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Quantification of Fluorine Content in AFFF Concentrates

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A simple direct method based on fluorine nuclear magnetic resonance (^{19}F NMR) for quantitative analysis of fluorine content in AFFF formulations is developed with model compounds and demonstrated for five commercial AFFF 3% concentrates. High resolution spectra with chemical shift and hyperfine features unique to individual fluorocarbon surfactants and their mixtures can provide a discriminating signature for AFFF formulations which may be later used to detect changes in identity and quantity of fluorocarbon surfactants used. The advantages of this fluorine analysis method are general availability of equipment and supplies, selective and non-destructive toward fluorine-containing analyte, AFFF component separation unnecessary, low expense, and rapid turnaround.

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Executive Summary:

Aqueous film-forming foams (AFFF) are used to rapidly extinguish fuel fires and are generated from commercial surfactant concentrates whose use in the military requires evaluation for MilSpec compliance. Fluorocarbon surfactants are the most active components in these concentrates, and analysis of the fluorine content in the AFFF concentrates is one of the requirements in the MilSpec evaluation. A simple direct method based on fluorine nuclear magnetic resonance for quantitative analysis of fluorine content in AFFF formulations is developed with model compounds and demonstrated for five commercial AFFF 3% concentrates. High resolution spectra with chemical shift and hyperfine features unique to individual fluorocarbon surfactants and their mixtures can provide a discriminating signature for AFFF formulations which may be later used to detect changes in identity and quantity of fluorocarbon surfactants used. The advantages of this fluorine analysis method are general availability of equipment and supplies, selective and non-destructive toward fluorine-containing analyte, AFFF component separation unnecessary, low expense and rapid turnaround. The currently used method of fluorine content analysis for AFFF MilSpec evaluation involves quantitative chemical decomposition of the fluorocarbon surfactant and analysis of the inorganic fluoride product. Comparative analyses for five commercial AFFF concentrates are reported.

QUANTIFICATION OF FLUROINE CONTENT IN AFFF CONCENTRATES

INTRODUCTION

Fluorocarbon surfactants are a critical component in aqueous film-forming foams (AFFF) used to extinguish fuel fires at fuel storage areas, airports, military bases and ships. When applied as a component in an AFFF foam onto a burning hydrocarbon pool fire, the fluorocarbon surfactant's unique contribution is its ability, through its combined oleophobic and hydrophobic character, to serve as a barrier to hydrocarbon fuel vapor diffusion between the liquid fuel surface and the combustion in the air above. Use of commercial AFFF concentrate formulations in military establishments requires conformity with MilSpec requirements [1]. In addition to hydrocarbon pool fire suppression testing, the MilSpec listing of chemical and physical requirements for AFFF concentrates includes a total fluorine content determination and a requirement for subsequent evaluations of this AFFF product wherein the fluorine content be monitored for variation of not greater than 15% [1]. The objective of the present work is to develop and demonstrate a fluorine nuclear magnetic resonance (^{19}F NMR) method for quantification of fluorine content in AFFF concentrates. As described below, current methods of fluorine analyses in general and specific to AFFF concentrates have issues of complexity (organofluorine digestion procedures, instrumentation and standards), accuracy, expense and turnaround time. The method reported here is directed at 3% AFFF concentrates containing fluorocarbon surfactants and is designed to be conducted on a common NMR spectrometer with readily available standards and solvents, rapid turnaround time and low expense. In addition to total fluorine content, the ^{19}F NMR spectrum provides a fluorocarbon surfactant "fingerprint" for a particular AFFF concentrate formulation that may be useful in detecting a concentrate aging instability or a later alteration of fluorocarbon surfactant in a particular formulation. Reported here are results for five commercial AFFF 3% concentrates, an analytical reference AFFF 3% concentrate and on two standard fluorocarbon surfactant compounds. At a time when fluorocarbon surfactant use is desired to be minimized or eliminated, this ^{19}F NMR analytical method can provide rapid and rigorously comparative fluorine content information for AFFF concentrate formulations.

Several methods for quantitative fluorine analysis of organic fluorine-containing materials are practiced. The traditional analysis method for total fluorine content is to decompose organofluorine compounds to fluoride ion then measure the fluoride ion by quantitative precipitation, by titration, by ion-selective electrode or by an absorption or emission spectroscopy [2-4]. These analysis techniques are very dependable when conditions are worked out for quantitative conversion of relatively stable fluorocarbon moieties to fluoride ion and for accurate calibration of the fluoride ion detection. These methods are also expensive and time consuming. Newer analytical methods focus on detection and measurement of the fluorine-containing molecule which frequently involve chromatographic separation and specific molecular detection. For gas chromatography, surfactant derivatization to a more volatile specie is frequently required along with a molecular specific detection method, usually mass

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spectroscopy. Liquid chromatography bypasses the derivatization, but the separation is more challenging. High performance/pressure liquid chromatography significantly improves separation, but quantifying molecular detection remains an issue. When mass spectroscopy is used, ionic fragments or parent ions need to be identified, and quantification is strongly dependent on instrument conditions and on use/availability of a calibrating internal standard. These more recent methods have been reviewed [5], and remarkable analytical work has been conducted on the identification of individual fluorocarbon surfactants via HPLC/MS in AFFF concentrates, foams and in water run-off samples [6-8]. While these chromatographic-molecular detection methods provide trace level organic fluorine molecular detection in dilute environmental samples, their complexity and expense for routine fluorine analysis in AFFF formulation concentrates may not be practical. The chromatography generally requires highly diluted sampling of an AFFF concentrate, and issues with respect to the diluent can arise. These include micelle formation in a water diluent and precipitation of a foam-stabilizing polymer component in a methanol diluent [9]. ^{19}F NMR as an analytical technique for simple fluorinated acids in environmental water samples was first reported by Mabury et al [10]. In a complex mixture it has the obvious advantage of detecting only fluorine-containing compounds with a wide 300 ppm chemical shift range which can resolve and discriminate resonances from many fluorocarbon substructures. The need for chromatographic separation can be bypassed, but its sensitivity is significantly lower than other detection methods used for trace analysis as comparative studies have shown [11-12]. However, in a fluorine analysis of an AFFF formulation concentrate for the objective stated above the ^{19}F NMR method appears to be well-suited.

EXPERIMENTAL DETAILS

The primary source of experimental information and data in this report is NRL Notebook No. N-10358.

Materials

Solvents, reference compounds, model compounds, AFFF components and concentrate formulations were obtained from a variety of sources as identified below and used as received.

Solvents. Solvents used for NMR include: Methanol-d_4 99.96%D (Aldrich: 444758); Chloroform-d 99.8%D (Aldrich: 151823); Deuterium oxide-d_2 99.9%D (Aldrich: 34,377-3).

^{19}F NMR References and Standards. Materials used as ^{19}F NMR chemical shift reference and calibrating standard addition compounds are fluorotrichloromethane ($CFCl_3$), 99+% (Aldrich: 25,499-1); 2,2,2-trifluoroacetamide (TFAcAm), 97% (Aldrich: 14,465-7); 2,2,2-trifluoroethanol (TFE), 99% (Polysciences, Inc.: #1258).

Model Compounds. Model compounds to assist in ^{19}F NMR spectra interpretations include perfluorooctanoic acid, PFOA, (3M Company, complementary sample); perfluorooctanamide (K&K Laboratories:17752); 1H,1H-pentadecafluoro-1-octanol (Peninsular Chemresearch Inc.: B16220); perfluoro-n-heptyl iodide (Pierce Chemical Co.: 65650).

Reference AFFF Components. Components for the analytical Reference AFFF concentrate formulation include Capstone® 1157 Fire Fighting Foam Fluorosurfactant (Chemours, complementary sample referred to as Capstone in this report); Glucopon® 215 UP an alkyl polyglucoside concentrate (BASF Corporation contributed sample referred to as Glucopon in this report); Butyl Carbitol®, diethylene glycol monobutyl ether, (Dow Chemical Company purchased from Sigma Aldrich and referred to as DGBE in this report).

AFFF Concentrate Formulations. The Reference AFFF formulation concentrate was prepared at a 3% proportioning rate by mixing by weight 2 parts Glucopon, 3 parts Capstone, 5 parts DGBE and 20 parts distilled water. Commercial 3% AFFF concentrates include Chemguard, Inc. 3% AFFF C-303, Fomtec AFFF 3% F(-15 C), National Foam Aer-O-Lite TMC6 3% AFFF, Buckeye Fire Equipment Company 3% MIL Spec AFFF (BFC-3MS) and Solberg Artic Foam 203 AFFF 3%. Composition information provided by MSDSs for the commercial AFFF concentrates are listed in Table 1.

Non-Volatiles Determination

The quantities of non-volatiles in the Capstone and Glucopon surfactant concentrates, in the Reference AFFF formulation and in the commercial AFFF 3% concentrates were measured by subjecting a small quantity of the liquid to sequential periods of increased vacuum at a rate such that foam formation and expansion beyond confines of the container does not occur. The general procedure is as follows. An analytical quantity of 600 mg concentrate is weighed into a 3 ml open top vial. The vial is placed in a 25 ml beaker, covered with a small watch glass to function as a foam expansion deflector if needed, and the vial-beaker-watch glass assembly is placed into a vacuum desiccator. The desiccator is very gradually evacuated while monitoring the liquid concentrates for bubble and foam formation until a pressure of 20 mm is attained without foam expansion filling more than half the 3 ml containing vial. This 20 mm vacuum is maintained for a 12 hr period after which the residual quantity of concentrate is weighed and the percent remaining solids calculated. This treatment is followed by a second 20 mm vacuum/12 hr treatment. The vacuum during subsequent 12 hr periods is progressively reduced from 20 mm to 12 mm to 7 mm to 2 mm and finally to a rotary pump maximum vacuum of ≤1mm for four 12 hr periods. The loss of volatiles is followed by residual mass measurements at the end of each 12 hr period.

^{19}F NMR Methods and Data Acquisition

^{19}F NMR spectra were recorded on a Bruker Advance 300MHz NMR spectrometer equipped with a standard BBO 300MHz S1 5mm probe and operating at 282.38 MHz with a 11.50 µsec 90° power pulse. For chemical shift calibrations (TFAcAm and TFE against $CFCl_3$ in CD_3OD and D_2O) and detection of resonances, a wide +10 to -300 ppm spectral window was scanned to observe aliphatic $–CF_3$ (-70 to -90 ppm), $-CF_2-$ (-110 to -135 ppm) and –CHF- & $-CH_2F$ (-175 to 250 ppm) substructures. For hyperfine structure resolution and quantitative integrations, a 100 ppm spectral window (FIDRes 0.215 Hz) was scanned using the following acquisition parameters: acquisition time, 2.32 sec; dwell time, 17.7 µsec; pre-scan delay, 25.29 µsec; relaxation delay, 2.000 sec ($\geq 5 \times T_1$ of $–CF_3$ and $–CF_2-$ resonances).

The TFAcAm and TFE secondary chemical shift reference compounds were calibrated with $CFCl_3$ (δ_F = 0 ppm) in D_2O and CD_3OD solvents. Solutions were prepared by dissolution of 3 mg quantities of these compounds in 500 mg of solvent, transferred to the 5 mm NMR cell, followed by three syringe additions of 1 ml quantities of head space vapor from the $CFCl_3$ container to the NMR cell. Results are: TFAcAm/D_2O, δ_F = -74.80 ppm; TFAcAm/CD_3OD, δ_F = -76.09 ppm; TFE/D_2O, δ_F = -75.72 ppm; TFE/CD_3OD, δ_F = -77.06 ppm.

The composition of solutions for the ^{19}F NMR fluorine content analysis was configured such that signal intensities were comparable from the TFE reference compound and the model compound or formulation of interest. For chemical shift analysis of the model compounds, solutions were prepared by dissolution of 11 to 12 mg quantities model compound and 1 to 2 mg TFE in 420 to 450 mg CD_3OD. For quantitative fluorine content analyses of PFOA, Capstone and Glucopon surfactant concentrates and of the AFFF formulation concentrates, TFE was used as the standard for fluorine content as well as the reference for chemical shift. For preparation of an NMR solution, it is important that the TFE concentration be known to at least two significant figures and that the intensity of its resonance be very comparable to the $-CF_3$ resonance of the surfactant being analyzed. A procedure using the Chemguard AFFF 3% concentrate was developed with feedback ^{19}F NMR information. The key numerical quantities are entered in Table 2. A stock solution was prepared by dissolving a ~50 mg quantity of TFE and ~150 mg of the AFFF concentrate. Two successive solutions with concentrations lowered by a factor of 10 (Sol'n #1) and by a factor of 100 (Sol'n #2) were prepared by diluting with the concentrate. Solutions for the ^{19}F NMR spectra were prepared by dissolution of ~20 and ~40 mg quantities in ~425 mg CD_3OD (NMR#1 and NMR#2 respectively). The corresponding weight fraction concentrations of TFE (C_{TFE}), of fluorine content derived from TFE ($C_{F(TFE)}$) and of the AFFF concentrate (C_{Conc}) are entered in Table 2. Note, the weight fraction of fluorine in TFE is 0.570 mgF/mgTFE. These concentrations directly factor into the calculation of the fluorine content in the AFFF concentrate from the integration of the ^{19}F NMR resonances. It should also be noted that many commercial AFFF formulations include a small quantity of dissolved polymer component, typically a polysaccharide, that is insoluble in polar fuels such as alcohols and will form a precipitated layer at a foam-fuel interface to which stabilizes the foam [9]. The commercial AFFF concentrates of this study form a small quantity of fine hazy precipitate when added to methanol which is readily separated by centrifugation. No fluorine was detected in the ^{19}F NMR spectra from D_2O solutions of this precipitate.

^{19}F NMR spectra from the NMR solutions of Table 2 display a series of resonances as described in the Experimental Results Section. The chemical shifts of these resonances are measured, and their corresponding areas are integrated and normalized relative to the TFE signal at -77.06 ppm. These data for Chemguard AFFF are presented in the center of Table 2. The last column headed by $\sum$Fconc is the summation of the AFFF concentrate fluorine signal integrations normalized to the TFE resonance area. The experimental conditions of interest affecting the integrated areas are the NMR solution concentration, the signal:noise in the spectrum and the spectrum resolution. The solution concentration effects were examined by comparing the results of the NMR solutions (19mg/476mg and 44mg/446mg). The difference between the two is negligible. The signal:noise was examined by comparing 1024 accumulated scan spectra with 4096

accumulative scan spectra. The lower noise from the greater number of scans results in slightly 5smaller integration numbers. This result appears to correlate with the narrow TFE signal being slightly enhanced in the higher signal: noise spectrum. The spectrum sweep width and resolution were changed from the default parameters of 350 ppm and 0.755 Hz to 100ppm and 0.215 Hz. This resulted in much better resolution of the very narrow TFE triplet resonance and a smaller integrated value for it, thus lowering the ∑Fconc for the AFFF concentrate as depicted in Table 2. The consequent effect on the calculated fluorine concentration in the AFFF concentrate ($C_{F(conc)}$) and corresponding calculated fluorine weight fraction ($W_{F(conc)}$) and fluorine weight percent (F(wt%)) are presented in the bottom of Table 2.

For the remainder of the AFFF concentrates, the Capstone concentrate and PFOA model compound, the NMR solution concentrations employed corresponded to that of the higher concentrated Chemguard example in Table 2 and are presented in Table 3. Likewise the spectrometer acquisition conditions also corresponded (100 ppm spectral window, 0.215 Hz resolution, 4096 scans). Using these conditions, ^{19}F NMR data obtained for the five commercial AFFF concentrates, the Capstone concentrate and the PFOA model compound are presented in Table 4. Also presented is the -CF_3 normalized integration of resonances in the PFOA spectrum which serves as an internal check on the integration. The corresponding spectra are presented in the Experimental Results Section along with discussion of the data in Table 4.

Calculation of Fluorine Content

The data in Tables 3 and 4 were used to calculate the fluorine content in the AFFF concentrates, Capstone concentrate and PFOA model compound as follows:

$$\frac{\sum F_{conc}}{\sum F_{TFE}} = \frac{C_{F(conc)}}{C_{F(TFE)}}$$

$$W_{F(conc)} = \frac{C_{F(conc)}}{C_{conc}}$$

$$F(wt\%) = 100 \times W_{F(conc)}$$

Where: $\sum F_{conc}$ ≡ summation of integrated areas of concentrate ^{19}F resonances

$\sum F_{TFE}$ ≡ integrated area of TFE ^{19}F resonance (usually normalized to 1.00)

$C_{F(conc)}$ ≡ concentration of concentrate derived fluorine in NMR solution (mg/mg)

$C_{F(TFE)}$ ≡ concentration of TFE derived fluorine in NMR solution (mg/mg)

C_{conc} ≡ concentration of concentrate or model compound in NMR solution (mg/mg)

$W_{F(conc)}$ ≡ Weight fraction fluorine in concentrate or model compound

F(wt%) ≡ Weight percent fluorine in concentrate or model compound

The fluorine contents defined above were calculated from the experimental data of Tables 2 and 3 and are entered in Table 5. These results are discussed in the Experimental Results Section.

Table 1. MSDS Information of Commercial AFFF 3% Concentrates

Buckeye

Product Name: Buckeye 3% MIL SPEC AFFF (BFC-3MS)
Manufacturer: Buckeye Fire Equipment Company

Component	Weight %	CAS #
Water	> 56	7732-18-5
Hexylene Glycol	< 19	107-41-5
Proprietary mixture of surfactants	< 25	N/A

Chemguard

Product name: Chemguard 3% AFFF C-303
Manufacturer: Chemguard, Inc.

Component	Weight %	CAS #
Water	85 - 90	7732-18-5
Propylene glycol t-butyl ether	2 - 4	57018-52-7
Magnesium sulfate	1 - 2	7487-88-9
Hydrocarbon surfactant mixture	proprietary	N/A
Fluorocarbon surfactant mixture	proprietary	N/A

National Foam

Product name: Aer-O-Lite TMC6 3% Aqueous Film Forming Foam
Manufacturer: National Foam

Component	Weight %	CAS #
Water	65 - 75	7732-18-5
Propylene glycol	10 - 20	57-55-6
Dipropylene glycol monomethyl ether	1 - <5	34590-94-8
Hydrocarbon surfactants	1 - <5	N/A
Synthetic detergent	1 - <5	N/A
Fluorocarbon surfactants	1 - <5	N/A

Fomtec

Product name: Fomtec AFFF 1% (-15), 3% F (-15 C) & 6% F (-15 C)
Manufacturer: Dafo Fomtec AB

Components	Weight %	CAS #
Water	balance	7732-18-5
Dipropylene glycol monobutyl ether	5 - 15	112-34-5
Hydrocarbon surfactants	1 - 5	N/A
Fluorocarbon surfactants	<5	N/A
Polyethylene glycol	1 – 5	25322-68-3
Monopropylene glycol	1 – 12	57-55-6
Urea	1 – 10	57-13-6

Solberg

Product name: Artic Foam 203 AFFF 3%
Manufacturer: Solberg Scandinavian AS - Norway

Components	Weight %	CAS #
Water	balance	7732-18-5
Dipropylene glycol monobutyl ether	<20	112-34-5
1,2-ethanediol	<25	107-21-1
Sodium octyl sulfate	<5	142-31-4
Betaine fluorocarbon surfactant	<25	161278-39-3
Ethanol	>0.1	64-17-5

Table 2. Chemguard AFFF ^{19}F NMR Solution Preparation, Spectral Data and Analyzed Fluorine Content

Chemguard Concentrate (conc) – TFE Solution Preparations and Concentrations

Sol'n	mg(solute)	mg(solvent)	mg(Total)	C_{TFE} $\frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}$ $\frac{mg\ F(TFE)}{mg\ Sol'n}$	C_{Conc} $\frac{mg\ Conc}{mg\ Sol'n}$
Stock	51 (TFE)	154 (conc)	205	0.249	0.142	0.751
#1 Sol'n	23 (Stock)	208 (conc)	231	0.0248	0.0142	0.974
#2 Sol'n	21 (#1)	192 (conc)	213	0.00245	0.00140	0.998
NMR#1	19 (#2)	457 (CD_3OD)	476	0.0000978	0.0000559	0.0398
NMR#2	44 (#2)	402 (CD_3OD)	446	0.000242	0.000138	0.0985

Chemguard Concentrate (conc) – TFE ^{19}F NMR Data

Chem shift (ppm)	-77.06	-80.70	-113.65	-121.30	-122.25	-122.71	-125.66	∑Fconc
NMR#1 (1024scan, sw 350 ppm)	1.00	2.97	1.39	1.82	1.83	2.02	1.95	11.98
NMR#2 (1024scan, sw 350 ppm)	1.00	2.88	1.74?	1.92	1.93	1.86	1.92	12.25
NMR#1 (4096scan, sw 350 ppm)	1.00	2.57	1.30	1.61	1.75	1.69	1.64	10.56
NMR#2 (4096scan, sw 350 ppm)	1.00	2.54	1.46	1.62	1.65	1.67	1.68	10.62
NMR#2 (4096scan; sw 100 ppm)	1.00	2.28	1.13	1.26	1.24	1.27	1.31	8.49

Chemguard Concentrate (conc) – TFE ^{19}F NMR Fluorine Content Analysis

^{19}F NMR Solution #	$C_{F(conc)}$	$W_{F(conc)}$	F (wt%)
NMR#1 (1024scan, sw 350 ppm)	0.000670	0.0168	1.7%
NMR#2 (1024scan, sw 350 ppm)	0.00169	0.0172	1.7%
NMR#1 (4096scan, sw 350 ppm)	0.000590	0.0148	1.5%
NMR#2 (4096scan, sw 350 ppm)	0.00147	0.0149	1.5%
NMR#2 (4096scan; sw 100 ppm)	0.00117	0.0119	1.2%

Table 3. Solution Preparations and Concentrations for ^{19}F NMR Analysis of AFFF Concentrates and Model Compounds

Chemguard						
Sol'n	**mg(solute)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ Conc}{mg\ Sol'n}$
Stock	51 (TFE)	154 (conc)	205	0.249	0.142	0.751
Sol'n #1	23 (Stock)	208 (conc)	231	0.0248	0.0142	0.974
Sol'n #2	21 (#1)	192 (conc)	213	0.00245	0.00140	0.998
NMR Sol'n	44 (#2)	402 (CD_3OD)	446	0.000242	0.000138	0.0985
Fomtec						
Sol'n	**mg(solute)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ Conc}{mg\ Sol'n}$
Stock	54 (TFE)	165 (conc)	219	0.247	0.141	0.753
Sol'n #1	31 (Stock)	271 (conc)	302	0.0254	0.0145	0.975
Sol'n #2	39 (#1)	349 (conc)	388	0.00255	0.00146	0.997
NMR Sol'n	43.5 (#2)	453 (CD_3OD)	496.5	0.000223	0.000128	0.0874
Buckeye						
Sol'n	**mg(solute)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ Conc}{mg\ Sol'n}$
Stock	55 (TFE)	165 (conc)	220	0.250	0.1425	0.750
Sol'n #1	32 (Stock)	286 (conc)	318	0.0252	0.0143	0.975
Sol'n #2	37 (#1)	327 (conc)	364	0.00256	0.00146	0.997
NMR Sol'n	41 (#2)	439 (CD_3OD)	480	0.000219	0.000125	0.0852
National Foam						
Sol'n	**mg(solute)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ Conc}{mg\ Sol'n}$
Stock	51 (TFE)	160 (conc)	211	0.242	0.138	0.758
Sol'n #1	34 (Stock)	305 (conc)	339	0.0243	0.0145	0.976
Sol'n #2	33 (#1)	299 (conc)	332	0.00242	0.00138	0.998
NMR Sol'n	41 (#2)	442 (CD_3OD)	483	0.000205	0.000117	0.0849
Solberg						
Sol'n	**mg(solute)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ Conc}{mg\ Sol'n}$
Stock	51 (TFE)	155 (conc)	206	0.248	0.141	0.752
Sol'n #1	33 (Stock)	302 (conc)	335	0.0244	0.0139	0.976
Sol'n #2	30 (#1)	305 (conc)	335	0.00219	0.00125	0.998
NMR Sol'n	42 (#2)	450 (CD_3OD)	492	0.000187	0.000107	0.0854
Reference AFFF						
Sol'n	**mg(solute)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ Conc}{mg\ Sol'n}$
Stock	50 (TFE)	152 (conc)	202	0.248	0.141	0.752
Sol'n #1	34 (Stock)	331 (conc)	365	0.0231	0.0132	0.977
Sol'n #2	38 (#1)	358 (conc)	396	0.00222	0.00126	0.998
NMR Sol'n	39 (#2)	428 (CD_3OD)	467	0.000185	0.000106	0.0833
Capstone						
Sol'n	**mg(solute)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ Conc}{mg\ Sol'n}$
Stock	54 (TFE)	331 (conc)	385	0.140	0.0799	0.860
Sol'n #1	31 (Stock)	311 (conc)	342	0.0127	0.00723	0.987
Sol'n #2	39 (#1)	349 (conc)	388	0.00128	0.000728	0.999
NMR Sol'n	42 (#1)	443 (CD_3OD)	485	0.00110	0.000627	0.0856

PFOA – TFE Solution Preparations and Concentrations							
Sol'n	**mg(solute)**	**mg(PFOA)**	**mg(solvent)**	**mg(Total)**	$C_{TFE}\ \frac{mg\ TFE}{mg\ Sol'n}$	$C_{F(TFE)}\ \frac{mg\ F(TFE)}{mg\ Sol'n}$	$C_{Conc}\ \frac{mg\ PFOA}{mg\ Sol'n}$
Stock	24 (TFE)	92 (solid)	306 (CH_3OH)	422	0.0569	0.0324	0.218
Sol'n #1	38 (Stock)	-----	380 (CH_3OH)	418	0.00517	0.00295	0.0198
Sol'n #2	388 (#1)	30	-----	418	0.00480	0.00274	0.0901
NMR Sol'n	42 (#2)	-----	426 (CD_3OD)	468	0.000473	0.000270	0.00809

Table 4. ^{19}F NMR Spectral Data

Chemguard								
Chem shift (ppm)	-77.06	-80.70	-113.65	-121.30	-122.25	-122.71	-125.66	∑**F**conc
Integrated area	1.00	2.28	1.13	1.26	1.24	1.27	1.31	8.49
Fomtec								
Chem shift (ppm)	-77.06	-80.75	-113.68	-121.33	-122.30	-122.76	-125.72	∑**F**conc
Integrated area	1.00	1.95	0.97	1.03	1.07	1.10	1.13	7.25
Buckeye								
Chem shift (ppm)	-77.06	-80.72	-113.10/-113.63	-121.26	-122.27	-122.64	-125.69	∑**F**conc
Integrated area	1.00	1.61	0.43/.04	0.98	0.71	0.82	0.65	5.24
National Foam								
Chem shift (ppm)	-77.06	-80.73	-113.09/-113.67	-121.28	-122.28	-122.65	-125.69	∑**F**conc
Integrated area	1.00	1.88	0.35/0.15	0.97	1.02	0.99	1.01	6.37
Solberg								
Chem shift (ppm)	-77.06	-80.73	-113.11/-113.67	-121.27	-122.27	-122.64	-125.69	∑**F**conc
Integrated area	1.00	2.47	1.05/-0.07	1.34	1.39	1.31	1.41	9.04
Reference AFFF								
Chem shift (ppm)	-77.06	-80.72	-113.11	-121.26	-122.27	-122.63	-125.68	∑**F**conc
Integrated area	1.00	2.39	1.30	1.34	1.38	1.33	1.40	9.14
Capstone								
Chem shift (ppm)	-77.06	-80.71	-113.09	-121.23	-122.23	-122.60	-125.65	∑**F**conc
Integrated area	1.00	4.01	2.51	2.57	2.60	2.52	2.60	16.81
PFOA								
Chem shift (ppm)	-77.06	-80.62	-1183.37	-120.96	-121.32	-122.03	-122.31	-125.55	∑**F**conc
Integrated area	1.00	4.17	2.61	2.57	2.58	2.66	2.66	2.59	19.84
CF_3:normalized	-----	3.0	1.9	1.8	1.9	1.9	1.9	1.9	

Table 5. ^{19}F NMR Based Fluorine Content

AFFF Concentrate	∑**F**conc	$C_{F(conc)}$	$W_{F(conc)}$	**F(wt%)**
Chemguard	8.49	0.00117	0.0119	1.2%
Fomtec	7.25	0.000928	0.0106	1.1%
Buckeye	5.24	0.000655	0.00769	0.77%
National Foam	6.37	0.000745	0.00878	0.89%
Solberg	9.04	0.000967	0.0113	1.1%
Reference AFFF	9.14	0.000969	0.0166	1.7%
Capstone	16.81	0.1215	0.123	12.3%
PFOA	19.84	0.00536	0.662	66.2%

EXPERIMENTAL RESULTS

The results to be described in this section include a simple non-volatiles content determination for AFFF concentrates, the development and demonstration of a facile ^{19}F NMR method to determine organofluorine content in AFFF formulations, an analysis ^{19}F NMR spectra wherein profiles somewhat unique to individual commercial AFFF can be identified and a fluorine content comparison of five commercial AFFF formulations.

AFFF Concentrate Non-Volatile Content

A commercial AFFF concentrate is a complex mixture of many components designed to produce a foam when mixed with water usually at a 3% or 6% proportioning rate that, when deposited onto the surface of a burning organic liquid, will rapidly extinguish the fire. These formulations are water based and include hydrocarbon surfactants, fluorocarbon surfactants, organic solvents, water-soluble polymers, inorganic salts, buffers and preservatives [9]. A regimented vacuum-assisted evaporation procedure is useful in establishing a volatiles profile along with a non-volatiles or solids content for an AFFF concentrate. These concentrates have a strong potential for foaming, and very gradual application of vacuum in necessary to avoid uncontrolled foam expansion from the samples under examination. Such a procedure is provided in the Experimental Details Section and presented in summary form along with the volatiles profile for the five commercial AFFF 3% concentrates in Figure 1.

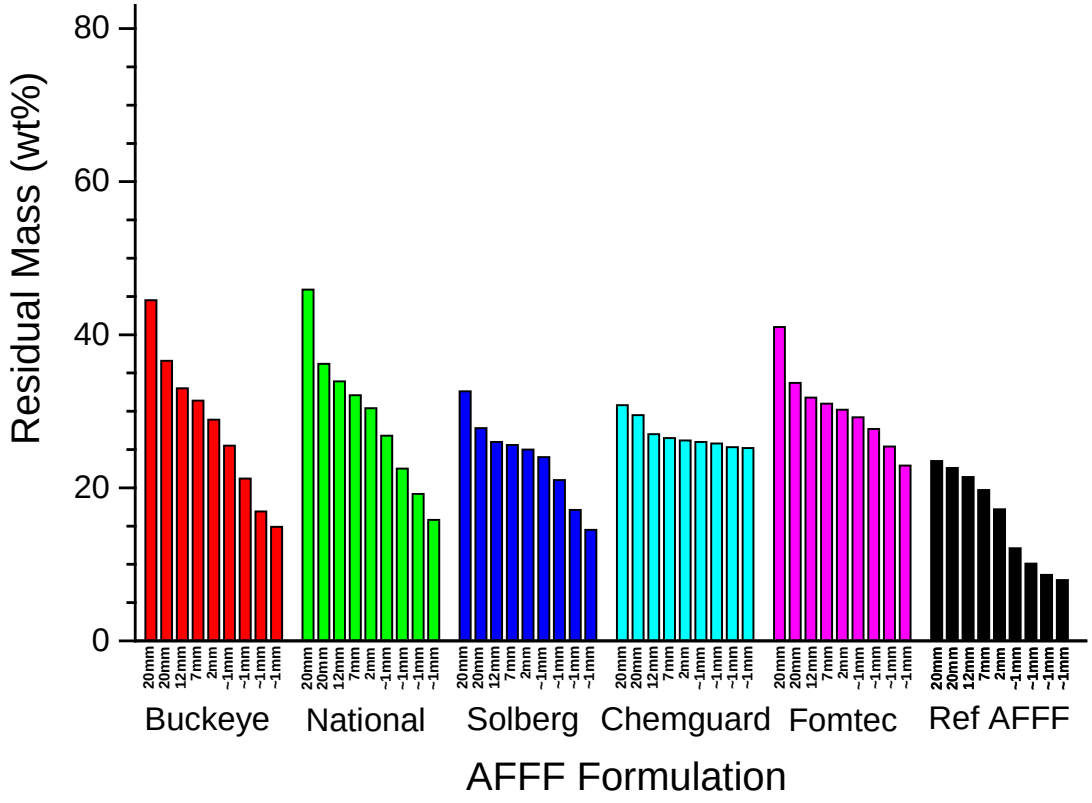

Figure 1. Non-volatiles profile of commercial and Reference AFFF formulations for successive 12 hr periods at progressively reduced pressures (20mm→12mm→7mm→2mm→<~1mm).

The patterns of volatile removal reflect significant similarities and differences between AFFF formulations. All commercial AFFF formulations contain components of variable volatility some of which have relatively low volatility as reflected by the continual weight loss over four 12hr/<~1mm treatments. Buckeye and National Foam are remarkably similar in profile and reduce to a 15% solids content. Solberg, while more volatile also reduces to the 15% solids content. Chemguard and Fomtec are significantly different with the highest levels of solids content, 25% and 23% respectively. While this characterization does not reflect the fluorine content, it is a good indicator of water-soluble solids that will not evaporate. The profile for the Reference AFFF formulation reflects its minimal number of components (four: Capstone, Glucopon, DGBE and water) and their volatility. Capstone and Glucopon are concentrates whose individual volatiles profiles indicate a complete separation with respective solids components of 27.5% and 63.6% as depicted in Figure 2. As an accuracy check on this method of non-volatiles content, knowledge of the Reference AFFF formulation content (3:2:5:20 Capstone:Glucopon:DGBE:water by weight), the non-volatile content of Capstone and Glucopon and assumption of 100% volatility of Butyl Carbitol yields a calculated non-volatiles content of 7.0% which is in good agreement with the 7.3% result in Figure 1.

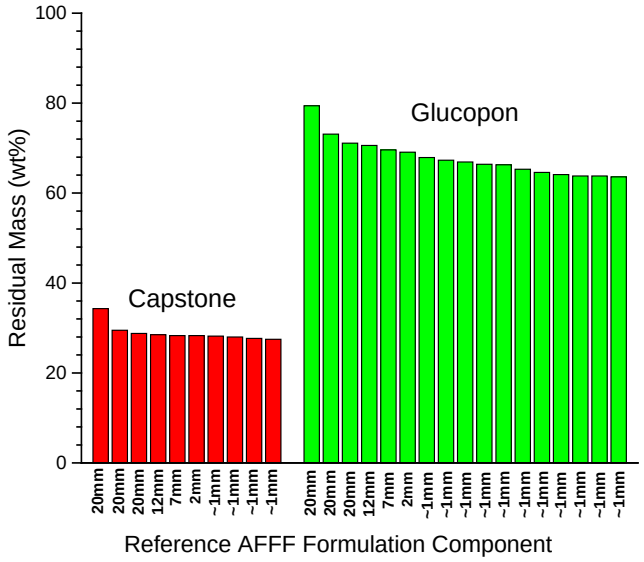

Figure 2. Non-volatiles profile of Reference AFFF Capstone and Glucopon components derived from successive 12 hr periods at reduced pressures (20mm→12mm→7mm→2mm→<~1mm).

^{19}F NMR Spectra

Qualitative and quantitative analyses of fluorine in ^{19}F NMR spectra require some form of chemical structure assignment of resonances, analyses of chemical shifts and line shapes and measurement of the quantities of fluorine generating such resonances. In this section are described the selection and use of ^{19}F NMR standard and reference compounds for chemical shift

measurement and fluorine quantification, use of model compounds for chemical shift assignments, and spectra of the AFFF 3% concentrates.

a) Experimental Standards and Model Compounds.

Below are described the development of procedures for chemical shift measurement and spectra analysis useful for interpreting spectra of the AFFF concentrates.

i) 1,1,1-Trifluoroethanol Calibrating Reference.

The commonly used primary reference compound for chemical shift determination is $CFCl_3$ with a defined chemical shift of 0 ppm [13]. In this work it was desired to employ a secondary chemical shift reference compound whose resonance is closely situated but not interfering or overlapping with resonances from model compounds and AFFF concentrates. It was also desired that this compound serve as a reference for quantitative standard addition determination of the fluorine content in the AFFF concentrates. As such, the compound CF_3CONH_2 was identified as having the attractive characteristics of a $–CF_3$ derived singlet resonance (-76.09 ppm) approximately 5 ppm shifted downfield from the $–CF_3$ terminal resonance observed in model compounds. This compound is also miscible with water and methanol which are the solvents used for the NMR spectra of the AFFF concentrates. Unfortunately, it was observed that CF_3CONH_2 slowly hydrolyzes over a period of several hours in water and methanol with the appearance and growth of a $–CF_3$ resonance at -75.23 ppm attributed to the trifluoroacetate product [14]. As a stable and water- and methanol-miscible secondary reference for chemical shift and fluorine content determination, trifluoroethanol (TFE), CF_3CH_2OH, was selected. A well-resolved triplet (TFE/CD_3OD: δ_F = -77.06 ppm, triplet J_{FH} = 9.5 Hz ; TFE/D_2O, δ_F = -75.72 ppm, triplet J_{FH} = 9.0 Hz). Solutions for quantitative ^{19}F NMR fluorine analyses were prepared by dissolution of a two significant figure analytical quantity of TFE into a model compound solution or concentrate with dilutions made such that the $–CF_3$ resonances of TFE and of the analyte were of closely comparable intensity as described in the Experimental Detail Section.

ii) Perfluorooctanoic Acid and Analog Model Compounds

To assess the utility and accuracy of this ^{19}F NMR method an analysis of perfluorooctanoic acid (PFOA) and the related model compounds perfluorooctylamide, perfluorooctyl alcohol and perfluorooctyl iodide was conducted. The spectrum of PFOA-TFE/CD_3OH with high resolution expansions of the individual resonances is depicted in Figure 3. In addition to the -77.06 TFE resonance there are seven resonances corresponding six $–CF_2$- and one $–CF_3$ moieties. The high resolution expansions show resolved hyperfine structures. The reference TFE $–CF_3$ resonance is a narrow triplet, and the PFOA $–CF_3$ is a triplet of triplets attributable to the splitting of the closest two $-CF_2$- groups. The six PFOA $-CF_2$- groups display varying degrees of resolved hyperfine splitting with the resonance at -118.37 assignable to the terminal $-CF_2$- group at the -COOH chain end by virtue of its triplet of triplets splitting from its nearest two $-CF_2$- groups. The interior $-CF_2$- groups display varying levels of resolved hyperfine structure and splitting complexity making assignments less straightforward. PFOA has been analyzed in detail by ^{19}F-^{19}F NMR correlation spectroscopy (COSY) and by nuclear Overhauser effects to make definitive assignments for each of the fluorine resonances [15,16]. These assignments and

results are presented in Table 6 along with the assignments of this work. Although different solvents and concentrations were used, the agreement is good.

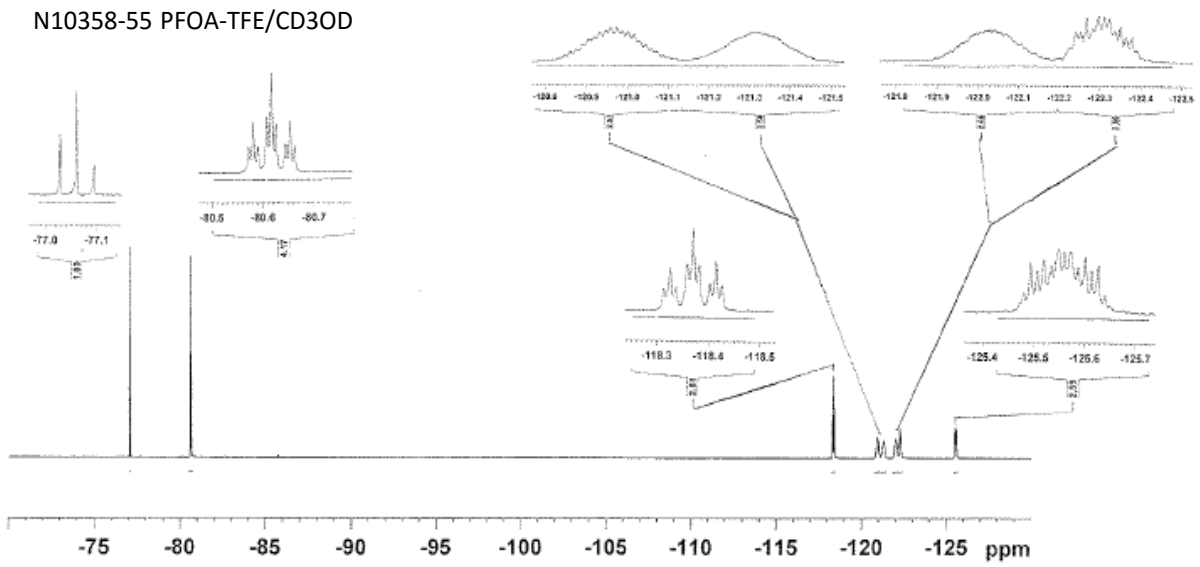

Figure 3. ^{19}F NMR spectrum of PFOA+TFE/CD_3OD (0.00809mg+0.000473mg/mg sol'n)

Table 6. ^{19}F NMR Chemical Shifts (ppm) of PFOA

CF_3—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	O ‖ COH
-80.9	-126.2	-122.9	-122.2	-121.9	-123.4	-117.6	2.5mg/0.5ml D_2O [15]
-81.0	-126.0	-123.7	-121.9	-121.6	-123.9	-119.0	?.?mg/?.?ml $CDCl_3$ [16]
-80.8	-125.7	-122.1	-121.4	-121.17	-122.40	-118.6	49mg/455mg CD_3OD *Current Work*

Table 7. ^{19}F NMR Chemical Shifts (ppm) of PFOA Analogue Model Compounds

CF_3—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	O ‖ CNH_2	
-80.65	-125.63	-122.15	-122.15	-121.35	-120.93	-118.98		11mg/448mg CD_3OD
CF_3—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	CH_2OH	
-80.66	-125.62	-122.80	-122.09	-121.41	-121.41	-121.41		11mg/426mg CD_3OD
CF_3—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	CF_2—	I	
-80.63	-125.62	-122.07	-121.28	-120.29	-113.05	-64.94		12mg/418mg CD_3OD

Of importance to derivative and analog surfactants to PFOA is the perturbation of the chemical shifts in the perfluorocarbon tail when the head group is altered. In Table 7 are presented the amide, alcohol and iodide analog model compounds and the corresponding chemical shifts in the fluorocarbon tail resonances. As expected from its close positioning, the resonance corresponding to the terminal $–CF_2$- (indicated in Table 6) experiences the greatest variation in chemical shift. This is particularly useful in obtaining a discrimination between similar but different fluorocarbon surfactants as is the case when conducting analyses of commercial AFFF concentrates having proprietary formulations.

Finally, PFOA is a compositionally well-defined surfactant that can serve as an evaluation for the ^{19}F NMR method to determine fluorine content. The integration of the TFE and PFOA fluorine resonances (Figure 3 and bottom of Table 4) for the analytically prepared NMR solution (bottom of Table 3) are used to calculate a wt% fluorine in PFOA. The result (66.2 wt%, Table 5) compares well with that calculated from the $C_8HF_{15}O_2$ composition formula (68.8 wt%).

iii) Capstone 1157

Capstone® 1157 is a Chemours™/DuPont™ product also having earlier tradename of Forafac® 1157 [17]. It is a structurally defined 6:2 fluorocarbon telomer sulfonamide alkylbetaine surfactant and more closely related to fluorocarbon surfactants in current AFFF formulations than is PFOA [6]. Its synthesis was reported in the 1970's in the patent literature [18] and has been structurally characterized by NMR and mass spectroscopy [19,20]. For the purposes of comparison of the spectrum of this known structure with spectra of the AFFF formulations and as a second check on the accuracy of the ^{19}F NMR fluorine content measurement method, the spectrum of Capstone-TFE/CD_3OH was obtained and is depicted in Figure 4.

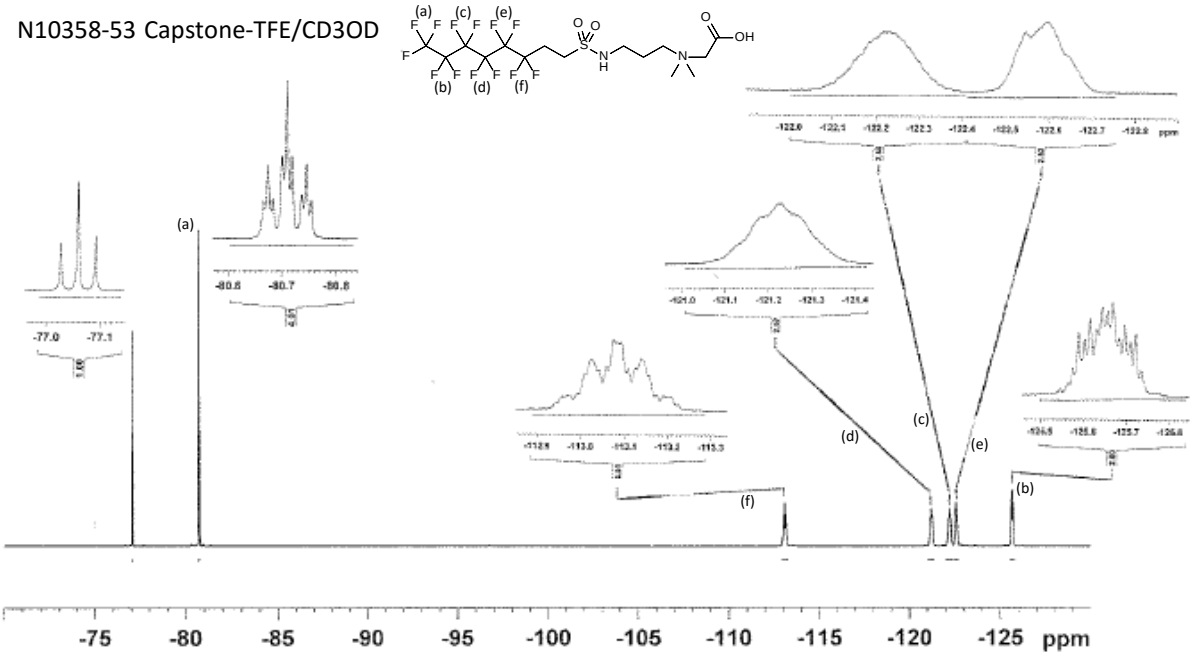

Figure 4. ^{19}F NMR spectrum of Capstone®+TFE/CD_3OD (0.00856mg+0.00110mg/mg sol'n).

The Capstone-TFE spectrum is similar to the PFOA-TFE spectrum (Figure 3) in that the $–CF_3$ resonances are a triplet and a triplet of triplets, but different in that there is one less $–CF_2$- resonance and the terminal $–CF_2$- resonance at -113.09 ppm is not a first order triplet of triplets but more complicated by additional hyperfine splitting from the adjacent $–CH_2$-CH_2- substructure. The other four $–CF_2$- resonances from the central region of the fluoromethylene chain display symmetrical but more broadened hyperfine structure. With regard to the ^{19}F NMR fluorine content measurement in the Capstone concentrate, the integration of the TFE and Capstone fluorine resonances (Figure 4 and Capstone entry in Table 4) for the analytically prepared Capstone-TFE NMR solution (Capstone entry in Table 3) are used to calculate a wt% fluorine as indicated in the Experimental Details Section. This result (12.3 wt%, Table 5) compares well with that calculated from the $C_{15}H_{19}O_4F_{13}S$ composition formula and the 27.5 wt% solids in the Capstone concentrate (12.5 wt%).

b) Reference AFFF Concentrate.

The reference AFFF Concentrate is a minimal component analytical AFFF formulation composed of 2:3:5:20 parts by weight Glucopon:Capstone:DGBE:water which passes the 28 ft^2 MilSpec fire-extinction test and has been developed as a tool to evaluate fluorine-free surfactant substitute candidates for the Capstone [21]. The inclusion of this ref AFFF concentrate in the ^{19}F NMR fluorine content measurement development serves the purpose of determining whether the inclusion of known hydrocarbon surfactants and organic solvents alter the ^{19}F NMR spectrum of the fluorocarbon surfactant and as a third check on the accuracy of this measurement with a known analyte in a mixture that mimics commercial proprietary AFFF formulations. The spectrum of Ref-TFE/CD_3OH with high resolution expansions of the individual resonances is depicted in Figure 5.

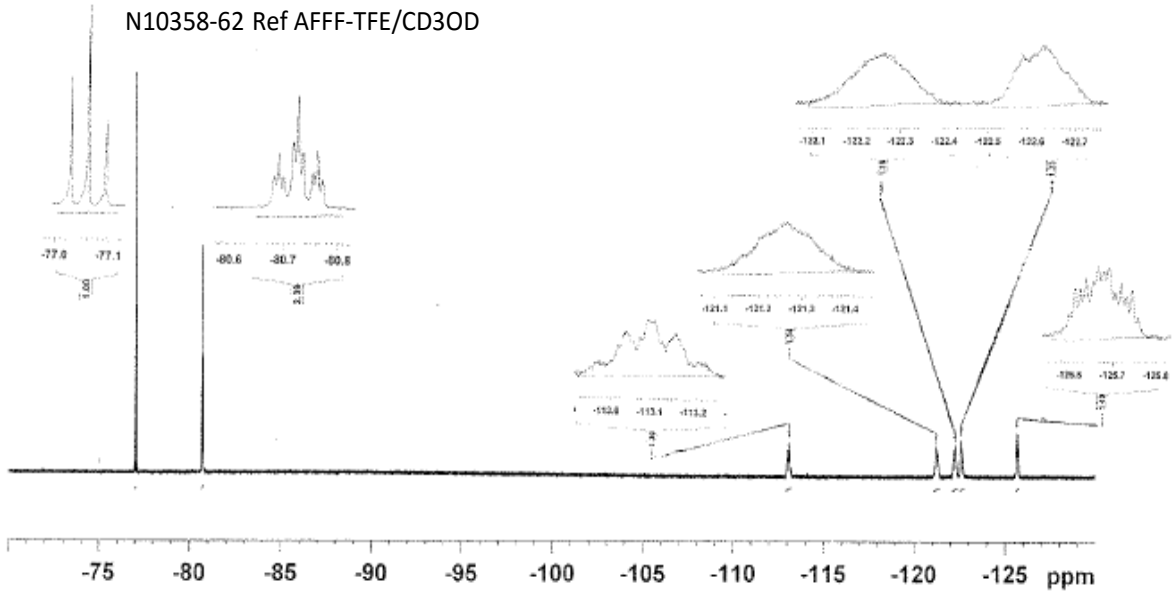

Figure 5. ^{19}F NMR spectrum of Ref AFFF+TFE/CD_3OD (0.0833mg+0.000185mg/mg sol'n).

For the six Capstone resonances comparison of chemical shifts (Table 4) and expanded spectral hyperfine features (Figures 4 and 5) indicate that the Glucopon, DGBE and water in the Ref AFFF concentrate have negligible effect on the Capstone surfactant fluorocarbon tail. The ^{19}F NMR fluorine content measurement in the Ref AFFF concentrate as calculated from the integrations of the TFE and Capstone resonances (Figure 5 and Ref AFFF entry in Table 4) for the analytically prepared Ref AFFF-TFE NMR solution (Reference AFFF entry in Table 3) yields a value of 1.7 wt% fluorine (Table 5). This compares closely with a value of 1.6 wt% calculated from the 2:3:5:20 Glucopon:Capstone:DGBE:water Ref AFFF composition, the 27.5 wt% Capstone concentrate solids composition and the 45.54 wt% F in the $C_{15}H_{19}O_4F_{13}S$ Capstone surfactant formula composition.

c) Commercial AFFF Concentrates.

In an analogous manner, the ^{19}F NMR fluorine content measurement method was applied to the five proprietary Commercial AFFF 3% concentrates (Chemguard, Fomtec, Buckeye, National Foam and Solberg). The ^{19}F NMR spectra of the respective commercial AFFF-TFE/CD_3OH solutions with high resolution expansions of the individual resonances is depicted in Figures 6, 7, 8, 9 and 10 below. While these spectra are very similar to that of Capstone in that a pattern of resonances corresponding to a CF_3-CF_2-CF_2-CF_2-CF_2-CF_2- surfactant tail is observed, it is immediately apparent that there are small but significant differences in the chemical shifts of the individual resonances and in the hyperfine line shapes of these resonances. This results from an array of variations in surfactant head group structures (for examples see [9,19,22]). The -CF_2- resonances most perturbed are those closest to the head group.

To illustrate the effect of this variation the spectra of Figures 5-10 have been consolidated in an expansion of -113 to -125 ppm with individual structural assignments made to illustrate these effects as depicted in Figure 11. The terminal -CF_2- group connected to the surfactant head structure displays the largest effect. In the Capstone structure, this resonance at -113.08 ppm displays a distinct and symmetrical 5-line structure with each of the five lines barely resolved into three more lines. The spectra of the commercial AFFF concentrates have been arranged in a progression wherein a second resonance at -113.7 ppm emerges with the apparent diminishing of the resonance at -113.1 ppm. This does not appear to be an equilibrium situation as warming or cooling the sample does not affect the spectrum. The next most affected resonance is the one originating from the -CF_2- adjacent the terminal -CF_2- substructure at -122.6 ppm. It appears to correlate with two overlapping signals which are resolved in resonances from the terminal -CF_2- at -113.1 and -113.7 ppm. This is best illustrated in the National Foam spectrum in Figure 11. The remaining three -CF_2- resonances displayed much smaller effects from attachment to different head groups.

While not easy to interpret, the patterns in these fluorocarbon surfactant tail spectra can be useful for discriminating or identifying a particular commercial AFFF concentrate among several possibilities. Along with a fluorine content measurement, this spectral signature could be used to detect changes in commercial AFFF concentrate formulations.

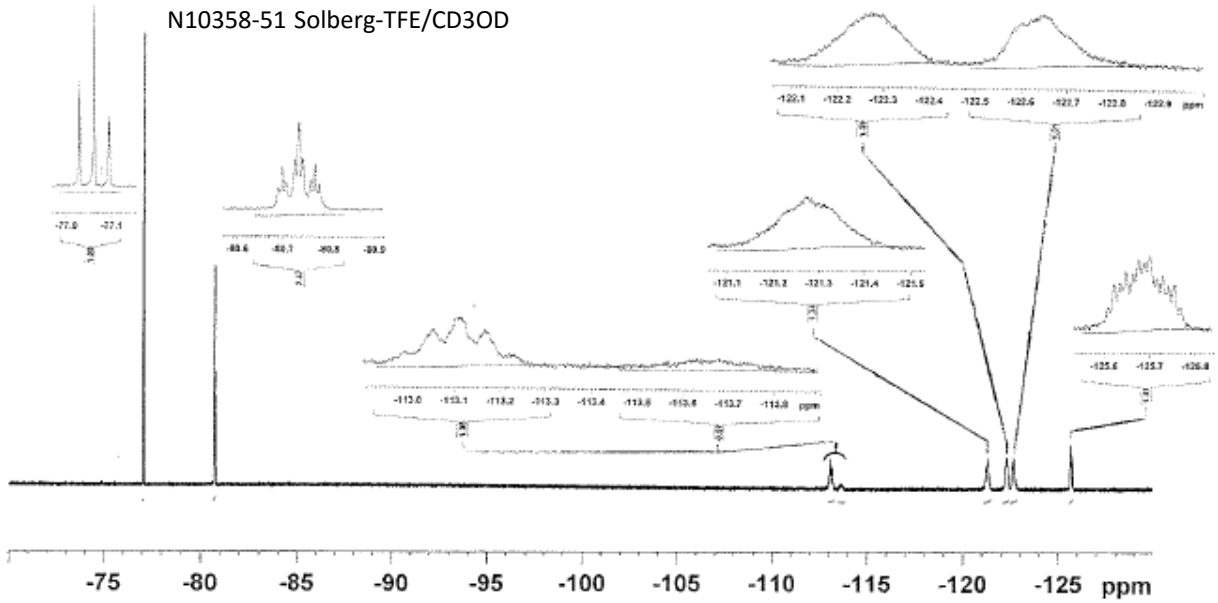

Figure 6. ^{19}F NMR spectrum of Solberg+TFE/CD_3OD (0.0854mg+0.000187mg/mg sol'n).

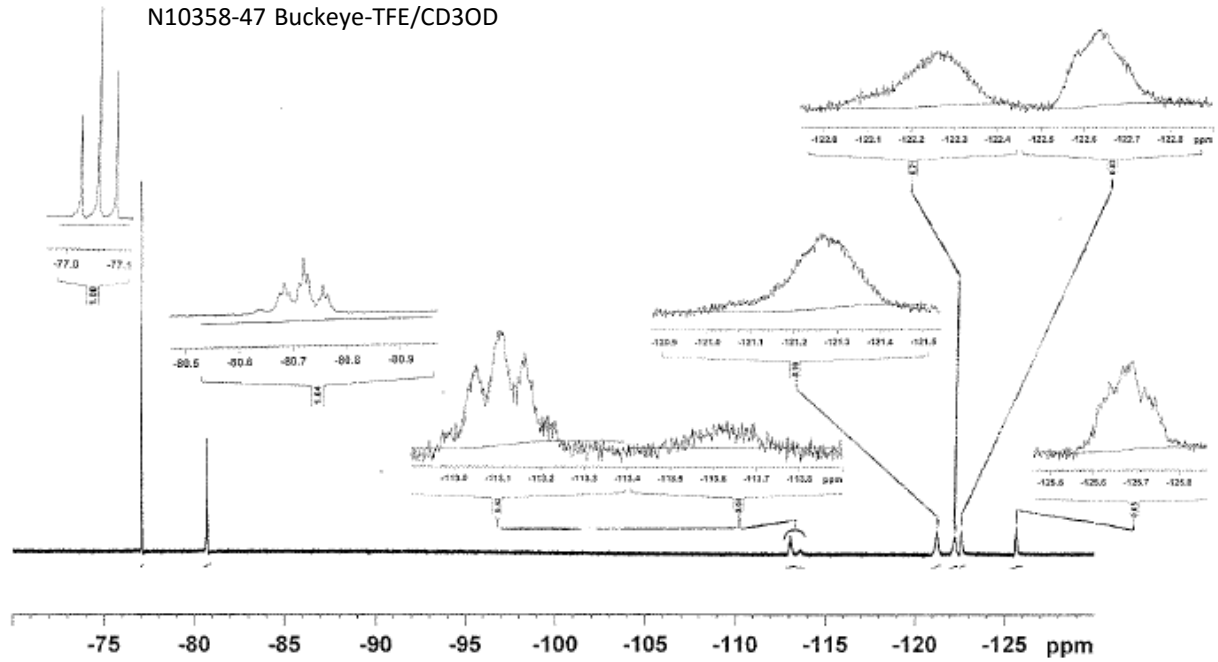

Figure 7. ^{19}F NMR spectrum of Buckeye+TFE/CD_3OD (0.0852mg+0.000219mg/mg sol'n).

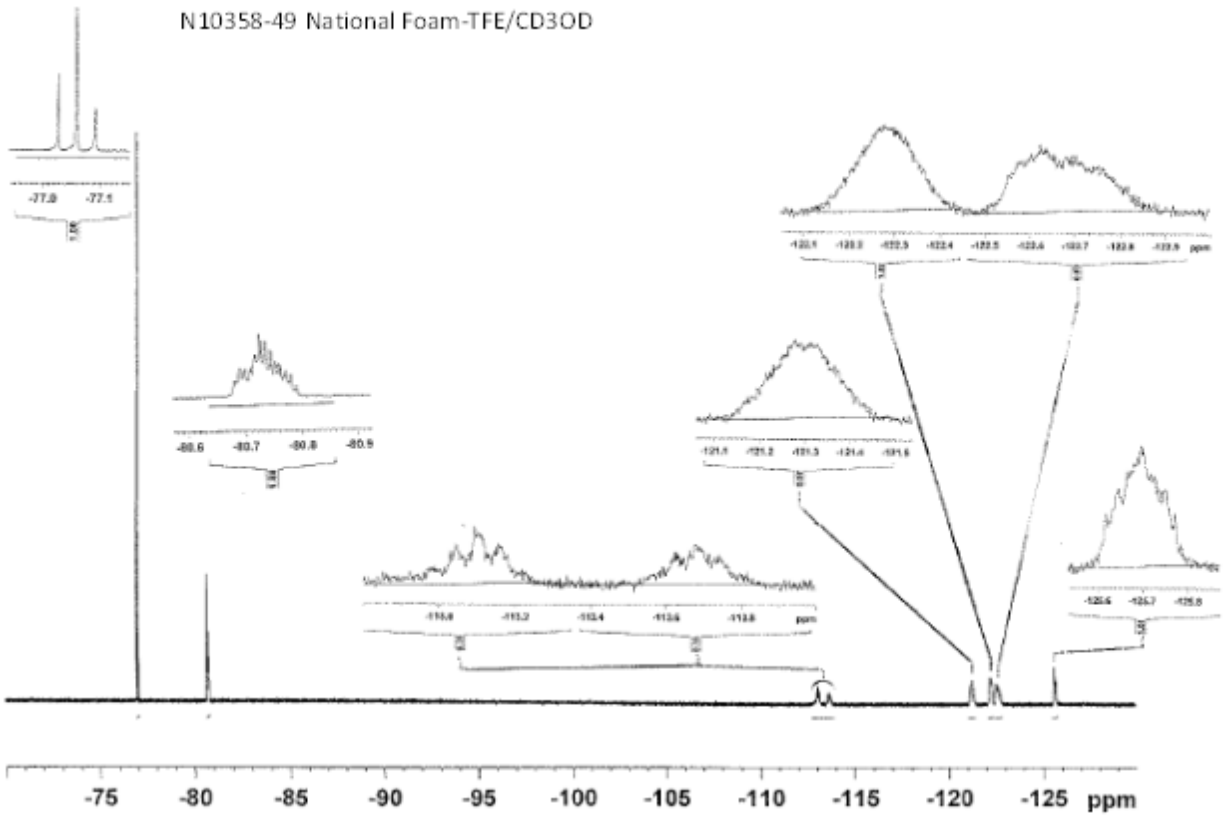

Figure 8. ^{19}F NMR spectrum of National Foam+TFE/CD_3OD (0.0849mg+0.000205mg/mg sol'n).

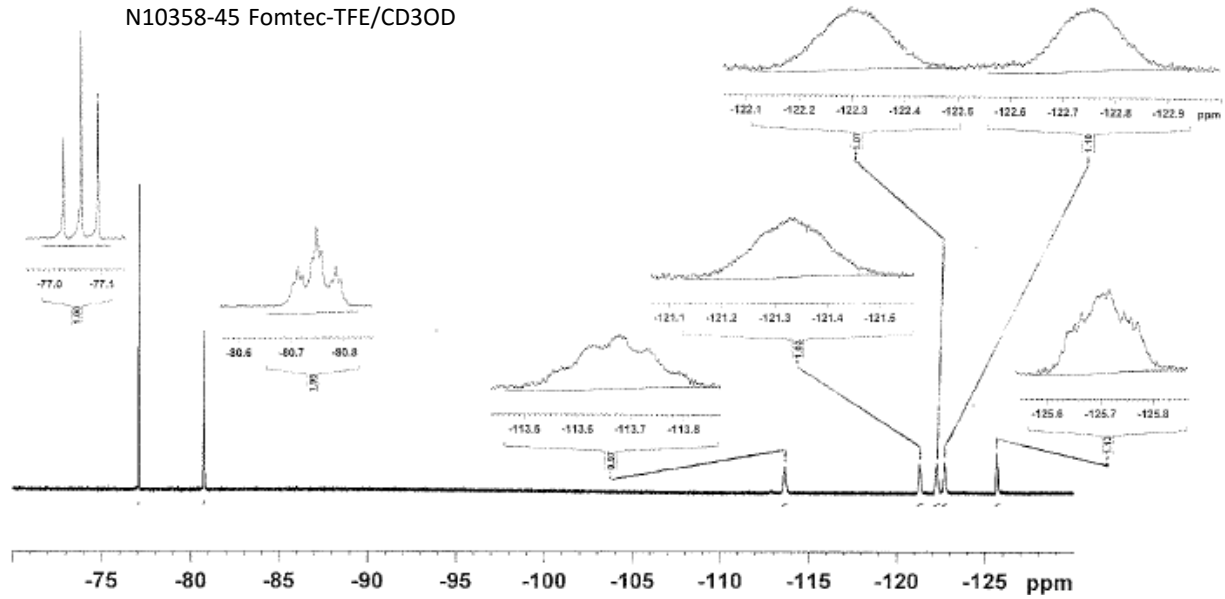

Figure 9. ^{19}F NMR spectrum of Fomtec+TFE/CD_3OD (0.0874mg+0.000223mg/mg sol'n).

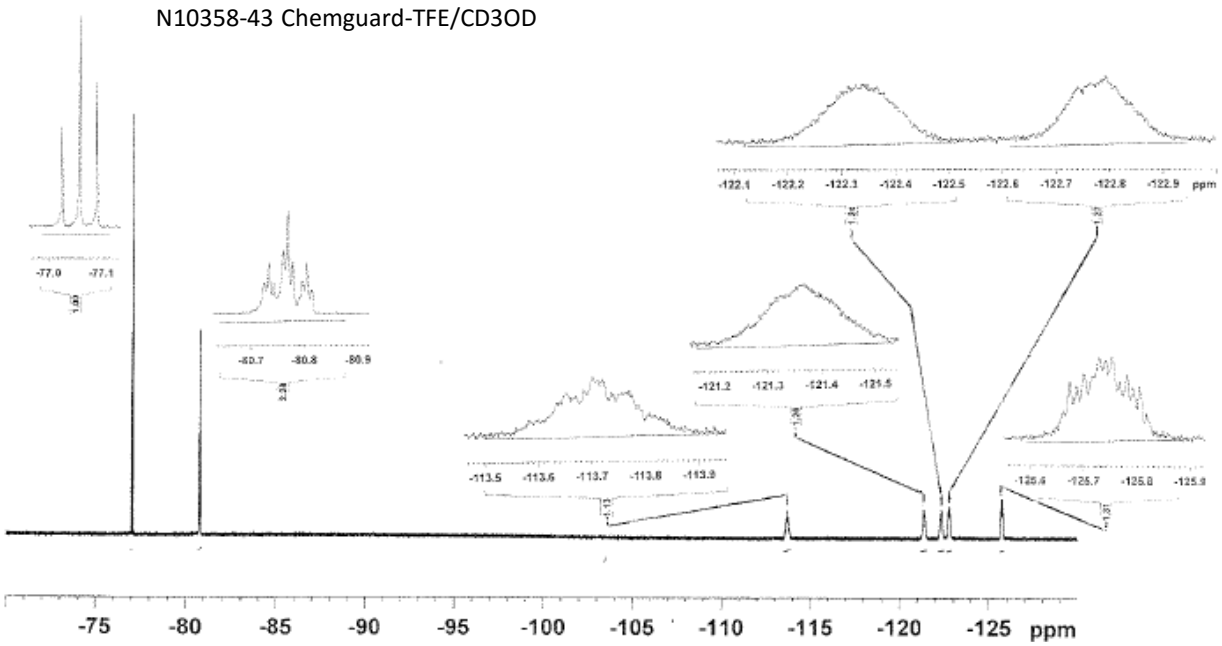

Figure 10. ^{19}F NMR spectrum of Chemguard+TFE/CD_3OD (0.0985mg+0.000242mg/mg sol'n).

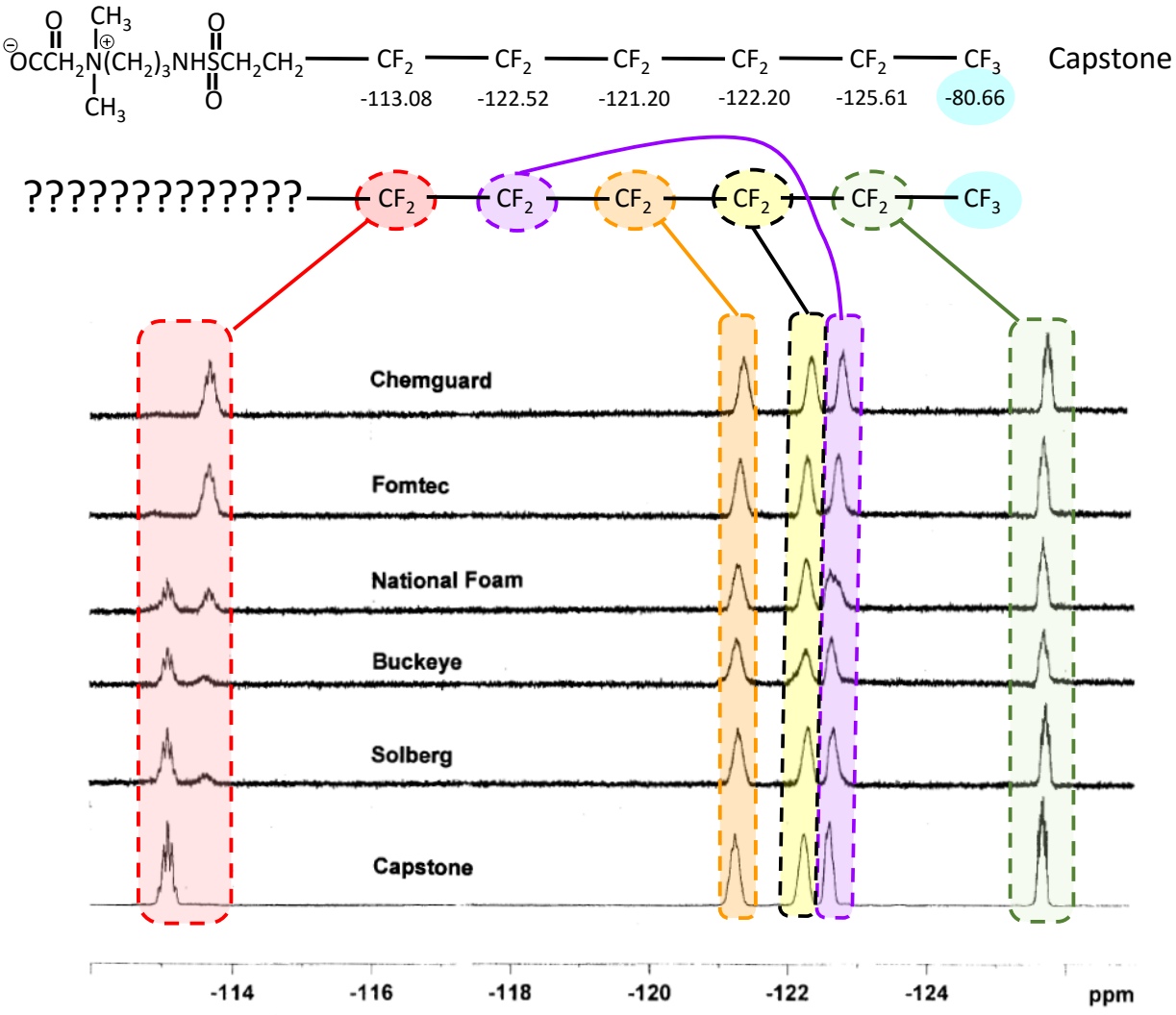

Figure 11. Comparative ^{19}F NMR spectra of expanded -CF_2- region for AFFF concentrate formulations. The Capstone surfactant in the Reference AFFF concentrate is depicted in the bottom scan and spectra of the five commercial AFFF concentrates are depicted above. The chemical structure of the Capstone surfactant is entered at the top, and chemical shifts assigned to structural elements in its fluorocarbon tail are listed under the structure. The fluorocarbon surfactants in the commercial AFFF concentrates have an unknown head structure, but the resonance assignments for the tail structure can be made as indicated. The highlighted areas depict spectral variations caused by differences in unknown head group.

Fluorine Content Measurement

The fluorine content of the commercial AFFF concentrates is measured by making a 50 mg standard addition of TFE to 150 mg of the AFFF concentrate, adjusting the relative quantities of the TFE and AFFF concentrate surfactant by analytical dilutions of this stock solution with AFFF concentrate until the ^{19}F NMR resonances for TFE and the AFFF surfactant are of comparable intensity, and then integrating the relative areas of the TFE resonance and sum of the AFFF surfactant resonances. The weight percent of fluorine in the AFFF concentrate is calculated from a proportionality between integrated area of fluorine resonance and concentration of fluorine compound and quantity of fluorine within the compound. Numerical data and calculation method are presented in the Experimental Detail Section. As measured by this ^{19}F NMR method, the numerical results of fluorine content in the AFFF concentrates and model compounds are presented in Table 8 below. They are compared with results obtained by an analytical services company using traditional fluorine analysis for the AFFF concentrates and by calculation from known composition of the Ref AFFF and model compounds. The agreement of these results from different sources of measurement or with known references is validation for the ^{19}F NMR method.

Table 8. Measured Fluorine Content of AFFF Concentrates and Model Compounds

Sample	Chemguard	Fomtec	Buckeye	National	Solberg	Ref AFFF	Capstone	PFOA
^{19}F NMR	1.2%	1.1%	0.77%	0.89%	1.1%	1.7%	12.3%	66.2%
Other		0.9%*	0.53%*ǂ	0.90%*	1.1%*	1.6%#	12.5%#	68.8%#

* Galbraith Laboratories, Inc.; # Calculated from known composition; ǂ Result considered specious

SUMMARY

A ^{19}F NMR method for quantitative measurement of fluorine content in AFFF 3% concentrate formulations is developed using PFOA and Capstone as model compounds, an analytical reference AFFF concentrate and TFE as a reference standard. Fluorine analysis was demonstrated for a series of five commercial AFFF 3% concentrates. Chemical shift information and hyperfine structure in expanded spectra can provide a selective identifier for subtle changes in the fluorocarbon surfactant components of AFFF concentrates. Procedures and complete data sets are provided for replication and expansion of this analysis method.

ACKNOWLEDGEMENT

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