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LETTER

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Liquid Chromatography/Mass Spectrometry Method for Determination of Perfluorooctane Sulfonyl Fluoride upon Derivatization with Benzylamine

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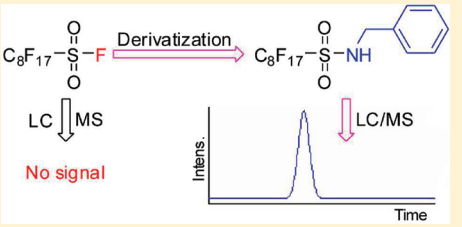
Supporting Information

ABSTRACT: Perfluorooctane sulfonyl fluoride (PFOSF) is a main precursor of environmentally ubiquitous perfluorooctanesulfonate (PFOS), and the quantity released to the environment is substantial. Determination of PFOSF, particularly at low concentrations, presents significant challenges for high-performance liquid chromatography and liquid chromatography/mass spectrometry (LC/MS) analyses due to the lack of chromophore and ionizable functional group, respectively. In this study, a new method was developed by derivatizing PFOSF with benzylamine to allow rapid quantitative analysis by using LC/MS. The method demonstrated good linearity in the range from 2 to 80 ng mL^{-1} with r^2 > 0.994 for the derivatization product while the absolute detection limit was 2.5 pg. Liquid−liquid and liquid−solid extraction procedures were established for analysis of water and soil samples, and recoveries were in the range of 51−128%. In addition, the derivatization was selective for PFOSF, whereas PFOS did not nearly react. The developed simple analytical method with good reproducibility might not only be applied for analysis of PFOSF in the environment but also be applicable for supporting investigations on environmental fate of PFOSF, particularly its environmental and biotransformation to PFOS.



Perfluorinated compounds (PFCs), a class of compounds with excellent surface activity and chemical and thermal stability, are widely used in the production of fluoropolymers, inks, water repellents, and as coatings on paper and textiles during the past 50 years.[1,2] PFCs were found to be persistent, bioaccumulative, toxic even at trace amount, and ubiquitous in the environment.[3,4] Among PFCs, the eight carbon chained perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) were found to be environmentally persistent and globally distributed in soil,[5,6] waters,[7,8] atmosphere,[9,10] and even in the bloodstream of the general population and wildlife,[11−13] typically with PFOS at higher concentrations than PFOA.[14,15] PFOS is extremely persistent and has substantial bioaccumulating and biomagnifying properties, although it does not follow the classic pattern of other persistent organic pollutants (POPs) by partitioning into fatty tissues but instead binds to proteins in the blood and liver. The chemical has a capacity to undergo long-range transport and also fulfills the toxicity criteria of the Stockholm Convention. Therefore, PFOS, perfluorooctane sulfonyl fluoride (PFOSF), and PFOA were added as new POPs in the Stockholm Convention in 2009.[16]

Although PFOS is often found at the highest levels in environmental monitoring compartments, PFOSF was produced in much greater quantities because it is the main precursor of PFOS. The commercial production of PFOSF began over half a century ago, and the total amount produced from 1970 to 2002 was estimated to be ∼100 000 tons. PFOSF is volatile with an estimated global release of 6 800 to 45 250 tons between 1970 and 2002 to the air and water from various sources.[17] It has been hypothesized that, during the life cycles of PFOSF, the chemical could potentially degrade to PFOS in the environment to an undetermined degree.[18,19] However, there have been no published reports on a successful methodology for the quantitative determination of PFOSF and its pathway of transforming to PFOS.

PFOSF cannot be easily protonated or deprotonated due to the lack of ionizable functional group and thus may not be directly amenable to electrospray ionization mass spectrometry (ESI-MS). Although a direct probe mass spectrometric analysis with chemical ionization showed the PFOSF molecular ion peak, the subsequent relevant analysis by gas chromatography mass spectrometry (GC/MS) did not produce any chromatographic peaks under either the positive or negative ion mode.[20] Furthermore, the direct analysis of PFOSF by using high-performance liquid chromatography with visible, UV, or fluorescence detection may be impossible due to the lack of chromophore in the molecule. No successful method for the quantitative determination of PFOSF has been reported, to the best of our knowledge. Because of the unavailable analytical methodology, studies on the environmental fate, degradation, and transport of PFOSF in the

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environment are extremely limited. It is also currently unknown how much PFOSF contributes to the burden of environment, due to lack of a suitable method for the quantitative determination by HPLC, LC/MS, and GC/MS.

Although GC/MS analysis combined with chemical derivatization might provide good quantitative ability, the derivatization procedure applied for LC/MS quantitative analysis is less known. Compared with GC, LC can tolerate much higher sample loading and avoid sample degradation during the analysis. A general derivatization LC/MS methodology has been developed for determination of a class of commonly encountered alkyl esters of sulfonates or sulfates by using trialkylamines as the derivatization agents with good linearity and recoveries.[21] Fatty alcohol, neurosteroids, and vitamin D could be detected with amines as a derivatizing agent to improve the ionization activity in the ESI sourse.[22,23]

PFOSF can be easily transformed into sulfonamides with good yield. *N*-alkylperfluorooctane sulfonamides have been in commercial production for insecticide applications since the 1950s.[24,25] PFOSF-based substances such as perfluorooctanyl sulfonamides including *N*-ethylperfluorooctane sulfonamide (*N*-EtFOSA), *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), *N*-methyl perfluorooctane sulfonamidoethanol (*N*-MeFOSE) can be directly amenable to GC/MS analysis using electron ionization or chemical ionization.[26] Recently, Arsenault used ^{19}F nuclear magnetic resonance (^{19}F NMR) spectroscopy to elucidate the structure of PFOSF isomers by converting the analytes to sulfonamides with good yield.[27] Benzylamine was chosen as the key nucleophile to build the S−N bond.[28] To contribute this knowledge to the trace analysis of PFOSF, the objective of this study was to develop a simple and sensitive LC/MS method upon the derivatization of PFOSF with benzylamine.

EXPERIMENTAL SECTION

Chemicals and Standards. PFOSF (98%) was purchased from Sigma-Aldrich (St. Louis, MO). PFOS (>98%) was purchased from TCI Chemical (Shanghai, China). Triethylamine (99%), anhydrous sodium sulfate, and benzylamine (99%) were purchased from Acros Organics (Geel, Belgium). Ultragrade dichloromethane was purchased from Duksan Pure Chemicals (Gyungkido, Korea). HPLC grade acetonitrile was obtained from Merck Co. (Darmstadt, Germany), and distilled water was further purified by a Milli-Q purification system (Millipore, Bedford, MA).

Sample Preparation for Stability Investigations of PFOSF. PFOSF was diluted with acetonitrile to the concentration of 100 μg mL^{-1} as a stock solution. The solution was diluted with tap water to achieve a final concentration of 20 ng mL^{-1}. The PFOSF samples were analyzed on days 0, 5, and 10 by LC/MS for the purpose of stability examination. In order to investigate the stability of PFOSF in water, PFOS standard working solutions at eight calibration levels in the range of 0.5−50 ng mL^{-1} were prepared by suitable dilutions of the PFOS stock solution with tap water.

Synthesis of Benzylperfluorooctane-1-Sulfonamide (BFOSA). PFOSF (2.50 g, 4.98 mmol) was carefully added dropwise to a vigorously stirred solution of benzylamine (3.43 g, 32.0 mmol) in anhydrous dichloromethane (10 mL) and Et_3N (2.45 g, 24.2 mmol) at 0 °C. The reaction mixture was stirred at the temperature for 1 h before letting it warm up to room temperature within 20 h. Then, 8 mL of aqueous HCl (10%) was added. The aqueous phase was extracted with dichloromethane, and the combined organic layers were dried over Na_2SO_4. Filtration and solvent evaporation left a crude product which was further purified by chromatography on silica gel (hexane to hexane/ethyl acetate = 10/1) to give the produced BFOSA product that was mixed amides including line and branch chain isomers because the reaction agent PFOSF was a technical mixture.

Line amide (L-BFOSA) was separated and prepared on a Varian Prostar semipreparative HPLC (Varian Co.). A reversed-phase Shim-pack PRC-ODS column (20 mm × 250 mm, 10 μm) was used for the separation. A mixture of water and acetonitrile (35:65, v/v) was used as the mobile phase. The collected fractions were evaporated to dryness for subsequent MS and NMR analyses. L-BFOSA was obtained as a white solid with a mp of 115.5−116.5 °C. The calculated elemental compositions for $C_{15}H_8F_{17}NO_2S$ were C, 30.57; H, 1.37; N, 2.38, while the detected values were C, 31.06; H, 1.40; N, 2.31.

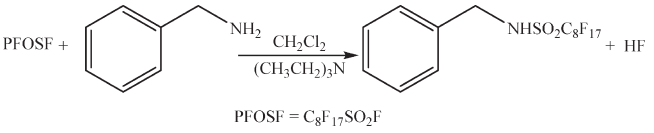
Derivatization of Trace PFOSF and Sample Extraction. An amount of 250 μg of benzylamine in 50 μL of triethylamine was added into 1−100 ng PFOSF in 1 mL of anhydrous dichloromethane solution. The reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated to dryness using a nitrogen evaporator. The residue was dissolved in 1 mL of acetonitrile, vortex mixed, and centrifuged at 12 000 rpm for 20 min prior to the LC/MS analysis.

The sample preparation procedure for environmental analysis included extraction of target compounds from water and soil. Environmental soil collected from a local land field was used for the method development with the property of the air-dried soil: pH 6.4 when adding into distilled water; 1.5% total organic matter; 0.84% total organic carbon; 56.4% sand, 22.2% silt, and 21.4% clay. Briefly, 10 mL of distilled water or 10 g of soil was spiked with PFOSF at a concentration of 100 ng mL^{-1} or 100 ng g^{-1}. The sample was extracted with 10 mL of dichloromethane two times. The combined organic layers were dried over Na_2SO_4. A volume of 1 mL of the combined supernatant was then transferred into another tube for the derivatization described above.

LC/MS Analysis and FTICRMS Analysis of BFOSA. An Agilent 1100 series HPLC system (Agilent Technologies, Palo Alto, CA) coupled to a Bruker Esquire 4000 ion trap mass spectrometer (Bruker−Franzen Analytik GmbH, Bremen, Germany) with an ESI source was used for LC/MS analysis. An Agilent extend C-18 column (2.1 mm × 150 mm, 5 μm) was used for the separation. Mobile phase consisted of water and acetonitrile (25:75, v/v) at a flow rate of 0.2 mL min^{-1} with the detection wavelength of 254 nm. A volume of 5 μL of sample was injected for analysis. The ion source temperature was set at 250 °C, and the ESI needle voltage was set at 4.0 kV. Nitrogen was used as the nebulizing gas at a pressure of 25 psi and the drying gas at a flow rate of 8 L min^{-1}. The effluent in the first 2.5 min was diverted to waste to minimize the contamination of the ion source.

The accurate mass measurement on the molecular and fragment ions of L-BFOSA was performed on an Apex III (7.0 T) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (Bruker, Billerica, MA) by infusing L-BFOSA in methanol into the FTICR MS source at a flow rate of 3 μL min^{-1}. The precursor ion was generated in the negative ion mode by using an ESI source. XMASS software, version 6.1.1, was used for instrument control, data acquisition, and processing. The spray voltage was 4.5 kV. The temperature of the capillary was 250 °C.

Scheme 1. Synthesis of Benzylperfluorooctane-1-sulfonamide



Nitrogen was used as the nebulizing and drying gases, and argon was used as the collision gas.

Nuclear Magnetic Resonance Analysis of BFOSA. ^{1}H NMR and ^{13}C NMR spectra of the produced BFOSA and L-BFOSA were recorded on a Bruker Advance 500 NMR spectrometer instrument with a QNP probe head at ambient temperature using $CDCl_3$ as the solvent. ^{19}F NMR spectra of both L-BFOSA and the produced BFOSA were recorded on a Bruker Avance DPX 400 (375.50 MHz) NMR spectrometer equipped with a Bruker SEF ^{19}F/^{1}H dual probehead. The data were acquired on Silicon Graphics O2 workstations using XWINNMR, version 2.1 (Bruker Analytik, GmbH, Germany).

RESULTS AND DISCUSSION

Stability of PFOSF in Water. It has been hypothesized that PFOSF could potentially degrade to PFOS in the aqueous environment.[18,19] PFOS was proposed as the terminal transformation product for the stability study because it was extremely stable. Thus, there have been significant concerns on the transformation of PFOSF to PFOS under various environmental conditions. In order to investigate the stability of PFOSF in water, determination of PFOS in water samples with a certain time period of PFOSF exposure was performed. Because PFOS has been widely considered as the major degradation product of PFOSF, the stability experiment on PFOSF was performed by determining and comparing the PFOS levels in the control and PFOSF-exposed water samples. A series of calibration standard solutions of PFOS were prepared and analyzed by using LC/MS for the investigation on the possibility of transformation of PFOSF to PFOS. The analysis of PFOS was performed based on the reported LC/MS method.[29,30] PFOS showed good linearity at the range from 0 to 50 ng mL^{-1} with r^2 of 0.998. The method demonstrated high sensitivity with the limit of detection (LOD) of 0.05 ng mL^{-1} for the PFOS analysis. The obtained results from LC/MS analysis of the stability experiments indicated that the PFOS level did not increase after PFOSF existed in tap water for 5 and 10 days at temperature below 30 °C. PFOSF was also found to be stable in organic solvents of dichloromethane and acetonitrile at room temperature. The obtained result of PFOSF stability agreed with the data reported from previous studies demonstrating that PFOSF was only slowly hydrolyzed in water. For example, PFOSF is minimally hydrolyzed in water at 180 °C, even after several days.[31] It was reported that only partial hydrolysis of short-chain sulfonyl fluoride such as difluoromethanesulfonyl fluoride was observed after being in water for 4−5 h at 25 °C, although the short-chain sulfonyl fluoride should theoretically be more readily hydrolyzed than the long-chain sulfonyl fluoride like PFOSF.[32] Degradation of the short-chain sulfonyl fluoride was found after its exposure in water for several days at room temperature.[33] Therefore, PFOSF might stay in the environment including the aqueous environment for a certain time period and thus result in environment pollution.

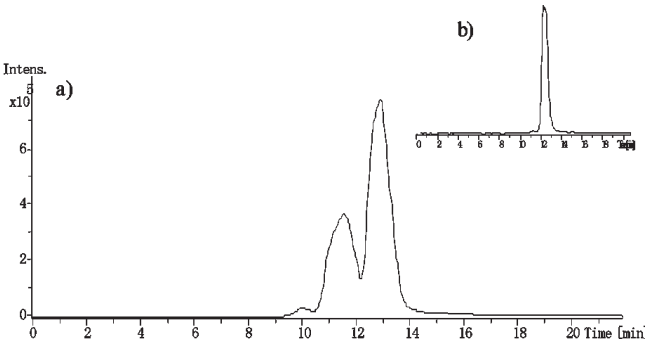


Figure 1. SIM chromatogram of sulfonamide: (a) the produced BFOSA and (b) L-BFOSA.

Benzylperfluorooctane-1-sulfonamide (BFOSA). Although PFOSF is stable in water, the chemical is found to be reactive with benzylamine to produce benzyl perfluorooctane sulfonamide (Scheme 1). Triethylamine was used as a base to the catalytic benzylamine reaction with PFOSF. It should be noted that the commercial standard of PFOSF was actually a mixture of about 30% branch and 70% line PFOSF.[34,35] Therefore, the produced BFOSA was mixed amides including line and branch chain isomers. The pure line amide (L-BFOSA) was separated from the reaction product mixture for its structure identification. Proton signal at δ4.48 in the ^{1}H NMR spectrum (Supporting Information, Figure S1) was obtained along with carbon signal at δ48.9 in ^{13}C NMR spectrum (Supporting Information, Figure S2) showing a methylene group. Five protons at δ7.30−7.50 and one at δ5.28 corresponded to benzyl and amine protons, respectively. No obvious difference was observed between L-BFOSA and the produced BFOSA product in ^{1}H NMR and ^{13}C NMR spectra. Only three signals in the range from −60 to −80 in the ^{19}F NMR spectrum of L-BFOSA (Supporting Information, Figure S3) suggested the presence of just one CF_3 unit. No signal observed at about δ−190 indicated that there was no CF unit in the molecule. While the structure of L-BFOSA was readily identified, many isomer signals could be observed in the ^{19}F NMR spectrum of the produced BFOSA (Supporting Information, Figure S4). BFOSA is very stable for the S−N bond possessing double-bond character, which is increased by the high electron-withdrawing effect of the perfluoride group.[36,37]

Most of sulfonamides are prepared from sulfonic acids by initially converting them into sulfonyl chloride or fluoride and then reacting with primary or secondary amines because sulfonic acid is inactive for the direct amide production.[38] Reaction of PFOS with benzylamine was also investigated by comparing its reaction with that of PFOSF under similar conditions. In the case of PFOS, no amide was produced even after the 48 h reaction. Therefore, the sulfonamide reaction was selective for PFOSF analysis that was not interfered with by PFOS.

LC/MS Analysis of BFOSA. Full-scan ESI-MS analysis in the negative ion mode was performed for the determination of the produced BFOSA product. A total of 65% L-BFOSA was detected in the amide product based on quantification with L-BFOSA. To increase the sensitivity, selected ion monitoring mode (SIM) was used for quantitative analysis of the produced BFOSA by monitoring the $[M - H]^-$ ion at m/z 588. A typical

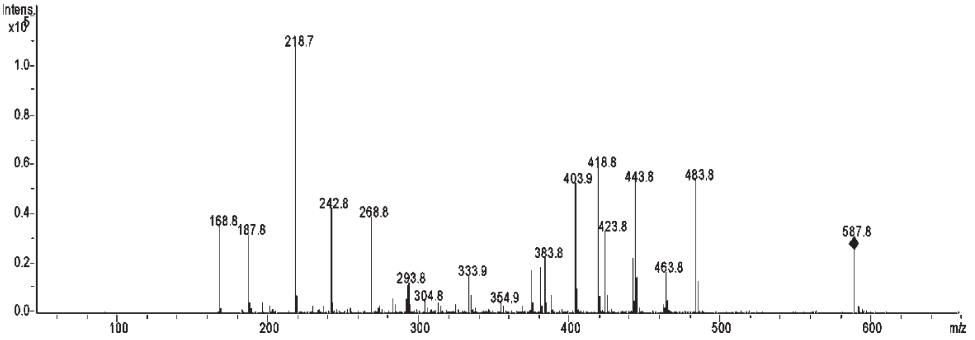


Figure 2. MS/MS spectrum of deprotonated L-BFOSA.

SIM chromatogram of the produced BFOSA and L-BFOSA is shown in Figure 1. Three peaks of the produced BFOSA including L-BFOSA were detected in the corresponding chromatograms, indicating that all PFOSF isomers mixture could be derivatized with benzylamine and detected by LC/MS.

Analysis of the product ion spectrum of L-BFOSA indicated that the precursor ion was fragmented with two fragmentation routes (Figure 2). One route involved cleavage of the S−C bond and yielded the product ion at m/z 419 or cleavage of the C−C bond to yield a series of product ions at m/z 269, 219, 169. The second route involved loss of a molecule of SO_2 first and then lost two molecules of HF, yielding the product ion at m/z 484. The production of ions at m/z 464, 444, 424, 404, and 384 suggested the consequent neutral losses of HF. Therefore seven molecules of HF extruded from the precursor ion could be observed. Because no proton existed in perfluorooctane unit, the loss of HF might be a result of the proton transfer or rearrangement from the benzyl or methylene unit. The accurate masses of both the molecular ion and fragment ions were measured by using FTICR/MS/MS. The most probable elemental compositions of the ions were obtained with a high degree of confidence. The relative errors between experimental masses and theoretical masses were within ±1.08 ppm (Supporting Information, Table S1).

Optimization of PFOSF Trace Derivatization. Application of different amines for the derivatization reaction, including benzylamine, 4-methylaniline, 4-nitroaniline, 4-hydroxyaniline, and 2-hydroxyaniline as derivatization reagents, was investigated and compared. As a result, the anilines were found not effective due to the decreased electronegative character at the nitrogen. Benzylamine was selected as the derivatization regent for its proper polarity and good reaction yield. It was found that the excess concentration of benzylamine was critical for the derivatization process. Particularly for the reaction with a trace level of PFOSF, a higher concentration of benzylamine benefited the reaction and thus provided a better reaction yield.

Although the derivatization method has been used for quantitative determination of some other compounds with the combination of GC/MS analysis, the reaction yield was often not evaluated. This is because many derivatization products were not suitable for being separated and purified. In this study, the produced BFOSA was used to generate the calibration curve for the quantitative analysis of the PFOSF derivatization products. The derivatization of PFOSF at concentrations of 2.0, 5.0, 10.0, and 20.0 ng mL^{-1} were investigated. Good reaction yield was achieved at the range from 72% to 85%. As a control, the derivatization of a blank sample was investigated. No background interference such as inherent contamination from the solvent and instrument was found when the derivatization reaction was stopped.

Validation of the Method and Application. A series of calibration standard solutions of the produced BFOSA were prepared and analyzed to evaluate the dynamic linear response for the analysis with the SIM mode. BFOSA showed good linearity in the range from 2 to 80 ng mL^{-1} (sum (Σ) amide) with $r^2 > 0.994$. The detection limit of the derivatization product as defined at S/N = 3 was 2.5 pg with the injection of 5 μL. It should be pointed out that the method of combining derivatization and LC/MS analysis provided a good detection signal when the PFOSF concentration was 1 ng mL^{-1} in dichloromethane. To assess the quantitative reproducibility, replicate analysis (n = 6) of 10 ng mL^{-1} PFOSF was carried out. The obtained relative standard deviation (RSD) was 10.8%.

In addition to the analysis of PFOSF by using LC/MS after its derivatization, the existing aromatic group in the derivatization product of PFOSF also allowed detection with UV due to the introduction of a chromophore. The HPLC−UV determination at the wavelength of 254 nm showed good linearity with r^2 of 0.990 for the concentration range from 20 to 100 μg mL^{-1} (sum (Σ) amide), with the detection limit of 25 ng when the injection volume was 5 μL.

In order to assess recovery of sample preparation, the distilled water and soil were spiked with a known amount of PFOSF, respectively. The sample was extracted with dichloromethane that was also the reaction solvent. The extract was then analyzed by using the developed derivatization LC/MS method. The obtained recovery ranged from 55.4% to 128% for water and 51% to 109% for soil analysis. The sample extraction required only the one-step liquid−liquid extraction (LLE) or liquid−solid extraction (LSE) by omitting the filtration and removal of solvent by vacuum, the probable losses of the analyte from adsorption on the sample vessels and possible vaporization were minimized as much as possible, particularly considering the volatility of PFOSF. In addition, background interference from the solvent and glassware might be eliminated after the derivatization.

CONCLUSIONS

Derivatization of PFOSF with benzylamine allowed the quantitative analysis of PFOSF by using LC/MS because the produced benzyl perfluorooctane sulfonamide could be ionized by ESI-MS and detected with good sensitivity. The developed derivatization LC/MS method is novel, rapid, simple, and reproducible for the indirect analysis of PFOSF through the determination of the derivatization product. Furthermore, the

derivatization procedure combined with LLE and LSE enabled the analysis of PFOSF in water and soil samples. Because of the specific derivatization of PFOSF with benzylamine, the developed method might overcome the universal interference problem of PFOS that might coexist in the sample and sample preparation system. The obtained results from the stability tests demonstrated that PFOSF was stable in water, and thus it is possible to exist in the global environment. The developed method may be applied for the urgently needed investigations on environmental fate, degradation, and transformation of PFOSF.

■ ASSOCIATED CONTENT

Supporting Information. Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) 3M. U.S. EPA Docket No. 2002-0043-0008, 1999.
(2) Renner, R. *Environ. Sci. Technol.* **2004**, *38*, 264a–265a.
(3) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, P. D.; Helle, E.; Nyman, M.; Giesy, J. G. *Environ. Sci. Technol.* **2001**, *35*, 1593–1598.
(4) Lau, C.; Butenhoff, J. L.; Rogers, J. M. *Toxicol. Appl. Pharmacol.* **2004**, *198*, 231–241.
(5) Russell, M. H.; Berti, W. R.; Szostek, B.; Buck, R. C. *Environ. Sci. Technol.* **2008**, *42*, 800–807.
(6) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. *Environ. Sci. Technol.* **2005**, *39*, 3946–3956.
(7) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Anal. Chem.* **2001**, *73*, 2200–2206.
(8) Richardson, S. D. *Anal. Chem.* **2009**, *81*, 4645–4677.
(9) Shoeib, M.; Harner, T.; Wilford, B. H.; Jones, K. C.; Zhu, J. *Environ. Sci. Technol.* **2005**, *39*, 6599–6606.
(10) Loewen, M.; Wania, F.; Wang, F.; Tomy, G. *Environ. Sci. Technol.* **2008**, *42*, 2374–2379.
(11) Kannan, K.; Corsolini, S.; Falandysz, J.; Oehme, G.; Focardi, S.; Giesy, J. P. *Environ. Sci. Technol.* **2002**, *36*, 3210–3216.
(12) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, *35*, 1339–1342.
(13) Stock, N. L.; Furdui, V. I.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2007**, *41*, 3529–3536.
(14) Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. *Toxicol. Sci.* **2007**, *99*, 366–394.
(15) Loos, R.; Wollgast, J.; Huber, T.; Hanke, G. *Anal. Bioanal. Chem.* **2007**, *387*, 1469–1478.
(16) POPRC. Decision SC-4/10 to SC-4/18: The 9 new POPs under the Stockholm Convention; Stockholm Convention on Persistent Organic Pollutants, May 2009.
(17) Paul, A. G.; Jones, K. C.; Sweetman, A. *Environ. Sci. Technol.* **2009**, *43*, 386–392.
(18) Olsen, G. W.; Burris, J. M.; Mandel, J. H.; Zobel, L. R. *J. Occup. Environ. Med.* **1999**, *41*, 799–806.
(19) 3M. AR226-0681, 2000; pp 1063−1072.
(20) Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. *Anal. Chem.* **2002**, *74*, 584–590.
(21) An, J.; Sun, M.; Bai, L.; Chen, T.; Liu, D. Q.; Kord, A. *J. Pharm. Biomed. Anal.* **2008**, *48*, 1006–1010.
(22) Mitamura, K. *Chromatography* **2000**, *21*, 254–255.
(23) Ji, Y.; Morris, M. E. *Anal. Biochem.* **2003**, *323*, 39–47.
(24) Banks, R. R., Smart, B. E., Tatlow, J. C. *Organofluorine Chemistry. Principles and Commercial Applications*; Plenum Press: New York, 1994.
(25) Key, B. D.; Howell, R. D.; Criddle, C. S. *Environ. Sci. Technol.* **1997**, *31*, 2445–2454.
(26) Richardson, S. D. *Anal. Chem.* **2006**, *78*, 4021–4045.
(27) Arsenault, G.; Chittim, B.; Gu, J.; McAlees, A.; McCrindle, R.; Robertson, V. *Chemosphere* **2008**, *73*, S53–S59.
(28) Toulgoat, F.; Langlois, B. R.; Debielle, M. M.; Sanchez, J. Y. *J. Org. Chem.* **2008**, *73*, 5613–5616.
(29) Richardson, S. D. *Anal. Chem.* **2010**, *82*, 4742–4774.
(30) Benskin, J. P.; Bataineh, M.; Martin, J. W. *Anal. Chem.* **2007**, *79*, 6455–6464.
(31) Gramstad, T.; Haszeldine, R. N. *Dalton Trans.* **1957**, 2640–2645.
(32) Chen, Q. Y.; Wu, S. W. *J. Fluorine Chem.* **1990**, *47*, 509–514.
(33) Sokol, G. A.; Knunyants, I. L. *Russ. Chem. Bull.* **1961**, 1606–1610.
(34) Arsenault, G.; Chittim, B.; McAlees, A.; McCrindle, R.; Riddell, N.; Yeo, B. *Chemosphere* **2008**, *70*, 616–625.
(35) Vyas, S. M.; Kania-Korwel, I.; Lehmler, H. J. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*. **2007**, *42*, 249–255.
(36) Lyapkalo, I. M.; Reissig, H. U.; Schafer, A.; Wagner, A. *Helv. Chim. Acta* **2002**, *85*, 4206–4215.
(37) Jennings, W. B.; Spratt, R. *J. Chem. Soc. D* **1970**, *21*, 1418–1419.
(38) Lehmler, H. J. *Chemosphere* **2005**, *58*, 1471–1496.