

Examination of Commercial Samples of Perfluoroethylcyclohexane Sulfonate: Another Source of PFOS Isomers

Riddell N¹, McAlees A¹, McCrindle R², Stefanac T¹, Chittim B¹

¹ Research Division, Wellington Laboratories Inc., Guelph, ON, Canada, N1G 3M5

² Department of Chemistry, University of Guelph, Guelph, ON, Canada, N1G 2W1

Introduction

Perfluoro-4-ethylcyclohexanesulfonates (PFECHS) have been utilized extensively as hydraulic fluid additives in order to inhibit the occurrence of erosion in hydraulic systems. In 2011, the use of phosphate-based hydraulic fluids in aircraft was identified as a likely source of this product in surface waters and fish from the Great Lakes of North America [1]. Scientific interest in this contaminant has recently increased since research groups from Australia and Asia reported its presence in local samples. Indeed, PFECHS has been detected in water, sediment, and fish samples in an area surrounding Beijing International Airport in China [2], in soil cores close to Brisbane Airport in Australia [3], and even the Devon Ice Cap [4]. Unfortunately, the only reference standards that have been available to the authors of these studies for quantification of PFECHS in environmental samples are technical grade products which are known to contain appreciable quantities of by-products formed during commercial production [1]. The use of impure/uncharacterized reference standards results in increased uncertainty associated with reported concentrations. Therefore, the goal of the present work was to elucidate the structures and relative concentrations of the major impurities present in these commercial PFECHS products using ¹⁹F nuclear magnetic resonance (NMR) spectroscopy and liquid chromatography coupled to mass spectrometry (LC/MS).

Materials and Methods

A sample of technical grade PFECHS was fractionated using flash column chromatography on reversed phase silica. Continued flash chromatography of the major fractions obtained from this initial column provided material in which individual components were enriched to the point where they could be identified by ¹⁹F NMR spectroscopy. This allowed the proportion of each of these compounds in commercial mixtures to be estimated by integration of relevant signals in their ¹⁹F NMR spectra. All ¹⁹F NMR experiments were performed using methanol-d₄ as the sample solvent at ambient temperature on a 600 MHz Bruker NMR Spectrometer (data acquired at a frequency of 564.62 MHz using a TXO probe). LC/MS experiments were performed using a Waters Acquity Ultra Performance Liquid Chromatography System coupled to a Micromass Quattro micro API MS. MS data were acquired in full scan mode and optimal separations were performed using a Waters CSH Fluoro Phenyl column (1.7 μm, 2.1 x 100 mm). Briefly, gradient elution started at 60% water, 40% 80:20 methanol: acetonitrile (both containing 10mM ammonium acetate) and was ramped to 90% organic over 13 min at a flow-rate of 0.3 mL/min.

Results and Discussion

This study revealed the presence of fourteen constituents in technical grade PFECHS samples at levels equal to, or greater than, 0.5% in terms of molar contributions. Separation of such a sample by LC/MS on a C₁₈ column resulted in a cluster of peaks consisting of four major signals (typical of available PFECHS reference standards) associated with a mass-to-charge ratio (m/z) of 461. These peaks, in order of elution, corresponded to perfluoro-4,4-dimethylcyclohexanesulfonate (PFdiMeCHS), perfluoro-3-ethyl-3-methylcyclopentane-sulfonate (PFEtMeCPS; *anti* and *syn*), PFECHS (*cis* and *trans*), and perfluoro-3-propylcyclopentane-sulfonate (PFPrCPS; *cis* and *trans*). The structures of these seven isomers (see Figure 1) were assigned on the basis of their ¹⁹F NMR spectra.

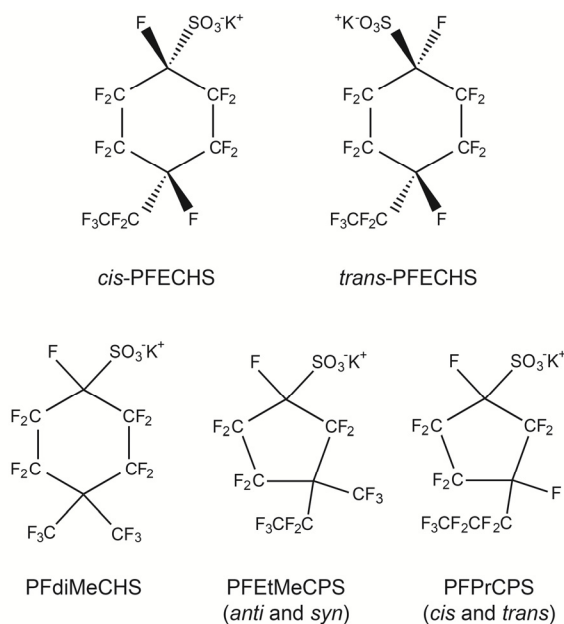


Figure 1: Structures of the compounds in technical grade PFECHS with LC/MS m/z 461.

In the two commercial samples examined, *cis*- and *trans*-PFECHS accounted for between 55 and 60% of the total components present. Although the *cis* and *trans* isomers of PFECHS co-elute by LC on a C₁₈ column, analysis using a pentafluorophenyl (PFP) stationary phase resulted in the isomers of PFECHS being partially resolved (see Figure 2). Also underlying the major cluster of peaks in the chromatogram of commercial material are those arising from minor amounts (*ca* 1%) of *cis*- and *trans*-perfluoro-3-ethylcyclohexanesulfonate. Further components of the mixtures with molar contributions of 1-3% were *cis*- and *trans*-perfluoro-3-methylcyclohexanesulfonate (PFMeCHS) and perfluorocyclohexane-sulfonate (PFCHS).

It is also important to note that additional constituents (ca 0.2-2%) were determined to be isomers of perfluorooctanesulfonate (PFOS). Two of the PFOS isomers characterized are branched/structural isomers not present in commercial PFOS and the other is linear PFOS itself. Other minor components of the PFECHS commercial material (as yet not identified with confidence) have been tentatively identified as: two additional isomers of PFMeCHS ($m/z = 411$); compounds showing $m/z = 423$ ($F_{13}C_8SO_3^-$) and thus having one more double bond equivalent than PFECHS; at least four isomers arising from compounds with $m/z = 439$ [$F_{13}C_8(O)SO_3^-$] in which two fluorine atoms in a PFECHS-like molecule are replaced by an oxygen: several hydrido isomers with $m/z = 441$ ($F_{14}C_8HSO_3^-$); at least two ring-opened isomers containing an oxygen atom, with $m/z = 477$ [$F_{15}C_8(O)SO_3^-$]; and traces of several compounds containing C_9 skeletons.

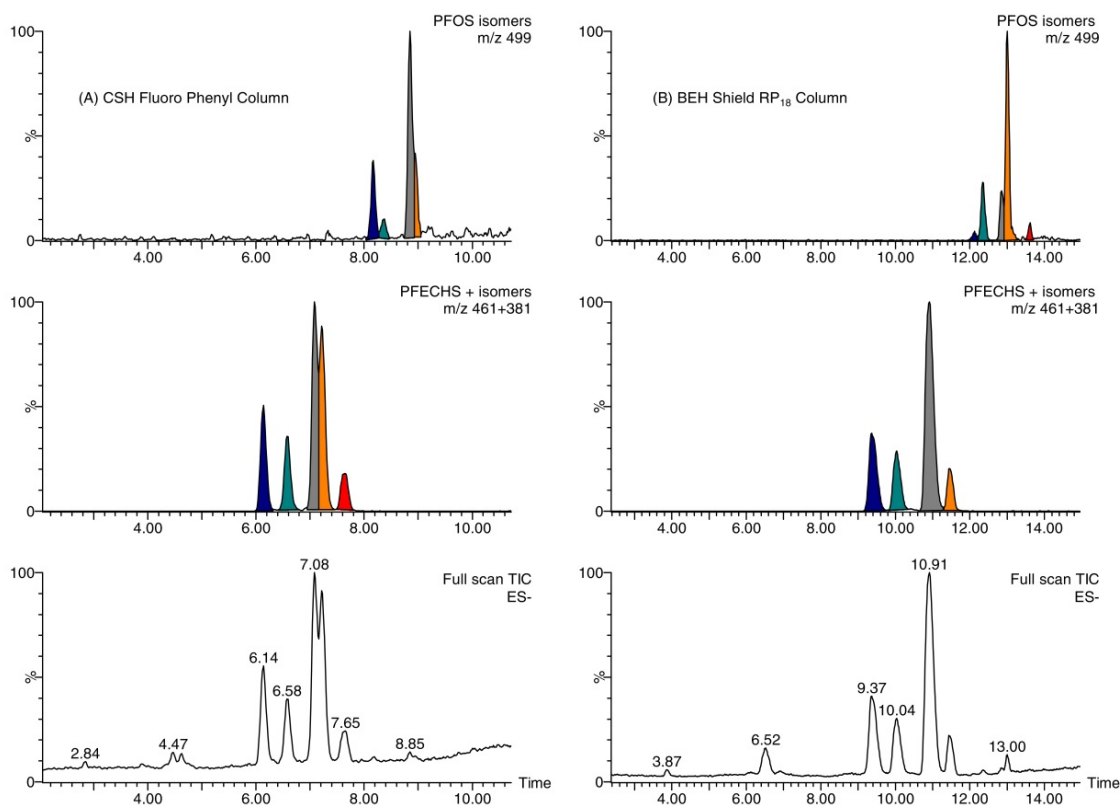


Figure 2: Illustration of the LC separation of technical grade PFECHS achieved using (A) CSH Fluoro Phenyl column and (B) BEH Shield RP₁₈ column [isomers associated with m/z 461+381 (PFECHS) and m/z 499 (PFOS) are highlighted]

References

1. De Silva AO, Spencer C, Scott BF, Backus S and Muir DCG (2011) *Environmental Science & Technology*, **45** 8060-8066.
2. Wang Y, Vestergren R, Shi Y, Cao D, Xu L, Cai Y, Zhao X, and Wu F (2016) *Environmental Science & Technology*, **50** (20) 10923-10932.
3. Baduel C, personal communication, August 2016.
4. MacInnis JJ, French K, Muir DCG, Spencer C, Criscitiello A, De Silva AO, Young CJ (2017) *Environmental Science-Processes & Impacts*, **19**, 22-30.