

Study on the generation of perfluorooctane sulfonate from the aqueous film-forming foam

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Abstract

Perfluorooctane sulfonate ($C_8HF_{17}SO_3$) and perfluorooctane acid ($C_8HF_{15}O_2$) are artificial chemicals and have been used all over the world, mainly as water repellent agents, fluorochemical surfactants, coating agents, etc. However, perfluorooctane sulfonate and perfluorooctane acid are environmental contaminants because of their stability, bio-accumulativeness, and long-term persistence in the ecological environment. At the present day, they are diffused all over the world. Lately, this diffusion is viewed with suspicion and there is a movement towards their restriction, even if the environmental fate of them is still under investigation. Fluorochemical surfactants are key compounds in the aqueous film-forming foam (AFFF) formulations. AFFFs are used for massive conflagration such as industrial fire and petroleum fire because of their efficient fire control. On the other hand, a lot of AFFFs are used in case of massive conflagration and most of them enter ocean and groundwater. Actually, perfluorooctane sulfonate and perfluorooctane sulfonate related substances were detected from the fire-fighting facility of US forces. Therefore, there is the possibility of generating perfluorooctane sulfonate and perfluorooctane sulfonate related substances from fluorochemical surfactants in the AFFFs. In this study, activated sludge added AFFF were analyzed for perfluorooctane sulfonate and perfluorooctane acid with time. And the perfluorooctane sulfonate was directly detected after 2 days using LC–MS. This shows that AFFF can be decomposed perfluorooctane sulfonate by microorganisms easily. However, perfluorooctane sulfonate would not decompose at all. Additionally, activated sludge added *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide which is one of the fluorochemical surfactants used in the AFFF was analyzed for perfluorooctane sulfonate and perfluorooctane acid with time and the perfluorooctane sulfonate was detected too.

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1. Introduction

Fire disaster produces a lot of harmful gases such as nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), and some hydrocarbons, and can cause severe environmental pollution such as acid rain, greenhouse effect, and so on. The petroleum fire also may produce them massively and endanger the lives and properties. Therefore the fire fighting is required to bring a fire under control effectively from the view point of preventing environmental destruction by toxic chemical compounds and protecting lives and properties.

However, the fire fighting has potential of destroying environment. For example, the halon fire extinguishants are high

fire control performance, low in cost, and superior in versatility and has low toxicity. But, they were banned by international agreements starting 1994, including the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer because halon is one of the ozone depleting substance same as CFCs. The fire-fighting forms are used for industrial fire and petroleum fire. Surfactants are major component of fire-fighting forms. But some surfactants, such as branched alkyl benzene sulfonate (ABS) are not resolved easily in the environmental water. Nowadays, the aqueous film-forming foams (AFFFs) including fluorochemical surfactants are used widely [1,2]. Fluorochemical surfactants are key compounds in the AFFF formulations. AFFFs are used for massive conflagration such as industrial fire and petroleum fire because of their efficient fire control. On the other hand, a lot of AFFFs are used in case of massive conflagration and most of them enter ocean and groundwater.

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Mainly, fluorochemical surfactants are made from perfluorooctane sulfonate and/or perfluorooctane acid. Perfluorooctane sulfonate and perfluorooctane acid are very important chemicals because of their versatility. However, perfluorooctane sulfonate and perfluorooctane acid are environmental contaminants because of their stability, bio-accumulativeness, and long-term persistence in the ecological environment [3]. They have been shown to bioconcentrate in fish, and appear to be toxicity to aquatic organisms, and especially have high toxicity to honey bees [4]. And they are referred to as carcinogens [5]. At the present day, they are diffused all over the world. Lately, this diffusion is viewed with suspicion and there is a movement towards their restriction. 3M Company, a major manufacturer of perfluorooctane sulfonate and related compounds, announced the phase out of producing them because they may generate perfluorooctane sulfonate in the environment [6].

AFFFs including fluorochemical surfactants have proven to be effective at extinguishing liquid-fuel fires and are widely and routinely used by civilian and US military fire-fighters. Historically, effluents from AFFF fire-fighting activities were neither impounded nor pre-treated prior to discharge to the environment. Therefore, perfluorooctane sulfonate may be generated from AFFFs. Actually, perfluorooctane sulfonate and perfluorooctane sulfonate related substances were detected from the fire-fighting facility of US forces [7].

In this study, activated sludge added AFFF were analyzed for perfluorooctane sulfonate and perfluorooctane acid with time using LC–MS. And activated sludge added *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide which is one of the fluorochemical surfactants used in the AFFF was analyzed too.

2. Experimental

2.1. Materials

AFFF and fluorochemical surfactant were added to activated sludge. AFFF included: fluorochemical surfactant (about 10–15 wt.%), hydrocarbon surfactant (about 15–20 wt.%), organic solvent (about 25 wt.%), antifreeze agent (about 10 wt.%), and water (about 30 wt.%). However name and chemical formulas were unknown because of business secret. *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide was added to activated sludge as a representative of the fluorochemi-

cal surfactants. AFFF and hydrocarbon surfactant were obtained from Hatsuta Seisakusho (Osaka, Japan). *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide was obtained from JEMCO Inc. (Akita, Japan). Aniline was purchased from Wako pure Chemicals (Tokyo, Japan) and used as a reference material. HPLC-grade methanol and perfluorooctane sulfonate (98% purity) were also purchased from Wako Pure Chemicals (Tokyo, Japan). To prepare mineral medium, buffer solution (pH 7.2), magnesium sulfate solution, calcium chloride solution, and iron (III) chloride solution were purchased from Kanto Chemical (Tokyo, Japan).

2.2. Methods

The preparation of activated sludge from collected sludge, mineral medium, and test solution cultures were followed OECD 301C.

The sludge which was sampled from 10 sites including five sewage treatment plants and five sites from river and the sea for this study was obtained from Ochiai wastewater treatment plant in Tokyo.

To prepare mineral solutions, 10 ml of buffer solution (pH 7.2) was mixed with 1000 ml deionized water and 1 ml of magnesium sulfate solution, calcium chloride solution and iron (III) chloride solution was added. And six test cultures were prepared every test article using mineral solutions and activated sludge.

Test culture 1: 300 ml purified water and 30 mg of test material.

Test cultures 2, 3, and 4: 300 ml mineral medium and 30 mg of test material.

Test culture 5: 300 ml mineral medium and 30 mg of aniline.

Test culture 6: 300 ml mineral medium (blank).

Thirty milligrams per liter of activated sludge was added to test cultures 2, 3, 4 and 5. They were stirred under conditions of darkness at 25 ± 1 °C. Biochemical oxygen demand (BOD) was calculated and perfluorooctane sulfonate and perfluorooctane acid were analyzed with time.

2.3. Perfluorooctane sulfonate and perfluorooctane acid analysis

The activated sludge (10 µl injection volume) were chromatographed by LC–MS at a flow rate of 0.2 ml/min as shown in Table 1 [8,9]. The total runtime was 20 min. The

Table 1
An optimized analytical condition for perfluorooctane sulfonate by LC–MS

HPLC		MS	
Instrument	Agilent 1100	Instrument	Agilent 1100 MSD SL
Column	Zorbax XDB C-18	Ionization	ESI
Mobile phase	Methanol 20% solution	Nebulizer	N ₂ (50 psig)
Flow rate	0.3 mL/min	Drying gas	N ₂ (12.0 L/min, 200 °C)
Oven temperature	40 °C	Polarity	Negative
Injection volume	10.0 µL	Fragmentor	180 V
		Vcap	4000 V

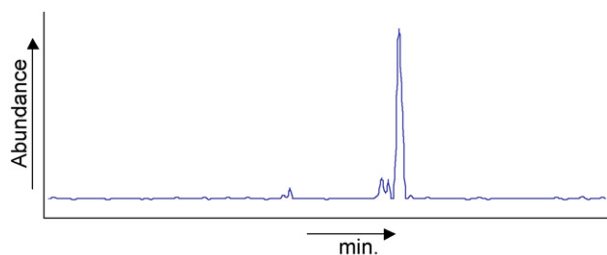


Fig. 1. Typical LC–MS chromatograms of perfluorooctane sulfonate in deionized water.

column temperature was maintained at 40 °C. Mass spectra were taken on an LC–MS system equipped with an orthogonal spray interface, employing electrospray ionization in the negative mode. The nebulizer pressure was 50 psig and the drying N₂ gas flow rate was 10.0 l/min. The selected ion monitoring (SIM) mode was employed for quantification of analytes (Table 1).

In the selected negative-ion mode monitoring of ions, the fragment ions for perfluorooctane sulfonate ion 499 (C₈F₁₇SO₃[−]) was monitored for quantification. The monitoring revealed a major peak with a retention time of 9.05 min for perfluorooctane sulfonate.

2.4. Validation study

Accuracy was evaluated by determining perfluorooctane sulfonate in quality control sample. In order to assay the quality control samples, three calibration curves spanning concentration from 0 mg/l to 100 mg/l were prepared along with the samples. The calibration curves used for quantification, consisting of five points covering 0–100 mg/l in deionized water, were plotted using a linear fit.

The accuracy of the calibration method at each concentration was expressed as a coefficient determination calculated by Microsoft Excel.

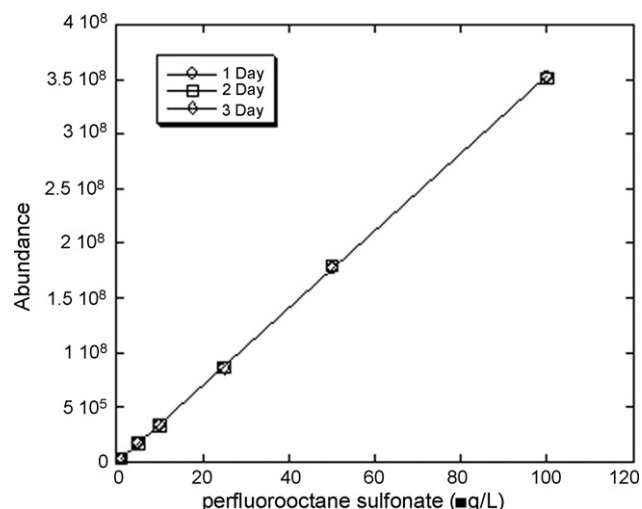


Fig. 2. Calibration curve for deionized water on three different days.

3. Results and discussion

3.1. Chromatographic identification of perfluorooctane sulfonate

Fig. 1 shows typical chromatographic patterns of PFOS in a deionized water sample spiked at 10 mg/l.

The 13.05-min peak had the parent ion, *m/z* 499 (C₈F₁₇SO₃[−]), and three daughter ions [ions 130 (CF₂SO₃[−]), 99 (FSO₃[−]) and 80 (SO₃[−])] [10], and confirming that it corresponded to perfluorooctane sulfonate.

3.2. Calibration curve and accuracy of LC–MS

The calibration curves were obtained in the ranges from 0 mg/l to 100 mg/l showed excellent linearity with a coefficient of determination 0.999. Fig. 2 shows the calibration curves relating peak area to concentration of perfluorooctane sulfonate on five different days.

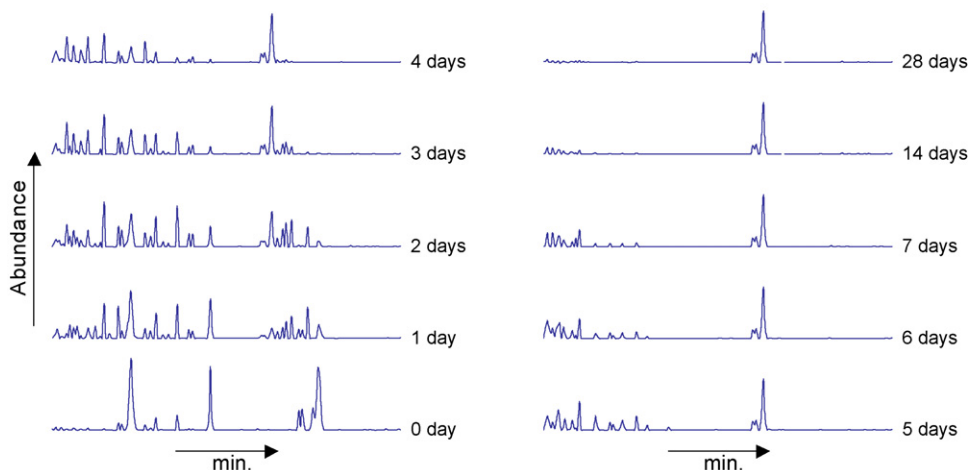


Fig. 3. LC–MS chromatograms of AFFF.

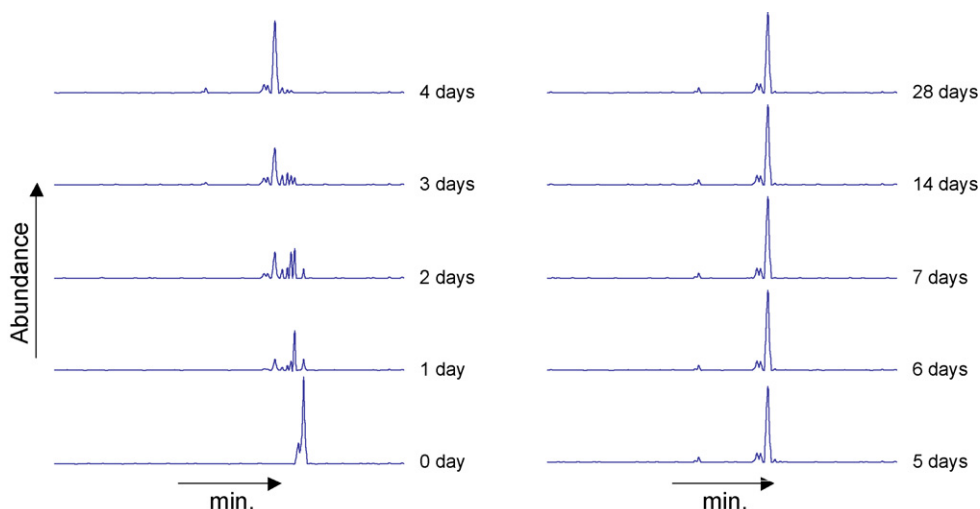


Fig. 4. LC-MS chromatograms of fluorochemical surfactant.

3.3. Practicability of this test method

The practicability of this test method was demonstrated with aniline. If the degradation rate of aniline is over 60%, this test method is practical followed OECD 301C. The degradation rate was calculated using following scheme. BOD was calculated from dissolved oxygen (DO)

$$\text{Degree of degradation (\%)} = \frac{(\text{BOD} - B)}{\text{TOD}} \times 100$$

where BOD is the biochemical oxygen demand of sludge plus test material, B the biochemical oxygen demand of blank, TOD is the theoretical oxygen demand required when the test substance is completely oxidized.

All degradation rate of aniline were about $87 \pm 5\%$ in this study. Therefore, all test method was practical.

3.4. AFFF

Fig. 3 shows chromatographic patterns of AFFF. It indicated that the AFFF test cultures underwent rapid loss of the fluorochemical surfactant over the 4 days of incubation by the biodegradation of microorganisms, as determined by decreasing peak area response. And the peak area response of perfluorooctane sulfonate increased with decrease of fluorochemical surfactant. That is to say, AFFF could be decomposed perfluorooctane sulfonate by microorganisms easily. However, perfluorooctane sulfonate could not be decomposed at all. And perfluorooctane acid was hardly generated in this test. It means this AFFF was not made from perfluorooctane acid but made from perfluorooctane sulfonate.

3.5. Fluorochemical surfactant

Fig. 4 shows chromatographic patterns of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide. The 14.25-min peak had the parent ion, m/z 672 ($\text{C}_{17}\text{NH}_{19}\text{F}_{17}\text{SO}_5^-$), and some daughter ions.

This test cultures underwent rapid loss of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide over the 4 days of incubation by the same token. And the peak area response of perfluorooctane sulfonate also increased with decrease of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide. Transiently, the intermediate compounds were observed at early time points following the initial exposure of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide to the activated sludge. Table 2 shows the MS ions and retention times observed for the intermediate compounds. That is to say, the fluorochemical surfactants like *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide could be decomposed perfluorooctane sulfonate by microorganisms easily and the fluorochemical surfactant in AFFF can be one of the causative agents of perfluorooctane sulfonate emission and diffusion.

3.6. Mixture of fluorochemical surfactant and hydrocarbon surfactant

Generally, the fluorochemical surfactant in AFFF is coexistent other organics like hydrocarbon surfactant. To clarify that other organics effects the generation of perfluorooctane sulfonate from AFFF in the environmental water, the mixture of fluorochemical surfactant and hydrocarbon surfactant was added to the activated sludge.

Fig. 5 shows chromatographic patterns of the mixture of fluorochemical surfactant and hydrocarbon surfactant. The

Table 2
MS ions and retention times of the intermediate compounds

Chemical formula	Retention time (min)	LC/MS anions observed
$\text{C}_{17}\text{NH}_{19}\text{F}_{17}\text{SO}_5^-$	14.25	672
$\text{C}_{15}\text{NH}_{15}\text{F}_{17}\text{SO}_4^-$	13.97	628
$\text{C}_{13}\text{NH}_{11}\text{F}_{17}\text{SO}_3^-$	13.77	584
$\text{C}_{11}\text{NH}_7\text{F}_{17}\text{SO}_2\text{N}^-$	13.41	540
$\text{C}_{11}\text{NH}_7\text{F}_{17}\text{SO}_3\text{N}^-$	13.55	556
$\text{C}_9\text{NH}_4\text{F}_{17}\text{SO}_2\text{N}^-$	13.18	513
$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}^-$	13.05	499

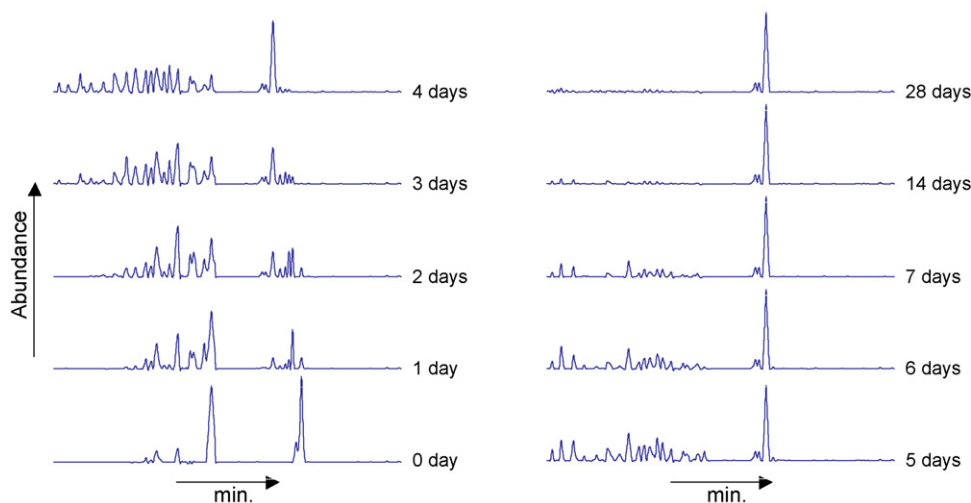
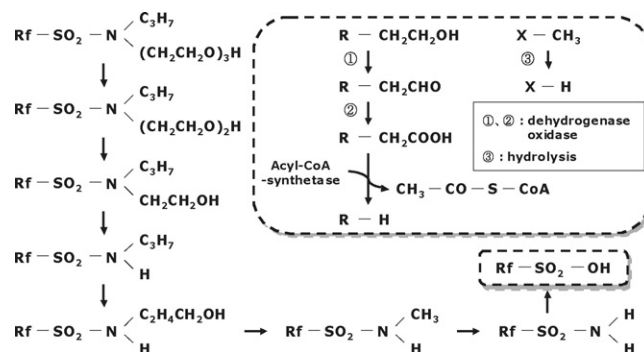


Fig. 5. LC-MS chromatograms of mixture of fluorochemical surfactant and hydrocarbon surfactant.

behavior of perfluorooctane sulfonate generation from fluorochemical did not have big difference between with and without hydrocarbon surfactant. Fig. 6 shows the consumption rate of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide and incidence rate of perfluorooctane sulfonate. This also indicated that coexistent hydrocarbon surfactant did not effect the generation of perfluorooctane sulfonate at all.

3.7. Metabolism of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide

Based on the results of LC-MS, the biogenetic pathway of perfluorooctane sulfonate from *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide was proposed (Scheme 1). Generally, end alcohol group is oxidized to aldehyde group and to carboxyl group by the dehydrogenase and/or the oxidase in the environmental water. Finally, carboxyl group is taken away by acyl-coenzymeA-synthetase, etc. and the carbon number is reduced [11]. End methyl group is also taken away by hydrolysis in the environmental water [12]. Therefore, the end alcohol



Scheme 1. The biogenetic pathway of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide.

and methyl group of *N*-polyoxyethylene-*N*-propyl perfluorooctane sulfonamide was also biodegraded by the same token and finally perfluorooctane sulfonate was generated. Eventually perfluorooctane sulfonate was not biodegraded in 28 days at all.

4. Conclusions

Generation of perfluorooctane sulfonate from AFFF could be confirmed by biodegradation test provide from OECD 301C. Since the activated sludge is used as pseudo-environmental water, it is believed that AFFF can be one of the causative agents of perfluorooctane sulfonate emission and diffusion in the environment. Perfluorooctane acid hardly was generated because AFFF may be originated from perfluorooctane sulfonate in this study. Although the fire fighting is required to bring a fire under control effectively, some fire extinguishants, such as AFFF and the halon fire extinguishants, have possibility of environmental destruction and it may be necessary to assess the environmental risks of them.

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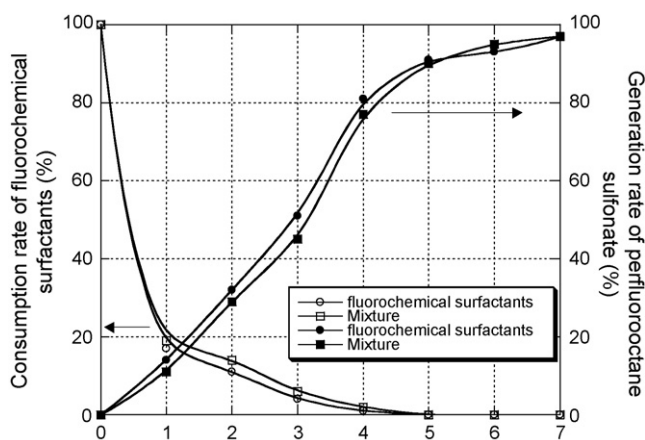


Fig. 6. Consumption rate of fluorochemical surfactant and generation rate of perfluorooctane sulfonate.

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