Methodological and analytical challenges for PFAS monitoring in environmental media

Update from the frontline

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Agenda

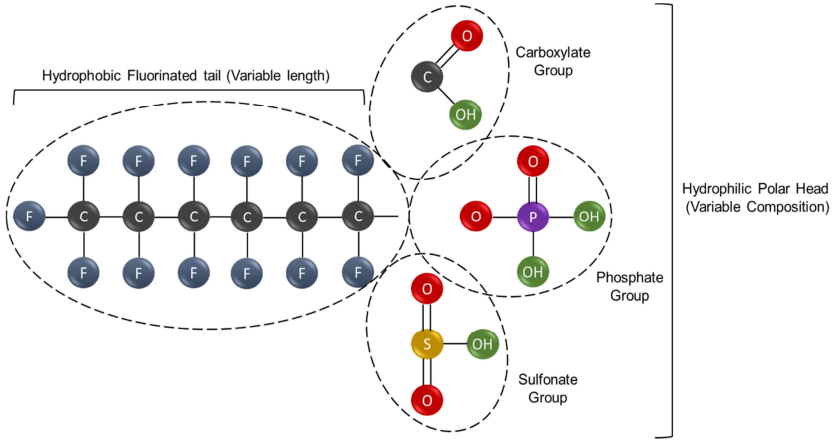
- PFAS: more than 1 compound (class)
- PFAS: more than 1 analytical method
- Challenges
- Possible solutions
- Caveats and restrictions
- Answers or questions ?

"you can only find what you search for"

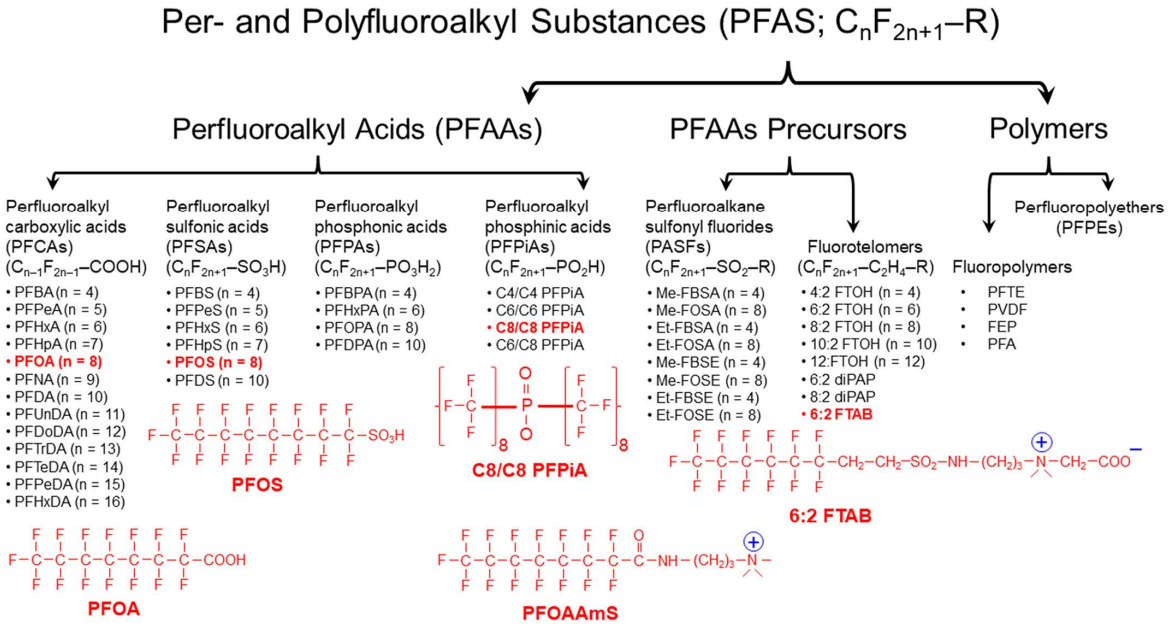
PFAS: More than 1 compound (class)

WHAT?

- Molecules with varying (i) carbon chain length, (ii) functional groups and (iii) number of fluor atoms
- PFAA + Polymers + Precursors **+ polyfluorinated cpds**
- Water, soil, air**, soil improver, waste, consumer products, industrial intermediates, animals, food, humans, …**
- Particle-bound, semi-volatile and volatile



https://doi.org/10.3390/toxics10020044



https://doi.org/10.1029/2021RG000765

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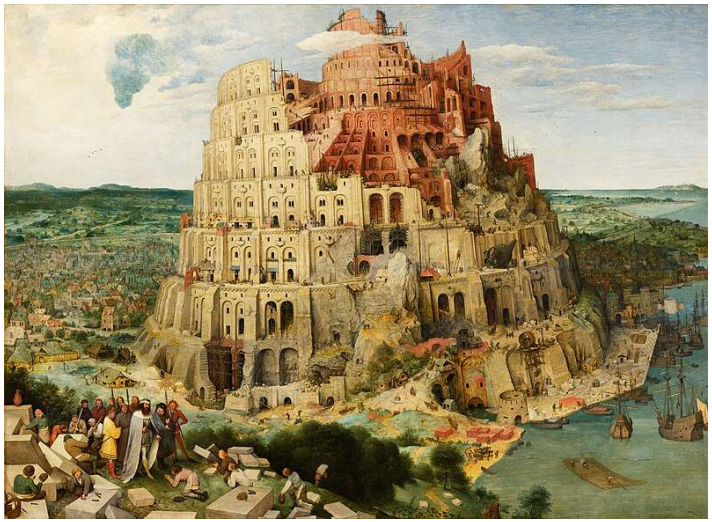
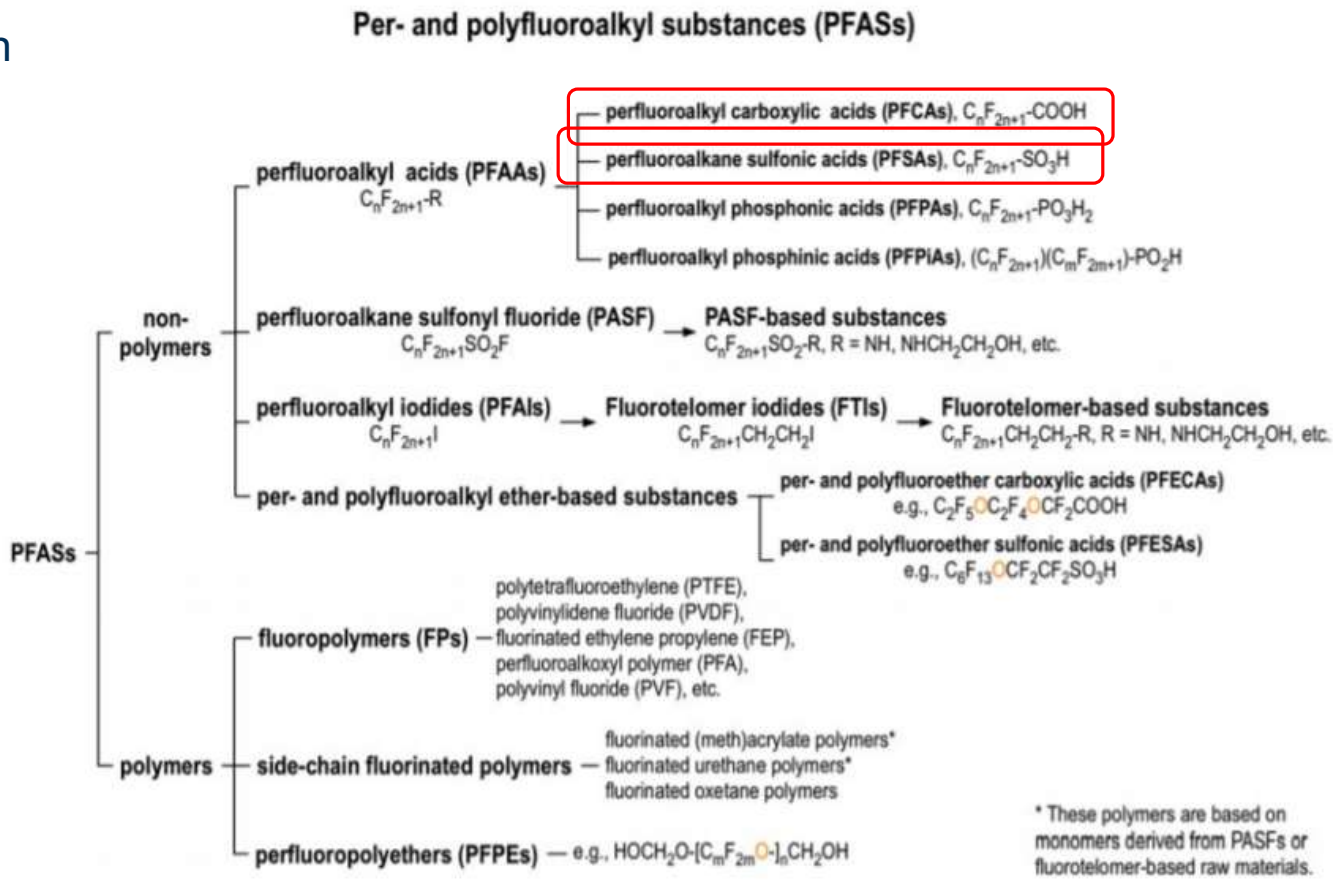
PFAS: More than 1 compound … more than 1 classification

OECD 2020 classification



Pieter Brueghel de Oude - https://en.wikipedia.org/wiki/The_Tower_of_Babel_(Bruegel)



https://web-archive.oecd.org/2017-08-02/250024-synthesis-paper-on-per-and-polyfluorinated-chemicals.htm

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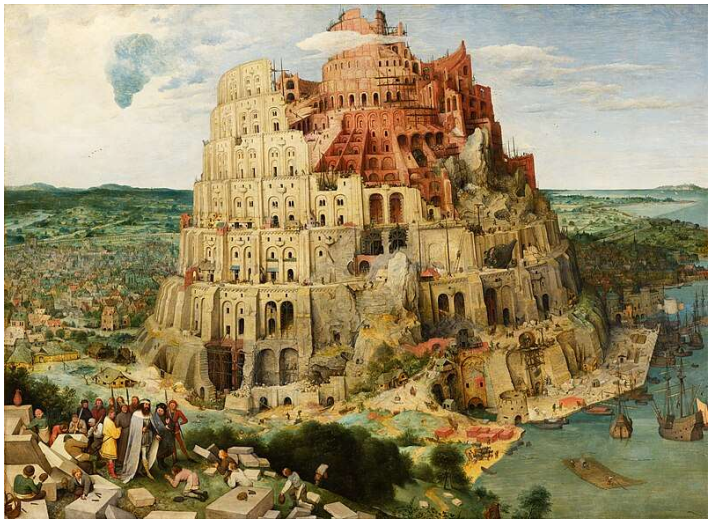
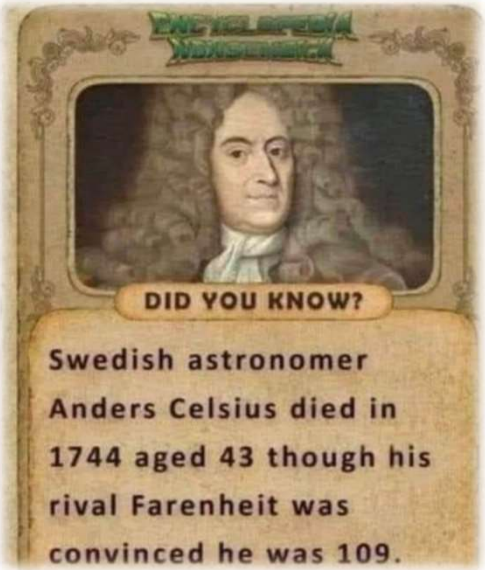
PFAS: More than 1 compound … more than 1 classification



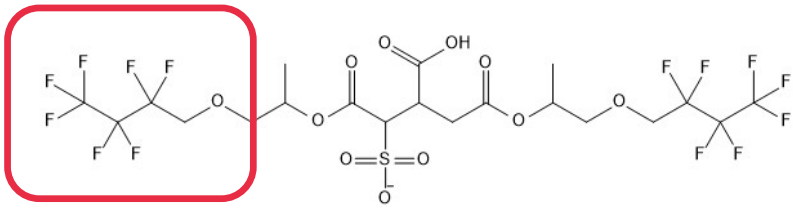
Pieter Brueghel de Oude - https://en.wikipedia.org/wiki/The_Tower_of_Babel_(Bruegel)

- Unique ID
- IUPAC
- PFOS = 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoroctane-1-sulfonic acid
- CAS #
- e.g. ADONA, NaDONA, DONA
- What with:
  - Polymers
  - Break-down products
  - Derivatives
  - PolyF-cpds
  - …
  - Quantification & Reference compounds ???



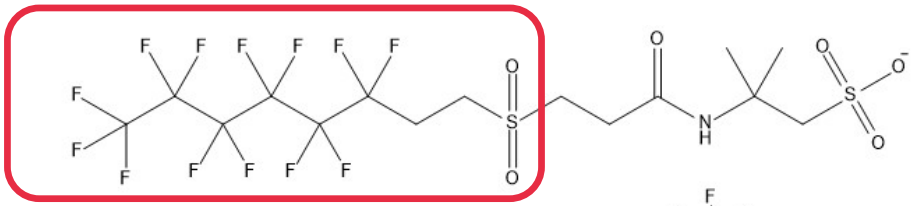
https://www.facebook.com/groups/encyclopedia.nonsensica/

PFAS: More than 1 compound … more than 1 classification



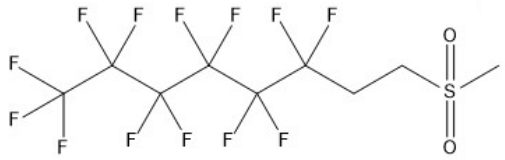
PFBA-precursor

Chemical Formula: $C_{20}H_{21}F_{14}O_{11}S^-$
Exact Mass: 735,0587

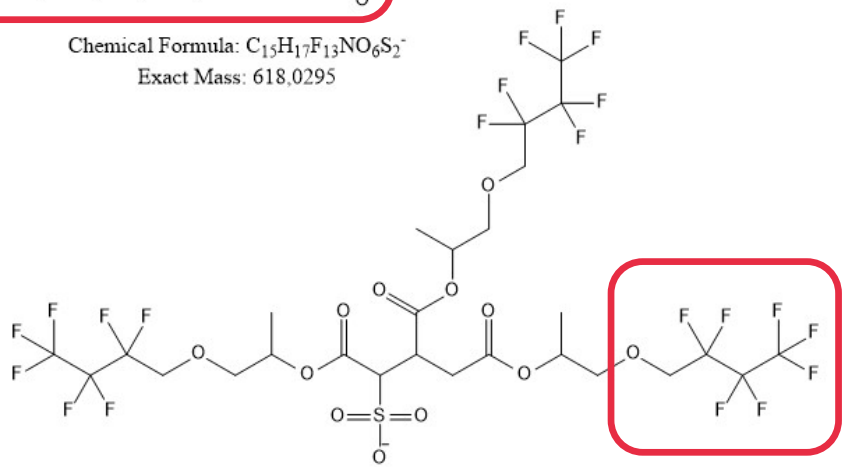


Chemical Formula: $C_{15}H_{17}F_{13}NO_6S_2^-$
Exact Mass: 618,0295

Chemical Formula: $C_{27}H_{28}F_{21}O_{12}S^-$
Exact Mass: 975,0972



Chemical Formula: $C_{11}H_{10}F_{13}O_4S^-$
Exact Mass: 485,0098
Acetate adduct



Chemical Formula: $C_{27}H_{28}F_{21}O_{12}S^-$
Exact Mass: 975,0972

PFAS: More than 1 method

Intended for
NORDIC WORKING GROUP FOR CHEMICALS, ENVIRONMENT, AND HEALTH (NKE)

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Final Report

Date
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ANALYSIS OF NEEDS FOR ENFORCEMENT OF PFAS IN ARTICLES AND CHEMICAL PRODUCTS

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Section 2.1

Total fluorine content

- CIC
- PIGE
- XPS
- LIBS
- INAA
- WDXRF
- HR-CS-GF-MAS

All fluorinated compounds
No individual identification/quantification

Section 2.2

Non-targeted and suspect screening analysis *via* HRMS

- LC- and GC-MS(MS)
- SPE-coupling
- direct infusion ESI
- MALDI
- DART
- FT-ICR
- IM-MS
- ICP-MS

Several PFAS simultaneously
High sensitivity and specificity

Section 2.3

Targeted analysis

- LC- and GC-MS
- pyr-GC-MS
- SFC-MS
- Sensors
- Sensors
- TOPA

Individual PFAS
High sensitivity and specificity

Section 2.4

Structural analysis & additional methods

- ^{19}F-NMR
- FTIR
- SERS
- XANES
- MIP-OES

Individual PFAS
High specificity

Resource quantifiers

- Time investment
- Costs
- Expertise

➔ **quantification possible**
… if reference compounds available

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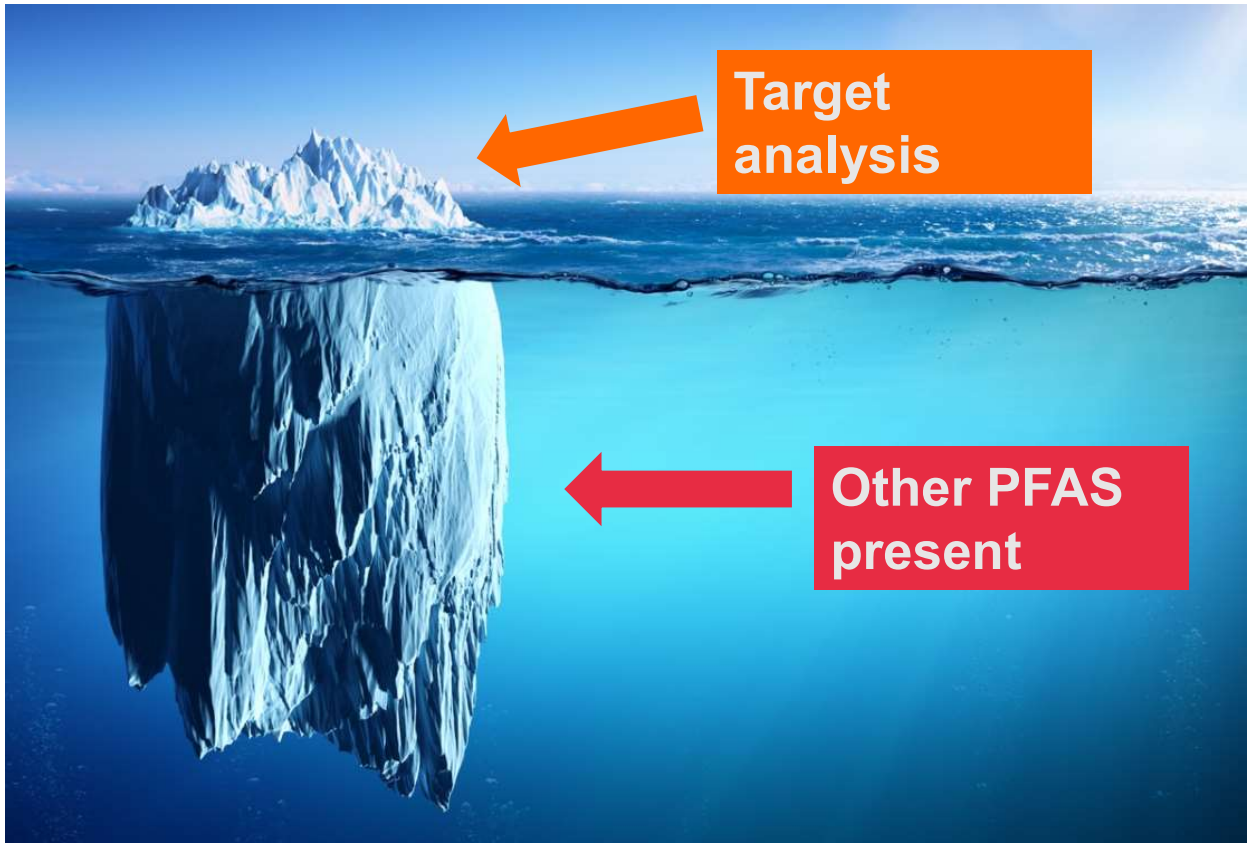
PFAS: More than 1 method

Quantification of PFAS – Target analysis

- Multiple methods needed: legacy cpds,ultra-short chain cpds, volatile PFAS, … !
- It will ***NEVER*** be possible to quantify all PFAS we encounter
- Applicability of target method is different according to corresponding matrix and PFAS class
  - WAC/IV/A/025 – Determination of PFAS in water with LC-MS/MS - #43
  - WAC/IV/A/026 – Determination of ultra-short chain PFAS in water with LC-MS/MS - #7
  - CMA/3/D – Determination of PFAS in soil and sediment - #43
  - CMA/3/O – Determination of PFAS in soil improvers - #42

  - Expected updates
    - Suspect and non target analysis (S/NTA) → selection of new relevant target compounds
    - Depends on the availability of reference standards and internal standards

PFAS: More than 1 method



Romolo Tavani | Dreamstime.com

Challenges and solutions

Total PFAS methods

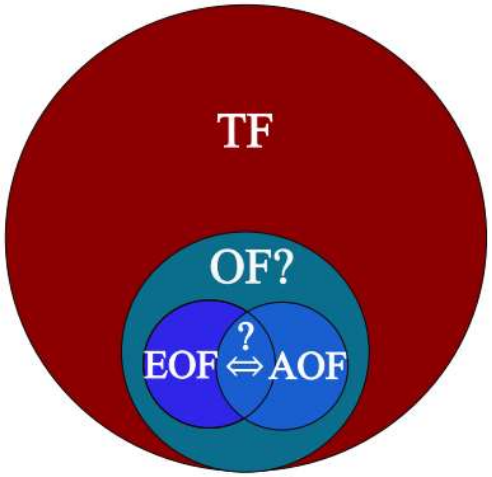
TOF-techniques

The GOOD

- Measuring total F, but for EOF and AOF the inorganic fluorine should be removed (extraction/adsorption)
- Can give a quick idea of the total fluorine content
- ISO standard is under development (AOF)

The BAD

- Not all techniques distinguish between inorganic and organic F (false positives)
- The limit of F detection mg/L range
- Molecular technique vs SI-data reporting
- Not (yet) wide-spread in commercial labs.
- CIC and HR-CS-GF-MAS can be used but these are destructive methods where often sample preparation is needed
- Ultrashort-chain PFAS remain a blind spot even for these “total PFAS” methods



Gehrenkemper et al., 2021
DOI: 10.1007/s00216-020-03010-y

Challenges and solutions

Suspect and non target analysis (S/NTA)

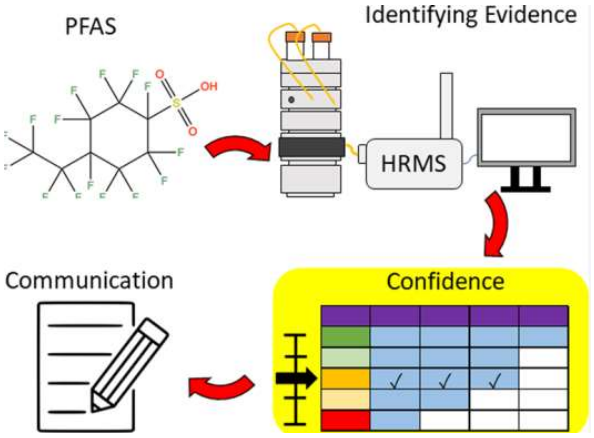
NTA-techniques

The GOOD

- HRMS allows identification of new and suspected PFAS
- HRMS can measure both multiple known and unknown analytes in a single analysis
- LOD factor 10 or more lower than target analysis
- Developments for high-throughput ongoing
- Results will direct future developments of target methods

The BAD

- High cost of technology acquisition, operation and maintenance
- High training and experience level of scientists
- Large datasets
- Slower process than target analysis
- Not (yet) assimilated in commercial labs

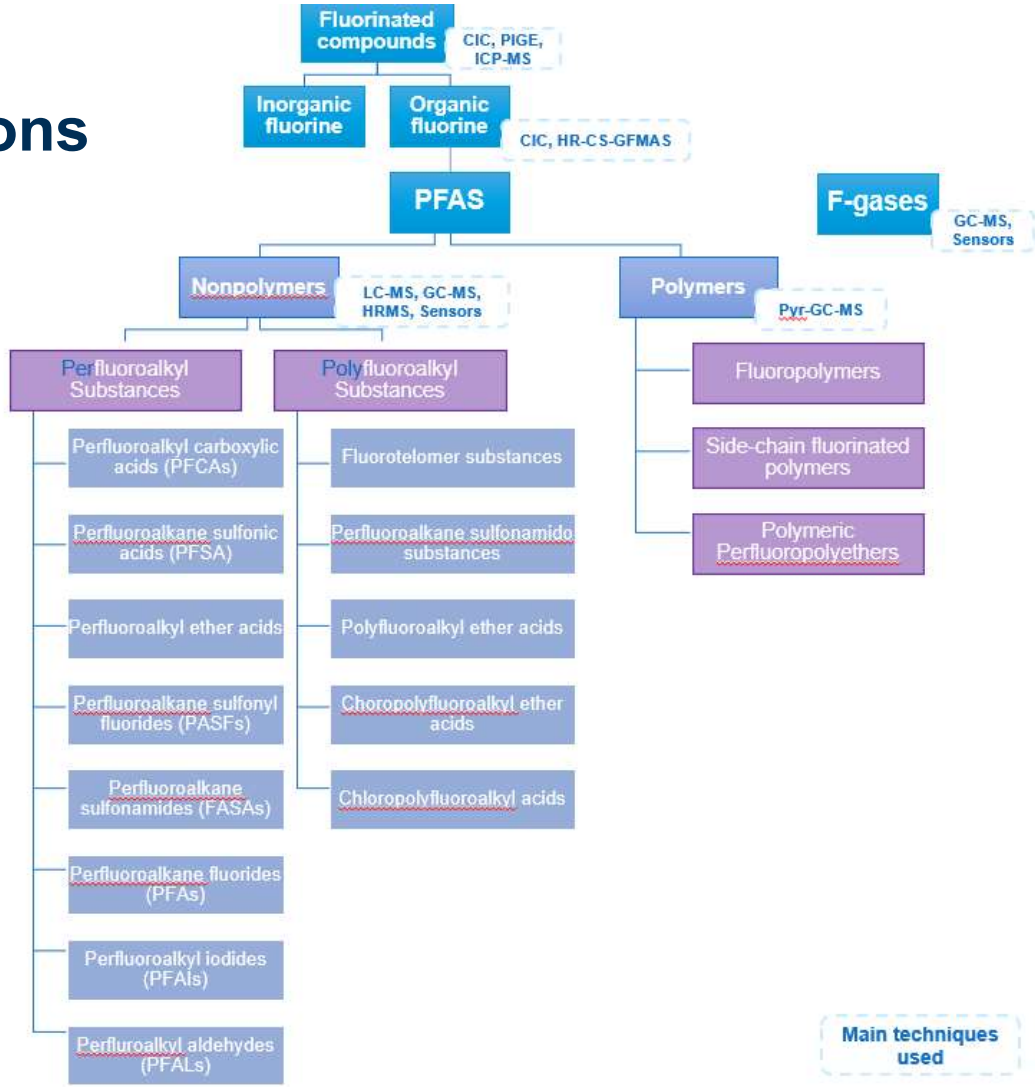


Charbonnet et al., 2022

DOI: 10.1021/acs.estlett.2c00206

Challenges and solutions

- Complementary techniques are needed
- Orthoganol approaches
- Complexity tailored to the need
- Target methods will not become obsolete but will require maintenance and updates
- … the inherent limitations of every analysis applies …



Challenges and solutions

Update from the frontline

- Expansion of Targeted methods LC-MS/MS
  - More compound classes
- Development, validation and implementation of TOP assay
- Development/improvement of GC-MS method for the analysis of neutral and volatile PFAS
- Development/improvement of AOF and EOF (total PFAS methods)
- Further development and application of the NTA PFAS platform
- Development of a methodology for the quantification of PFAS in flue gasses
- …


Uncertainty
Just Ahead

“***Uncertainty is unpleasant, but certainty is absurd***”

Voltaire (1694-1778)

https://en.wikipedia.org/wiki/Voltaire

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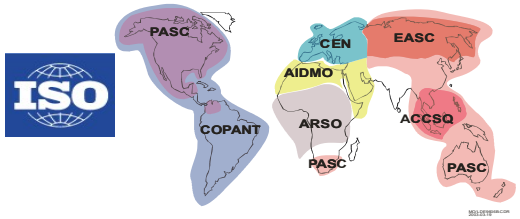
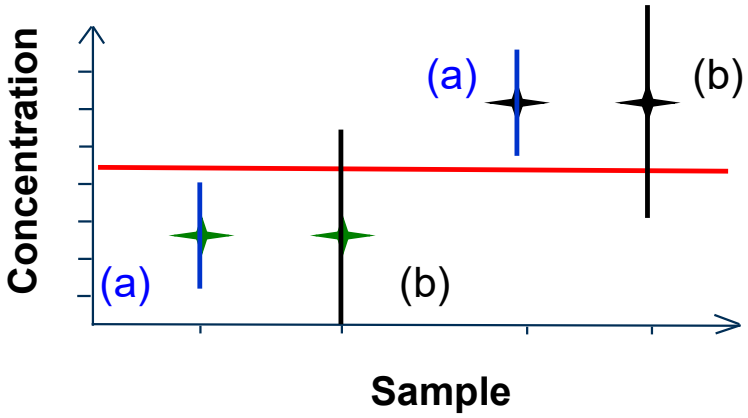
Caveats and restrictions

- Uncertainty of:
  - Compound ID
  - Compound quantity



fit-for-purpose measurement uncertainty



Meta-data

5 %

20 %

50 %

Analytical result: **x ± U**

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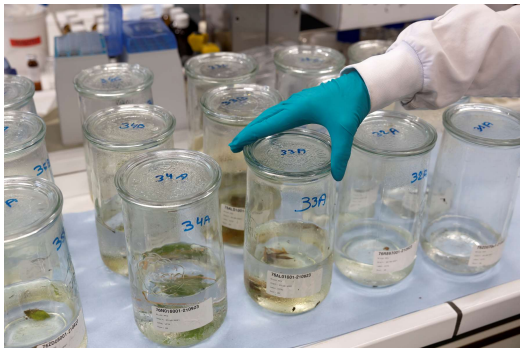
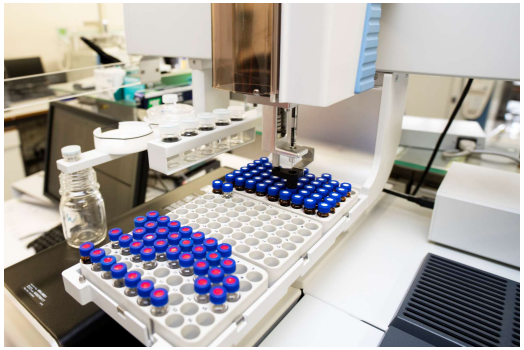
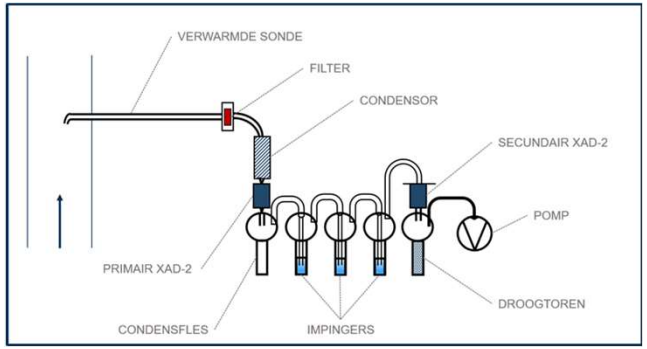
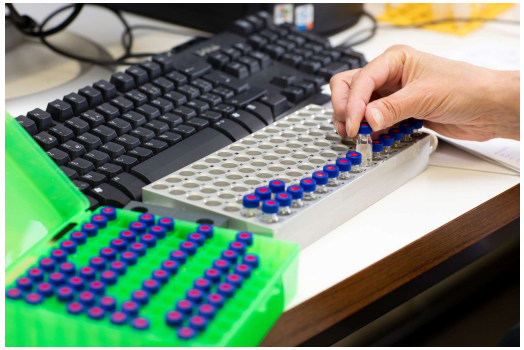
Caveats and restrictions – uncertainty

sampling – preparation – measurement – data interpretation









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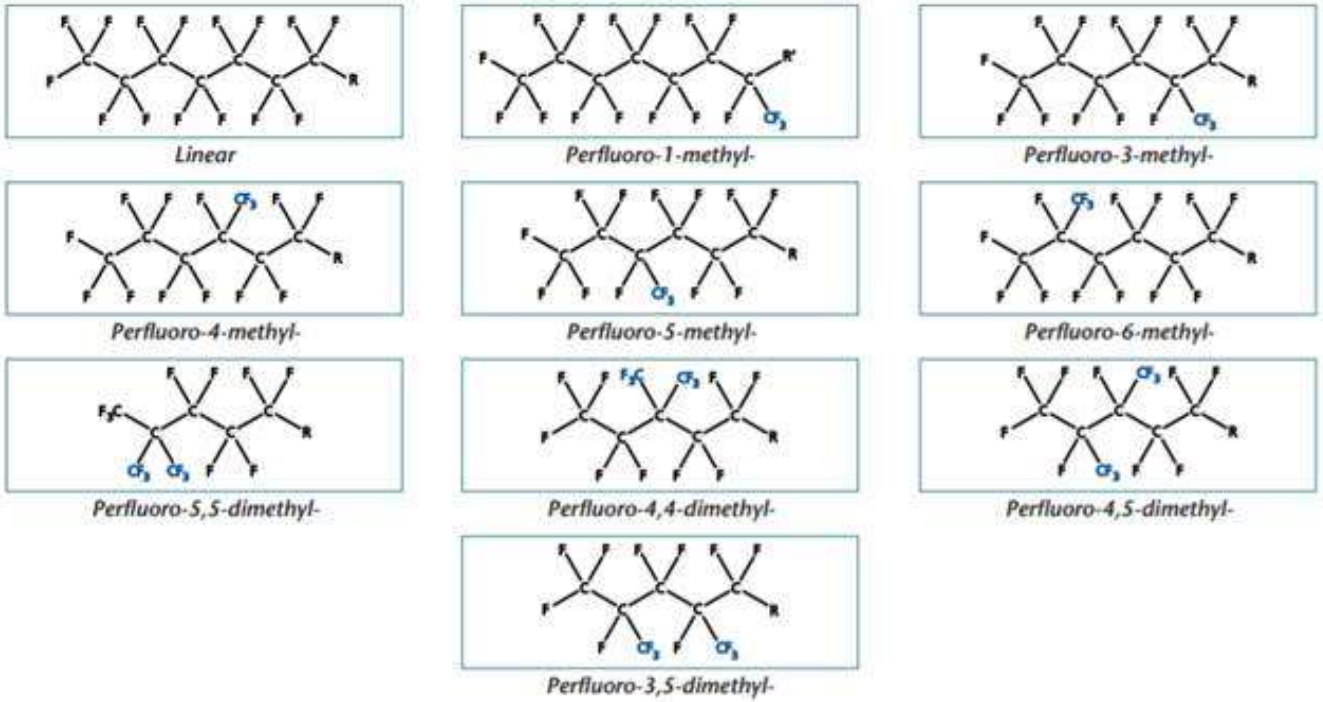
Caveats and restrictions – uncertainty

Caveats and restrictions – uncertainty

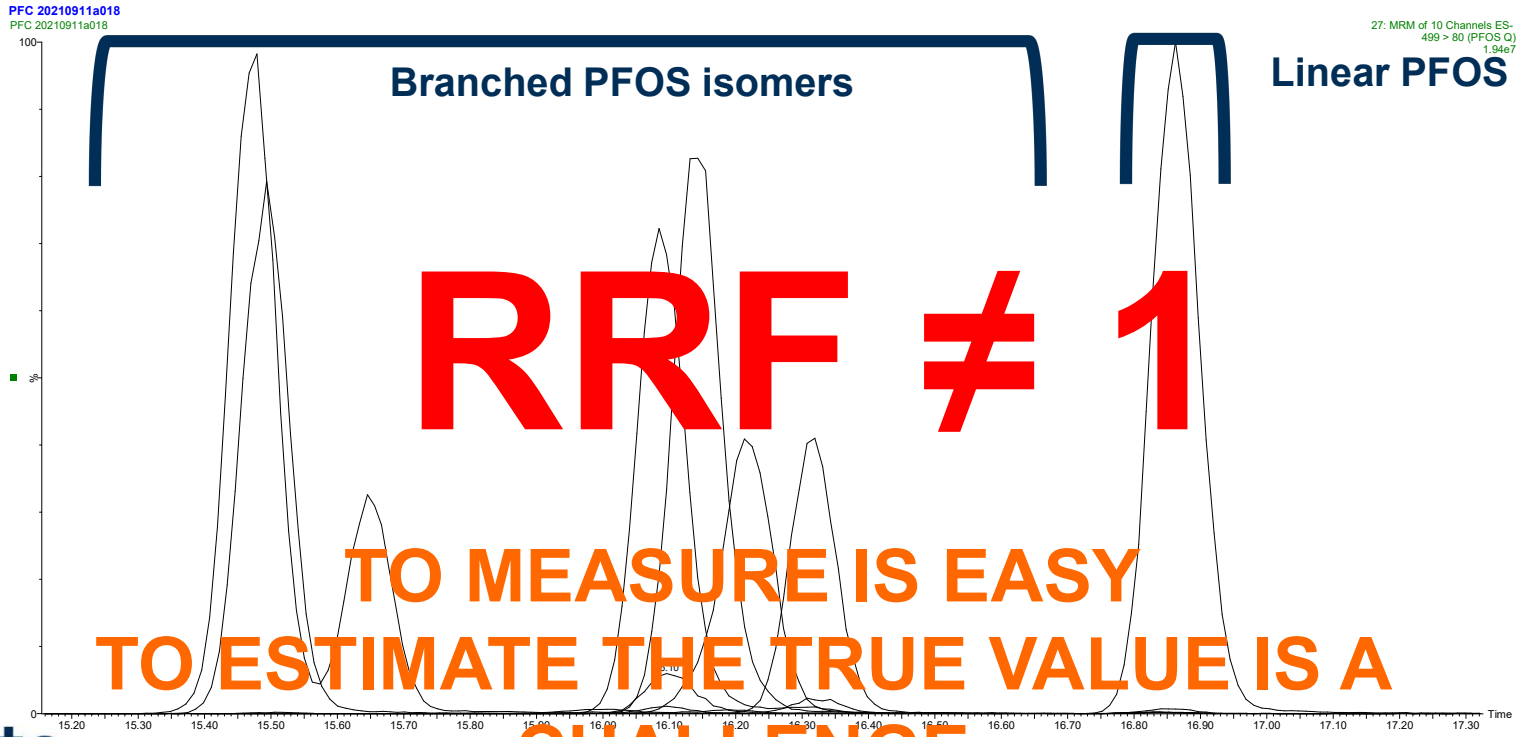
The curious case of PFOS-isomers (aka branched vs linear)



NOTE: R= CO_2^- and $CF_2SO_3^-$
R'= SO_3^- only

Caveats and restrictions – uncertainty

The curious case of PFOS-isomers (aka branched vs linear)



RRF ≠ 1

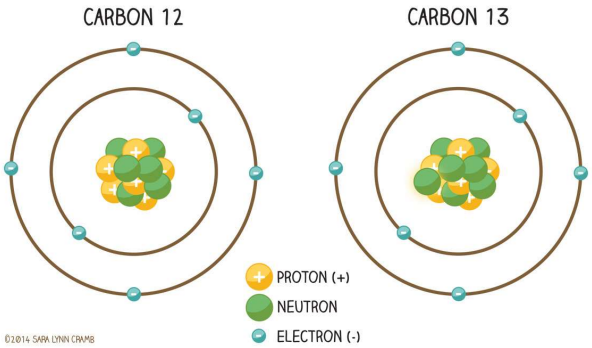
TO MEASURE IS EASY

TO ESTIMATE THE TRUE VALUE IS A CHALLENGE

Caveats and restrictions

- Knowing what to count → > 6000 PFAS
- Specificity matters
- **Isomers – linear vs branched**
- Qualitative analysis → identity + present or not (LOD)
  - How to identify?
- Quantitative analysis → identity + mass fraction (amount)
  - How to identify?
  - How to quantify? → calibration – **reference (SI-traceable)** – reproducible data (comparison)

Caveats and restrictions



- Reference compounds of known purity needed
  → huge response factor differences, even for closely correlated structures
- For true quantification: matching mass-labelled IS standards essential
- Every analytical measurement is only an estimation
  → Measurement uncertainties range from 15 – 50 % (k = 2)
  → But: Fit-for-purpose data
- Setting realistic expectations (read: quality)

“*Analytical chemistry is an exact science, as long as it is exact enough*”

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