High purity native and deuterated reference standards for short-chain perfluoroalkane sulfonamide derivatives and their preparation

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Introduction: The work focuses on the synthesis of new reference materials for short-chain PFASs namely perfluorobutane (C4) and perfluorohexane (C6) sulfonamido derivatives, which is part of the REVAMP PhD project. C4 and C6 based fluoropolymer compounds were introduced as short chain replacement to perfluorooctane sulfonyl derivatives, known for their impact of the environment and human health. But these short chain PFASs could be also potential contaminants. Among them, N-methyl or N-ethyl perfluorobutane sulfonamidoethanol (MeFBSE or EtFBSE) or N-methyl perfluorobutylsulfonamideoacetic acid (MeFBSAA) are building blocks for a broad range of fluorotelomer products. MeFBSAA can also be formed when certain fluorinated compounds break down in the environment[1]. Short chain equivalent of perfluooctanesulfonamidoethyl (meth)acrylate could be also interesting to synthesize in order to analyse their degradation. Thus, synthesis of different native and stable isotope-labelled short chain perfluoroalkane sulfoamide derivatives namely N-methyl and N-ethyl perfluoroalkylsulfonamidoacetic acid (C4 and C6, MeFBSAA, EtFBSAA, MeFHxSAA and EtFHxSAA), N-methyl and N-ethyl perfluoroalkane sulfonamidoethanol (C4 and C6, MeFBSE, EtFBSE, MeFHxSE and EtFHxSE), N-methyl and N-ethyl perfluoroalkylsulfonamidoethyl (meth)acrylate (C4 and C6, MeFBSEA, EtFBSEA, MeFBSEMA, EtFBSEMA, MeFHxSEA, EtFHxSEA, MeFHxSEMA and EtFHxSEMA) was developed as new reference materials that can be used for environmental analysis and toxicological study.

Materials and Methods: Synthesis of different native and labelled short chain PFAS was developed from perfluorobutane and perfluorohexane sulfonyl fluoride as starting matrials. MeFBSAA, EtFBSAA, MeFHxSAA, EtFHxSAA, MeFBSE, EtFBSE, MeFHxSE and EtFHxSE were synthesize via nucluophilic substitution. (Meth)acrylate derivatives could be obtained from esterification of the amino alcohol sulfonamide with methacryloyl or acryloyl chloride. Fluorine NMR amd GC/MS analyses were used for product identification and purity accessment, and also for confirming the presence of only one isomer after purification.

Results: 40 compounds were synthesized with a good yield, except for the acrylate derivatives, the general structures can be seen in figure 1. The main challenge in the synthesis was to get pure single chain PFASs especially for perfluorohexanesulfonamido derivatives due to an impure starting material. Indeed, the commercially available perfluorohexnaesulfonyl fluoride was received as an isomer mixture composed of branched and single chain molecules. This problem could be solved by succesive recrystalisations of N-methyl and N-ethyl perfluorohexanesulfonamide before adding the other functional groups, but leaded to a lower yield. All products have received purity above 98%, based on GC/MS analyses.

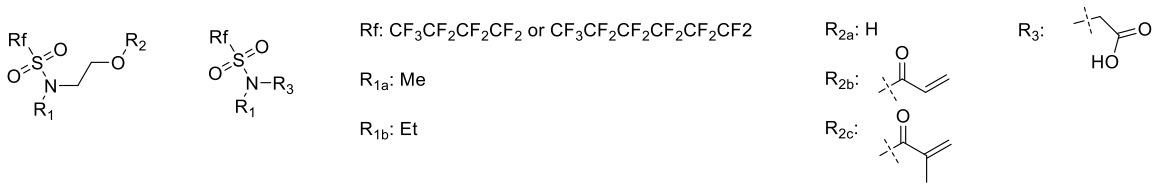

Figure 1: General structures of the different compounds synthesized

Conclusions: Synthesis of native and deuterated sulfonamide derivatives have been synthesized, purified and characterized with a high purity as new reference materials for analysis.

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References:

1. Huset CA, Barlaz MA, Barofsky DF, et al. (2011) *Chemosphere*. 82(10): 1380–1386.