PFAS by CIC workflow

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What does CIC replace?

Combustion (Oxygen) Bombs

- All hydrocarbons are oxidized to carbon dioxide and water by the reaction, and all sulfur compounds are converted to soluble forms and absorbed in a small amount of water placed in the vessel.

Schoniger Flask

- Combustion of a sample in pure oxygen, followed by the absorption of the combustion products by a solution of sodium hydroxide

Wickbold Apparatus

- Consists of a shell oven, a solid state burner, a burning chamber, a cooling device, an absorption tube, a solution tank, a rinsing device, and a flask for decomposition solution

Microwave-Induced Combustion (MIC)

- Burns the samples in pure oxygen and absorbs the analytes in small amounts of liquid

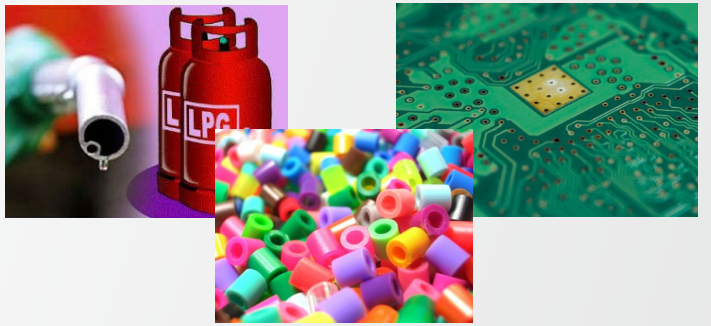
Analytical method for the determination of AOF

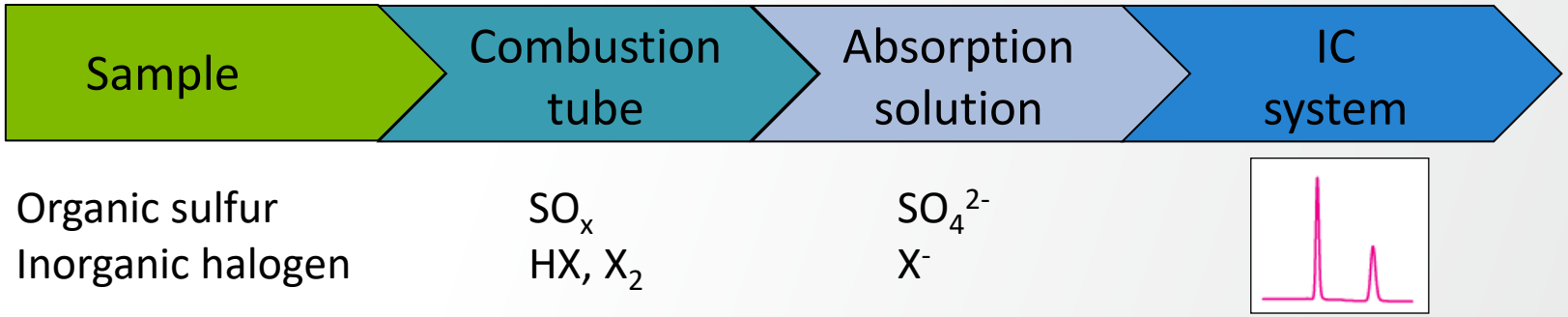
What is CIC?

Combination of Ion Chromatography (IC) with an automated sample preparation step (Combustion)

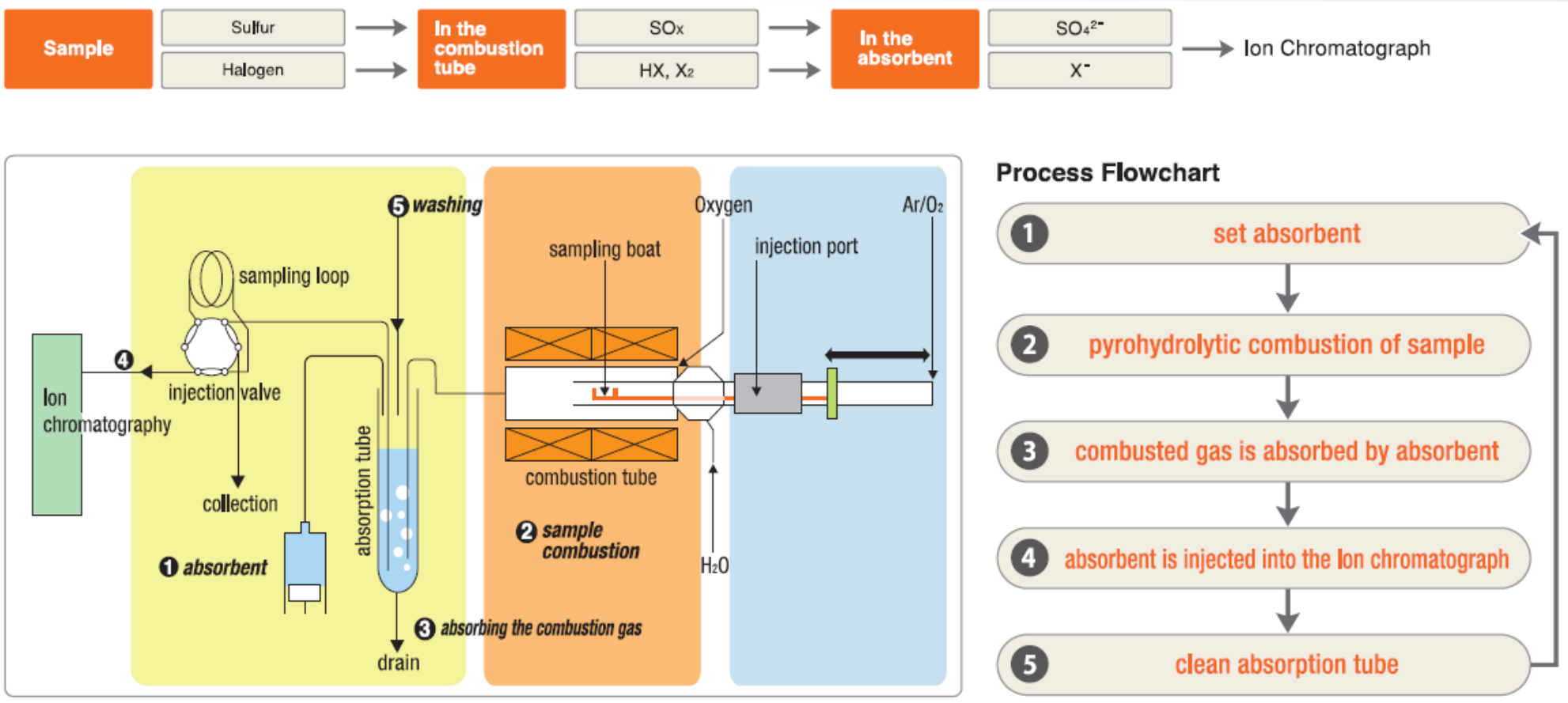
Combustion Ion Chromatography (CIC)

Total S, F, Cl, Br in liquid, solid and gas samples
Polymers, raw materials, oil, fuel, coal
Standard methods: ASTM, JIS, VDI, DIN, ISO





CIC theory

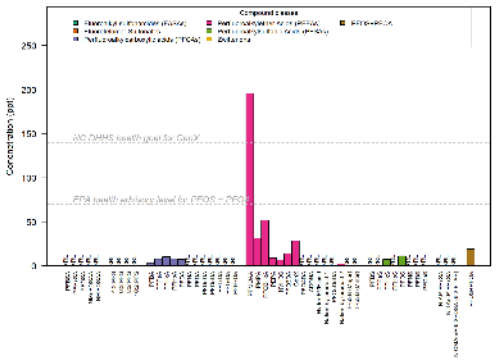


Schematic of a CIC system

PFAS analysis strategy for known and unknowns

Offline SPE

Triple Quadrupole MS/MS
(target quantitation)



Sample collection

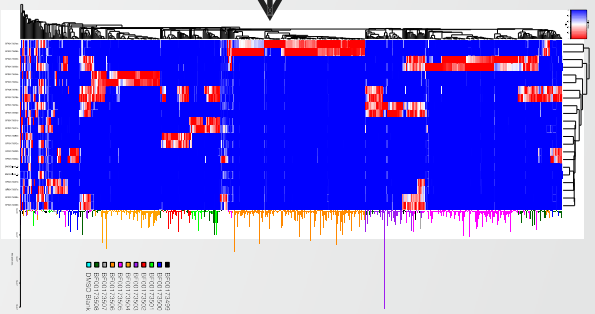
PFAS mass balance

Combustion IC
(Adsorbable Organic Fluorine (**AOF**))

\+

Online SPE or Offline SPE

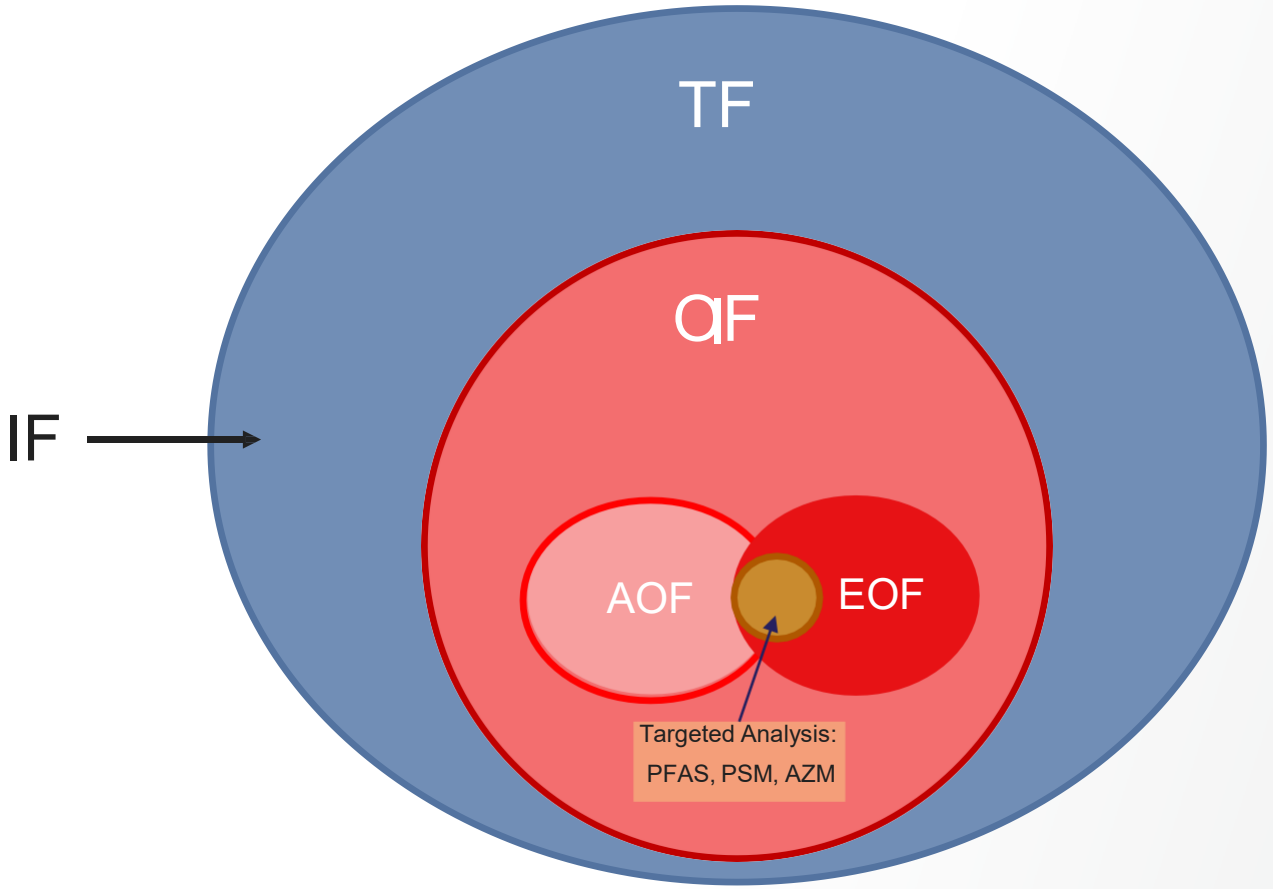
High-resolution MS
(suspect screening)



Why AOF?

- Covers fluoroorganic compounds not readily determined by LC-MS/MS
  - Identify additional potential sources contributing to PFAS contamination
- Complement to other approaches
  - Easy-to-use and economically attractive way to generate a cumulative parameter
- Optimize utilization of the more expensive LC-MS/MS and GC-MS/MS instrumentation
  - Selecting and only analyzing “suspicious” samples

Total fluorine mass balance



TF = Total Fluorine

IF = Inorganic F

OF = Organic F

AOF = Adsorbable OF

EOF = Extractable OF

PFAS: Fluorine measurement methods

Method	Notes	Instrumentation	Advantages	Disadvantages
Total Fluorine (TF)		CIC	All F (PFAS incl.)	• Both IF and OF • Indiscriminate
Inorganic Fluorine (IF)		IC		
Organic Fluorine (OF)	TF - IF	CIC + IC	• Inorganic F excluded • PFAS incl.	• Non-PFAS org. compounds incl. • 200 ppb LOD
Adsorbable OF (AOF)	Adsorbed onto activated carbon	CIC	• Inorganic F excluded • PFAS bound • Concentration • 10 ppb DL	Only a portion of OF adsorbed; i.e. not all PFAS captured
Extractable OF (EOF)	Solid phase extraction	SPE + LC-MS/MS (Targeted) or LC-HRAM (non-targeted)	• Inorganic F excluded • PFAS bound • Concentration • ~ 1ppt DL	Only a portion of OF extracted; i.e. not all PFAS captured

AOF by CIC workflow

Sample Adsorption → Carbon combustion/ Gas absorption → Ion Chromatography → Data Analysis

Nittoseiko TXA-04
AOX Adsorption Unit

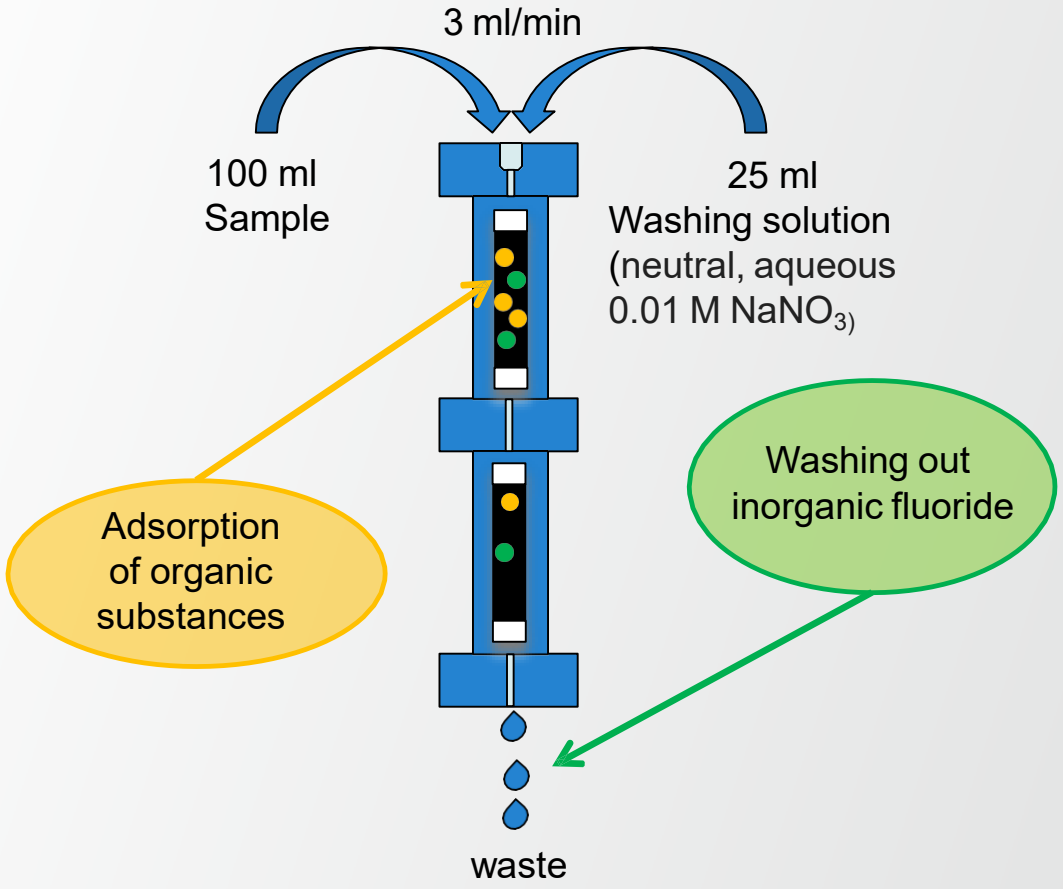
Nittoseiko AQF-2100

Thermo Scientific™ Dionex™ Integrion™ HPIC system

Thermo Scientific™ Chromeleon™ Chromatography Data System

AOF adsorption onto activated carbon

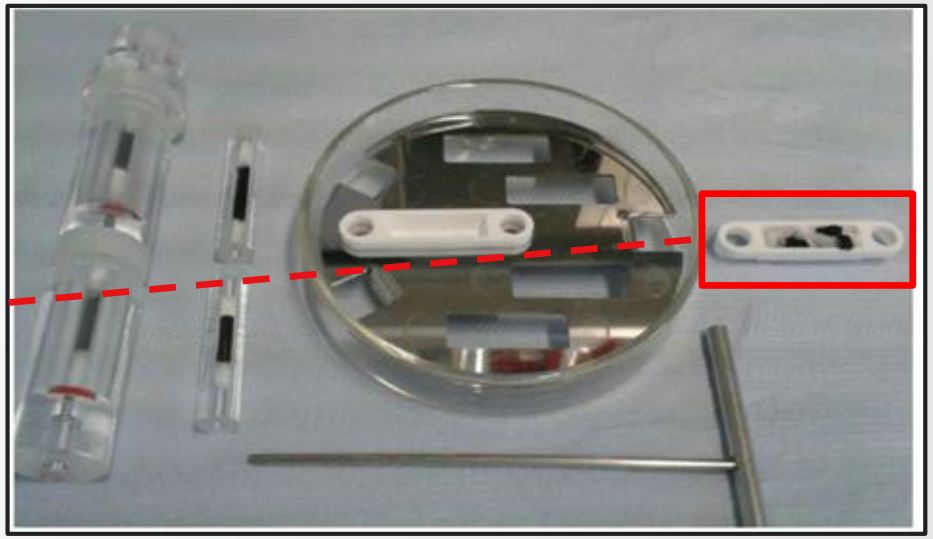
Nittoseiko TXA-04
AOX Adsorption Unit



Combustion and halogen determination

Dionex Integrion HPIC system

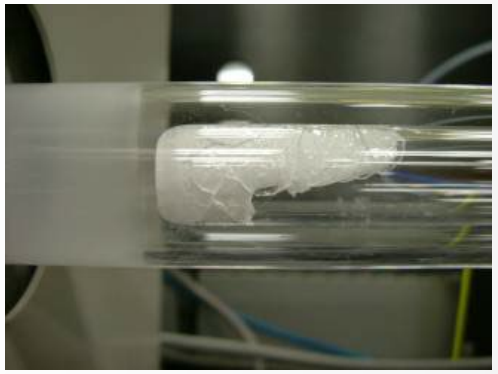
AQF-2100



Transfer of carbon to combustion boats.

Ceramic tube to prevent devitrification

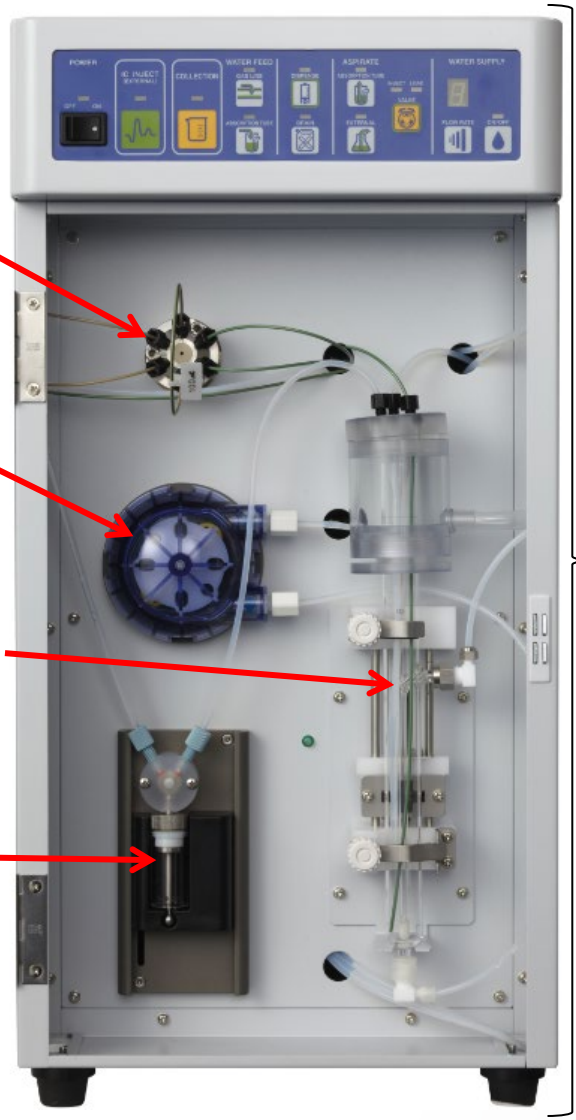
- Combustion of samples with high sodium or alkali earth metals levels will rapidly damage the quartz tube



Problem solved!

- Ceramic inner tube
  - Protects Quartz tube
  - Improved accuracy and recovery

Combustion gas absorption module



Gas absorption

- Absorption tube
  - Heat-resistant glass,10 or 20 mL
- Syringe burette

Channel Indicator LED

External solution selector

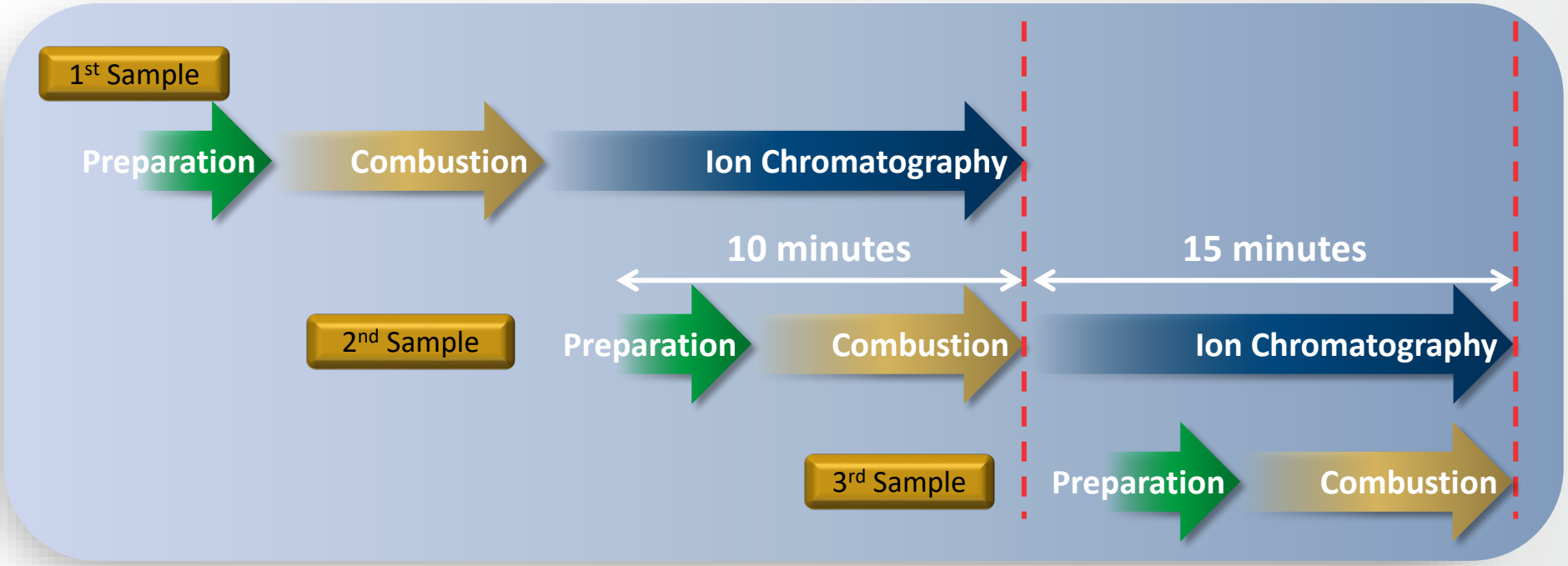
- Four aqueous solutions/standards can be injected without combustion

Combustion monitor

- Determines sample burn rate by oxygen consumption
- Optimizes boat program

Software based automation to increase productivity

- Established program controls total analysis
  - Capable of starting combustion of next sample to reduce waiting time



CIC system components

- Nittoseiko TXA-04 AOX Adsorption Unit
  - Mitsubishi Chemical Analytech prepacked active carbon columns (ca. 50 mg x 2)

- Nittoseiko AQF-2100H
  - ASC-240S Solid Autosampler or ASC-270LS Liquid/Solid Autosampler
  - HF-210 Horizontal furnace
    - Ceramic insert, ceramic boats
  - GA-211 Gas absorption unit
  - ES-210 External solution selector

CIC system components and reagents

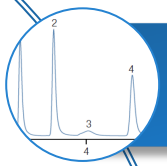
- Dionex Integrion HPIC system
  - Dionex IonPac AS20 column set (2 mm; P/N 063065, 063066)
  - Dionex EGC 500 KOH Potassium Hydroxide Eluent Generator Cartridge (P/N 075778)
  - Dionex CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
  - Dionex ADRS 600 Anion Dynamically Regenerated Suppressor (2 mm; P/N 088667)
  - *Optional* (IC sample preconcentration)
    - Dionex UTAC-XLP1 concentrator column (P/N 063459)
    - Dionex IonPac ATC-HC Anion Trap Column (P/N 059604)
    - Dionex AXP auxiliary pump (P/N 063973)

- Calibration standard
  - Dionex Fluoride Standard, 1000 mg/L, 100 mL (P/N 037158)

- Reagents
  - Nitric acid (65%, Merck KGaA, Darmstadt, Germany)
  - Sodium nitrate (99.5%, VWR Chemicals, Germany)
  - Ammonium perfluorobutanesulfonate (PFBS) (98%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany)
  - 4-Fluorobenzoic acid (≥98%, Merck KGaA, Darmstadt, Germany)

Thermo Scientific CIC strengths

Dionex Integrion HPIC system

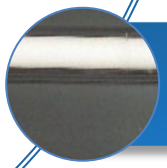


Sensitivity – 2 -10 ppb

Column offerings (variable capacities, 4 µm resin,…)

Eluent generation technology

Ease of use with Chromeleon CDS Software



Ceramic inner tube, ceramic boats

Combustion conditions

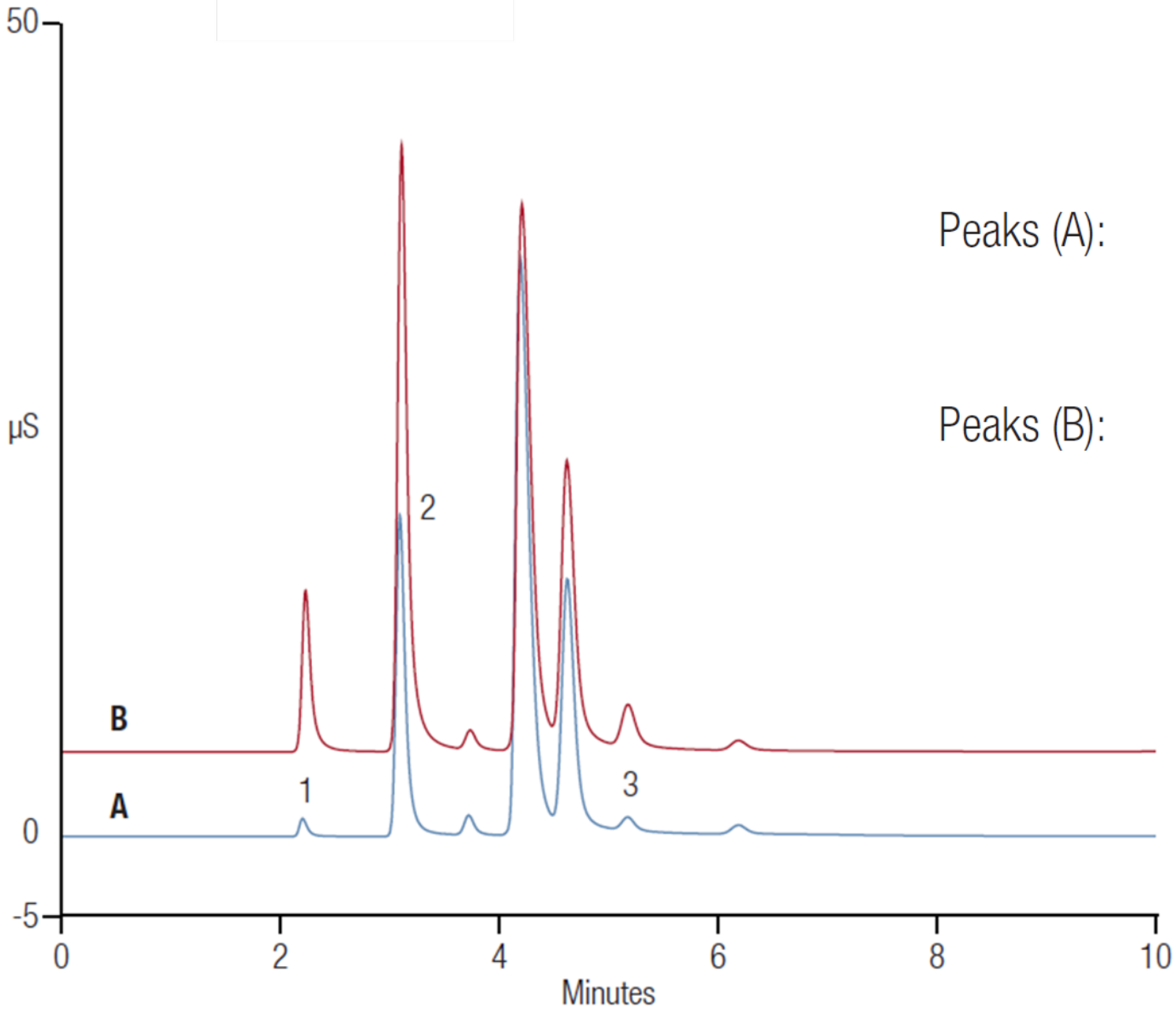
Furnace Inlet Temp.	900 ° C
Furnace Outlet Temp.	1,000 ° C
Argon Flow (Carrier)	200 mL/min
Oxygen Flow (Combustion Agent)	400 mL/min
Humidified Argon Flow	100 mL/min
Pyrolysis Tube	Quartz tube with ceramic insert and quartz wool
Sample Boat	Ceramic
Absorption Solution	Water
Absorption Solution Volume	3.5 mL
Mass Combusted	Contents of the GAC column (40–50 mg)

IC Conditions

Thermo Scientific™ Dionex™ Integrion™ HPIC™ System

IC Conditions	
Columns	Thermo Scientific™ Dionex™ IonPac™ AG18-4µm column set, 4 mm
Eluent Source	Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge
Eluent Concentration	30 mM KOH
Flow Rate	1.0 mL/min
Column Temp.	30 ° C
Inj. Volume	100 µL
Detection	Suppressed conductivity

Determination of AOX in (A) wastewater and (B) spiked wastewater



Peaks (A):	1. Fluoride	0.0425 mg/L
	2. Chloride	1.90
	3. Bromide	0.340
Peaks (B):	1. Fluoride	0.543 mg/L
	2. Chloride	3.92
	3. Bromide	0.908

Thermo CIC system advantages

- KOH eluents with eluent generation and column technology
  - Lower background, minimal or no water dip and F well separated from water.

- HF-210 Horizontal furnace
- Combustion of samples with high sodium or alkali earth metals levels will rapidly damage the quartz tube
  - Ceramic insert, ceramic boats

- System is ready to meet upcoming DIN/ISO and U.S. EPA standards using CIC to determine AOF; additionally, an ASTM method is under development

Recoveries of PFAS compounds from various water

Table 4. Recovery data for PFBS and 4-FBA

Surface water		Wastewater		
Sample	PFBS recovery	Sample	PFBS recovery	4-FBA recovery
1	94	1	102	90
2	105	2	91	83
3	99	3	86	82
4	92	4	89	n.d.
5	109	5	93	n.d.
6	98	6	85	83
7	98	7	94	127
8	99			

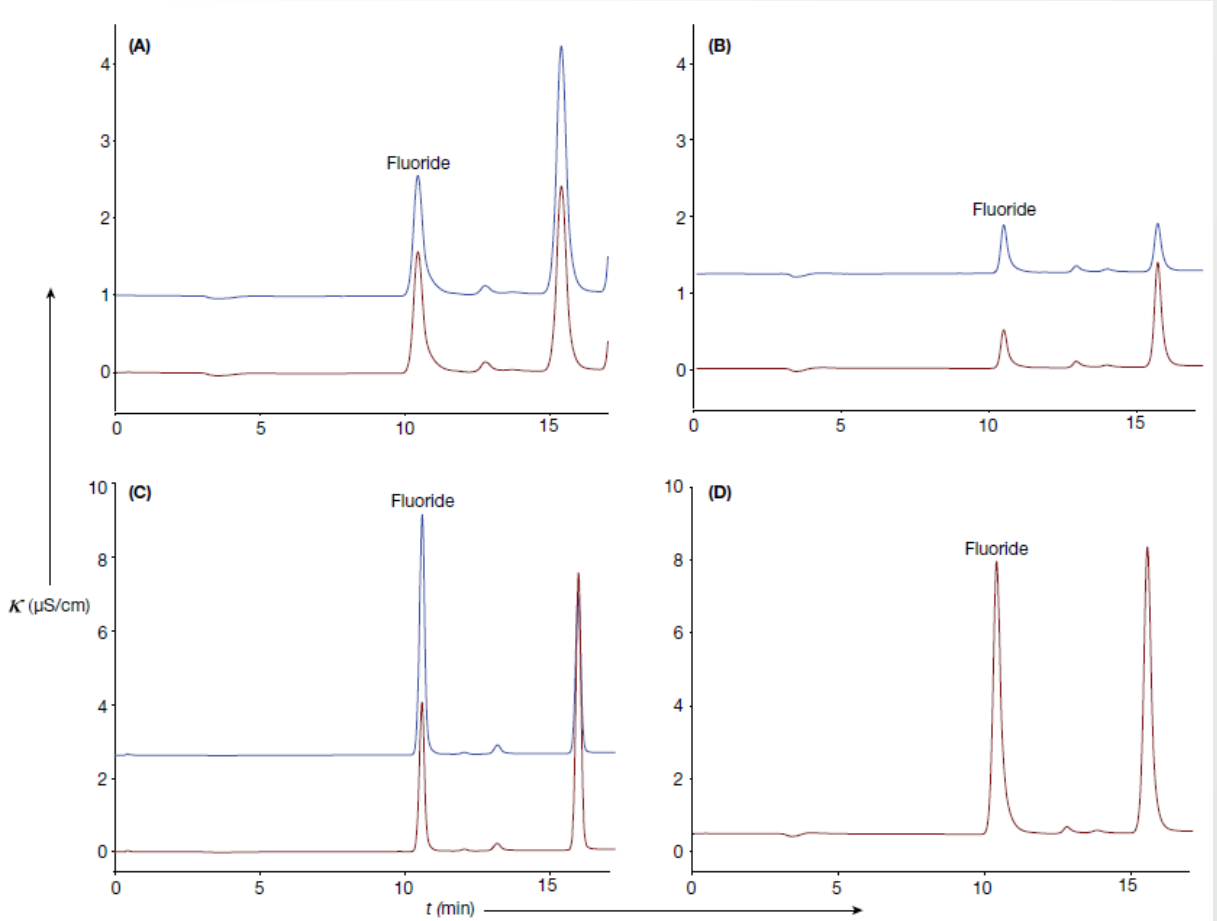
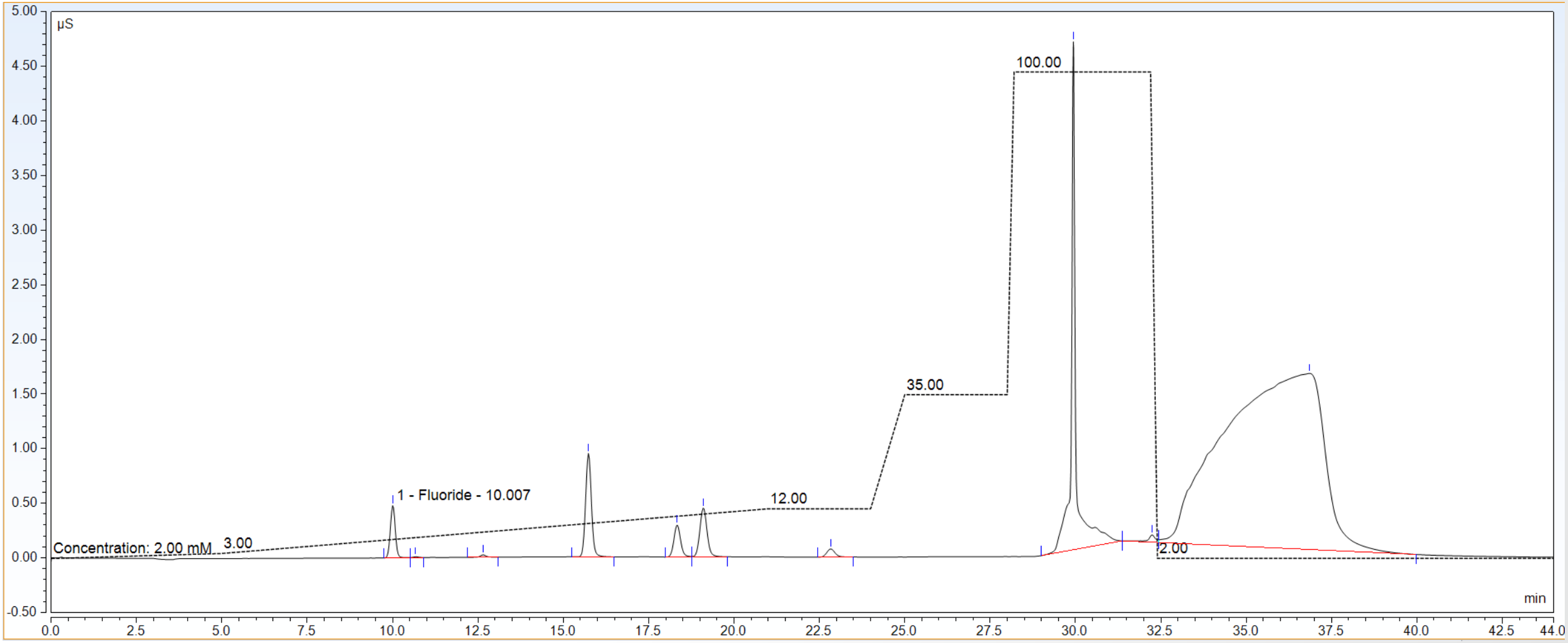
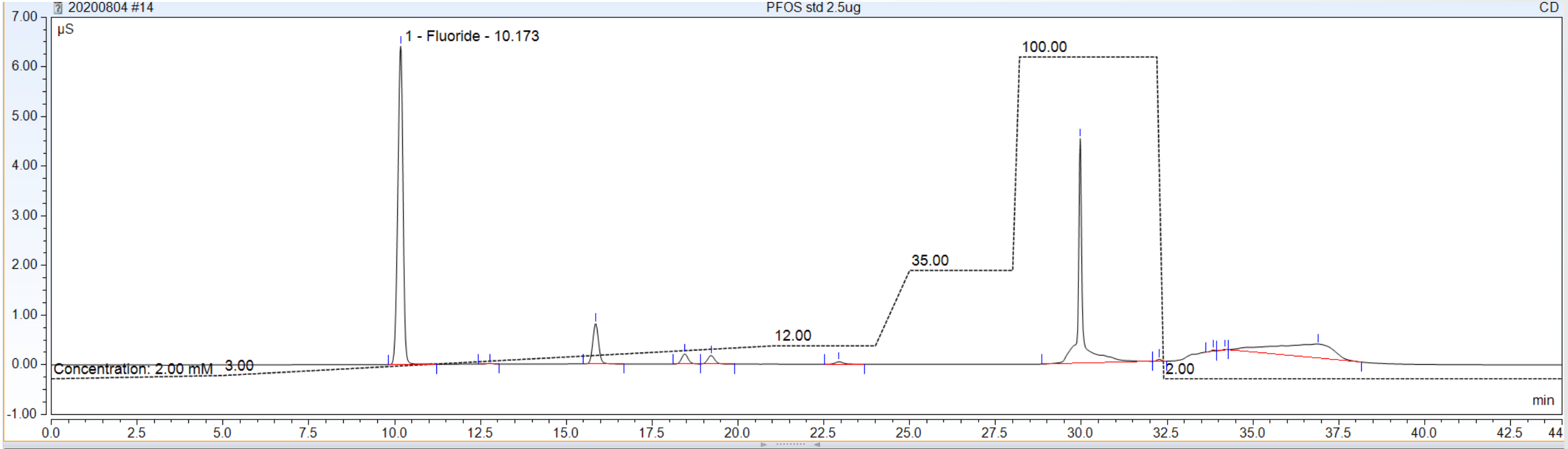


Figure 4. Selection of representative chromatograms obtained after adsorption on activated carbon and combustion. (A) municipal wastewaters, (B) groundwaters, (C) surface waters, (D) industrial wastewater (diluted 1 to 10)

0.1 ug/L F

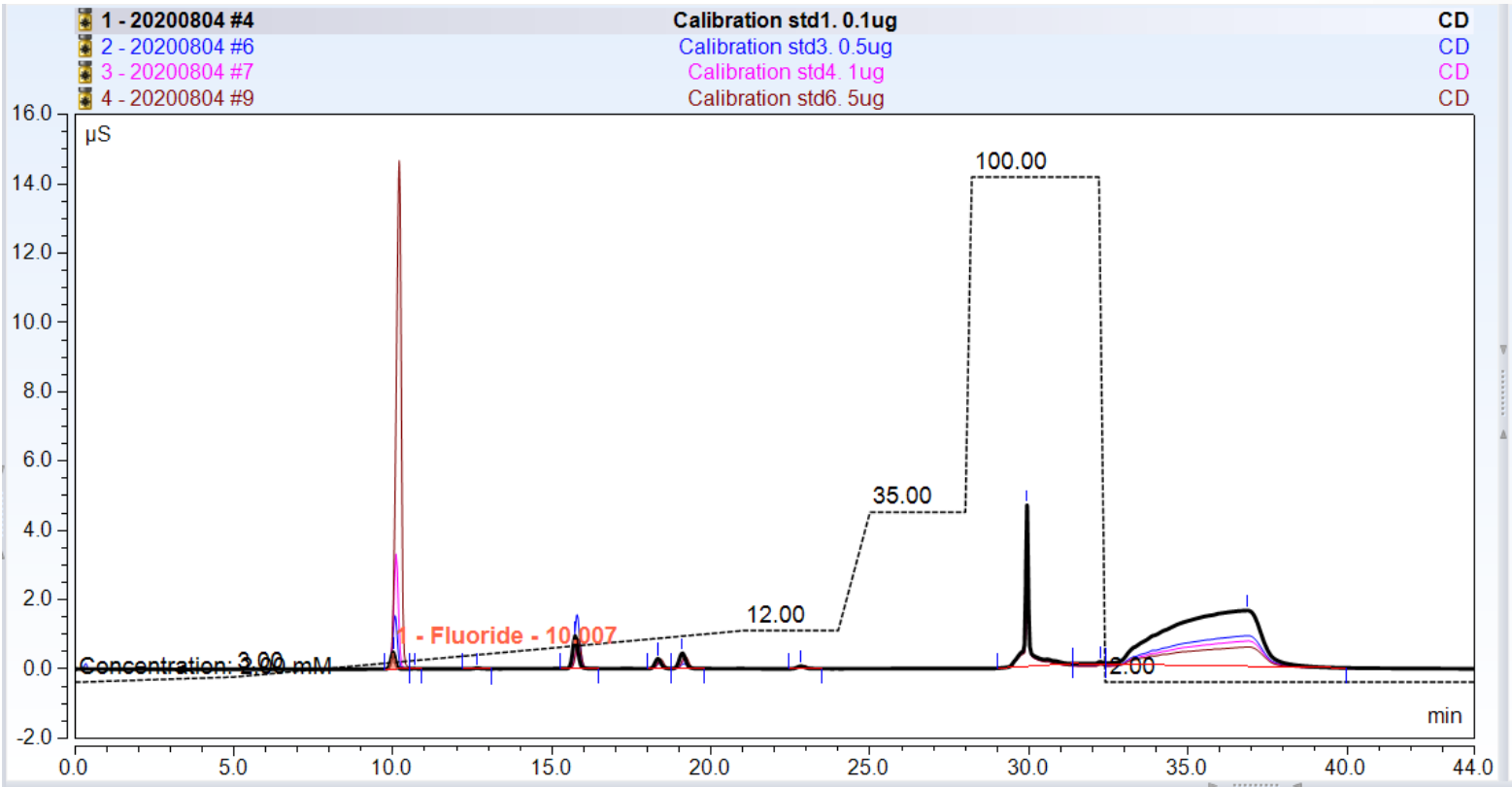

µS
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
1 - Fluoride - 10.007
Concentration: 2.00 mM
3.00
12.00
35.00
100.00
2.00
min
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0
42.5
44.0

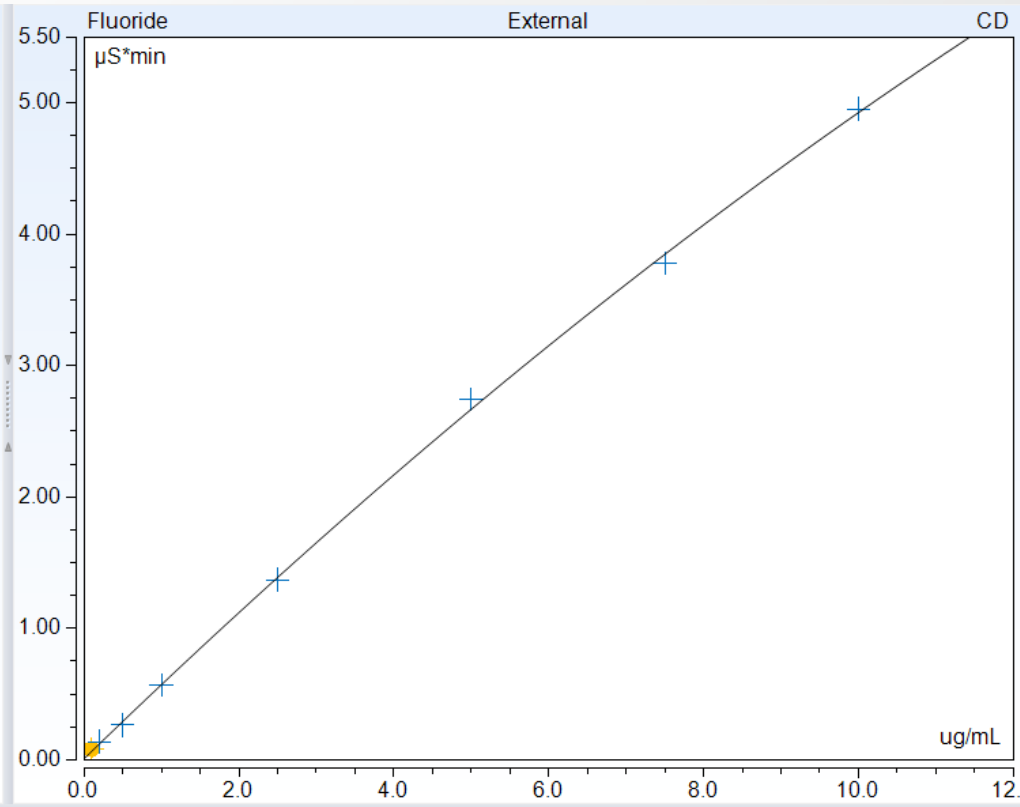
PFOS standard



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	Peak	Peak Name	Ret.Time	Amount	Rel.Area	Area	Height	Type	Width (50%)	Asym.	Resol.	Plates			
2	No.		min	ug/mL	%	µS*min	µS		min	EP	EP	EP			
4	1	Fluoride	10.173	2.0088	42.26	1.1251	6.41	BMB	0.163	0.92	9.02	21539			
6	Maximum			2.0088	42.26	1.1251	6.41		0.163	0.92	9.02	21539			
7	Minimum			2.0088	42.26	1.1251	6.41		0.163	0.92	9.02	21539			
8	Sum			2.0088	42.26	1.1251	6.41								

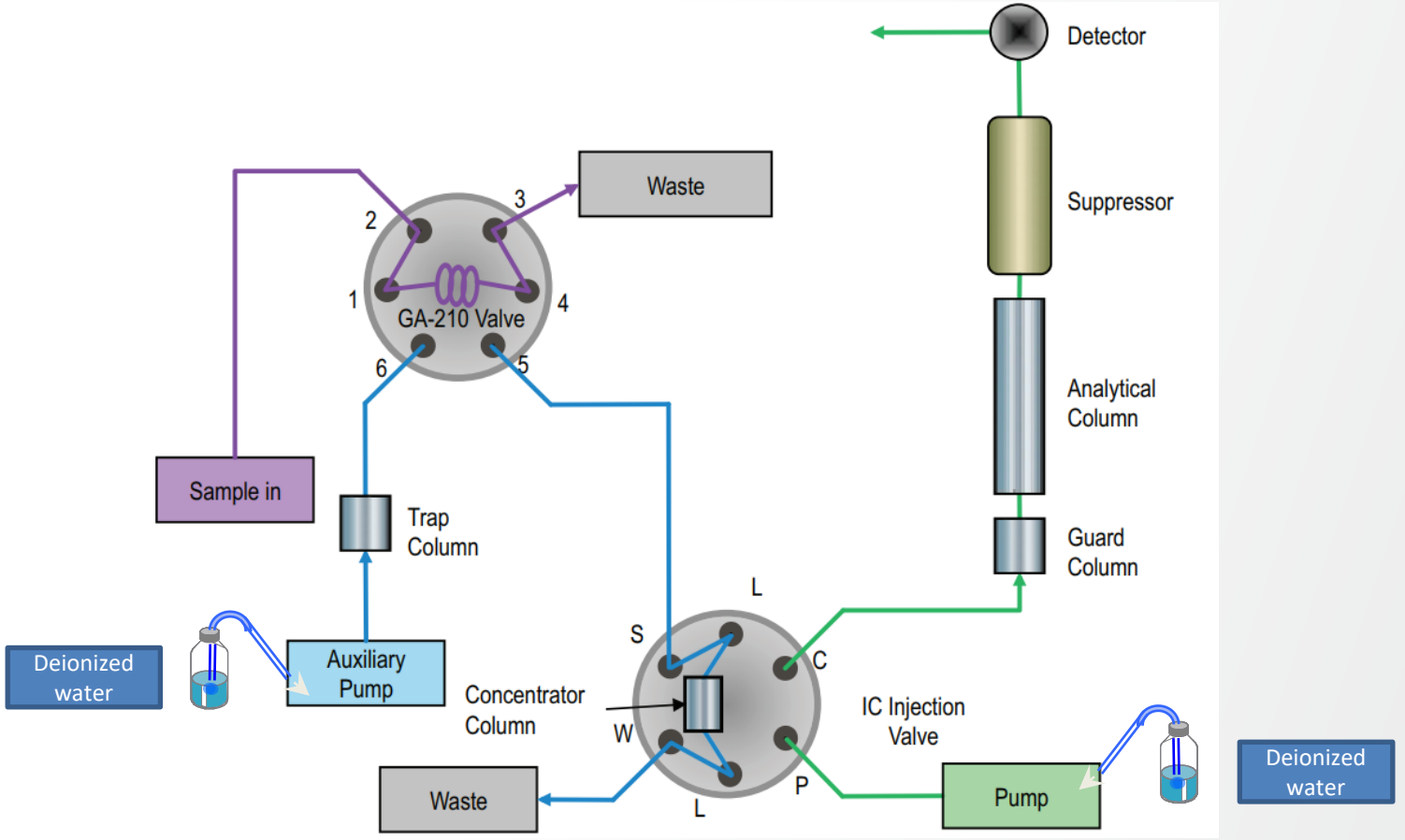
Calibration data





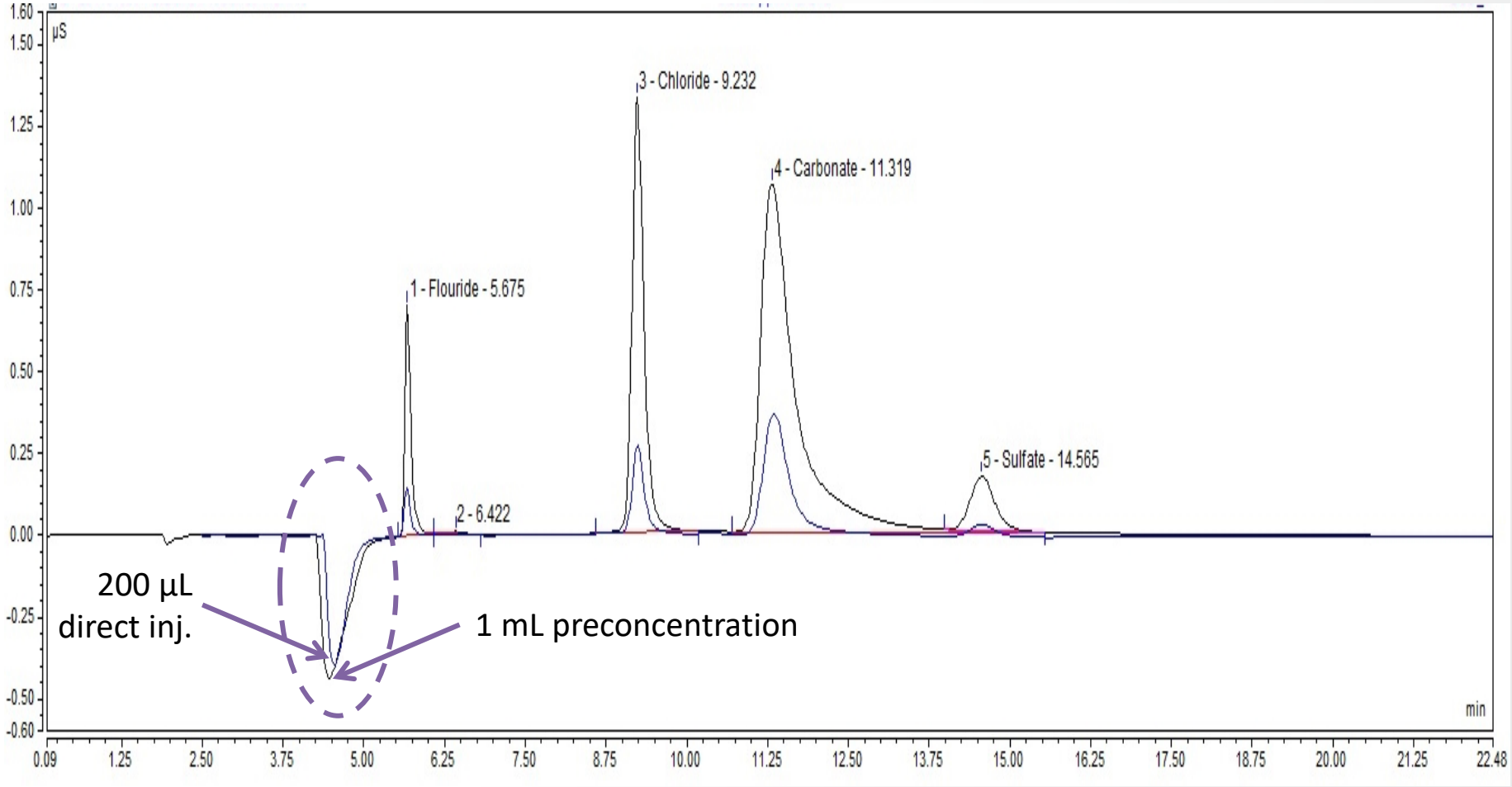
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	Peak No.	Peak Name	Ret.Time min	Cal.Type	Eval.Type	Number of Points	Rel.Std.Dev. %	Coeff.of Determination	C0 (Offset)	C1 (Slope)	C2 (Curve)				
4	1	Fluoride	10.007	Quad, WithOffset,	Area	8	2.9277	0.99947	0.0082	0.5722	-0.0081				
6	Maximum						2.9277	0.99947							
7	Minimum						2.9277	0.99947							

Flow diagram for Integrion HPIC system using – preconcentration with matrix elimination



Preconcentration

2.5 ppb preconcentration (1.0 mL) vs. direct inj. (200 µL)



Conclusions

- Combustion ion chromatography can be used for precise and accurate determination of AOX and total fluoride in environmental water samples
- The Dionex Integrion IC system provides a high performance, integrated solution that uses eluent generation to free the analyst from the need to prepare eluent, eliminates the handling of strong base, and removes a possible source of error
- The AOF-CIC-method, as a complement to existing approaches, provides an easy-to-use and economically attractive screening tool to generate a cumulative parameter, and can help to optimize the utilization of the more expensive LC-MS/MS and GC-MS/MS instrumentation by selecting and only analyzing “suspicious” samples

Thermo Scientific Combustion IC System

Thank you