Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Chromatography A, 1082 (2005) 110–119

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

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

Horst Fr. Schröder*, Roland J.W. Meesters

Institut für Siedlungswasserwirtschaft, RWTH Aachen University, Templergraben 55, D-52056 Aachen, Germany

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”

---

* Corresponding author. Tel.: +49 241153252; fax: +49 2418092500.
E-mail address: schroeder@isa.rwth-aachen.de (H.Fr. Schröder).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
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)