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Journal of Chromatography A, 1082 (2005) 110–119
JOURNAL OF CHROMATOGRAPHY A
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Stability of fluorinated surfactants in advanced oxidation processes—A follow up of degradation products using flow injection–mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry

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Available online 7 March 2005

Abstract

The advanced oxidation process (AOP) reagents ozone (O_3), O_3/UV, O_3/H_2O_2, and H_2O_2/Fe^{2+} (Fenton's reagent) were applied to the anionic and the non-ionic fluorinated surfactants perfluorooctanesulfonate (PFOS) and *N*-ethyl-*N*-(perfluoroalkyl)-sulfonyl-glycinic acid (HFOSA-glycinic acid) or *N*-ethyl-*N*-perfluoroalkyl sulfonylamido-2-ethanol polyethoxylates (NEtFASE-PEG), their methyl ethers (NEtFASE-PEG methyl ether) and partly fluorinated alkyl-ethoxylates (FAEO) dissolved in ultrapure water. To monitor the efficiencies of destruction samples were taken during the treatment period of 120 min. After sample concentration by C_{18}-solid phase extraction (SPE) and desorption MS, coupled with atmospheric pressure chemical ionisation (APCI) or electrospray interface (ESI) was applied for detection. No elimination of PFOS was observed while HFOSA-glycinic acid and AOP treated non-ionic surfactants were eliminated by oxidation. Degradation products could be detected and identified. So PFOS was observed during HFOSA-glycinic acid oxidation. Polyethylene glycols (PEG) and PEG methyl ethers were generated from non-ionic fluorinated surfactants beside their oxidation products – aldehydes and acids – all identified by tandem (MS–MS) or multiple stage mass spectrometry (MS^n). AOP treatment of FAEO blend resulted in a mixture of partly fluorinated alcohols, separated and identified using GC–MS.

Keywords: Advanced oxidation process (AOP); Degradation; Destruction; Elimination; Surfactants; Fluorinated; Organofluorine compounds

1. Introduction

In the late sixties, after organic fluorine in human serum had been detected using nuclear magnetic resonance (NMR) spectroscopy, Taves postulated that perfluoroalkyl substances were widespread environmental contaminants [1,2]. The low concentration of these compounds, a lack of authentic standards, and the unusual physical and chemical properties of perfluoroalkyl chemicals, however, made it difficult to confirm their identity [3]. Liquid chromatography coupled with mass spectrometry (LC–MS) using electrospray ionisation (ESI) confirmed the contamination of wildlife and human population with perfluorinated acids (PFOA) and other perfluoroalkyl substances, e.g., heptadecafluorooctane sulfonamide (HFOSA) [4]. In addition it became obvious that many of these compounds in the meanwhile had become distributed globally [4,5] and therefore perfluorooctane sulfonate (PFOS) came to rank among the most prominent organohalogen contaminants [3]. In animal experiments toxic effects of certain perfluorinated acids in vitro [6,7] as well as in vivo [8] were observed while tumor promotion also was reported [9,10].

The anionic fluorinated surfactant PFOS besides other partly fluorinated or perfluorinated surfactants is known to resist heat, acids, and bases, as well as reducing and oxidizing agents. Therefore, these fluorinated surfactants are applied in media "where conventional surfactants do not survive"

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doi:10.1016/j.chroma.2005.02.070

[11,12]. Their unique properties made fluorinated surfactants irreplaceable in many applications.

Their greatest disadvantage, however, is that they exhibit persistence also under biochemical attack [13–15]. Fate studies after dosage of these compounds or their potential primary bio-degradation products during wastewater treatment were not so promising because of a lack of radioactive labelled standards that were not yet available though essential for a reliable follow up and balancing studies. Mineralization of these compounds or the degradation of part of the fluorinated alkyl chains could be excluded because no fluoride ions were detected [15]. Volatile fluorinated organics confirming primary degradation could be observed for some of these compounds when waste air sampling during aerobic and after anaerobic treatment according to Martin et al. [16] was performed. The whereabouts of most of the compounds spiked during biodegradation experiments could not be cleared up. Further elimination experiments – removal or degradation – of fluorinated surfactants from wastewater to prevent discharges into the environment were examined applying different physical, chemical and biochemical techniques [17–21]. Reliable methods to confirm results only partly were applied and proved the high stability of fluorinated surfactants against degradation though elimination was observed.

On the one side outstanding properties of these compounds in industrial applications and on the other side their non-ecological-friendly behaviour in the environment induced us to think about alternatives in the elimination of these compounds and thus to allow their licenced partial application where they are hardly replaceable. Though fluorinated surfactants resist conventional oxidative chemical reagents, advanced oxidation processes (AOP) with their high oxidation potential seemed to be a promising alternative to classical physico-chemical and biological processes. AOPs have been defined broadly as those aqueous phase oxidation processes which are based primarily on the intermediacy of the very powerful and non-selective oxidising species, the hydroxyl radicals ($^{\bullet}$OH) [22] in the mechanism(s) resulting in the destruction of the target contaminants, e.g., refractory and hazardous pollutants observed in industrial wastewater, surface waters, and groundwater [23].

Our objectives were either an elimination of these compounds from aqueous media by oxidation or a modification of the molecules as viable support for an improved biological treatability of these pollutants of concern. In parallel intermediates generated during AOP and precursor surfactants should be followed up in gas and water phases using substance specific gas chromatography (GC), flow injection analysis (FIA), LC–MS and MS^n examinations.

Techniques with a more powerful degradation potential should therefore be applied. Different reagents, e.g., ozone (O_3), O_3 in combination with UV radiation (O_3/UV), O_3 combined with hydrogen peroxide (O_3/H_2O_2), and H_2O_2 mixed with ferrous ions (H_2O_2/Fe^{2+}; Fenton's reagent), all known from different AOP treatment but not yet having been applied for the oxidative removal of anionic and non-ionic

Table 1
AOP treatment methods and determinations of fluorinated surfactants—interfaces, ionisation modes and ions recorded for qualitative and quantitative determinations

No.	Type of surfactant	General formula/(abbreviation)	Systematical name	Trade name	AOP methods applied	Interface/ionisation mode/(+/−)	Molecular or adduct ion(s) (*m/z*)	Recorded ion(s) (*m/z*)
1	Anionic	C_8F_{17}—$SO_3^-H^+$/(PFOS)	Perfluorooctanesulfonate (potassium salt)	Fluorad FC-95	O_3 O_3/UV O_3/H_2O_2 Fenton	ESI/(−)	499	499
2	Anionic	C_8F_{17}—SO_2—$N(C_2H_5)$—CH_2—COO^- H^+/(HFOSA-glycinic acid)	*N*-Ethyl-*N*-(heptadecafluoro-octane)-sulfonyl-glycinic acid (potassium salt)	Fluorad FC-129	O_3/UV	ESI/(−)	584	584
3	Non-ionic	C_8F_{17}—SO_2—$N(C_2H_5)$—$(CH_2)_2$—$(OCH_2CH_2)_x$—OH/(NEtFASE-PEG)	*N*-Ethyl-*N*-sulfonylamido- perfluoroalkyl-2-ethanol polyethoxylate	Fluorad FC-170C	O_3/UV	APCI/(+)	677 + Δ44	677–941 (Δ44)
4	Non-ionic	C_8F_{17}—SO_2—$N(C_2H_5)$—$(CH_2)_2$—$(OCH_2CH_2)_x$—OCH_3/(NEtFASE-PEG methyl ether)	*N*-Ethyl-*N*-sulfonylamido- perfluoroalkyl-2-ethanol polyethoxylate methyl ether	Fluorad FC-171	O_3/UV	APCI/(+)	691 + Δ44	691–1131 (Δ44)
5	Non-ionic	C_nF_{2n+1}—$(CH_2)_2$—O—$(CH_2CH_2O)_x$—OH (n = 6, 8, 10)/(FAEO)	2-Perfluoroalkyl-ethanol polyethoxylates (partly fluorinated alkyl-polyethoxylates)	Fluowet OTN	O_3 O_3/UV O_3/H_2O_2 Fenton	APCI/(+)	514 + Δ44	514–954 (Δ44)

fluorinated surfactants of environmental concern as listed in Table 1 were examined.

2. Experimental

2.1. Materials

Ultra-pure water used in AOP treatment was prepared by a Milli-Q system (Millipore, Milford, MA, USA). Ammonium acetate ($CH_3CO(O)NH_4$), and acetic acid (CH_3COOH) for ionisation support were of "analytical reagent grade" (Merck, Darmstadt, Germany). The linear fluorinated alcohols 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecyl-fluoro-1-octanol (purity: 97%), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecyl-fluoro-1-octanol (purity: 98%) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecy-fluoro-1-decanol (purity: 97%) were purchased from Aldrich (Steinheim, Germany) while the mixture of C_6, C_8, C_{10} and C_{12} branched perfluoroalkyl-2-ethanols (Foralkyl EOH-6N LW) was a gift of BYK Chemie (Wesel, Germany). The anionic surfactant blends (cf. Table 1) perfluorooctanesulfonate potassium salt (PFOS; Fluorad FC-95), *N*-ethyl-*N*-[(heptadecafluoro-octane)-sulfonyl]-glycinic acid potassium salt (Fluorad FC-129) and the non-ionic surfactant blends *N*-ethyl-*N*-sulfonylamido-2-perfluoroalkylethanol polyethoxylate (Fluorad FC-170C) *N*-ethyl-*N*-sulfonylamido-2-perfluoroalkylethanol polyethoxylate methyl ether (Fluorad FC-171) were gifts from 3M (Germany) while the non-ionic surfactant blend 2-perfluoroalkylethanol polyglycolether (partly fluorinated alkyl-ethoxylates; Fluowet OTN) was a gift of Hoechst AG (Germany). With the exception of PFOS (Fluorad FC-95) all fluorinated surfactant blends were mixtures of compounds with different alkyl chain length, partly (Fluowet OTN) or perfluorinated (Fluorad FC-129, FC-170C, and FC-171).

Diethyl ether, hexane, and methanol used for desorption of fluorinated surfactants and potential degradation products from the solid-phase materials, as well as acetone and methanol for SPE-conditioning purposes were Nanograde solvents purchased from LGC Promochem (Wesel, Germany). Methanol used as mobile phases were of HPLC grade (LGC Promochem) and was used in gradient elution in combination with Milli-Q-purified water (Millipore). Hydrogen peroxide solution 30% (H_2O_2) applied in AOP examinations was of "medical extra pure" grade (Merck).

Nitrogen for drying of solid-phase cartridges was of 99.999% purity, nitrogen used as sheath gas in APCI ionisation was of 5.0 purity. Oxygen for ozone generation was of "medical grade" while argon used as collision gas was of technical grade. All these gases were Linde (Germany) products.

Commercially available solid-phase extraction (SPE) cartridges filled with C_{18} material from Baker (Deventer, Netherlands) were used for concentration of the surfactants and their AOP degradation products. Prior to use the cartridges were conditioned as prescribed by the manufacturer. Depending on the degree of pollution as calculated from spiking concentrations different amounts of water were used in SPE procedure. The quantity of sample solution used for extraction was chosen that a maximum load of 7 mg DOC per 100 mg of SPE C_{18}-material was not exceeded. The load of the water samples to be concentrated were calculated from spiking quantities because neither by chemical oxygen demand (COD) nor by dissolved organic carbon (DOC) determination methods reliable results could be obtained because of the stability of fluorinated surfactants against chemical or thermal oxidation. After water samples for GC–, FIA– and LC–MS analysis had been forced through the SPE cartridges the columns were rinsed with one volume of purified water before they were dried in a stream of nitrogen. To ensure complete concentration of dissolved carbon on the SPE material random distributed sample extracts which were obtained from solutions after passage of the SPE cartridges and which then again were submitted to MS detection after a preceding SPE procedure.

The adsorbed compounds from SPE were desorbed sequentially by applying three column volumes of organic solvents of different polarities (hexane-diethyl ether (8:2, v:v), diethyl ether, and methanol; [24]). This procedure ensured a widely selective elution according to the polarities of the pollutants. All eluates from the solid-phase extraction were evaporated to dryness in a gentle stream of nitrogen at 30 °C. According to polarity of the SPE-eluents the residues were taken up in 1 ml of hexane or methanol, respectively. Concentrates could be used for injection in GC–, FIA– or LC–MS analysis.

2.2. Standards

For AOP treatment and quantification purposes methanolic stock solutions of each fluorinated surfactant as listed in Table 1 were prepared containing 10 g l^{-1} of the surfactant blend mixtures. Calibration standards were obtained by dilution of these stock solutions first containing 1 g l^{-1} of each surfactant, then working solutions with concentrations of 1, 5, 10, 50 and 100 μg ml^{-1} for FIA–MS and 1, 2, 3, 5, 10 and 25 μg ml^{-1} for LC–MS were prepared by means of serial dilution and stored in lockable polypropylene test tubes.

Each standard solution was analysed by mass spectrometry in flow injection analysis mode or after LC separation on a reversed phase (RP) C_{18} column applying gradient elution.

2.3. Sample preparation

All AOP-treatment steps were performed in a three-necked cylindrical glass reactor with a capacity of 2000 ml. A 15 W medium pressure mercury lamp (Heraeus, Germany), surrounded by a quartz thimble, was used when UV radiation was applied. The flask and the quartz thimble were double walled and water was used in a cooling circuit during reaction to maintain a constant temperature of 25 °C. This reactor was used to apply different AOP reagents as listed in Table 1.

To perform oxidation 4 ml of the stock solutions with concentrations of 10 g l^{-1} of the different fluorinated surfactants were spiked into 2 l of Milli-Q-water contained in the reaction flask resulting in an overall concentration of 20 mg l^{-1} prior to AOP treatment of surfactants as listed in Table 1.

During ozonation experiments, ozone was produced continuously from oxygen in an ozone generator (Sander, Germany). With the fixed gas flow and the voltage adjusted, 2.6 g O_3 h^{-1} were generated. The gas consisting of O_2 and O_3 was fed into the pH-adjusted wastewater (pH 11; NaOH) using a sintered glass plug located at the bottom of the reactor while the aqueous surfactant mixture was thoroughly mixed by stirring.

Application of hydrogen peroxide in combination with ozone (H_2O_2/O_3) was carried out as mentioned before using O_3 with an in-parallel addition of 3 ml of H_2O_2 l^{-1} aqueous sample (pH 11; NaOH).

For AOP treatment using Fenton's reagent the solution containing the fluorinated surfactants was adjusted to pH 3.5 by sulfuric acid before 500 mg of ferrous sulfate ($FeSO_4$) were dissolved in this mixture. The mixture was vigorously stirred for 1 min while in parallel 5 ml of H_2O_2 l^{-1} were added. Prior to a sedimentation period of 30 min the samples were stirred for 120 min.

In the course of the application of the AOP treatment reagents O_3, O_3/UV, H_2O_2/O_3 and Fenton 20 ml samples were taken every 15 min from the reaction flask for monitoring concentration of fluorinated surfactants and their degradation products. Samples from Fenton treatment were filtered prior to SPE whereas the other samples could be extracted by SPE without any pre-treatment. After elution into lockable polypropylene test tubes SPE concentrates could be used for GC, FIA or LC–MS analyses.

2.4. Methods

2.4.1. Quantification procedure

Quantification for degradation monitoring of AOP treated surfactants was performed by means of calibration curves and reconstructed by results obtained in selected ion monitoring (SIM) detection mode (selected ions (cf. Table 1) in APCI(+) and ESI(−)).

Elimination rates were determined by summation of areas of the fluorinated surfactants in the SIM traces of the confirmation ions in FIA–MS or LC–MS mode. Retention times (T_R) observed with calibration standards were used for additional confirmation in LC–MS mode.

In FIA–MS mode the calibration curves for anionic PFOS and *N*-ethyl-*N*-(heptadecafluoro-octane)-sulfonyl-glycinic acid as well as *N*-ethyl-*N*-sulfonylamido-2-perfluoroalkyl-ethanol polyethoxylate, *N*-ethyl-*N*-sulfonylamido-2-perfluoroalkyl-ethanol polyethoxylate methyl ether, and non-ionic fluorinated AEO (cf. Table 1) were linear over a concentration range of 5–100 μg ml^{-1} (FIA–MS: $r^2 \geq 0.98$).

Calibration curves for the same fluorinated surfactants obtained after separation on RP-C_{18} phase prior to LC–MS also were linear over a concentration range of 2–25 μg ml^{-1} (LC–MS: $r^2 \geq 0.995$).

The detection limits (LODs) in LC–MS mode were calculated by a signal-to-noise ratio of 3 (S/N 3:1) taking into account the amount of sample extracted, the volume of the extract analysed and the absolute quantities spiked.

Each concentration of fluorinated surfactant standards in Table 1 applied to establish calibration curves had been checked by a 10- or 3-fold determination in the FIA–MS or LC–MS SIM mode, respectively. Then the entire procedure of solid phase extraction and determination of these compounds was validated by five-fold FIA or three-fold LC–MS determinations.

2.4.2. Gas chromatographic analysis

A GC equipped with an ion-trap mass spectrometer (Finnigan MAT GCQ) and an auto sampler (A 200 S) was used for GC–MS analyses. The mass spectrometer was tuned by perfluorotributylamine (PFTBA) using the auto-tune program. GC separations were performed on a fused silica capillary column (Carbowax 20 M; film thickness 0.25 μm; 50 m × 0.32 mm I.D.) purchased by CS Chromatographie Service (Langerwehe, Germany). The conditions were as follows: carrier gas, helium; linear gas velocity, 40 cm s^{-1}; injector temperature, 250 °C; transfer line temperature, 275 °C; ion source temperature, 200 °C. For analyses 2 μl split injections (1:10) were carried out. GC conditions were programmed as follows: initial oven temperature 50 °C, held for 3 min, then increased at a rate of 10 °C min^{-1} to 200 °C and held at 200 °C for 8 min. Full scan positive electron impact ionisation (EI(+)), positive chemical (PCI) as well as negative chemical ionisation (NCI) with methane gas as reactant gas, were selected for ionisation purposes. GC–MS analysis was performed by scanning at 1 s from 50 to 750 U. Solvent delay, 4 min; EI-electron energy, 70 eV; emission current, 200 μA; electron multiplier voltage, 1100 V.

Data analyses were performed using Finnigan Xcalibur software.

2.4.3. Flow injection analysis

For coupling of FIA, APCI or ESI both from Finnigan were applied for the determination of the fluorinated surfactants. The conditions in FIA–MS and MS–MS on a TSQ 700 bypassing the analytical column were as follows: injection volume: 10 μl; mobile phase methanol–water (30:70) containing 0.05 M ammonium acetate. The overall flow-rate was 0.6 ml min^{-1} (Waters Model 510 pump).

FIA–MS analysis was performed by scanning at 1 s from 100 to 1200 U.

2.4.4. Liquid chromatographic conditions

LC-separations were carried out with a Kromasil 100–5 C 18 column (RP-C_{18}, 5 μm, spherical; 250 mm × 4.6 mm I.D.) from CS Chromatographie Service. Gradient elution by means of methanol in combination with Milli-Q-purified water was applied. The gradient was programmed as follows:

Starting with 30% A/70% B the concentration was increased linearly to 90% A/10% B within 12 min. Up to 30 min the composition was kept constant. The overall flow rate was adjusted to 0.8 ml min^{-1}.

LC separations coupled with MS, MS–MS (TSQ 700; Finnigan MAT), and UV detection were achieved with a Waters (Milford, MA, USA) Model 600 MS system or a SpectraSystem P4000 pump (Thermo Separation Products (TSP), San Jose, CA, USA). A Waters Model 510 pump was used for post-column addition of 0.1 M ammonium acetate solution in the APCI mode. A Waters 996 photodiode array detector system (DAD-UV) in combination with a Millenium 2010 data system (Millipore) was connected in-line with the APCI or ESI interfaces (Finnigan MAT).

Applying APCI ionisation, 0.2 ml min^{-1} of 0.1 M ammonium acetate was added after passing the DAD system, resulting in an overall flow-rate of 1.0 ml min^{-1}. In ESI mode 0.2 ml min^{-1} of eluent was added after passing the column prior to DAD. The flow split ratio then was 1:2 in favour of the MS in the ESI mode compared to waste.

The overall flow-rate was 0.5 ml min^{-1} in the APCI mode and 0.2 ml min^{-1} in the ESI mode.

2.4.5. MS and MS–MS systems and analysis

A TSQ 700 mass spectrometer combined with a DEC 5000/33 data station (Finnigan MAT) was used for research work. The atmospheric pressure chemical ionisation (APCI) interface and the electrospray (ESI) interfaces were obtained from Finnigan MAT.

For coupling the LC-system with the TSQ 700 mass spectrometer, the following conditions for APCI ionisation using ammonium acetate were chosen: vaporizer temperature, 400 °C, capillary temperature, 180 °C. Corona voltage was operated at 5 kV. The potential of capillary, tube lens and API octapole were chosen as 50, 50 or −3 V, respectively. Sheath gas pressure was operated at 2.81×10^5 Pa. Under the above-mentioned conditions, the ion source pressure was 0.3 Torr, and the pressure in the vacuum system of the mass spectrometer was 2×10^{-5} Torr.

The electron multiplier operated at 1200 V and the conversion dynode at 15 kV. In the MS–MS mode, too, the ion source pressure was 0.5 Torr. Under CID conditions the pressure in quadrupole 2 (collision cell) was, unless otherwise specified in the captions to the figures, 1.3 mTorr. The collision energy was adjusted from −10 to −50 eV. The electron multiplier voltage in quadrupole 3 varied between 1200 and 1800 V with a conversion dynode voltage at 15 kV.

FIA and LC analyses on the TSQ 700 were performed, recording APCI or ESI mass spectra scanning from 100 to 1200 U at 1 or 3 s, respectively. FIA bypassing the analytical column with MS or MS–MS (product- and parent ion-mode) detection was performed while we accumulate a maximum of 50 scans after injection.

The mass spectrum averaging the total ion current from the beginning of the signal up to the end in FIA–MS mode was termed “overview spectrum”. APCI and ESI ionisation on the TSQ 700 were first checked in positive and negative MS or MS–MS mode followed by determinations adjusting the conditions with highest sensitivity and efficiency.

Identification of PEG oxidation products by MS^n was performed using the methanolic SPE-C_{18} eluates of AOP treated non-ionic surfactant blends. So degradation products of *N*-ethyl perfluoroalkyl sulfonylamido-2-ethanol polyethoxylate (Fluorad FC-170C; NEtFASE-PEG), its methyl ether (Fluorad FC-171; NEtFASE-PEG methyl ether), and the partly fluorinated alkyl-polyethoxylates (Fluowet OTN) were continuously injected (25 μl min^{-1}) into the ESI source of a MAT 95 XL hybrid sector field-ion trap mass spectrometer (Finnigan MAT) by means of a syringe pump. For MS^n examinations in positive ESI mode ions with calculated ion masses of ammonium adduct ions of PEG, PEG methyl ether, and their oxidation products (aldehydes and acids) were selected and analysed. Fragmentation behaviour of was monitored.

The positively generated full scan data were acquired under the following conditions: ion source temperature, 20 °C; mass range, *m*/*z* 100–800; scan time, 2 s; mass resolution ($M/\Delta M$), 1000; sprayer voltage 3 kV and electron multiplier voltage, 1500 V; capillary temperature, 200 °C, sheath gas pressure, 3.2 bar. In the MS–MS SRM mode, the formation of product ions generated from selected parent ions was monitored. The parameters for the MS–MS SRM studies were as follows: Automatic gain control, off; injection waveform, off; injection time, 500 ms; scan time, 1.76 s; *m*/*z*; variable.

PEG oxidation products were identified by using by their characteristic product ions applying SRM in MS^n mode: (parent transitions (PEG aldehyde) $298^+ \rightarrow 281^+ \rightarrow 263^+$: 239^+, 253^+; (PEG) $300^+ \rightarrow 283^+ \rightarrow 265^+$: 195^+, 239^+; (PEG mono acid) $314^+ \rightarrow 297^+ \rightarrow 279^+$: 239^+, 191^+; (PEG di-acid) $328^+ \rightarrow 311^+ \rightarrow 293^+$: 117^+; 161^+).

3. Results and discussion

Fluorinated surfactants play an important role in many special applications [12]. Their use, e.g., in fire-fighting foams extinguishing high temperature fires has made these compounds irreplaceable because of their outstanding stability against heat. Nevertheless, a method is overdue to remove these pollutants of high concern from aqueous phase as completely as possible after their use in order to protect the environment against these compound. Elimination by adsorption onto sewage sludge seems to be one alternative, but results of biochemical degradation under these conditions were not quite promising [15]. Incineration of sewage sludge polluted with these compounds may destroy the fluorinated surfactants to a certain extent but complete destruction will not be achieved [14]. Moreover, fluorinated surfactants would spread out by flue gas. Deposition on a waste disposal site temporarily would immobilise these compounds but after matrix where they are adsorbed on will be degraded, pollutants will be re-mobilised again thus they will be enabled to reach groundwater and surface waters. The same effects will be ob-

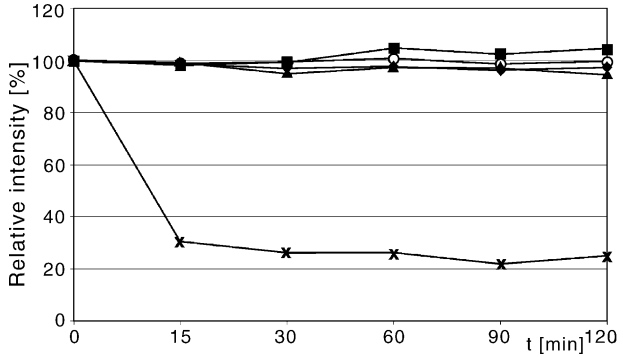

Fig. 1. Graphs of elimination for PFOS and HFOSA-glycinic acid under AOP treatment over a period of 120 min applying different AOP reagents (PFOS treated with: O_3 ▲; O_3/UV ■; O_3/H_2O_2 ♦; Fenton ◯; HFOSA-glycinic acid treated with: O_3/UV ×).

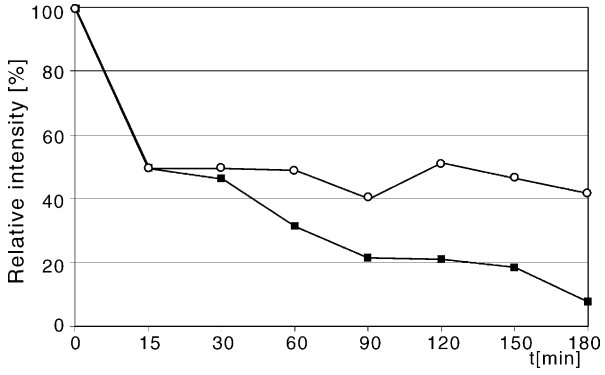

Fig. 2. Graphs of elimination for *N*-ethyl perfluoroalkyl sulfonylamido-2-ethanol polyethoxylate (NEtFASE-PEG) and its methyl ether (NEtFASE-PEG methyl ether) under AOP treatment over a period of 120 min applying the AOP reagent O_3/UV (◯ NEtFASE-PEG and ■ NEtFASE-PEG methyl ether).

servable if contaminated sewage sludge is used as fertiliser in agriculture.

Therefore, AOP techniques with an elevated degradation potential were applied for an oxidative removal of selected fluorinated surfactants as listed in Table 1. To judge elimination results APCI and ESI interfaces were used in combination with FIA–MS and LC–MS in positive or negative mode for the analytical determination and quantification of fluorinated surfactants and their potential degradation products. As AOP treatment was performed in aqueous phase after fluorinated surfactant blends had been spiked into ultra pure water matrix-free samples were obtained. So precursor surfactants and their oxidation products could be concentrated using SPE while comprehensive clean up steps were unnecessary. FIA–MS bypassing the analytical column was used providing quick results. So semi-quantitative information about oxidation was obtained whereas LC–MS as the more time-consuming method later on was used for an exact quantification performed by mass trace analysis of characteristic parent ions of fluorinated surfactants. These examinations proved that the results we obtained by means of FIA–MS quantification were in good accordance with the LC–MS quantification results.

3.1. AOP treatment of anionic fluorinated surfactants monitored by FIA and LC–MS

The protonated anionic surfactant blends PFOS and *N*-ethyl-*N*-(heptadecafluoro-octane)-sulfonyl-glycinic acid (HFOSA-glycinic acid) were submitted to the AOP reagents as listed in Table 1 over a period of 120 min. While O_3,

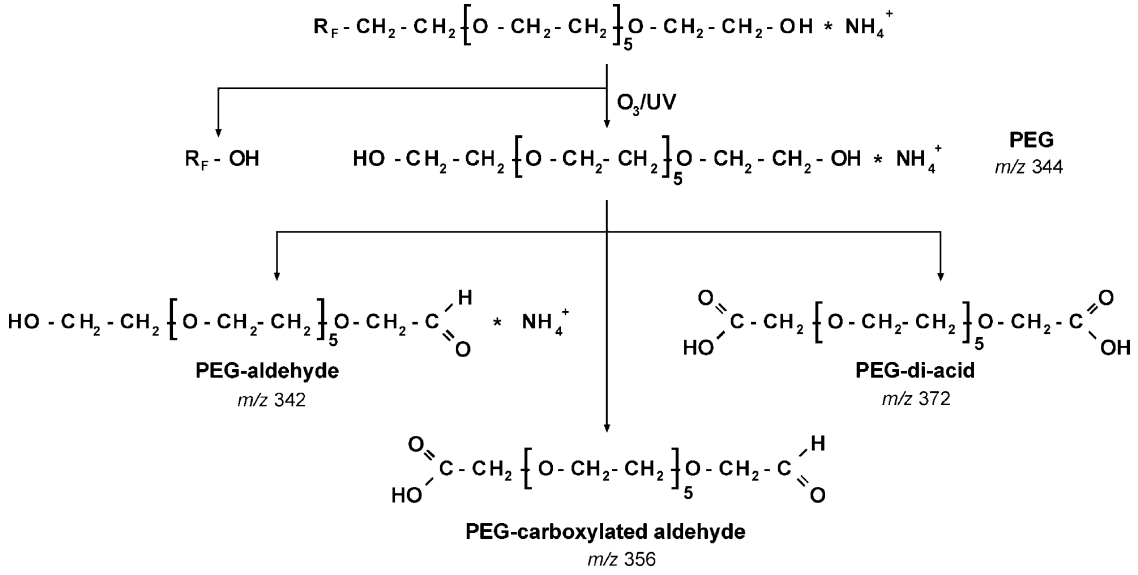

Fig. 3. Scheme of alternative AOP degradation pathways for 2-perfluoroalkyl-ethanol polyglycolether (partly fluorinated alkyl-ethoxylates) detected by means of GC–MS (partly fluorinated alcohols), APCI-FIA–MS overview spectrum, and APCI-LC–MS total and selected ion current traces (PEG and PEG derivatives) as shown in the Fig. 5(b) and in the Fig. 7(e)–(i), respectively.

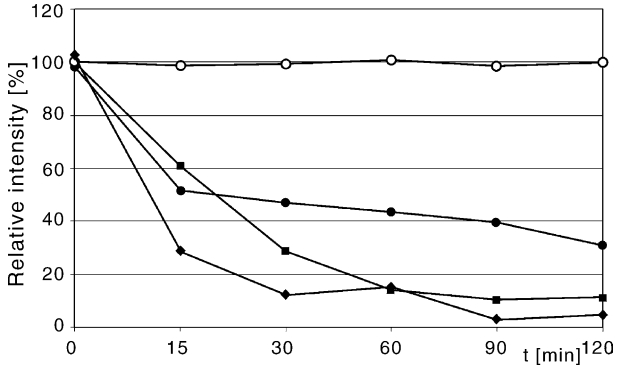

Fig. 4. Graphs of elimination for perfluorinated alkyl-polyethoxylates under AOP treatment over a period of 120 min applying different AOP reagents (perfluorinated alkyl-polyethoxylates treated with: O_3 ●; O_3/UV ■; O_3/H_2O_2 ♦; Fenton ○).

O_3/UV, O_3/H_2O_2, and Fenton's reagent were applied to PFOS as the compound of highest environmental concern HFOSA-glycinic acid only was treated with O_3/UV. As is easily recognisable from results obtained by FIA–MS and by LC–MS both molecules resisted chemical attack in a quite different manner.

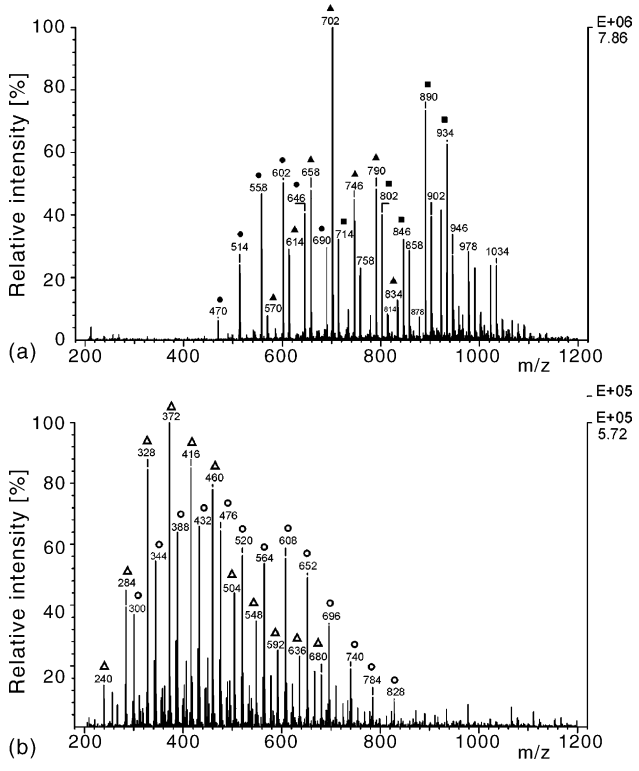

Fig. 5. (a) APCI-MS(+) loop injection spectrum for untreated 2-perfluoroalkyl-ethanol polyglycolether blend (partly fluorinated alkyl-ethoxylates; C_nF_{2n+1}—(CH_2)—O—$[CH_2$—CH_2—$O]_x$—H) bypassing the analytical column (FIA–MS), subsequently termed "overview spectrum". Blend consists of three series of homologues, marked as ● (C_6F_{13}–), ▲ (C_8F_{17}–), and ■ ($C_{10}F_{21}$–). (b) APCI-FIA–MS spectrum for AOP degradation products generated by oxidative bond cleavage (○ PEG) and oxidation of PEG resulting in PEG di-acid (△), C_{18} SPE; eluent, methanol. Positive APCI ionization. For FIA and MS conditions, see Section 2.

The graphs (Fig. 1) of elimination of PFOS and HFOSA-glycinic acid under AOP treatment recorded by ESI-LC–MS(−) render that the PFOS molecule resisted all chemical attacks without (O_3) or with the involvement of the hydroxyl radical •OH (O_3/UV,O_3/H_2O_2, and Fenton's reagent) as one of the most powerful chemical oxidation reagent. So PFOS could be recovered without any reduction in concentration. The application of O_3/UV to HFOSA-glycinic acid, however, partially resulted in an elimination of this surfactant blend during AOP treatment. HFOSA-glycinic acid was reduced to 20% of initial spiking concentration within a treatment period of 120 min and an in-parallel generation of PFOS

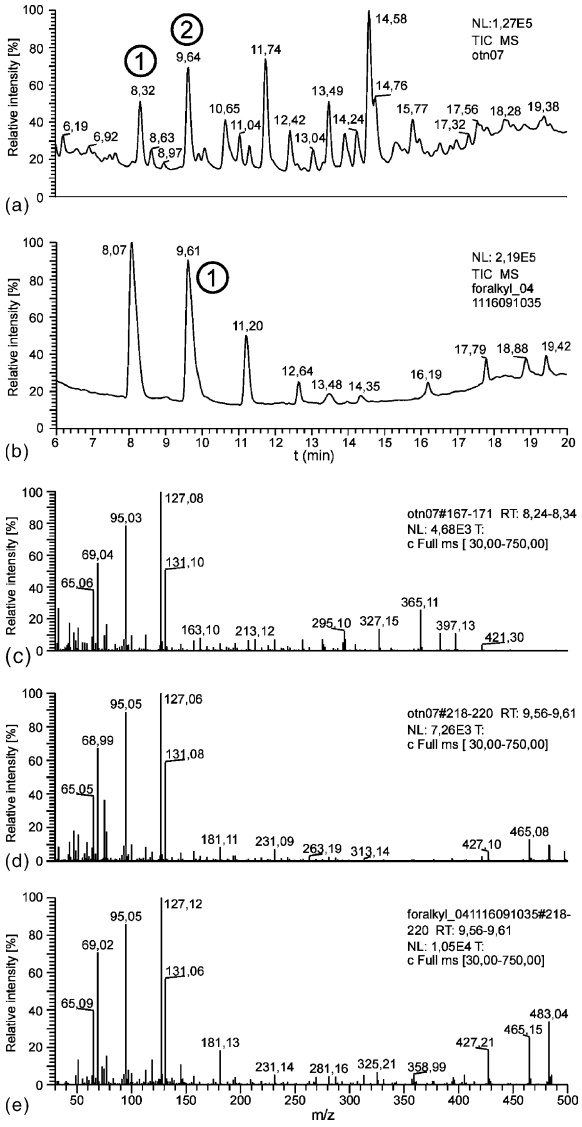

Fig. 6. EI(+)-GC–MS total-ion current tracings (a) for SPE extract of AOP treated 2-perfluoroalkyl-ethanol polyglycolether blend, and (b) for methanolic standard mixture of partly fluorinated alcohols (C_nF_{2n+1}—(CH_2)—OH; $n = 6$, $T_R = 8.07$ s; $n = 7$, $T_R = 9.61$ s; $n = 8$, $T_R = 11.20$). (c–e) Positive El mass spectrum (EI(+)-MS) (c) for peak 1, and El(+)-MS (d) for peak 2 of AOP treated 2-perfluoroalkyl-ethanol polyethoxylate in (a), (e) EI(+)-MS spectrum for peak 1 in standard mixture in (b). Concentration by C_{18} SPE; eluent, methanol. For EI-GC–MS conditions, see Section 2.

from the precursor molecule by an oxidative S–N-bond cleavage could be confirmed by recording the extract in negative LC–MS mode. Exact quantification of generated PFOS was complicated because of stripping effects caused by waste gas—O_3, O_2 and carbon dioxide (CO_2) from methanol oxidation, respectively.

3.2. AOP treatment of non-ionic fluorinated surfactants monitored by FIA and LC–MS

The AOP treatment of the non-ionic surfactant blends *N*-ethyl-*N*-perfluoroalkyl sulfonylamido-2-ethanol polyethoxylate (Fluorad FC-170C; NEtFASE-PEG), its methyl ether (Fluorad FC-171; NEtFASE-PEG methyl ether), and the partly fluorinated alkyl-polyethoxylates (Fluowet OTN) resulted in the generation of oxidation products with an inparallel reduction of precursor surfactants concentrations as shown in their graphs of elimination (Figs. 2 and 4). After AOP degradation of the perfluorinated compounds NEtFASE-PEG and NEtFASE-PEG methyl ether applying O_3/UV only degradation products of the hydrophilic part of the molecules could be observed. So homologues of polyethylene glycols (PEG) or their PEG methyl ethers, their oxidation products, aldehydes and acids of PEG or PEG methyl ethers as shown in the degradation scheme in Fig. 3 were detected and confirmed by MS. All these types of intermediates could be determined applying APCI-FIA–MS or LC–MS in positive mode. For identification and structural confirmation MS^n was applied to oxidative degradation products as later on described for partly fluorinated alkyl-

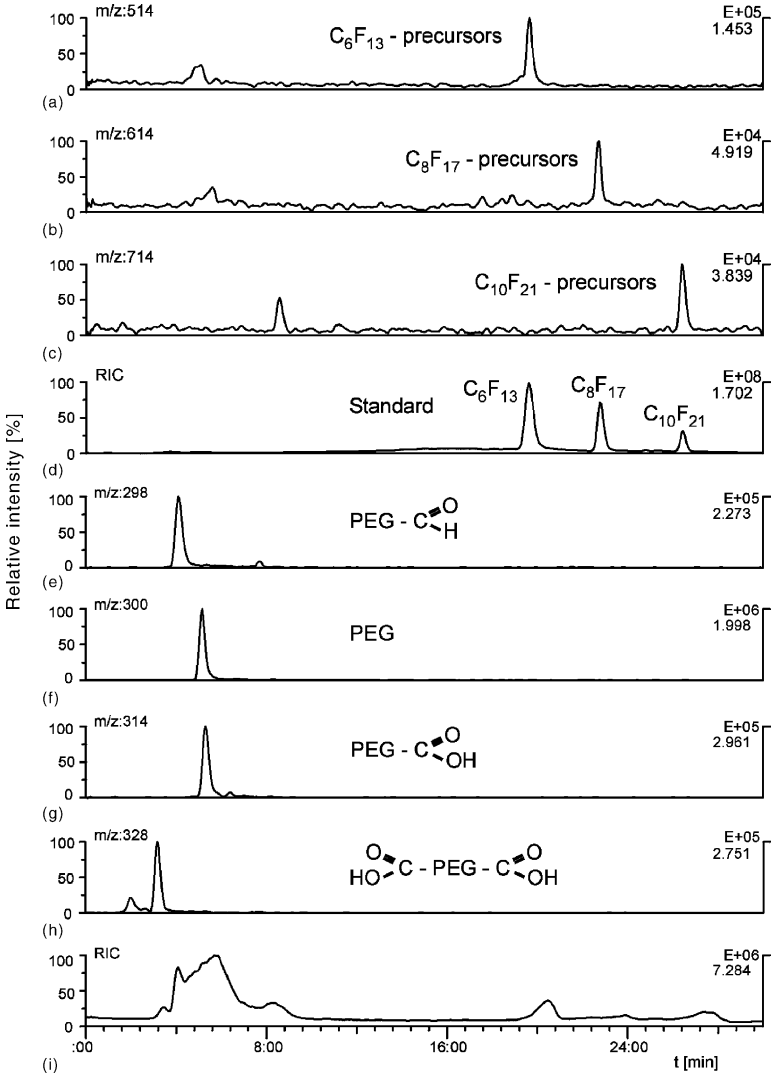

Fig. 7. LC–APCI(+)-MS total-ion current tracing (d) for standard mixture containing the non-ionic fluorinated surfactant blend C_xF_{2x+1}—$(CH_2)_2$—O—$[CH_2$—CH_2—$O]_z$—H ($x = 6$, 8, 10) and (i) for O_3/UV treated standard mixture as in (d). (a–c) LC–APCI(+)-MS selected ion current tracings for ammonium adduct ions of non-ionic fluorinated surfactant blend C_xF_{2x+1}—$(CH_2)_2$—O—$[CH_2$—CH_2—$O]_z$—H as in (d) ((a) $x = 6$, $z = 4$: *m*/*z* 514; (b) $x = 8$, $z = 4$: *m*/*z* 614; (c) $x = 10$, $z = 4$: *m*/*z* 714), (e–h) LC–APCI(+)-MS selected ion current tracings for ammonium adduct ions of PEG oxidation products as in (i) ((e) PEG aldehyde: *m*/*z* 298; (f) PEG: *m*/*z* 300; (g) PEG mono-acid: *m*/*z* 314; (h) PEG di-acid: *m*/*z* 328). Separation by gradient elution performed on RP-C18 column. For LC–MS conditions, see Section 2.

polyethoxylates (Fluowet OTN), too. Alcohols like *N*-ethyl-*N*-perfluoroalkyl sulfonamidoethanol observed by Martin et al. [16] as airborne fluorinated pollutants in ambient air which may result from an oxidation of the perfluorinated lipophilic moieties after cleavage of the hydrophilic polyether chains here could not be detected.

Under physico-chemical treatment conditions using O_3, O_3/UV, and O_3/H_2O_2 the partly fluorinated alkyl-polyethoxylates (Fluowet OTN) was almost eliminated completely. Application of Fenton's reagent, however, failed (cf. Fig. 4). Results of O_3/UV treatment recognisable by comparison of ion patterns of untreated and AOP treated mixtures are shown as FIA–MS overview spectra in Fig. 5. In contrary to biochemical oxidation where the terminal polyether chain links of the partly fluorinated alkyl-polyethoxylates had been converted into carboxylates [14,15] AOP treatment first seemed to induce a bond cleavage between the hydrophilic and the lipophilic parts of the amphiphilic perfluorinated alkyl-polyethoxylate molecules. This first step resulted in a oxidative bond fission between both moieties of the molecules. Under these conditions partly fluorinated alcohols (1-hydroxyethane-2-perfluoroalkanes) and polyethylene glycol homologue molecules (PEG) were generated. Both degradation products, branched or linear alcohols and PEG, could be confirmed by means of GC–MS (Fig. 6) or FIA (Fig. 5(b)) and LC–MS (Fig. 7(f)), respectively. While the lipophilic moieties, the partly fluorinated alcohols generated as primary degradation products under AOP conditions resisted further AOP treatment, a progressive oxidation of the hydrophilic parts, the PEG moieties, took place. So the oxidation products of the hydrophilic moieties were observable with their pattern of $\Delta m/z$ 44 equally spaced ions in FIA–MS overview spectrum (Fig. 5(b)) and by mass trace analysis in LC–MS mode (Fig. 7). Homologues of PEG, PEG aldehyde, PEG mono acid, and PEG di-acid were obtained as confirmed with their mass traces in Fig. 7 and by their characteristic product ions [25] observable by means of SRM in MS^n studies as listed in Section 2.

4. Conclusions

Those results of our examinations applying different AOP treatment techniques to destroy or to improve biological treatability of anionic and non-ionic fluorinated surfactants were disappointing. Despite the application of quite potential oxidation reagents the alternative AOPs provide to destroy fluorinated surfactants, lipophilic linear perfluorinated parts of the molecules remained unaltered. Moreover, with the AOP treatment of the anionic HFOSA-glycinic acid the most stable surfactant molecule, PFOS, was generated as observed and confirmed by means of ESI-LC–MS(−) and -MS–MS(−).

AOP treatment of *N*-ethyl-*N*-sulfonylamido-2-perfluoroalkylethanol polyethoxylates or their methyl ethers led to unknown or hardly detectable fluorinated compounds that had generated during an oxidative bond cleavage between lipophilic fluorinated and hydrophilic non-fluorinated parts of the molecules. In parallel precursor surfactant compounds were diminished as confirmed by APCI-FIA– and -LC–MS(+).

The fate of the partly fluorinated alkyl-polyethoxylates under AOP treatment could be cleared up. Results quite easy to follow up were obtained by GC–MS and LC–MS. So GC–MS proved that the lipophilic part of the surfactant molecules was oxidised resulting in partly fluorinated branched or linear alcohols with an increased volatility when O_3, O_3/UV, and O_3/H_2O_2 was used, while an oxidative destruction by means of Fenton's reagent failed in all cases. Neither a bond cleavage between lipophilic and hydrophilic part nor an oxidation at the terminal polyether chain links was observed.

Quite different was the behaviour of the polyether homologues after these compounds had been generated from these non-ionics and sulfonylamido compounds (NEtFASE and its methyl ether) by bond cleavage. By APCI-, ESI-MS, and -MS^n the successive oxidative degradation of PEG or PEG methyl ether in terminal position of the polyether chains resulting in aldehydes, mono-acids, and di-acids could be confirmed by means of LC–MS and MS^n. During AOP treatment the concentrations of these compounds reached a maximum before they ultimately were mineralised.

Acknowledgement

The authors thank Mr. Scheding for recording MS and MS^n spectra.

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