Total PFAS analysis using Combustion Ion Chromatography

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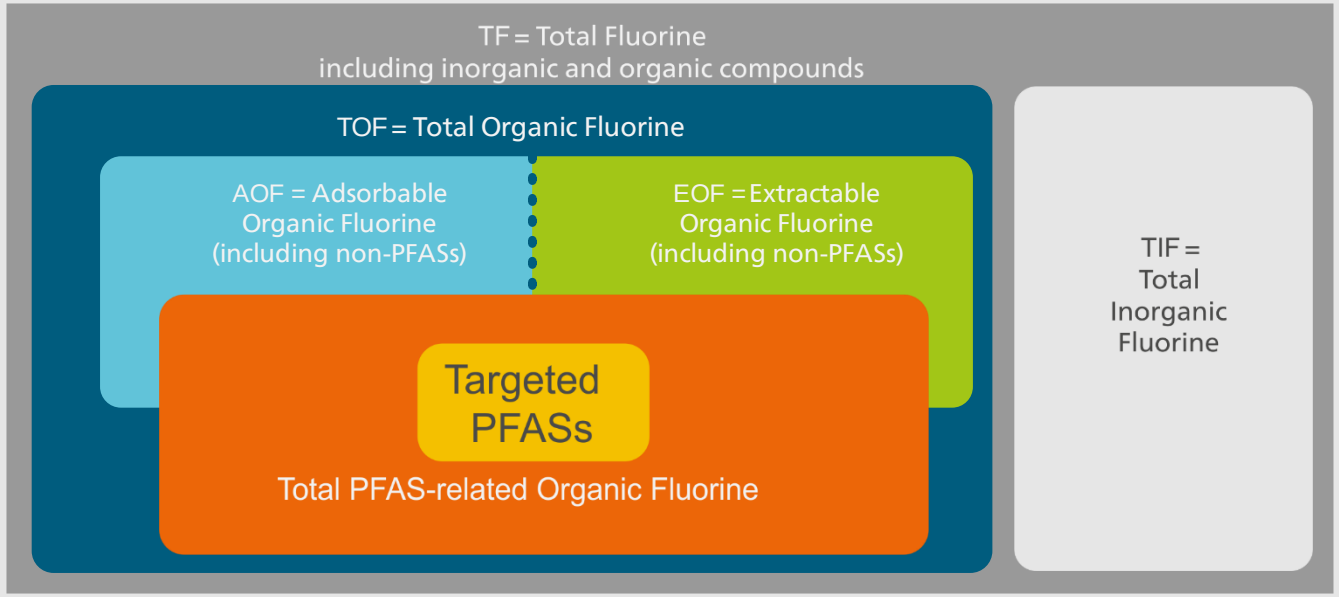
Fluorine in focus



Lanciki, A. Metrohm AG (2021): Adsorbable organic fluorine (AOF), WP-078EN

- US EPA lists >12'000 chemicals as per- and polyfluorinated alkyl substances (PFAS) (Source: CompTox Chemicals Dashboard (epa.gov))
- PFAS are persistent,ubiquitous, and bioaccumulative
- PFAS are used in industrial and consumer products
- Harmful to human health
- Monitoring individual substances difficult to impossible
- **Sum parameters to detect organic fluorine compounds**

What to expect…

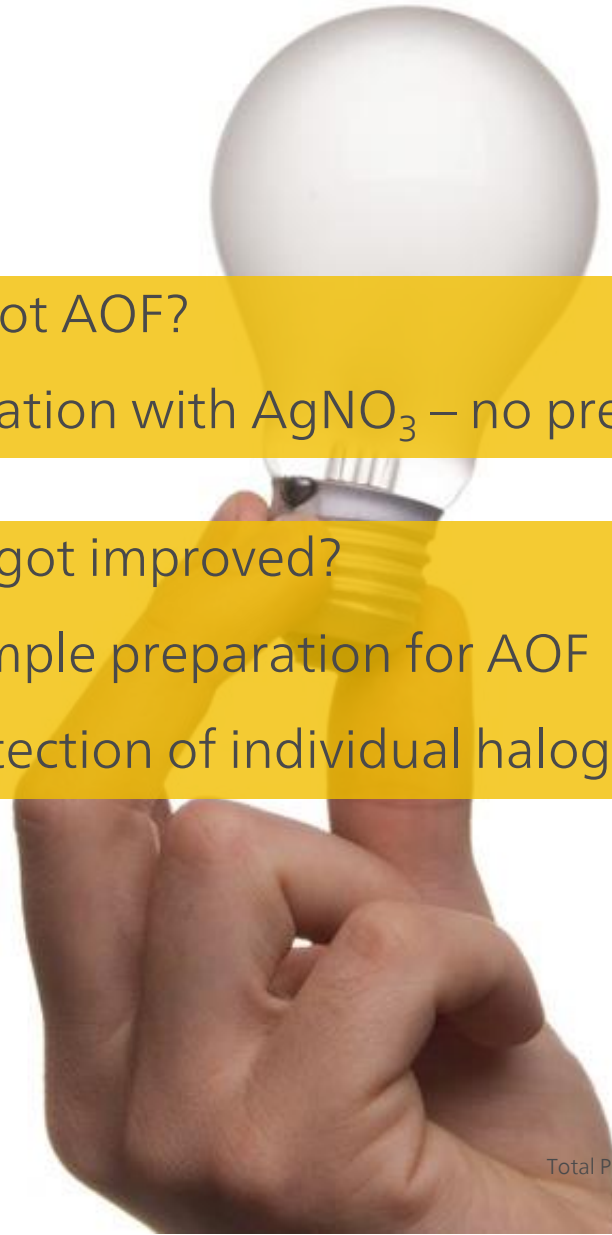
Why to use CIC for AOF analysis and why a dedicated sample preparation for AOF is needed.

Introduction to IC and Combustion IC.

Sample preparation and analysis of AOF.

Why use CIC for AOF analysis?

- **AOX** (adsorbable organic halogens, **Cl, Br, I**) combustion + microcoulometric titration after adsorption step (DIN 9562, EPA 1650)
- **DIN 38409-59: AOF**, AOCl, AOBr, and AOI after adsorption by **CIC**
- Improved and for AOF **optimized sample preparation** (neutralization)
- Superiority
  - Adsorption = preconcentration
  - Dedicated adsorption columns
  - IC – sensitive ion analysis
  - Beside TOP assay and EOF – 3rd approach for total PFASs assessment



Why not AOF?

- Titration with $AgNO_3$ – no precipitation

What got improved?

- Sample preparation for AOF
- Detection of individual halogen-species

Why dedicated sample preparation for AOF?

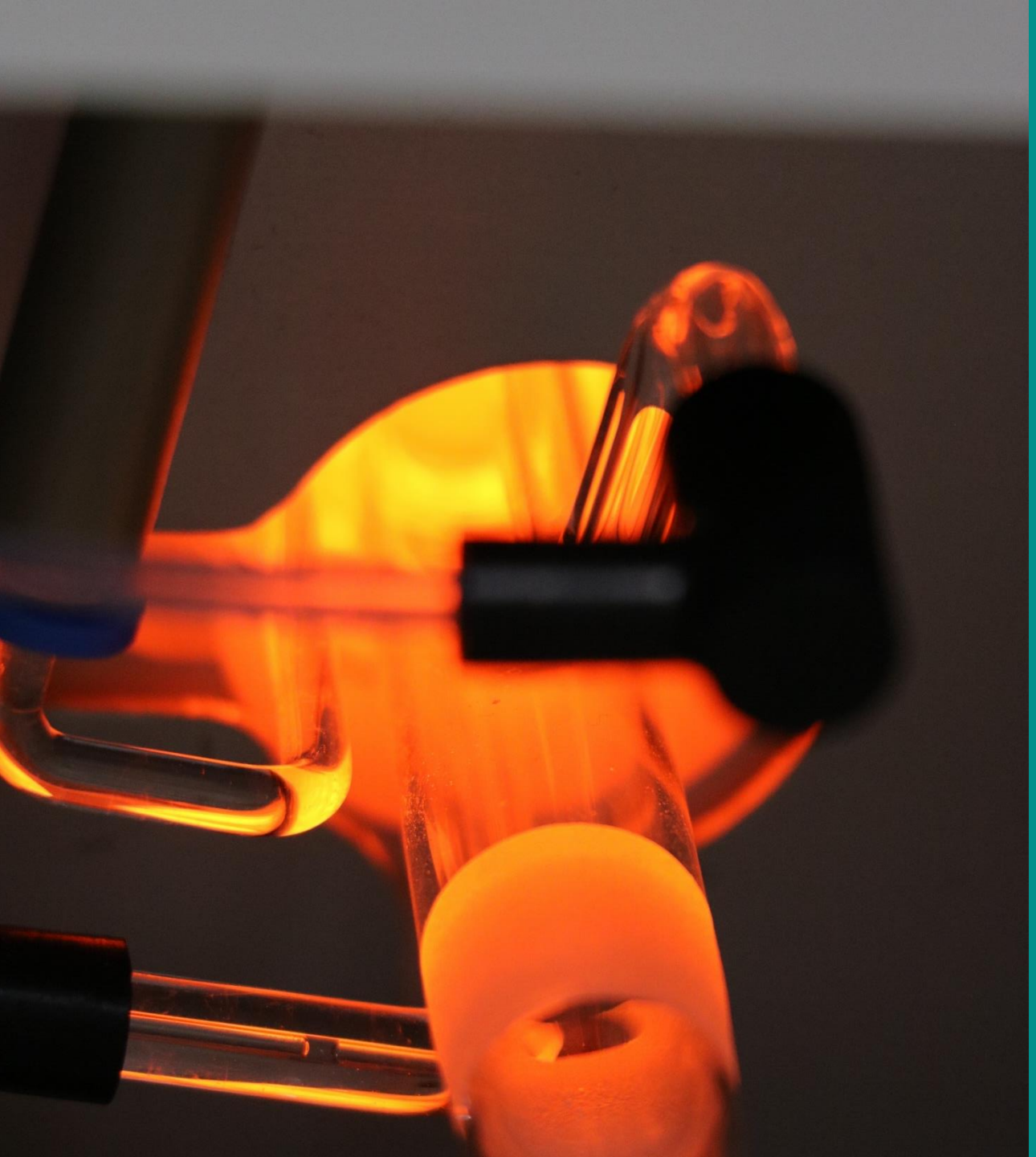
REMOVAL OF INORGANIC FLUORINE

- AOX: Sample and washing solution at pH < 2

  → Mostly non-dissociated HF
  → can adsorb to activated carbon

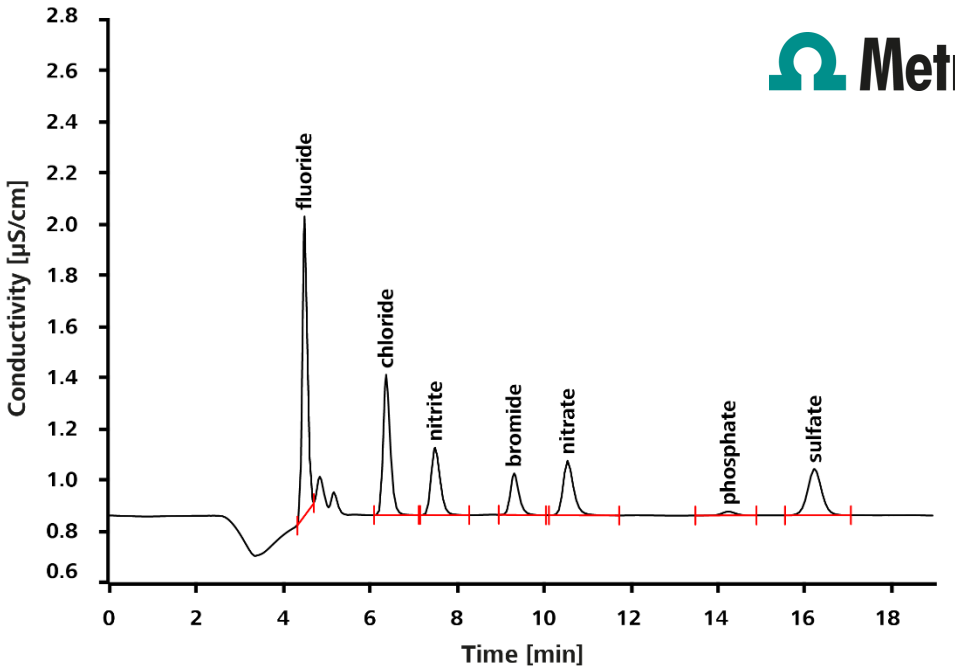
- AOF: Sample and washing solution at neutral pH

  → Inorganic fluorine can be removed



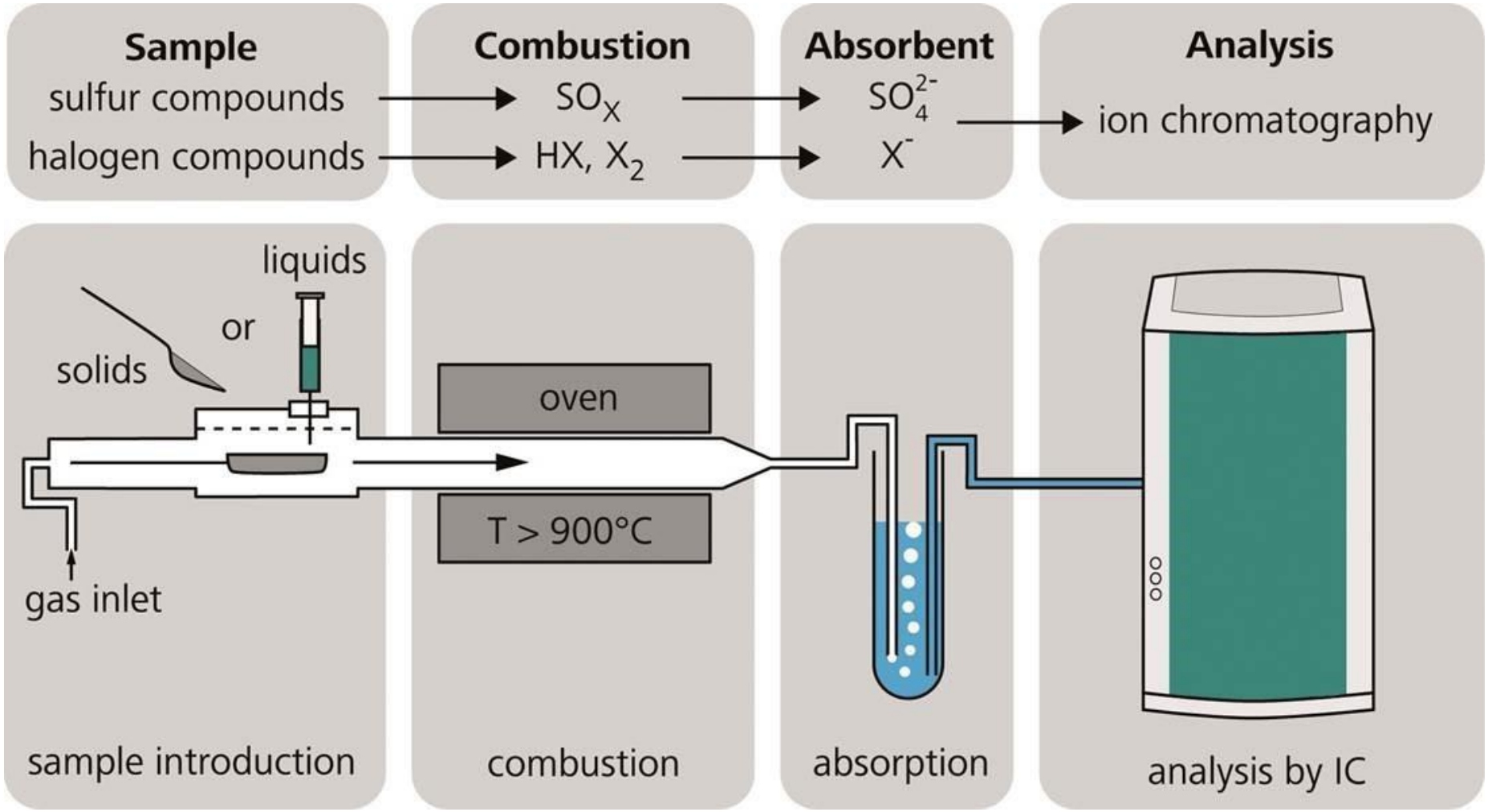
Introduction to IC and to Combustion IC

Ion chromatography in brief



- Analytical technique
- Separation of (chemically) similar substances in one run
- Specialized for anions, cations and polar substances
- Automated sample preparation as valuable feature

Theory of CIC – a sample preparation technique



Whole combustion process

- Sample is weighted in on boat
- Boat is picked up from rack by gripper and transferred into CIC tube
- Combustion happens according to light dispersion or fixed boat program
- Absorption in water or hydrogen peroxide after combustion
- Measurement of absorber solution by IC

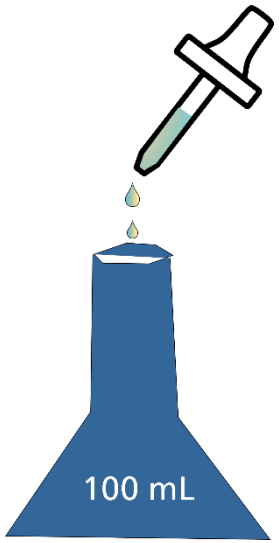
Samples for Combustion IC

- Combustible samples
- Samples can be in liquid, solid or gaseous form
- Samples can be analyzed for **halogens** (F, Cl, Br, I) and **sulfur** simultaneously
- Up and coming technique in norms and standards, especially in petroleum industry
- Breaks up organics which usually cannot be directly analyzed by IC

Sample preparation and analysis of AOF

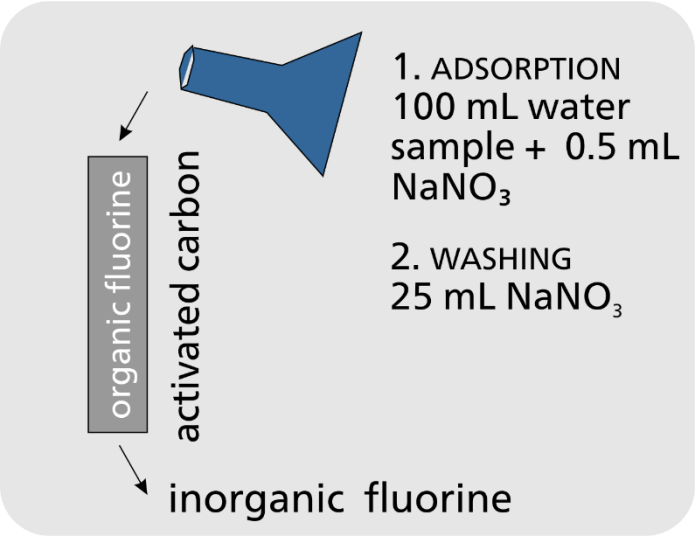
Don`t be sour - neutral is the solution

Sample preparation and preconcentration for AOF analysis (EDIN 38409-59)



Sample/blank neutralization with sodium nitrate

1

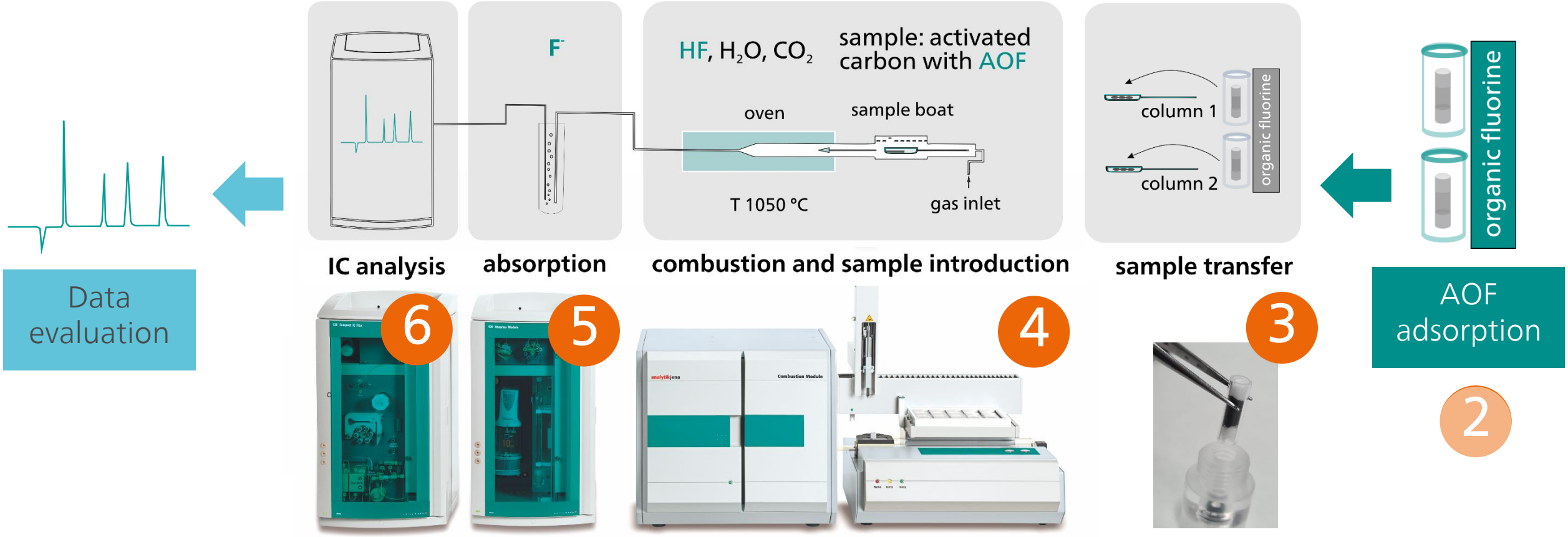


Adsorption step and rinsing (activated carbon columns for AOF)

2

Semi automation with APU *sim* (Analytik Jena)

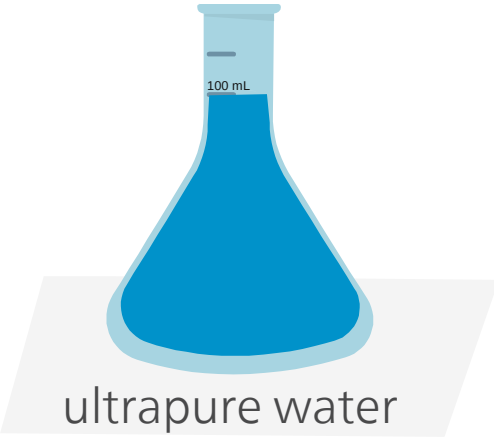
Complexity of sample preparation and sample analysis for AOF determination

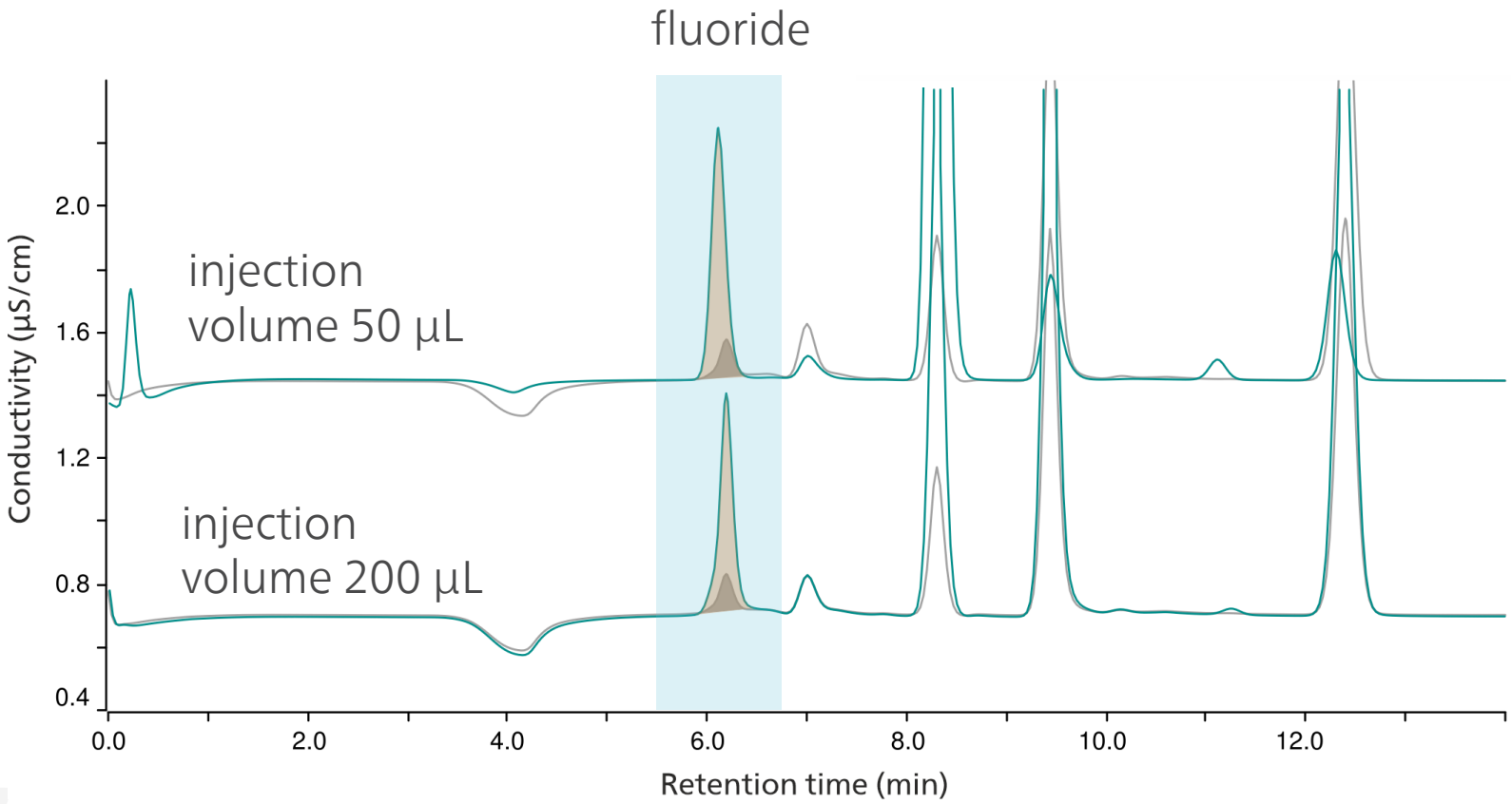


CIC analysis of a surface water sample

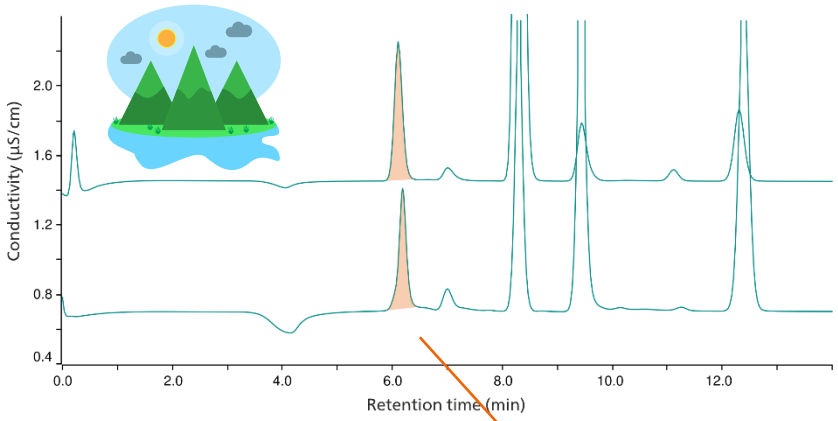
sample

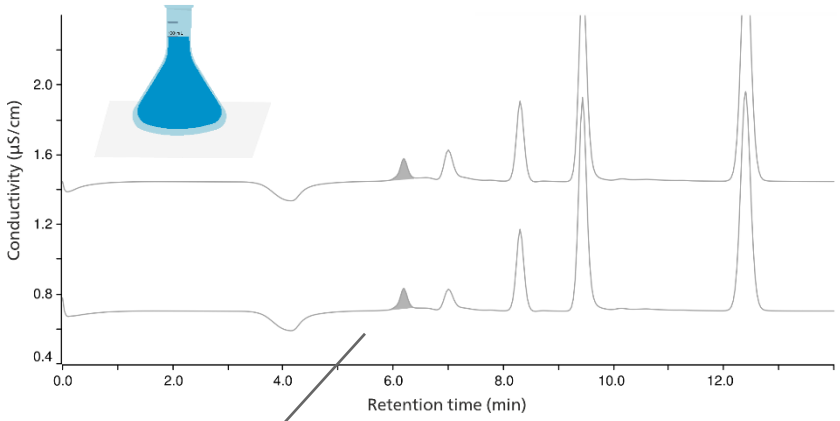
blank





Calculation of the AOF concentration from IC analysis





fluoride sample (µg/L)

fluoride blank (µg/L)

Volume absorption solution (mL)

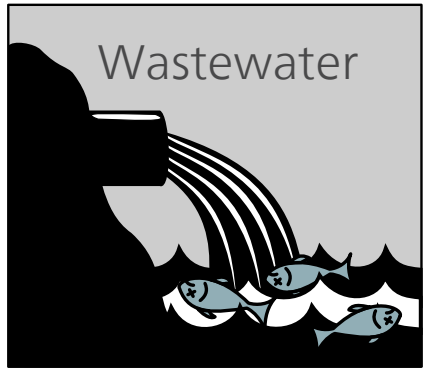
$$\sum_{column\ 1}^{column\ 2} c(AOF) = \left(c(F^-)_{IC} * \frac{V_{Abs}}{V_{Smpl}} \right) - \left(c(F^-_{BW})_{IC} * \frac{V_{AbsBW}}{V_{SmplBW}} \right)$$

Volume for adsorption on activated carbon (100 mL)

AOF (µg/L)

Replicate AOF measures in “natural” samples:

Excellent repeatability and performance for AOF analysis by CIC despite the complexity of this method



AOF #1 (µg/L)	AOF #2 (µg/L)	AOF #3 (µg/L)	AOF #4 (µg/L)	AOF_{AVG} ± SD (µg/L)	RSD (%)
6.3	6.3	6.8	6.8	6.5±0.3	5
10.2	10.0	9.3	9.2	9.7±0.5	5
7.4	7.0	7.6	7.2	7.3±0.3	4

Excellent repeatability with RSDs≤5%

Data evaluation

Combustion, absorption, and IC analysis

AOF adsorption

Will AOF also be your future solution for PFAS screening?