

Collection of Airborne Fluorinated Organics and Analysis by Gas Chromatography/Chemical Ionization Mass Spectrometry

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The ubiquitous detection of perfluorooctane sulfonate (PFOS) in humans and animals has produced a need for sensitive and compound-specific analytical methods to determine the environmental distribution of fluorinated organic contaminants. A suite of potential PFOS precursors (sulfonamides) and fluorotelomer alcohols (FTOHs) were separated by gas chromatography and detected by chemical ionization mass spectrometry (GC/CI-MS). Full-scan spectra were collected in both positive and negative chemical ionization (PCI and NCI, respectively) mode to determine retention time windows and fragmentation patterns. In selected ion monitoring (SIM) mode, instrumental detection limits ranged from 0.2 to 20 pg for individual analytes, depending on ionization mode. PCI mode was preferred for routine analysis because of the simple mass spectra produced, typified by the presence of a major molecular ion $[M + H]^+$. High-volume air samplers collected gaseous and particle-bound fluoroorganics on composite media consisting of XAD-2, polyurethane foam (PUF), and quartz-fiber filters. The combined collection efficiency for individual analytes was 87 to 136% in breakthrough experiments. Application of the method to the analysis of ambient air from urban and rural sites confirmed the presence of six novel fluorinated atmospheric contaminants at picogram per meter³ concentrations. Low concentrations of fluoroorganics were consistently detected in blanks ($<4 \text{ pg m}^{-3}$); however, this did not prevent confirmation or quantification of environmental concentrations.

Sensitive and compound-specific analytical methods^{1,2} in combination with extensive biological monitoring studies^{3–6} have recently revealed much about the global distribution of perfluorooctanesulfonate (PFOS). One curiosity to arise from these efforts

was the detection of PFOS in animals collected at remote geographical locations, such as the Arctic, Antarctica, and mid-North Pacific Ocean.^{3–5} These observations were unexpected, because PFOS is sparingly volatile⁷ and moderately water soluble,⁸ making it a poor candidate for long-range atmospheric transport. These facts have previously led to speculation that the global dissemination of PFOS must occur via an airborne neutral derivative that yields the free acid upon degradation.^{9,10} To test this hypothesis it was necessary to develop efficient air sample collection protocols in tandem with sensitive analytical techniques for the detection of neutral fluoroorganic compounds in the atmosphere.

Existing methods for the atmospheric monitoring of organofluorine compounds are largely restricted to low-molecular-weight chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs).^{11–16} An existing method for airborne collection and analysis of higher-molecular-weight fluoroorganics is insufficiently sensitive for environmental monitoring and is nonspecific, using total organofluorine as an indicator of concentration.¹⁷ In the context of this study, high-molecular-weight fluoroorganics were of interest, particularly neutral compounds that had the potential to volatilize and yield PFOS upon

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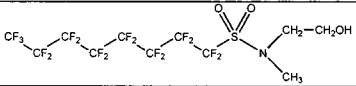
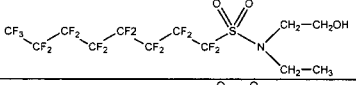
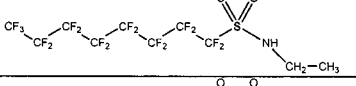
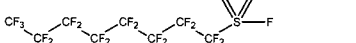
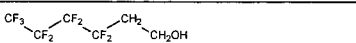
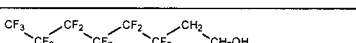
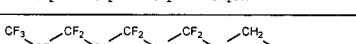
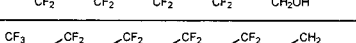
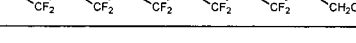
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Table 1. Target Analyte Acronym, Structure, Molecular Weight, Ions Monitored by PCI- and NCI-MS, and Mean Environmental Concentrations (pg m^{-3}) at Two Sampling Locations for n Samples^b

Analyte	Acronym	Structure	Molecular Weight (amu)	Ions Monitored (m/z)		Environmental Concentrations (pg m^{-3})	
				PCI	NCI	Toronto (n=4)	Long Point (n=2)
N-methyl perfluorooctane sulfonamidoethanol	NMeFOSE		557	558, 540	494, 483, 400	101 (86-123)	35 (34,36)
N-ethyl perfluorooctane sulfonamidoethanol	NEtFOSE		571	572, 554, 540	508, 483, 400	205 (51-393)	76 (68,85)
N-ethyl perfluorooctane sulfonamide	NEtFOSA		527	528	526, 483, 400	14 (n=2)	n.a.
perfluorooctane-1-sulfonyl fluoride	PFOSF		502	^a 503, 419, 169	^a 400, 362, 350	a	a
1-hydroxyethane-2-perfluorobutane	4:2 FTOH		264	265, 227	184, 204	n.d.	n.d.
1-hydroxyethane-2-perfluorohexane	6:2 FTOH		364	365, 327, 393	284, 304, 314	87 (30-196)	29 (41,16)
1-hydroxyethane-2-perfluorooctanol	8:2 FTOH		464	465, 427, 493	384, 404, 414	55 (9-123)	32 (40,25)
1-hydroxyethane-2-perfluorodecanol	10:2 FTOH		564	565, 527, 593	484, 504, 514	29 (7-46)	17 (20,15)
pentadecafluoro-1-octanol (internal standard)	PDFO		400	401, 381	360, 340		

^a Ions were obtained by direct probe mass spectrometry. PFOSF was not amenable to the GC conditions used and was not monitored in environmental samples by the developed method. ^b The range of environmental concentrations is shown below the mean for both sites. Abbreviations: n.d., not detected; n.a., not applicable. No attempt was made to detect NEtFOSA at Long Point.

degradation. Many such compounds find use in surface treatment of paper and textiles;^{18,19} as surfactants;¹⁹ as insecticides, such as *N*-ethyl perfluorooctane sulfonamide (NEtFOSA; Sulfluramid);^{20,21} and as intermediates in the synthesis of other fluorinated organics.²²

Synthesis of many higher-molecular-weight fluoroorganics, such as PFOS, proceeds via the intermediate, perfluorooctane-sulfonyl fluoride (PFOSF). Other PFOSF derived products include *N*-methyl perfluorooctane sulfonamidoethanol (NMeFOSE), and *N*-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE), both of which are incorporated as higher-molecular-weight derivatives into surface treatment formulations for paper and textile products to impart oil and water repellency.¹⁸ It is expected that PFOSF, NMeFOSE, NEtFOSE, and NEtFOSA will ultimately degrade to PFOS under environmental or biological conditions,²³ and as a result, they were the focus of the method development presented herein. Although PFOS-based products are voluntarily being phased out by their primary manufacturer because of concerns

about their environmental persistence,²⁴ similar compounds with long perfluorinated tails continue to be produced for comparable applications. Such compounds include fluorotelomer alcohols (FTOHs). FTOHs are primary alcohols, characterized by two nonfluorinated carbons adjacent to the hydroxyl function, and will be referred to herein as 4:2, 6:2, 8:2, and 10:2 FTOH, on the basis of the ratio of perfluorinated to nonfluorinated carbons. The telomerization process used in their manufacture results in only even-numbered carbon chain lengths.²⁵

We report here a quantitative, sensitive, and compound-specific method for the analysis of some fluorinated neutral compounds (Table 1) by gas chromatography/chemical ionization mass spectrometry (GC/CIMS). The applicability of this method to ambient atmospheric monitoring is described through breakthrough experiments using composite sampling media and through environmental sampling at distinct rural and urban locations.

EXPERIMENTAL SECTION

Chemicals, Standards, and Sampling Media. HPLC grade methanol (99.93%), HPLC grade ethyl acetate (99.8%), pentadecafluoro-1-octanol (PDFO, 98%), and PFOSF standard (98%), were purchased from Aldrich Chemical Co. (Milwaukee, WI). NEtFOSA standard (95%) was purchased from Lancaster Synthesis (Pelham,

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NH). NMeFOSE (96.32%) and NEtFOSE (97%) were donated by 3M Co (St. Paul, MN). FTOHs 4:2, 6:2, 8:2, and 10:2 (all 97%) were purchased from Oakwood Products, Inc. (West Columbia, SC). Amberlite XAD 2 resin was obtained from Supelco (Bellefonte, PA). Polyurethane foam (PUF) slices (2.5 cm) and quartz-fiber filters (10.16 cm, Whatman QMA) were purchased from Tisch Environmental Inc. (Cleveland, OH).

Safety Considerations. All handling of chemical standards and stock solutions should be performed in a fume hood to minimize inhalation exposure, because of the inherent volatility of these substances. Hands should also be protected with gloves to protect against dermal absorption. NEtFOSA is a registered insecticide, and its structural similarities to NEtFOSE and NMeFOSE warrants caution in the handling of all of them.

Sampling Media Preparation and Extraction. All handling of sampling media was performed under clean-room conditions (positive pressure, carbon and HEPA filtered air) at the National Water Research Institute (Burlington, ON) to minimize contamination. XAD resin was prepared by initial rinsing with purified water, 4-day Soxhlet extraction with methanol, rinsing twice with 1 N NaOH, and finally, by flushing with subsequent additions of methanol, dichloromethane, and ethyl acetate. The wet XAD was then dried under a flow of high-purity nitrogen. PUF slices were soaked consecutively in methanol and ethyl acetate, followed by drying under high-purity nitrogen. Quartz-fiber filters were rinsed several times with ethyl acetate in a Buchner funnel, dried under high-purity nitrogen, and wrapped in aluminum foil for transport to the sampling site.

For sample collection, 25 g of XAD was sandwiched between two sections of PUF inside a clean glass holder with a support screen. The glass holder was then contained inside a sealed, aluminum high-volume air sampler header (Tisch Environmental Inc., Cleveland, OH), that was modified by removing all fluorinated polymer materials, such as the sealing rings. The aluminum header also contained a quartz-fiber filter for collection of particles, placed upstream of the PUF and XAD. The entire unit was sealed inside a polyethylene bag and sent to the field for use in sampling or breakthrough experiments.

For extraction of samples, XAD was poured into glass columns containing 50 mL of methanol and allowed to soak for 1 h. The columns were then flushed with subsequent 50-mL additions of ethyl acetate (250 mL total), allowing 10 min for soaking between each aliquot. The eluting ethyl acetate and methanol were passed through dried sodium sulfate and combined. Both PUF slices were always analyzed together and were placed in Alihn funnels to be soaked for 30 min in 50 mL of ethyl acetate. This was repeated 5 more times (300 mL total), and the aliquots were collected and combined. Filters were placed in separatory funnels and shaken for 1 min with 50 mL of ethyl acetate. This was repeated three more times with additional ethyl acetate, and the volumes were combined (200 mL total) after filtering through glass wool.

The internal standard, pentadecafluoro-1-octanol (PDFO), selected because of its chemical and structural similarity to the analytes of interest, was then added to all extracts that were subsequently rotoevaporated to ~10 mL in round-bottom flasks. The concentrates were transferred to calibrated glass test tubes, rinsing the flask two times with 2 mL of clean ethyl acetate, and then evaporated under a gentle stream of high-purity nitrogen to

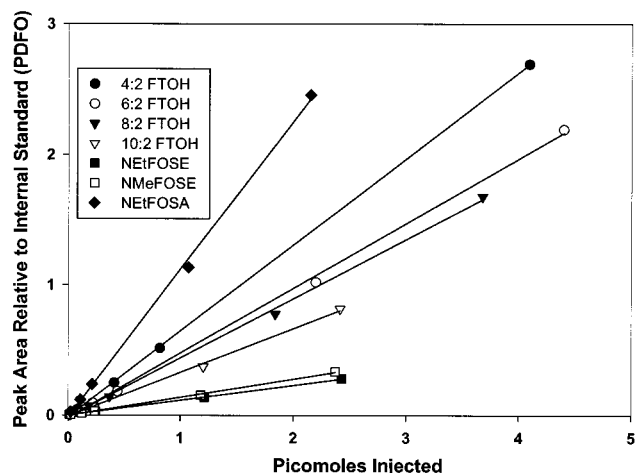


Figure 1. Calibration curves for all analytes in PCI mode. r^2 values were ≥ 0.998 for all compounds. The relative response was calculated as the ratio of peak areas between the analyte and internal standard molecular ions $[M + H]^+$. Analytical sensitivity (slope) was greatest for NEtFOSA > FTOHs > sulfonamidoethanols in PCI mode.

150 μ L and vialled for GC analysis. Final concentrates were filtered through 0.2- μ m Nylon syringe filters (Acrodisc, Pall Gelman) only if a precipitate was formed during concentration steps. All concentration steps were conducted without heating to protect against evaporative losses.

Instrumental Analysis and Quantification. Analysis of target analytes was performed by GC/CI-MS in both positive (PCI) and negative (NCI) chemical ionization modes. A Hewlett-Packard 5973 Mass Selective Detector, equipped with a chemical ionization source, acquired mass spectral data using methane as the reagent gas (PCI, 1 mL min^{-1} ; NCI, 2 mL min^{-1}). Gas chromatographic separation was performed on a 30m DB-Wax column (0.25 mm i.d., 250- μ m film thickness, J&W Scientific, Folsom, CA) using helium as the carrier gas. Pulsed splitless injections (1 μ L) were performed at an initial pressure of 40 psi and 200 $^{\circ}\text{C}$, returning to 10 psi at 1 min, and followed by an injector purge. The initial oven temperature was 60 $^{\circ}\text{C}$ for 1 min, ramped at 3 $^{\circ}\text{C min}^{-1}$ to 75 $^{\circ}\text{C}$, and subsequently at 20 $^{\circ}\text{C min}^{-1}$ to 240 $^{\circ}\text{C}$, followed by a 1-min hold. Standard injections were initially acquired in full-scan mode to determine the respective retention time window and fragmentation pattern of each analyte. All samples were acquired in selected ion monitoring (SIM) mode in either PCI or NCI mode, and the ions that were monitored are displayed in Table 1. Two to four ions were monitored at any given time in the chromatographic analysis, and only one analyte was monitored within each retention window, except for NMeFOSE and NEtFOSE, which could not be baseline-resolved. Quantification was performed by standard curve analysis by plotting the response of the respective molecular ion relative to PDFO versus the quantity of analyte in PCI mode (Figure 1).

Direct probe mass spectra of PFOSF were acquired with a Micromass 70S-250 operating at 6 kV in CI mode. Methane was the reagent gas employed for both PCI and NCI mode, and the source temperature was maintained at 210 $^{\circ}\text{C}$. The sample reservoir was maintained at 200 $^{\circ}\text{C}$.

Breakthrough Experiments. To examine the efficiency of target analyte collection, and the extent of sample blowoff, several breakthrough experiments were conducted under field conditions. This was performed by spiking 100–10 000 ng of each analyte in

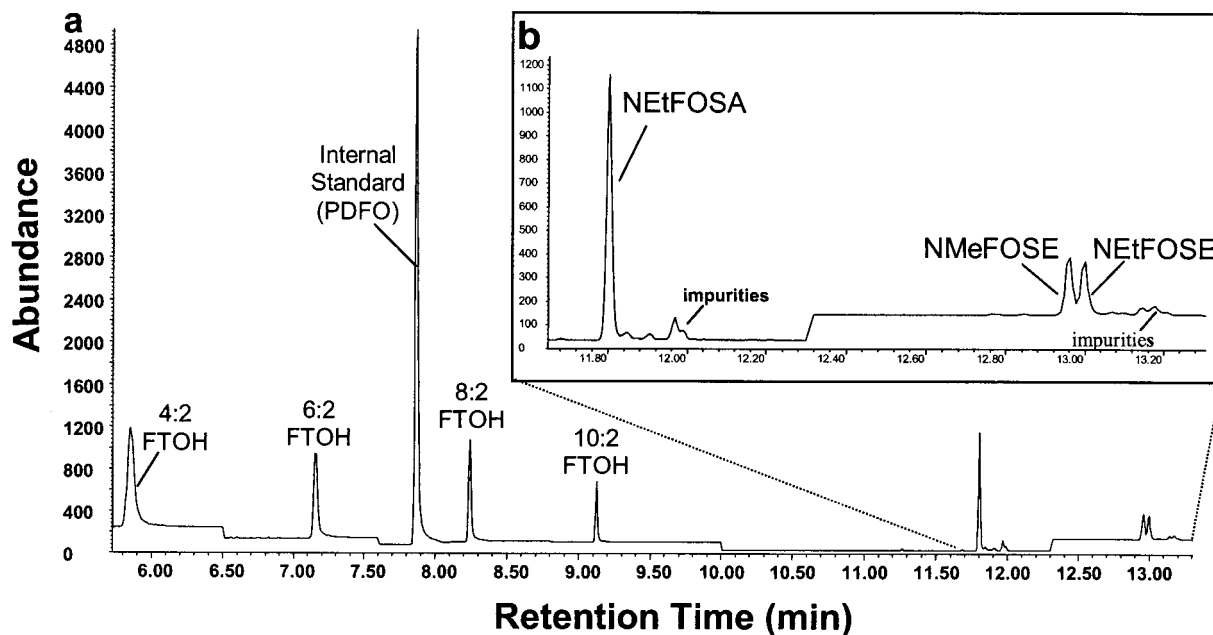


Figure 2. (a) Total ion chromatogram of fluorinated neutrals on a DB-Wax column, acquired in PCI mode employing SIM. In PCI mode, FTOHs and NEtFOSA were more responsive than NMeFOSE and NEtFOSE. Attempts to correct FTOH tailing were not successful with this column. (b) NEtFOSA, NMeFOSE, and NEtFOSE showed better chromatography; however, impurities of each standard (probably branched isomers) eluted 5–10 s after the main peak.

ethyl acetate (50 μL) onto the first (upstream) PUF and subsequently drawing ambient air for 3 days on a high-volume air sampler (TE-5000, Tisch Environmental Inc., Cleves, OH) for 3 days at 0.2 $\text{m}^3 \text{min}^{-1}$. Recovery was calculated relative to a "spiking duplicate", whereby the same quantities of target analytes were spiked directly into ethyl acetate in a 5 mL flask and concentrated to 150 μL at the time of analysis. The compounds examined in breakthrough experiments were NMeFOSE, NEtFOSE, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH. NEtFOSA standard was not available at the time of the breakthrough experiments.

Environmental Sampling. Air samples were collected at 2 sites in Southern Ontario, Canada, on high-volume air samplers (Tisch Environmental Inc., Cleves, OH) at approximate flow rates of 0.2 $\text{m}^3 \text{min}^{-1}$. The first site was highly urbanized, located at the University of Toronto's downtown campus (Gage Building, downtown Toronto, ON). The second site, Long Point, ON, was a rural environment on the north shore of Lake Erie, characterized by low population density. During the sampling periods, the sampler gauge pressures were monitored at predetermined intervals, and ambient pressure and temperature data was collected for correction of air volume. Six samples were collected at Toronto (February 26 to March 2, $n = 2$, 600 m^3 ; March 28 to April 3, $n = 2$, 850 m^3 ; and June 1–7, $n = 2$, 850 m^3); however, only the last four were analyzed quantitatively (i.e., with internal standard). The first two samples from Toronto were used for qualitative confirmation of all analytes (i.e., no internal standard). Two samples were collected at Long Point (March 28 to April 3, 850 m^3) and analyzed quantitatively.

Field blanks (XAD, PUF, and filters) were sent to the sample sites with each set of 2 samples, exposed briefly to ambient air, and returned to the laboratory with the environmental samples. The three sampling phase materials of each sample were analyzed separately; however, the respective concentrations were summed and reported as total airborne concentrations. No effort was made

to distinguish between gas phase (PUF, XAD) and particle-bound (filter) concentrations because of the well-established limitations of high-volume air sampler geometry, particularly "blowoff",²⁶ whereby particle-bound analyte can volatilize from the filter and diffuse into the gas-phase sampling media (XAD or PUF).

RESULTS AND DISCUSSION

Chromatography and Mass Spectrometry. Baseline chromatographic separation was easily achievable between each FTOH standard and PDFO; however, FTOH chromatographic peaks showed slight tailing that could not be improved by altering injection parameters or reinstallation of the column (Figure 2a). NMeFOSE, NEtFOSE, and NEtFOSA peaks had little tailing; however, the appearance of impurities was evident in standard injections (Figure 2b), eluting 10–20 s after the major chromatographic peak. We hypothesize that these impurities were structural isomers, because their spectra were not different from the major peak, and branched analogues are common (20%)⁸ in their production intermediate, PFOSF. NMeFOSE and NEtFOSE could not be completely resolved on the DB wax column (Figure 1b); however, the characteristic ions (m/z 558 and 572, respectively) allowed for mass separation and quantification.

Both PCI and NCI modes of operation were useful for the analysis of all target analytes, with the notable exception of PFOSF. Injections of a PFOSF standard did not produce any major chromatographic peaks under the conditions employed here in either PCI or NCI mode. Lower injection temperatures and pressures were investigated with no success; however, direct probe mass-spectral analysis revealed that PFOSF was ionizable (Table 1). In PCI mode, PFOSF yielded a significant relative abundance of the molecular ion $[M + H]^+$, but not in NCI mode, where the main ion was m/z 400.

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Table 2. Instrumental Detection Limit^a in NCI and PCI Mode and the Effective Limit of Detection^b Based on the Level of the Blank^c

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	NEtFOSA	NMeFOSE	NEtFOSE
PCI (pg)	2	5	2	0.8	0.3	0.6	0.6
NCI (pg)	20	8	7	0.9	0.2	0.2	0.2
LOD (pg m ⁻³)	0.4 ^d	4.5	4.0	0.15 ^d	1.6	4.2	6.2

^a Picograms. ^b LOD, picograms/meter³. ^c Average blank concentration + 3 σ and an 800 m³ sample. ^d There was no response detected in the blanks; therefore, LOD is based on the PCI mode absolute detection limit and an 800 m³ air sample.

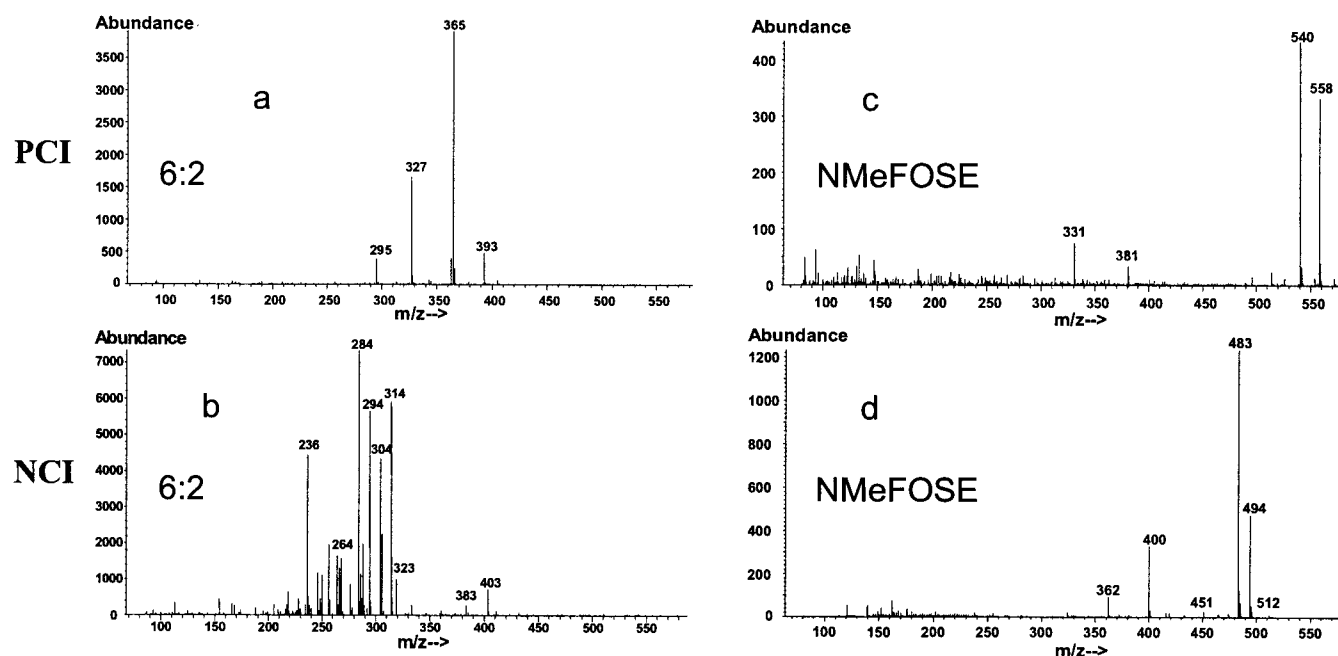


Figure 3. Mass spectra acquired for 6:2 FTOH in (a) PCI mode and (b) NCI mode, as compared to the mass spectra for NMeFOSE in (c) PCI mode and (d) NCI mode. PCI mode was favored because of the consistent presence of a molecular ion $[M + H]^+$ and because FTOH spectra were less complex (compare (a) to (b)).

Relative response was highly linear over 2.5 orders of magnitude for all standards (Figure 2). Linearity was not examined beyond this range, because it was appropriate for environmental monitoring. Instrumental detection limits, defined as the mass of analyte injected producing a peak with a signal-to-noise ratio (S/N) of 3, ranged from 0.2 pg (NEtFOSA) to 20 pg (4:2 FTOH), depending on the mode of ionization (Table 2). These values were extrapolated from the S/N of the respective peaks following an injection of the lowest standard concentration in either PCI or NCI mode (Table 2). Increased sensitivity could be expected from improved chromatography of FTOHs, and future studies will examine alternative stationary phases for their performance with this suite of compounds.

Typically, two or three ions were monitored for each analyte in PCI or NCI (Table 1). PCI was the most sensitive mode for detection of FTOHs, but NCI was the most responsive mode for NEtFOSA, NMeFOSE, and NEtFOSE (Table 2). Instrumental detection limits in NCI increased from 4:2 to 10:2 FTOH, but NEtFOSE, NMeFOSE, and NEtFOSA had the same detection limit (Table 2), indicating that sensitivity was dependent on the number of fluorine atoms per molecule. Overall, PCI was the ionization mode of choice for most analyses because it always produced the molecular ion $[M + H]^+$, and one or two characteristic fragment ions (with the exception of NEtFOSA). For example, FTOHs

always produced a fragment representing loss of 2 F, but both NMeFOSE and NEtFOSE generated a fragment representing loss of H_2O . Molecular adduct ions $[M + 29]^+$ were consistently present in FTOH spectra in PCI mode, indicating addition of CH_2CH_3 . NEtFOSA produced exclusively the molecular ion $[M + H]^+$ in PCI mode; therefore, confirmation of NEtFOSA in environmental samples was always made in NCI mode, wherein three fragments could be monitored.

NEtFOSA was the only analyte to generate an abundant molecular ion $[M - H]^-$ under NCI conditions, and mass spectra were very complex for all of the FTOHs, involving higher-molecular-weight adducts $[M + F_2]^-$ and even-mass fragments that may arise from interaction with HF in the source (Figure 3). For 6:2 FTOH, the major fragment ion was m/z 284, to which we have tentatively assigned the formula $[C_8HF_9O]^-$. The fragment at m/z 294 may be $[C_7F_{10}H_4O]^-$, with m/z 274 representing a subsequent loss of HF, and m/z 314, representing an HF adduct. The NCI mass spectra of 8:2 and 10:2 FTOH are generally analogous to 6:2 FTOH (Figure 3b), having fragment ions corresponding to +100 m/z (i.e., an additional CF_2CF_2) for each ion as we move from 6:2 to 8:2 to 10:2 FTOH. NMeFOSE, NEtFOSE, and NEtFOSA NCI mass spectra were relatively simple in comparison to FTOHs, with each producing a major fragment at m/z 483 and 400, characteristic of $[CF_3(CF_2)_7SO_2]^-$ and $[C_8F_{16}]^-$,

Table 3. Results of Breakthrough Experiments^a Showing Percent Recovery on the PUF and XAD Media, as Well as the Relative Standard Deviation of Each^b

	6:2 FTOH	8:2 FTOH	10:2 FTOH	NMeFOSE	NEtFOSE
	PUF				
mean recovery (%) ^c	not detected	16	9.1	28	31
% rsd		17	20	33	50
	XAD				
mean recovery (%)	120 ^d	120 ^d	78	68	58
% rsd	n.a.	n.a.	12	14	10
total recovery (%) ^b	120	136	87	96	90

^a $n = 3$. ^b The total recovery is the sum of the mean recovery on PUF and XAD relative to the spiking duplicate. ^c PUF 1 and 2 were combined for analysis. ^d XAD recovery of 6:2 and 8:2 FTOH was based on $n = 2$ samples because of contamination from background concentrations on 1 sample; thus, rsd could not be calculated (n.a.).

respectively. NMeFOSE (Figure 3d) and NEtFOSE spectra revealed a small abundance of the corresponding even-mass fragment $[M-CH_2CH_2OH]^-$ (i.e., m/z 512 and 526, respectively), and a larger abundance of the corresponding dehydrated ($-H_2O$) fragment (i.e., m/z 494 and 508, respectively). Electron ionization (EI) was not investigated in this study; however, a previous study described the spectra of 6:2 FTOH under EI mode;²⁷ wherein $[CF_3]^+$ and $[CH_2OHCH_2CF_2]^+$ were the major ions produced with only minor (4% relative abundance) production of the molecular ion.

Breakthrough Experiment. Total recovery of individual analytes ranged from 87% for 10:2 FTOH up to 130% for 8:2 FTOH (Table 3). For each compound, the majority of the spike that was added to the first PUF was recovered from the XAD resin. Less transfer from the PUF to XAD was evident for the sulfonamidoethanols than for either FTOH. Precision (relative standard deviation) was calculated for each sampling medium on the basis of the three breakthrough experiments performed and ranged from 10 to 33% (Table 3). Variability in the measurements may be partially attributed to ambient air temperature, whereby increased temperatures resulted in increased breakthrough. Average daily temperatures in the field during breakthrough experiments were between 20 and 24 °C. Recovery of 6:2 and 8:2 FTOH (Table 3) may be overestimated as a result of the addition of background concentrations, and this experiment should be replicated at higher concentrations in future studies.

Environmental Sampling. For positive confirmation of any analyte in the atmosphere, samples were monitored in both NCI and PCI modes to determine if all monitored fragment ions were produced in the correct ratio relative to a standard injection. Additionally, retention times had to be well-conserved (± 0.03 min) between standard and sample injections. All monitored analytes, with the exception of 4:2 FTOH and NEtFOSA, were confirmed at both sites (Table 1, Figure 4). NEtFOSA was confirmed only in Toronto, because the analytical standard was not obtained until the time of the final sampling campaign. NEtFOSE was the dominant PFOS derivative, followed by NMeFOSE and NEtFOSA (Table 1). In Toronto, the dominant FTOH was 6:2, followed by 8:2 and 10:2; however, this trend was not evident in Long Point (Table 1).

There was often a blank concentration associated with either XAD, PUF, or filter analysis; however, the response was always low enough ($< 4 \text{ pg m}^{-3}$) that it did not interfere with quantification of environmental samples (Figure 4). Field blank response was not significantly different from sampling media that remained in the laboratory, indicating that there was negligible contamination of sampling media transported to and from the field. Blank response differed among the three sampling media, and environmental samples were blank-subtracted with the corresponding field media blank before being summed and reported as total concentrations. The limit of detection (LOD), defined as the mean blank response $+ 3\sigma$ (and assuming an 800 m^3 sample), ranged from 0.4 (4:2 FTOH) to 6.2 pg m^{-3} (NEtFOSE) (Table 2). For LOD calculation, the mean blank response was the average response of any field blank media producing a quantifiable response. The method was appropriate for both rural and urban settings, based on the fact that blank-subtracted environmental concentrations always exceeded the LOD (Table 2).

High-volume air samplers equipped with PUF or XAD sorbents are standard apparatus for the routine monitoring of established atmospheric contaminants, such as PCBs, PAHs, and pesticides.²⁸ In general, our environmental sampling results indicated that collection efficiency on each medium was temperature-dependent, and the combination of XAD, PUF, and filter was necessary to ensure efficient collection in all temperature scenarios. For example, in February 2001, when average ambient temperature was < 0 °C, sulfonamidoethanols were primarily detected on PUF and particles. As the average daily temperature increased to above 20 °C in June, the sulfonamidoethanols were present primarily on XAD. Given these results, and the distribution on both phases in the breakthrough experiment, it is essential that a combination of XAD and PUF be utilized for the collection of this suite of fluorinated analytes. It is expected that the distribution of the detected compounds between XAD, PUF, and filter will be a function of vapor pressure, temperature, and particle concentration; however, there is a paucity of physical data for all of the compounds detected herein. The vapor pressure for NEtFOSE has been reported as 0.5 Pa at 20 °C,⁸ suggesting a significant proportion will be present in the gaseous phase.

CONCLUSIONS

This method provided efficient collection and adequate sensitivity for the analysis of a range of fluorinated neutral organics using GC/PCI- and GC/NCI-MS. PCI was the mode of choice for routine analysis; however, NCI mode was the most sensitive technique for sulfonamide derivatives of PFOS and provided straightforward confirmation of PCI mode data. Ambient air sampling in rural and urban locations confirmed the presence of six novel fluorinated environmental contaminants, three of which are expected to degrade to PFOS, and as such, have implications for its global dissemination. We have demonstrated that PFOSF is amenable to both PCI and NCI mode conditions; however, alternative columns or alternative chromatographic techniques must be examined before PFOSF can be routinely monitored. The successful analysis of this suite of compounds, having variable structure and physical properties, indicates that this technique

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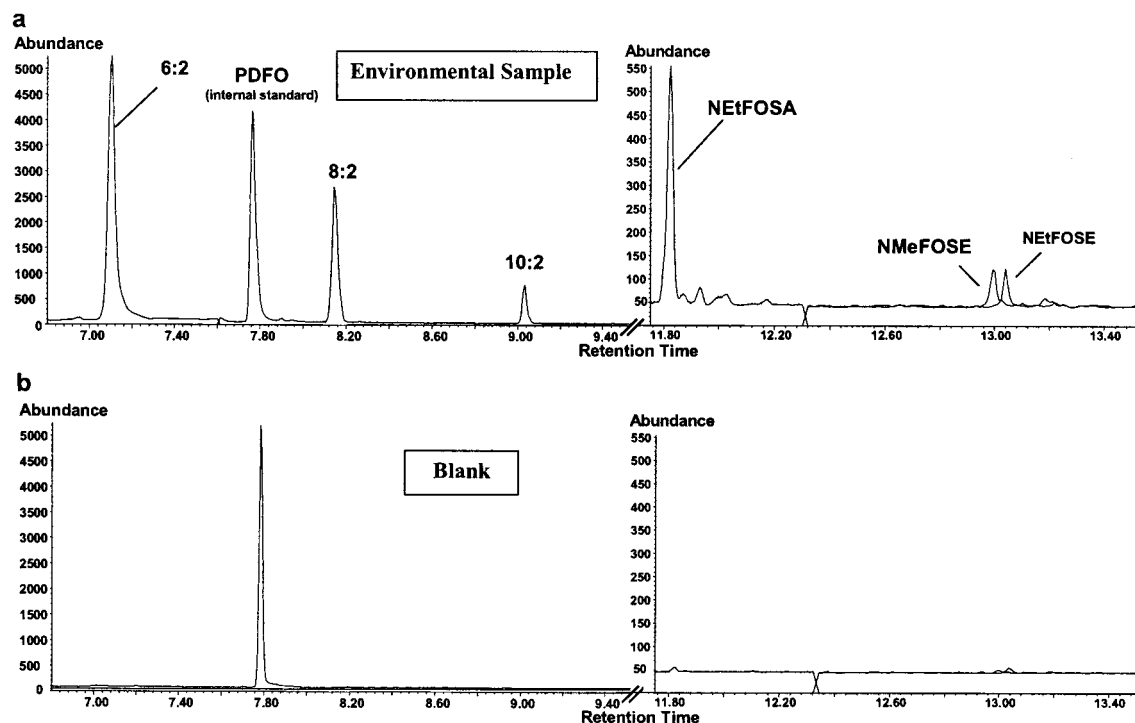


Figure 4. (a) Extracted and overlaid SIM chromatograms of an environmental sample (XAD fraction only) collected June 1–4, 2001, in Toronto (851 m³). All confirmed target analytes were detected in air above the corresponding limit of detection (Table 2). The internal standard PDFO was added for quantification. (b) A field blank (XAD fraction) showing that most analytes could also be detected in blanks; however, the concentrations were low (<4 pg m⁻³) and did not prevent quantification for any environmental sample.

may also be amenable to the analysis of many other fluoroorganic neutrals in commercial use,²⁴ whose environmental presence has not been previously investigated. Future studies should examine the use of annular diffusion denuders as a means of determining gas-particle partitioning and as a direct comparison to high-volume measurements.²⁹

ACKNOWLEDGMENT

This research would not have been possible without generous funding from the Toxic Substance Research Initiative (TSRI), administered through Health Canada (Ottawa, ON). Additional funding was provided by the Canadian Network of Toxicology Centers (CNTC, Guelph, ON). Dale Bacon (3M Co., St. Paul, MN) is thanked for donating sulfonamidoethanol chemical standards.

Camilla Teixeira (National Water Research Institute) is graciously thanked for the donation of precleaned sampling media and for the organization of high-volume sampling at Long Point. We thank Bob Wilkinson (National Water Research Institute) for valuable GC/MS support. Dr. Alex Young, (University of Toronto Mass Spectrometry Facility) is also thanked for direct probe mass analysis.

Note Added after ASAP. This article was inadvertently posted ASAP before final corrections were made. On the fifth page, column two, line 15, [C₈HF₉₀] was corrected to [C₈HF₉O]. The correct version was posted on January 8, 2002.

Received for review September 20, 2001. Accepted November 21, 2001.

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AC015630D