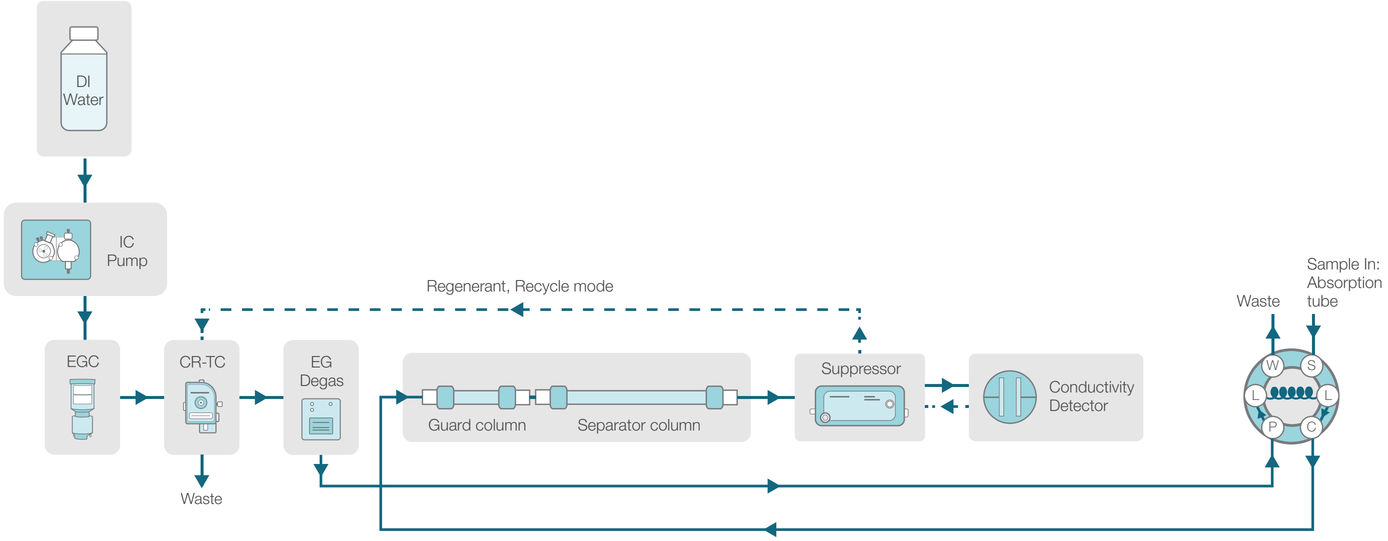

Figure 1. IC flow diagram

Operating the C-IC system

Operation of the Cindion C-IC system is thoroughly discussed in Thermo Scientific Technical Note TN003773.[33]

Assessing cleanliness

C-IC modules and C-IC consumables must be cleaned to remove residual contamination levels below the expected detection limits. To achieve this goal for the Cindion adsorption unit, the system and the empty GAC carriers are rinsed initially with 1% ammonium hydroxide in methanol followed by six cycles of DI water, 10% methanol in DI water, and DI water rinses. The cleanliness was determined by collecting a method blank (MB) on GAC for each channel and analyzing the carbon by C-IC.

To assess the baseline contamination of the furnace, run a sequence of 6–12 runs without combusting any cups. Clean the combustion cups using EPA Method 1621 Section 4.2.2.[28]

Results and discussion

The official EPA Method 1621 was updated from the draft method, and therefore, some of the section enumerations have changed. In addition, this method was updated from the EPA method by initiating the gradient at 4 min instead of 6 min to ensure that all anions are fully eluted from the column.

Initial demonstration of capability

In EPA Method 1621, the initial demonstration of capability (IDC) is required before analyzing samples. IDC includes determining the retention time windows of fluoride and chloride, calibration with relative standard error (RSE) <20%, initial demonstration of precision with RSD <20%, and accuracy within 20%. In EPA Method 1621, Section 10.2.2, fluoride must be separated >1 min from the water dip (void volume) and other peaks eluting near fluoride for accurate determinations. In hydroxide eluent separations with suppressed conductivity, as shown in Figure 2, the water dip is small and isolated from fluoride. Fluoride elutes away from the water dip in a flat baseline region. The results of these retention time experiments are summarized in Table 1. Fluoride meets the retention time criteria.

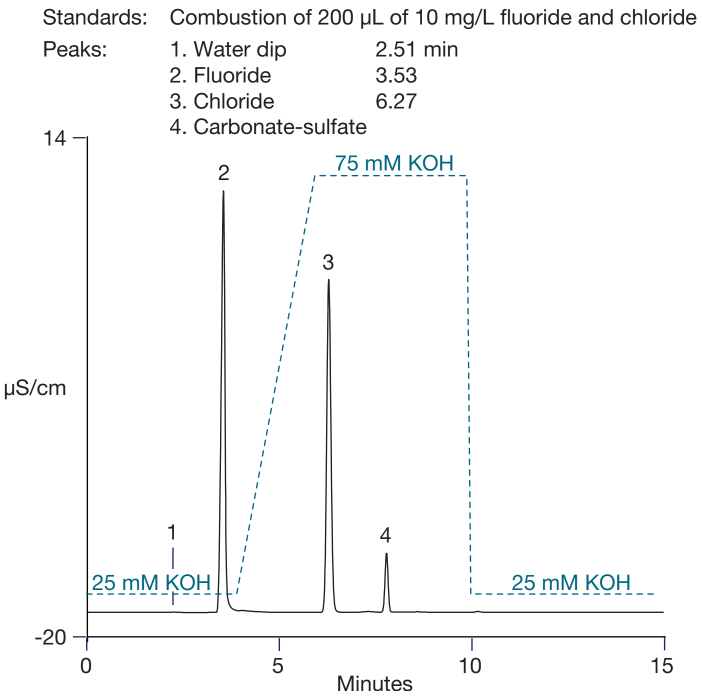

Figure 2. Determining retention time windows

Calibration

Calibration curves were determined according to EPA Method 1621, Section 10.3.0 by the peak area response of fluoride versus normalized concentration to the 100 mL sample volume. The concentration is first normalized for the 1/500-fold ratio of the volume of combusted standard to adsorbed sample, (0.2 / 100 mL). For example, the combustion of a 200 µL of 1 mg/L fluoride calibration standard is plotted as 2 µg/L fluoride. RSE is required to compare and select the best calibration fit per EPA Method 1621, Section 10.3.2. The advantages of using RSE to select the best calibration curve are discussed thoroughly in Thermo Scientific Application Note AN002748 and Technical Notes TN003056, TN003551, and TN003643.[29,30,37,38] The Chromeleon CDS RSE calculation table can be easily added to any Chromeleon CDS table. For ease of use, the table will be included in the "default" template for this application's eWorkflow found in the Thermo Scientific™ AppsLab™ Library.[39] For more information, the RSE formula is included in the Appendix.

Table 1. Determining fluoride retention time window

Peak	Retention time (min)	Peak window (min)	Separation (min)	EPA Method 1621 limit
Water dip	2.51 ± 0.04	--	--	--
Fluoride	3.55 ± 0.10	3.35–3.75	1.04	>1 min
Chloride*	6.23 ± 0.02	6.13–6.43	2.68	>1 min
EPA Method 1621 criteria		PASS		

*0.2 mL of 10 mg/mL fluoride and chloride, n = 3

Briefly, to determine the RSE, evaluate linear and quadratic fits by allowing offset from zero and calculating the curve fit related to area weighting (none, 1/A, 1/A^2). Select the calibration curve with the lowest RSE. In our experiments, we used a quadratic fit with offset and with 1/A^2 area weighting. This curve provided the lowest RSE (5.75) and complied with the RSE limit of 20% set by the EPA (Table 2). Figure 3 shows the resulting calibration plot.

Initial demonstrations of accuracy and precision

EPA Method 1621, Section 9.2.1 requires an initial demonstration of accuracy (IDA) and precision (IDP) before samples can be analyzed. The IDA and IDP demonstrate that the instrument and laboratory performances are suitable for this method. The IDA and IDP were determined by preparing and analyzing two MBs and four replicates of DI water fortified with 25 µg/L equivalent fluorine from a PFHxS standard. The IDA and IDP results demonstrate that the method and this laboratory meet the IDC requirements (Table 3). The results are also similar to those reported previously in AN002748 for both RSDs and recovery: RSD 4.5% vs. 4.6% in AN002748 and recovery 103% vs. 98% in AN002748.

Table 3. Initial demonstration of accuracy and precision

EPA Method 1621	Prescribed limit	Experimental value
IDA (Section 9.2.1)	Recovery within ± 20%	Recovery = 103.2%
IDP (Section 9.2.1)	RSD < 20 %	RSD = 4.47%

Method blanks and method detection limits

To assess the initial cleanliness of the Cindion adsorption modules after the cleaning process, MBs were determined on each channel. The results averaged 1.11 ± 0.046 and 2.02 ± 0.15 µg/L fluoride for the Cindion adsorption module #1 and #2, respectively.

MBs and method detection limits (MDLs) were determined over three days following EPA Method 1621 Section 9.2.2. Two to three replicate MBs and 5 µg/L equivalent fluorine (PFHxS) MDL standards were prepared and analyzed each day over three days. A total of n = 7 for each of MBs and MDL standards were analyzed.

Table 2. Comparison of relative standard error (RSE) and coefficient of determination (r^2)

	Linear			Quadratic			RSE limit
	No weighting	1/A	1/A^2	No weighting	1/A	1/A^2	
RSE*	38.76	20.47	7.25	13.22	5.94	5.75	20
r^2**	0.9967	0.9928	0.9900	0.9982	0.9977	0.9970	

n = 7

* RSE = Relative Standard Error, weighting = none, 1/area, or 1/(area)^2

** r^2 = Coefficient of determination

Calibration range = 2 µg/L to 100 µg/L based on a 100 mL sample

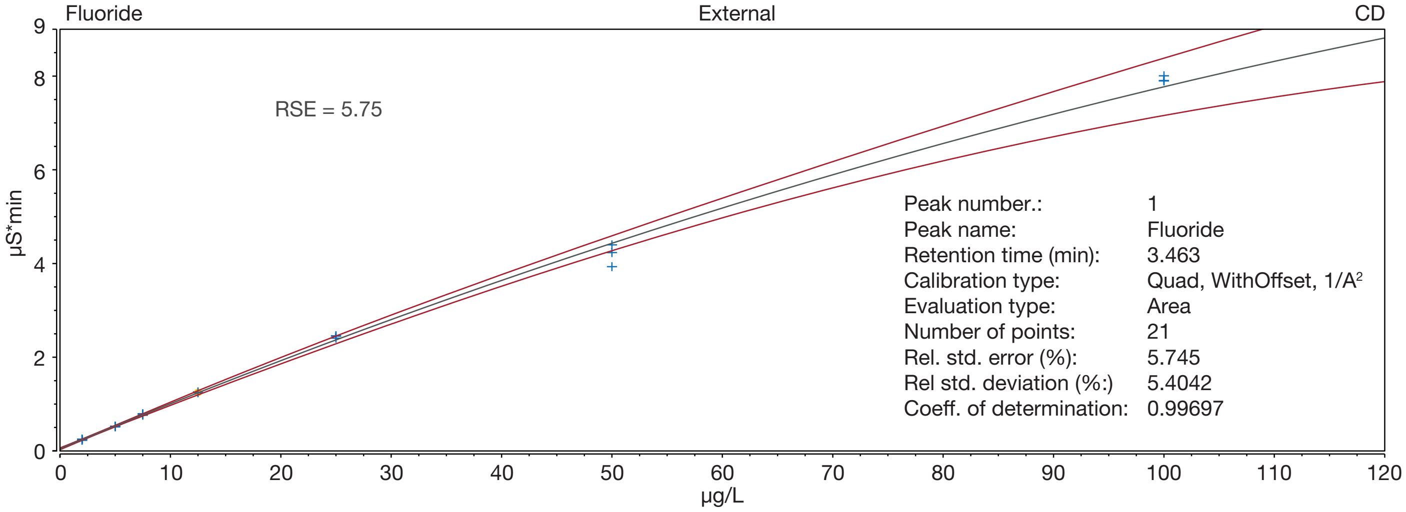

Figure 3. Calibration curve with RSE of 5.75

To calculate the MDL, the average MB of 2.167 µg/L fluoride was subtracted from the individual MDL results. The standard deviation of the average MDL, 0.54, was multiplied by the Student *t*-test constant of 3.14 (n = 7). Thereafter, the calculated MDL was 1.7 µg/L (Table 4). The MBs are slightly higher than the results previously reported in AN002748, which was attributed to the GAC material. The calculated MDLs are slightly lower than previously reported, demonstrating the advantages of the Cindion C-IC design for sensitivity.

Samples

The method was applied to municipal drinking water, blended wastewater, and percolation pond water samples. The results are shown in Table 5. Less than 5 µg/L of fluorine is present in the samples, ranging from 2 to 5 µg/L, with the wastewater containing the highest amount.

Determining recoveries of added PFHxS standard

To understand method accuracy, recoveries of added PFHxS standard were determined at two concentrations and in triplicate for the three samples (Table 5). The wastewater particulates were captured in the empty spaces of the GAC column. Therefore, no glass wool was needed, which provided the advantage of excluding a high and highly variable fluoride contamination.

Sample prep.: Adsorbed onto GAC columns using the Cindion adsorption module
Samples: A: DI water method blank
B: 5 µg/L equiv. Fluorine (PFHxS)

Peaks:	A	B
1. Fluoride	2.17	4.57 µg/L

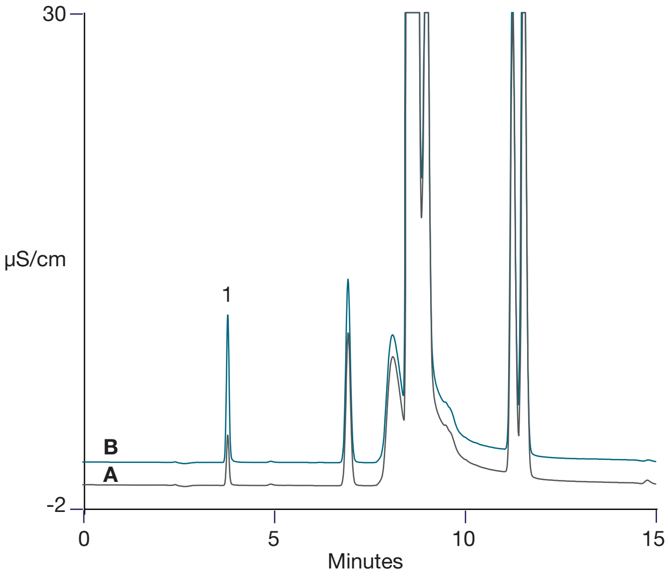

Figure 4. Method blank and 5 µg/L equivalent fluorine MDL standard

Table 4. Comparison of 3-day test of method blanks and 5 µg/L equiv. MDL standards

	Cindion C-IC and adsorption modules		Previous C-IC system reported in AN002748	
	Method blank F$^-$ (µg/L)	MDL standard* F$^-$ (µg/L)	Method blank F$^-$ (µg/L)	MDL standard* F$^-$ (µg/L)
Average over 3 days, X	2.17	4.57	1.23	4.76
Standard deviation (σ)	0.37	0.54	0.17	0.80
Calculated MDL**	--	1.7	--	2.5
Calculated ML (LOQ)	--	ML = 5	--	ML = 8

* Average method blank subtracted
**Section ii: MDL(s) = 3.14*σ [40]
Where MDL(s) is the MDL for spiked MDL standards, 3.14 is the Student's *t*-test value for n = 7, 99 percentile, and σ is the standard deviation.
Method limit (ML) = 3.18 * MDL

Table 5. Sample results and recovery results of added PFHxS standard

Sample	Total fluoride (µg/L)		Recovered (%)
	Measured*	Added	
Municipal dritnking water	1.81 ± 1.02	8.0	81.6 ± 1.6
		23.99	101 ± 16
Blended wastewater	4.86 ± 0.55	8.0	93.6 ± 14
		23.99	86.5 ± 5
Percolation pond water	0.29 ± 0.26	8.0	101 ± 5
		23.99	94.5 ± 7.3

*After MBs were subtracted

The method is accurate, as indicated by the 82% to 101% recoveries of added PFHxS standards, and this is improved over previous recovery results of 80% to 117% reported in AN002748. The chromatogram of wastewater is compared to an MB with the replicate recovery sample (Figure 5).

The MBs and process checks show that the method is working well and within the expected limits (Table 6).

Sample prep.: Adsorbed onto GAC columns using the Cindion adsorption module

Samples:
A: DI water method blank
B: Municipal wastewater
C: Sample B plus 9.99 µg/L equiv. Fluorine (PFHxS)

Peaks:	A	B	C
1. Fluoride	2.1	6.7	14.9 µg/L

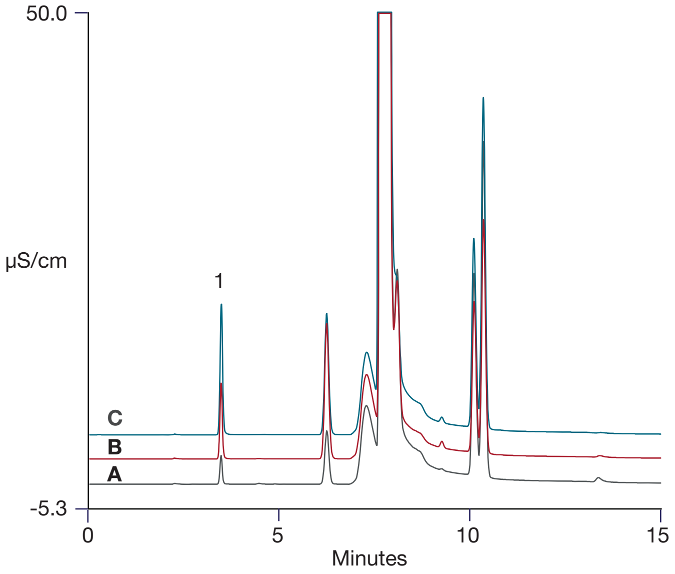

Figure 5. Determination of PFAS in wastewater by AOF and C-IC

Table 6. Quality control checks for sample sequences

	Sample sequences	Total fluoride (µg/L)		Recovered (%)
		Measured*	Added	
Method blanks	Drinking water	2.18 ± 0.28	--	--
	Wastewater	2.06 ± 0.09	--	--
	Pond water	2.59 ± 0.44	--	--
Low CV	Drinking water	4.45 ± 0.24	5.0	88.9
	Wastewater	5.05 ± 0.37	5.0	101
	Pond water	5.10 ± 0.12	5.0	102
OPR (n = 1)*	Drinking water	23.4	25	93.6
	Wastewater	20.5	25	81.9
	Pond water	21.5	25	85.9
Medium CV	Drinking water	21.4 ± 1.15	25	85.5
	Wastewater	22.5 ± 1.02	25	90.1
	Pond water	25.20 ± 0.1	25	101
Method limits				80–120% OPR: 70–130%

*After MBs were subtracted

Conclusion

This application note demonstrates U.S. EPA Method 1621 results using an improved C-IC workflow solution. The C-IC complete flow path includes the adsorption of PFAS in wastewater samples using the offline Cindion adsorption module, the combustion of the PFAS to fluoride using the Cindion combustion-absorption system, and quantitation using a Dionex Inuvion IC instrument with RFIC. The results were improved compared to previous implementation of EPA Method 1621 in Thermo Scientific Application Note AN002748. MDLs were improved (1.7 µg/L vs. 2.3 µg/L) with comparable reproducibility (4.5% RSDs vs. 4.6%) and improved accuracy (82–101% vs. 70–120%) as compared to previous results. This method showcases significant advantages of the Cindion C-IC system for measuring AOF and screening for PFAS in wastewater. In addition to ease of use, RFIC with hydroxide eluents provides more accurate reporting because fluoride easily elutes from the water dip, eliminating the need for manual integration. These data collectively highlight the power of C-IC in eliminating the sample matrix and measuring only adsorbable fluorine content in samples, successfully achieving the goals outlined in U.S. EPA Method 1621.

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Appendix

Table A1. Definitions

Term	Definition	Description
AOF	Adsorbable organic fluorine	Fluorocarbon and perfluorocarbon compounds in water or solvent that adhere to a sorbent like activated carbon or ion exchangers.
CV	Calibration verification standard	Check standards prepared from an inorganic fluoride standard that are from a different (second) source than the calibration standards. Added directly to combustion cups. Run at the beginning and the end of each sequence.
GAC	Granular activated carbon	Carbon material used for adsorbing organic compounds.
IPR	Initial precision recovery standard	Used to determine the expected process check value (OPR). Prepared by adding PFHxS standard to DI water. Processed through adsorption, combustion, absorption, and IC analysis.
MB	Method blanks	DI water processed through adsorption, combustion, absorption, and IC analysis. Indicates the lowest actual measurements possible and the baseline contamination of the C-IC and the filtration module. Always run at the beginning and the end of each sequence.
MDL	Method detection limit	The lowest reliable measurement, typically 3x S/N. In this test, the standard is processed through the adsorption on carbon, combusted, absorbed, and analyzed by IC.
MDL(b)	Method detection limit of blanks, n = 7	Defined as: (Mean of method blanks) plus (standard deviation x Student *t*-test factor).
MDL(s)	Method detection limit of 5 ng/mL PFHxS standard, n = 7	Defined as: (standard deviation) x (Student t-test factor).
OPR	Ongoing precision recovery standard	Check standard run at the beginning of each sequence. Prepared by adding PFHxS standard to 100 mL of DI water. Processed through the adsorption on carbon, combusted, absorbed, and analyzed by IC.
PFHxS	Perfluorinated sulfonate standard	Sodium perfluoro-1-hexanesulfonate standard. Used for MDL and QC check standards.
RSE	Relative standard error	Error from calibration line. Defines the best fit of a calibration curve.
TSS	Total suspended solids	Includes any loose particulates or precipitated solids in the water sample.

Relative standard error formula

Definition of the relative standard error to determine instrument linearity

with

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \frac{\left[\frac{x_i' - x_i}{x_i}\right]^2}{n-p}}$$

x_i = *Nominal concentration (true value) of each calibration standard*

x'_i = *Measured concentration of each calibration standard*

n = *Number of standard levels in the curve*

p = *Type of curve (2 = linear, 3 = quadratic)*

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