High purity and n-isomer specific PFAS reference standards

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Introduction:

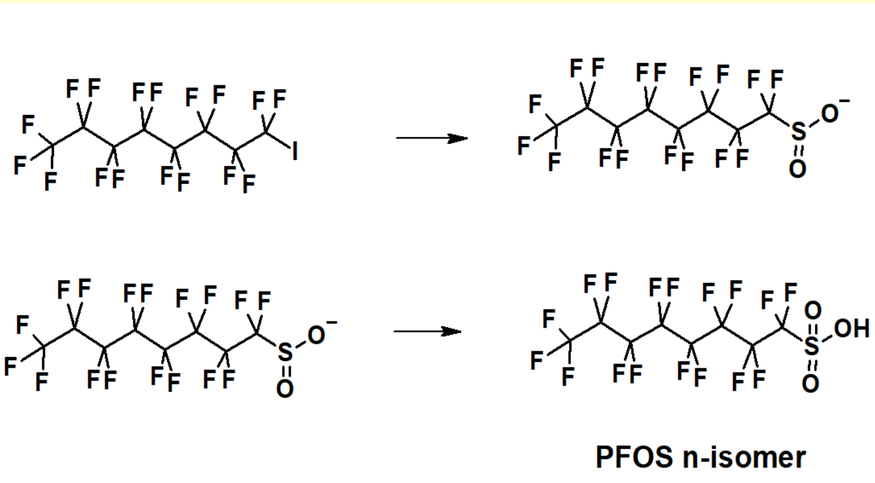
- **PFAS manufacturing results in products containing both linear and branched isomers, which are therefore found in the environment.**
- **Quantitative analysis of PFAS is normally conducted by eluting all isomers together, the mixture of linear and branched isomers presents challenges in providing an accurate quantification of many PFAS in environmental matrices.**
- **Isomer-specific analysis of PFAS is difficult due to the lack of analytical instruments and analytical reference materials**
- **Objective: the goal of this project is to synthesize, purify and characterize isometrically pure PFAS reference materials.**

Materials and Methods:

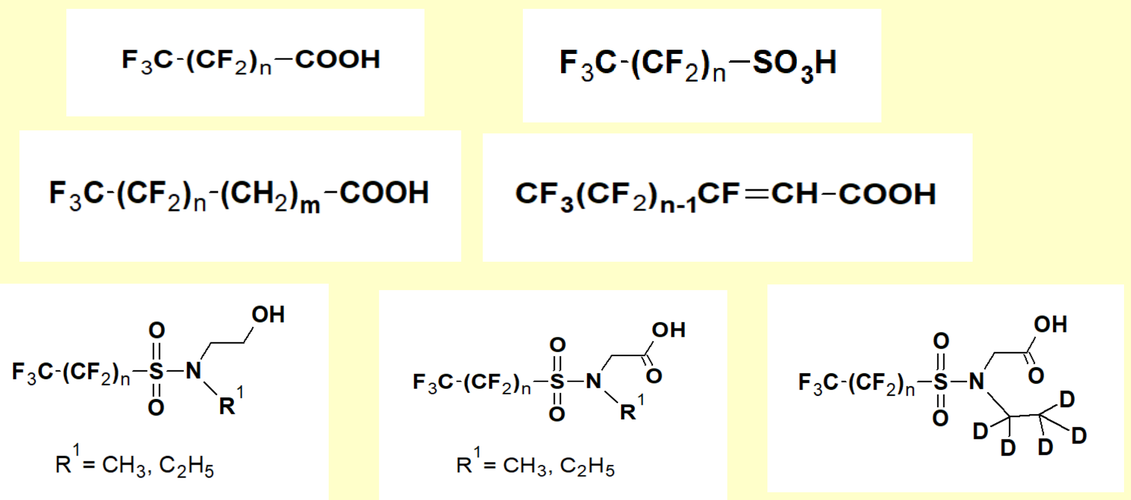
1. Chemical synthesis of n-isomer specific PFAS standards

Various n-isomer of PFASs were prepared by chemical synthesis, and/or purification of commercially available technical mixtures. Synthesis routes were designed for the individual PFAS group and the synthesized products have been purified by conventional purification techniques to remove chemical impurities and isomers. A flash column chromatographic method using flurorinated silica gel has also been developed.

Preparation of PFOS n-isomer, a synthesis example:



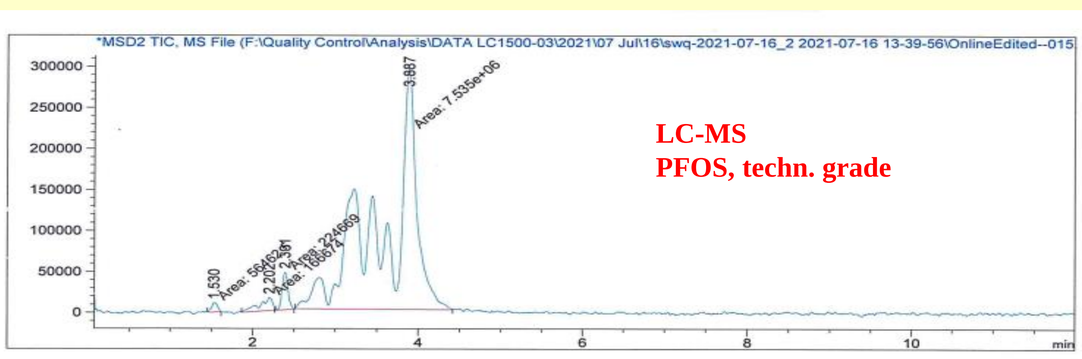
The PFAS synthesized with high quality/purity, general structures:

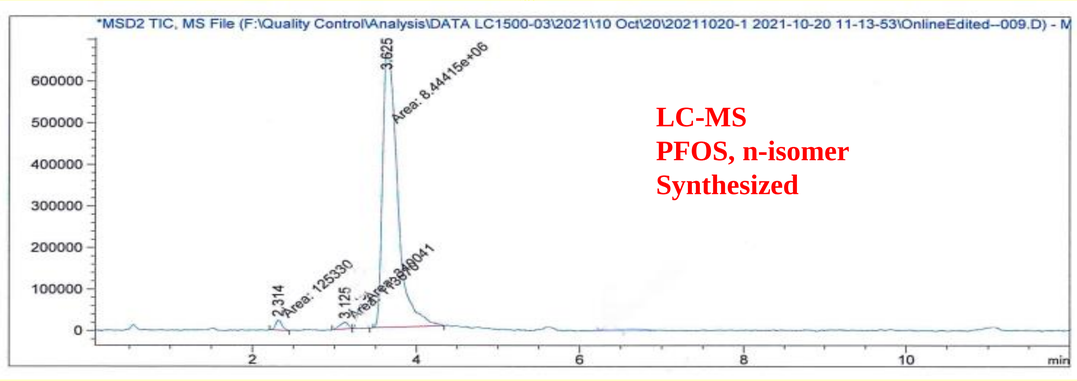


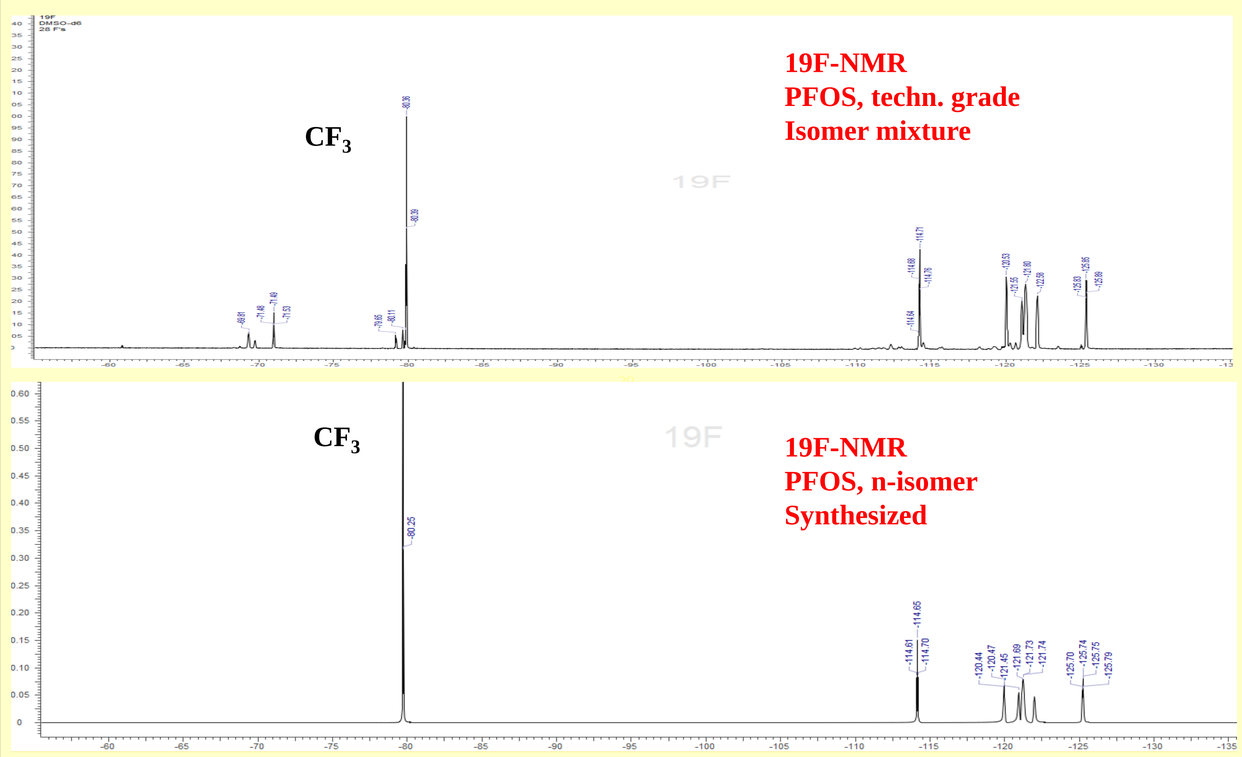
2. PFAS isomer purity, LC-MS and 19F-NMR analysis

LC columns: Phenomenex Kinetex (Pentafluorophenyl, PFP)

NMR: Bruker Avance III HD 400MHz, $CDCl_3$ with 0.03 v/v% TMS; (δ) ppm







Results and Discussion:

1) **Numbers of individual n-isomer of native PFAS have been synthesized in gram quantities.**
2) **The synthesis of perfluoroalkanesulfonates is challenging due to the low product yeild and difficulty in purification.**
3) **Isomer-profile of the PFAS synthesized is variable and depending on the carbon-chain length, the longer the chain (>C8), the more isomers in the synthesis.**
4) **Purification of all synthesized compounds have been performed in order to remove isomers and any other impurities.**
5) **Most of the compounds reached a purity of >98% for the n-isomer, based on both chromatographic analysis and NMR characterizations.**
6) **LC analysis with PFP column gave better isomer separation than with C18 biphenyl column.**
7) **Purification of commercial techn. PFAS have also been tried, but isolation of n-isomer is difficult, especially for long chain (>C8) PFAS.**

Conclusion:

1) **Both individual PFAS and some deuterium-labelled ones are prepared as n-isomer reference materials and internal standards.**
2) **Chemical synthesis gave high quality (purity >98%) PFAS standards.**
3) **Isomerically pure reference standards will give more accurate measurements and are more suitable reference materials.**

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