How linear and branched PFAAs are handled in the analysis of total PFAS

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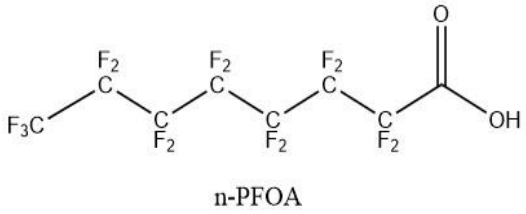
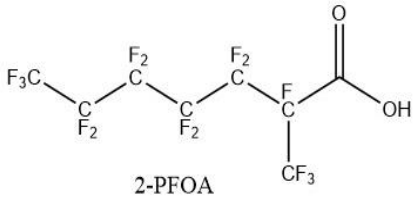
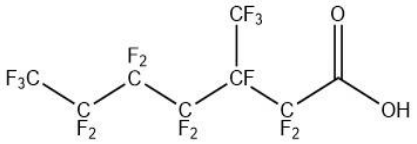
What do we mean by branched and linear?

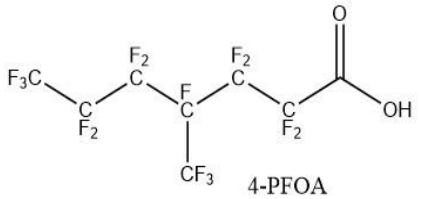
Branching of fluorinted carbon chain gives several possible structural isomers.

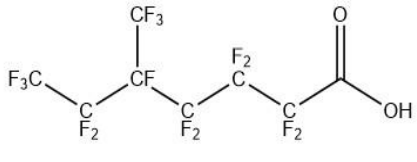


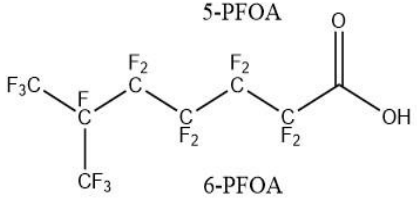
Linear PFOA











Branched PFOA

Normally refered to as sum of several branched isomers

Two manufacturing techniques

Gives different patterns in branching

Electrochemical fluorination (ECF)

PFSAs & FOSE/As

PFOS
Br/lin 30/70

PFOA
22/78

→ *Europe & US 1950s to 2000s*
China from 2000

Telomerisation

PFCAs & FTOHs → **PFOA**

100 % linear

Europe & US 2000-2015

(manufacture started in the 70s)

ECF PFOA
Generally historical pollution (unless in China)

Telomer PFOA
Generally more recent pollution

What affects distribution between isomers in the environment?

- Sorption
  - Preferential sorption of linear isomer to organic matter
  - Enrichment of branched isomers observed in surface waters
- Metabolism
  - Rates of precursor conversion and PFAA excretion differ between isomers
- Relative input of different types of sources of PFOA
  - ECF vs telomer
  - Can be used to understand sources to a specific environment

Analysis of branched and linear isomers

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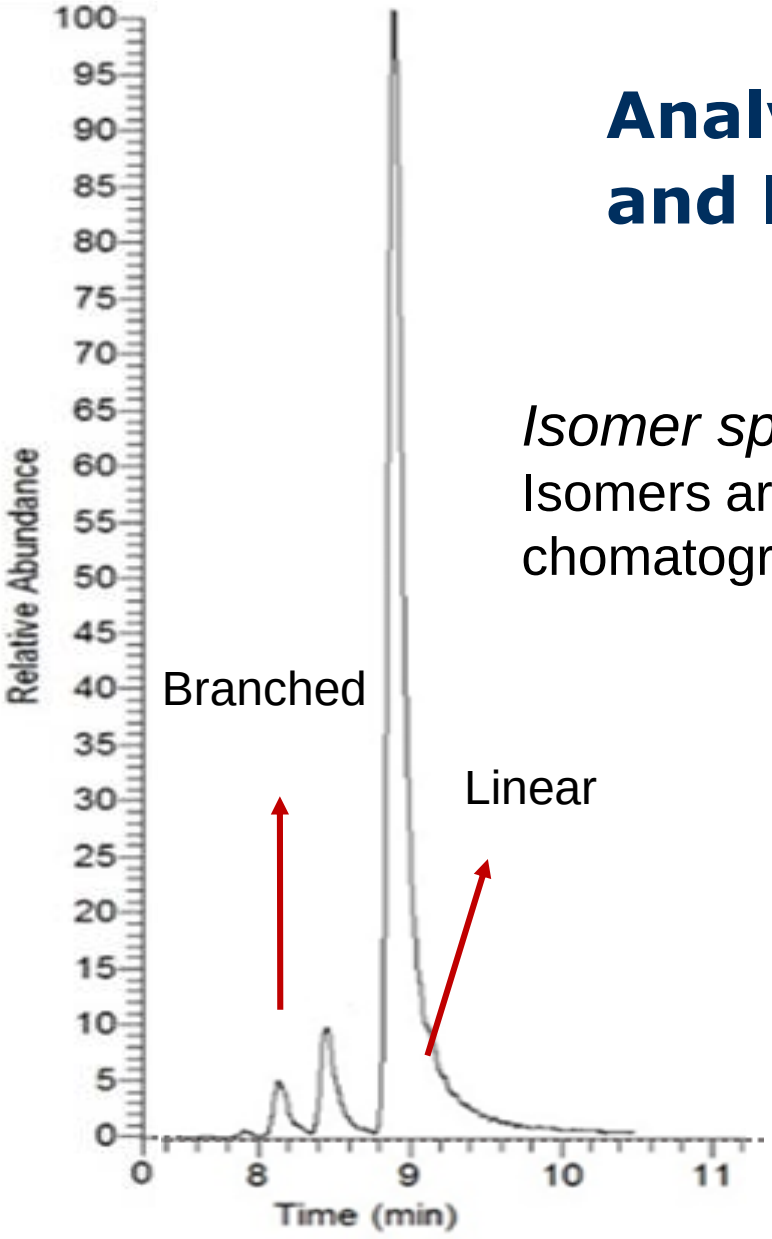
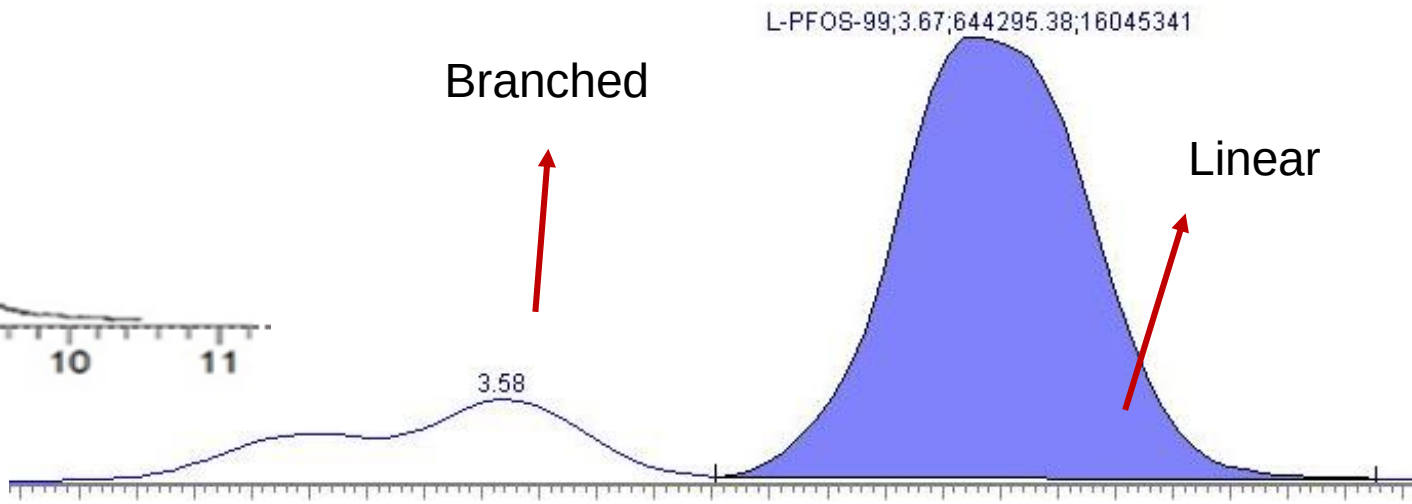
Isomer specific analysis
Isomers are separated chomatographically





Conventional method (C18 column) - Branched isomers coelute

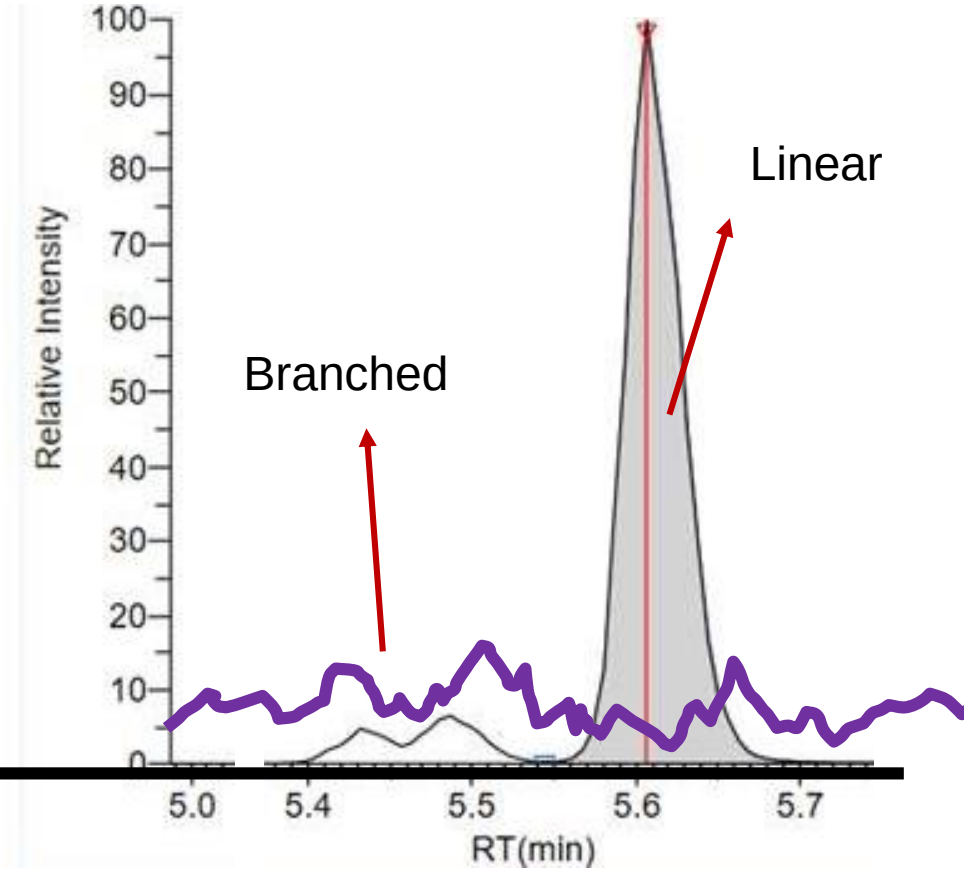
Challenges in analysis – Detection limits

- ∑branched and linear isomers have different limits of detection due to
  - different blank contamination (PFOA)
  - Signal/Noise will always be lower for the branched isomers

Linear > LOD
Branched < LOD

High noise

Low noise



Challenges in analysis - Quantification of Σbranched isomers

- Done vs linear or branched standard? Different labs may use different strategies – all produce data more uncertain than for linear isomer. Possible source of error if not done right!
- Technical standards (br + lin) available for PFOS, PFHxS, PFOA. For other PFAS any data on branched isomers will be uncertain.
- For details on analysis, see e.g.

  Riddell et al. (2009) Environ. Sci. Technol. 43
  Benskin et al. (2010) Environ. Sci. Technol. 44

What about other analytical techniques?

- Methods for total fluorine, total organofluorine, total absorbable organofluorine should cover all structural isomers equally well
- Total oxidisable precursor assay (TOP)

  Branched precursors → branched PFAAs → analysed by same methods as discussed here

In conclusion

- Check if the data you recieve from a lab is for total (branched + linear) or linear only.
  - Mostly relevant for PFOA, PFOS and PFHxS
  - No branched standards available for other PFAS
  - Observations of branched PFCAs (other than PFOA) are rare
- No reported ∑branched does not neccessarily mean there is none – detection limit higher than for linear!
- Reported concentration of ∑branched isomers more uncertain than that of linear. The error will depend on the method used by your lab and the isomer composition in your sample.
- Are there analytical guidelines in place?

You can ask lab about

- Chromatographic method (will likely be C18 column)
  - Branched and linear determined separately or co-eluted?
- How branched isomers were quantified (linear vs technical standard, use of confirmation/quantification ion in quantification, linearity) and estimated accuracy
- Determination of detection limit for branched isomers

For details on analysis, see e.g.

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Thanks for your attention