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Fang, Cheng; Megharaj, Mallavarapu; Naidu, Ravendra "Chemical oxidization of some AFFFs leads to the formation of 6:2FTS and 8:2FTS" Published in Environmental Toxicology and Chemistry Vol. 34, Issue 11, p. 2625-2628 (2015)

Available from: <http://dx.doi.org/10.1002/etc.3115>

This is the peer reviewed version of the following article: Fang, C., Megharaj, M. and Naidu, R. (2015), Chemical oxidization of some AFFFs leads to the formation of 6:2FTS and 8:2FTS. Environ Toxicol Chem, 34: 2625–2628, which has been published in final form at <http://dx.doi.org/10.1002/etc.3115>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

Accessed from: <http://hdl.handle.net/1959.13/1339815>

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Chemical oxidisation of some AFFFs lead to the formation of 6:2FTS and 8:2FTS

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All Supplemental Data may be found in the online version of the present study.

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Abstract: In this study, we tested some aqueous film-forming foam (AFFF) products for the presence or the potential to form 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (6:2FTS) and 1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2FTS). The results demonstrated the appearance of significant level of 6:2FTS and 8:2FTS after the oxidation of those AFFFs. We thus concluded that fluorotelomer skeletons exist but being derived from those formulations of AFFFs.

Keywords: Fluorosurfactant AFFF Fluorotelomer Oxidisation

INTRODUCTION

1 Aqueous Film-Forming Foams (AFFFs) contain fluorosurfactants and have been widely used to ex-
2 tinguish fuel and hydrocarbon fires since 1966 [1-3]. In the US market, 6.8 million liters of AFFFs was
3 produced in 1985 with a total revenue of ~10 million dollars [4]. Unfortunately, their widespread use, as
4 well as the emissions from other sources like fluoropolymer manufacture, ammonium perfluorooctano-
5 ate and fluoropolymer dispersion[5-8], has led to increase in perfluoroalkyl substances' global distribu-
6 tion and accumulation in the environment due to their fluoro-carbon skeletons being inert and resistant
7 to degradation under natural environmental conditions ($\text{CF}_3\text{-CF}_3$ of 99 kcal/mol vs. $\text{CH}_3\text{-CH}_3$ of 89
8 kcal/mol) [9, 10]. An example is that approximately 49,000 firefighting training sites around the world's
9 airports, including 450 civilian and military airports in Australia, have a high accumulation of AFFFs
10 that often escape into the surrounding urban or rural environment, resulting in people and the environ-
11 ment being potentially exposed with adverse effects at sufficient exposure thresholds[11]. In particular,
12 perfluorooctane sulfonate (PFOS), previously formulated in AFFFs, and was reported to enter ecosys-
13 tems and food chains, accumulating in animal and human tissue, including the liver and blood. Concerns
14 on the biological and environmental impacts of PFOS, coupled to its persistent nature, led to its phase
15 out in the early 2000s.

16 Subsequently, some alternative products based on fluorotelomer other than PFOS have been availa-
17 ble in the market. Although fluorine-free foams are obtainable too, fluorotelomer-based AFFFs have
18 been reported to be very efficient in extinguishing flammable liquid fires, their use as fluorosurfactants
19 will continue in the next decade[6, 12]. Sometimes, those fluorotelomers may be shielded by deriving or
20 tailing with groups that might introduce some new functions [3]. In this case, the derived groups, which
21 usually contain non-fluoro-carbon skeletons, should be easily degraded in the natural environment. Con-
22 sequently, the inert fluoro-carbon skeletons will become detectable in the form of degradation products,

23 such as 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (6:2FTS) and 1H, 1H, 2H, 2H-perfluorodecane
24 sulfonic acid (8:2FTS)[13].

25 To confirm the above hypothesis of derivation, we tested some AFFFs - branded as Angus-fire
26 Tridol (AF, S1), Ansulite (A, ICAO-B), and Angus-fire Tridol (T, S3). We intentionally oxidised these
27 AFFFs using chemicals (such as potassium permanganate or hydrogen peroxide). After 30 days of oxi-
28 disation, we measured the concentration of 6:2FTS and 8:2FTS from all 3 AFFF samples and compared
29 the values with those prior to their oxidation.

30

31 MATERIALS AND METHODS

32 All chemicals including potassium permanganate (KMnO_4), hydrogen chloride (HCl , 37%, w/w (kg
33 HCl/kg)), hydrogen peroxide (H_2O_2 , 30%, w/w ($\text{kg H}_2\text{O}_2/\text{kg}$)), methanol and ammonium acetate
34 (NH_4Ac) were purchased from Sigma-Aldrich (Australia). Three AFFFs samples of AF, A, T were col-
35 lected from the stockpile from Australia's Department of Defence, and they were delivered to our labor-
36 atory in common plastic containers (polyethylene terephthalate). Only polypropylene containers/pipette
37 tips were used throughout. Milli-Q water was used ($> 18 \text{ M}\Omega\cdot\text{cm}$) in the present study.

38 All samples were diluted in Milli-Q water in centrifuge tubes (polypropylene) without any pre-treat-
39 ment. 0.1 % KMnO_4 + 0.36 % HCl (w/w) was introduced into the tubes for the oxidation process [10,
40 14, 15]. The tubes were kept at room temperature ($\sim 24^\circ\text{C}$) without being shielded from the laboratory
41 fluorescent lamp for domestic lighting. The tubes were occasionally shaken (once per day) during oxidi-
42 sation. It should be noted that this oxidant exhibits a strong capacity under an artificial condition that
43 may not be expected to occur in the natural environment. Other oxidant such as H_2O_2 featured a similar
44 result but the concentration change was not significant as reported here (Figure S2 in Supplemental

45 Data), suggesting a lower efficiency [10]. Furthermore, H_2O_2 is not stable at room temperature, particu-
46 larly under an UV lamp illumination. We thus focused on the oxidant of 0.1 % KMnO_4 + 0.36 % HCl
47 due to its higher oxidation efficiency.

48 After the chemical oxidation, we heated samples (~0.1 mL) at ~105 °C for 2 hours to cease the oxi-
49 dation and remove the oxidant prior to HPLC analysis. This heating might be capable to accelerating
50 the oxidation process. In the end, the samples were dried into a white powder and dissolved into Milli
51 Q water for analysis, as indicated in the main text.

52 Samples were analysed using an astkCARE™ testing kit (CRC Care, Australia) [16][17] and HPLC-
53 MS (Agilent 1260 + Quadrupole 6130) before and after the oxidation [11, 18]. In general,
54 astkCARE™ testing kit needs 10 mL aqueous sample to be mixed with a 7 mL testing reagent. After
55 shaking for ~1 min and keeping it static for another 1 min, the top layer of organic phase extracted the
56 ion-pair of cationic dye and anionic surfactant. The colour is capable to being related to the anionic sur-
57 factant's concentration level in the aqueous solution (Supplemental Data, Figures S1 and S2). In princi-
58 ple, it works as an improved version of methylene blue active substrates (MBAS) [17]. That is, the ion-
59 pair of dye and anionic surfactant will be extracted into an organic layer. The brightness of the organic
60 phase corresponds with the ion-pair concentration and thus provides a visible test of anionic surfactant
61 concentration with a limit of detection 0.1 ppm.

62 For HPLC-MS analysis, we followed the standard method (EPA/600/R-08/092) [19]. In general, 10
63 μL sample solution was injected into Agilent 1260 high-performance liquid chromatography fitted with
64 an Eclipse plus-C18 column kept at 40°C with a dimensions of 4.6 mm internal diameter, 100 mm
65 length and 3.5 μm particle size. The flow rate was 0.5 mL/min for gradient mobile phase of methanol : 5
66 mM aqueous NH_4Ac for separation. Quadrupole 6130 detector was maintained under negative mode for
67 scanning. Extraction of the molecular ions was conducted at m/z 413 for perfluorooctanoic acid (PFOA),

499 for PFOS, 427 for 6:2FTS and 527 for 8:2FTS, respectively. Quantification was carried out by producing a calibration curve using standard solutions of PFOA, PFOS, 6:2FTS and 8:2FTS (only linear isomers) with correlation coefficients higher than 0.99 and limit of detection ~0.2 ppb (signal : noise > 3). Blank samples of HPLC-grade Milli Q water and methanol were run prior to each set of test to minimize the background contamination that might originate from the Teflon components of HPLC instrument itself. The nebulizer gas (nitrogen) pressure was set at 35 psi, drying gas flow rate was 10 L/min and temperature 350 °C, the capillary voltage was + 3500 V[20].

Free fluoride (F^-) was detected using ion chromatography (IC), which was carried out using DIONEX (ICS-2000, RFIC, Thermo Scientific). The ion exchange column was IonPacTM AS18, 2×250 mm and kept at 35 °C under the pump pressure of 2230 psi. After 25 μ L sample injection, 10 mM KOH was gradually flow at 0.25 mL/min. Conductivity detector was employed with a suppressor of 43 mA.

Note that each time we run at least 6 samples in parallel (3 samples without oxidant as controls whilst other 3 samples with oxidant) for quality assurance and quality control (QA/QC) [21]. Replicate experiments for HPLC-MS were carried out in two laboratories independently. The results were consistent whilst the data with a lower limit of detection (~0.2 ppb vs. ~2ppb) were reported here.

RESULTS AND DISCUSSION

Figure 1 shows the change in colour during the oxidation process. Herewith we selected 0.1 % $KMnO_4$ + 0.36 % HCl (all w/w) as the oxidant to break down non fluoro-carbon chains [14, 15] whilst retain most of the fluoro-carbon chains [10]. Sample AF experienced a fast oxidation because the darken colour was observed upon the addition of oxidant (< 5 min), which differed from the other two samples and was related with the individual active ingredients. From the released data sheet we know

the ingredients include diethylene glycol monobutyl ether, alkyl dimethylanine oxide and fluorosurfactants as well. The quickly darkened colour might originate from the oxidization of those additives given the stable fluoro-carbon chain of fluorosurfactants.

After 10 and 30 days of reaction at room temperature ($\sim 24^{\circ}\text{C}$), all colour changed from purple to dark and light brown, suggesting that oxidisation had occurred for all samples. We also observed the change in colour was slower for sample A compared to the others, suggesting the more difficult oxidisation that may be related to unknown chemicals.

We focus on those samples that have been oxidised for 30 days for the following tests. In parallel, samples without the addition of oxidant were considered as controls and marked as “before oxidisation”.

AstkCARE™ testing kit [16], an improved version of methylene blue active substrates (MBAS) [17], provides a visible test of anionic surfactant concentration. The results suggested Sample T has been darkened most significantly after the oxidization (Supplemental Data Figure S1), suggesting a concentration increase. Figure 2A shows the HPLC-MS spectra for Sample T (other samples are shown in Figure S3, Supplemental Data). Following oxidisation (including an aftermath heating), two obvious differences emerged: firstly enlarged peaks in 8-12 min region; and secondly, peak disappearing at ~ 13.2 min. The peak at ~ 13.2 min disappeared after oxidisation so it was assigned to the initial AFFF ingredient. After oxidisation, this initial ingredient was broken down. Due to the stable carbon-fluoride bonds [10, 22], the telomere-based skeleton could not be broken down as indicated in Figure 2B [3]. Subsequently, the peaks grew significantly in the 8-12 min region, which corresponded with 6:2FTS and 8:2FTS, as marked in the figure. The mass (m/z), presented in this figure confirmed the appearance of 6:2FTS and 8:2FTS after oxidization along with the peak position with the standard solutions. Note the multi-peaks are either due to the isomers or the oxidisation fragments.

Further heating of the sample containing the oxidants led to the 8:2FTS peaks shrinking (at ~11.2 min) or disappearing (at ~ 11.9 min) whilst the 6:2FTS peaks increased at ~9.8 min. Perhaps it is due to the further oxidization of 8:2FTS and initial ingredients (to 6:2FTS), or part of 8:2FTS may have been oxidised and converted into 6:2FTS, these hypotheses warrant further research [23]. Before the oxidation process, tiny peaks were observed for 6:2FTS at ~9.8 min and for 8:2FTS at ~ 10.6 min, and these may be the residue from the initial formulations [3].

Figure 3 shows the quantitative results of 3 samples based on HPLC-MS data where 4 targeted AFFF ingredients, including PFOS, PFOA, 6:2FTS and 8:2FTS, were identified by their molecular ions (m/z). The concentrations of 6:2FTS and 8:2FTS experienced a significant increase after oxidation, thus confirming the above hypothesis that fluorotelomer is produced during the oxidation. 6:2FTS was estimated to be 1010 ppm (mg/L) for sample T after oxidation, which was the highest for all 3 samples. Note this concentration may be smaller than the original formula because we could not guarantee that oxidation took place at the indicated positions in Figure 2B at 100% of yielding rate.

Meanwhile, PFOS was not detected (< 0.2 ppm) before and after the oxidation process for all samples. PFOA was very small concentration in Sample AF and Sample T, whilst a noteworthy increase occurred in sample A to 16.3 ppm following oxidation. Here, PFOA may have originated from an oxidation product, when it was oxidised at the indicated position in Figure 2B (smaller scissors) to break down the carbon chain. Note the samples “before oxidation” means there were no oxidants (0.1 % KMnO_4 + 0.36 % HCl) in the solution. However, as controls, considering they were stored (after dilution) at room temperature without being shielded from the laboratory lamp (staying parallel with the oxidising samples), they may have undergone partial oxidation due to the oxygen in air, which is responsible for the existence of 8:2FTS (AF) and 6:2FTS (T) “before oxidation”.

The existence of fluoro-carbon skeleton is also shown in Figure S4 (Supplemental Data) where free fluoride ion (F^-) was detected after the breakdown [19, 21, 24].

In summary, we found significantly increased concentrations of 6:2FTS and 8:2FTS after oxidation of AFFF formulations although these concentrations were not obvious before oxidation. It is thus recommended to conduct environmental risk assessment for the formulations of AFFF, particularly in the long term when the fluoro-carbon skeleton resists natural degradation whilst the derived groups (most likely non-fluorinated side chains) are subjected to degradation.

SUPPLEMENTAL DATA

Figures S1-S4.

Acknowledgment - The authors kindly acknowledge funding support from Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRCCARE) and the Australian Government Department of Defence.

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Figure legends

Figure 1. Images of samples subjected to oxidation of 0.1 % KMnO_4 + 0.36 % HCl at 10 and 30 days. All the sample concentrations were diluted with Milli-Q water to 0.1% (v/v) for the oxidation. Samples were marked as AF for Angus-fire Tridol (S1), A for Ansolite (ICAO-B), and T for Angus-fire Tridol (S3), respectively.

Figure2. HPLC-MS test results for sample T (a) and the possible molecular structure of fluorosurfactant (b). The concentration was 100 ppm (v/v) diluted from the original formula in (a). The possible positions to break down the carbon chain are indicated in (b).

Figure 3. HPLC-MS test results for sample AF (a), Sample A (b) and Sample T (c). The concentrations have been corrected using the dilution magnification to the values in the original formula without dilution.