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Development of Analytical Methods to Quantify Perfluorooctane Sulfonate and Related Compounds in the Environment

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Abstract

Analytical techniques based on ^{19}F NMR spectroscopy and HPLC-suppressed conductivity detection were developed to detect and quantify aqueous perfluoroctane sulfonate (PFOS), perfluoroctanoic acid (PFOA), and perfluorobutane sulfonate (PFBS). Chromatographic separation of the perfluoroalkyl surfactants (PFAS) was performed using a C^{18} reversed-phase column and a mobile phase consisting of a mixture of boric acid and acetonitrile. The detection limit for PFOS by ^{19}F NMR was 3.6 mg L^{-1}. The detection limit for PFOS, PFOA and PFBS by HPLC-suppressed conductivity detection was 1 mg L^{-1}. The detection limits were shown to improve considerably if samples were pre-concentrated by solid-phase extraction. The detection limits for PFOS of pre-concentrated samples were 3.6 mg L^{-1} and 10 ug L^{-1} by ^{19}FNMR and HPLC-suppressed conductivity detection, respectively. Comparison of these two methodologies showed that HPLC-suppressed conductivity detection should be preferred for routine quantification of these contaminants due to its simplicity, time efficiency, and accuracy. Conversely, ^{19}F NMR can be used to characterize changes in the chemical structure of fluorinated compounds due to its inherent advantage of high specificity and no matrix interferences. The feasibility of utilizing total organic carbon (TOC) and chemical oxygen demand (COD) analysis for the quantitative detection of PFOS in aqueous samples was also investigated. Although, the TOC analysis provided reliable quantification of PFAS in aqueous samples, the non-specificity is a drawback of the technique. The dichromate-based COD method was found unsuitable for the analysis of PFOS due to the incomplete oxidation of the highly stable perfluorinated compound under the conditions evaluated.

Keywords. PFAS, PFOS, PFOA, PFBS, ^{19}F NMR, HPLC, suppressed conductivity detector, TOC and COD.

Abstract

Métodos analíticos basados en ^{19}F NMR y HPLC con detector de conductividad suprimida fueron desarrollados para detectar y cuantificar sulfonato de perfluorooctano (PFOS), ácido perfluorooctanoico (PFOA) y sulfonato de perfluorobutano (PFBS) en muestras ambientales. La separación de los surfactantes perfluorinados (PFAS) se realizó con una columna C^{18} de fase reversa y una fase móvil compuesta de ácido bórico y acetonitrilo. El límite de detección para PFOS con ^{19}F NMR fue 3.6 mg L^{-1}, mientras que para PFAS con HPLC con detector de conductividad suprimida fue 1 mg L^{-1}. Los límites de detección mejoraron considerablemente si las muestras fueron pre-concentradas a través de una extracción en fase sólida (SPE) registrando valores para PFOS con ^{19}F NMR y HPLC con detector de conductividad suprimida de 3.6 mg L^{-1} y 10 ug L^{-1}, respectivamente. Esta última demostró ser la mejor técnica para análisis rutinario de cuantificación de contaminantes fluorinados debido a su simplicidad, rapidez y precisión. ^{19}F NMR fue muy efectiva para detectar y caracterizar cambios en la estructura química de los compuestos fluorinados ya que es una técnica analítica altamente específica en la que la matriz ambiental no interfiere con el análisis. El análisis de carbono orgánico total (TOC) y la determinación de la demanda química de oxígeno (COD) para la cuantificación de PFOS en muestras acuosas también fueron estudiados. A pesar de que los análisis de TOC permitieron cuantificar exitosamente PFAS, la falta de especificidad de este método es una limitación considerable. Finalmente, el análisis de PFOS a través de la determinación de COD no fue posible debido a una oxidación incompleta de los altamente estables compuestos fluorinados bajo las condiciones de operación evaluadas.

Palabras Clave. PFAS, PFOS, PFOA, PFBS, ^{19}F NMR, HPLC, detector de conductividad suprimida, TOC and COD.

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Introduction

Perfluoroalkyl sulfonates and perfluorocarboxylic acids such as perfluoroctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been the subject of numerous studies in recent years. These perfluorinated alkyl surfactants (PFAS) are of particular interest due to their tendency to bioaccumulate in higher organisms, persistence in the environment, and toxicity [1, 2, 3]. PFOS and PFOA have been detected in blood samples in various populations [4, 5], in wildlife throughout the world [6, 7, 8], and in aqueous and solid environmental matrices [9, 10].

Aqueous environments seem to be the primary sink for PFAS [11, 3] due to the relatively high solubility of these compounds (*i.e.*, 3.4 and 0.5 g L^{-1} for PFOA and PFOS in pure water, respectively [12, 13]), their negligible vapor pressure (*i.e.*, 1.33 x 10^{-5} and 3.31 x 10^{-4} Pa at 20°C and 25°C for PFOA and PFOS, respectively), and moderate sorption to organic matter [14, 15]. Literature studies have reported significant PFAS concentrations in surface waters [16, 17, 18, 19, 20, 21, 22]. For instance, Skutlarek and coworkers [22] measured total PFAS concentrations as high as 4.385 ng L^{-1} in the Moehne River at Heidberg, Germany. In the same study, PFOA and PFOS were detected at concentrations of 3.640 and 247 ng L^{-1}, respectively.

The analysis of perfluorinated surfactants in environmental samples has been primarily conducted by liquid chromatography coupled to mass spectrometry (LC-MS) or tandem mass spectrometry (LC-MS/MS) [23, 24, 25]. The accuracy and precision of these techniques make them very valuable for quantification of these pollutants. However, ion suppression due to matrix effects, sample contamination and elevated analysis cost limit the application of LC-MS or LC-MS/MS for routine analysis of environmental samples [26, 27]. Gas chromatography mass spectrometry (GC-MS) has also been employed for the analysis of PFAS [28, 25, 29]. The low volatility of the perfluoroalkane sulfonates requires the application of derivatization techniques to make them amendable to GC-MS analysis. Derivatization of PFOS compounds is problematic because esterified PFOS derivatives are not very stable [23, 30], and derivatization-reaction yields are often poor [31]. The derivatization-step makes this method time-consuming and not suitable for routine monitoring of non-volatile PFAS.

PFOS and related compounds have also been quantified by ^{19}F NMR spectroscopy. Moody and colleagues [32] reported the quantification of PFOA and PFOS in surface water samples by means of this spectroscopy technique. Recently, two studies have been published on the quantification of isomers in technical PFOS by ^{19}F NMR [33, 34].

The lack of reliable commercial standards limits the accurate analysis of PFAS in aqueous samples. Perfluoroalkyl sulfonyl-based chemicals commonly produced by electrochemical fluorination processes (ECF) are often mixtures of linear and branched isomer compounds [35, 36]. Commercial PFOS samples from fine-chemical manufacturers labeled as > 98% pure have been shown to contain 20-30 % branched PFOS isomers [34, 37, 38, 39]. The quality assurance of the analysis of perfluorinated surfactants might be improved by the use of commercially available ^{13}C-labeled and deuterium-labeled standards [23, 25]. However, ^{13}C-label standards are not optimal for all samples matrices, therefore careful selection of the internal standard for each type of matrix is required. In addition, traces of other PFAS can be found in these standards [25]. Currently, there are two mass-labeled standards for linear PFOS, ^{13}C-PFOS and $^{18}O_2$-PFOS [40, 5].

The objective of this research is to develop analytical methods relying on ^{19}F NMR spectroscopy and HPLC with suppressed conductivity detection to monitor PFOS and related compounds in aqueous environmental matrices. Quantification of perfluoroalkyl compounds was also investigated by means of TOC and COD analysis.

Materials and Methods

Chemicals

Perfluorooctane sulfonic acid potassium salt, PFOS (98% purity), and 1H,1H,2H,2H-tetrahydroperfluorooctane sulfonate, TH-PFOS (98%) were purchased from SynQuest Laboratories (Alachua, FL). Perfluorobutane sulfonic acid potassium salt, PFBS (98.2%), was kindly provided by the 3M Company (St. Paul, MN). Perfluorooctanoic acid, PFOA (96%), sodium fluoride (99%), chromium (III) acetylacetonate, $Cr(acac)_3$ (97%), and potassium hydrogen phthalate (99%) were obtained from Sigma - Aldrich (St. Louis, MO). 4'-(trifluoromethoxy)acetanilide, 4-TFMeAc (97%) was obtained from Matrix Scientific (Columbia, SC). Methanol-D4 was purchased from Cambridge Isotope Laboratories (Andover, MA). HPLC-grade acetonitrile, methanol, sulfuric acid, and boric acid (99.5%) were purchased from Mallinckrodt Chemicals (Phillipsburg, NJ). All chemicals were used as received.

^{19}F NMR quantification

The quantitative determination of PFOS by ^{19}F NMR was performed by a method adapted from Moody *et al.* [32]. Samples were dissolved in 0.7 mL of 90% H_2O / 10% CD_3OD or in 90% CH_3OH / 10% CD_3OD containing 4 mg mL^{-1} chromium acetylacetonate ($Cr(acac)_3$) and analyzed in 5-mm tubes. The internal standard, 4-TFMeAc, was present in all samples at a concentration of 140 mg L^{-1}, corresponding to a 1:1 molar 4-TFMeAc:PFOS ratio for the most concentrated PFOS sample. Samples containing PFOS and TH-PFOS in a 1:1 molar fluoride ratio (100 mg PFOS L^{-1}:112 mg TH-PFOS L^{-1}) were prepared as described above. Solid phase extraction (SPE) was conducted to preconcentrate analytes when required. SPE cartridges (3 mL, 500 mg

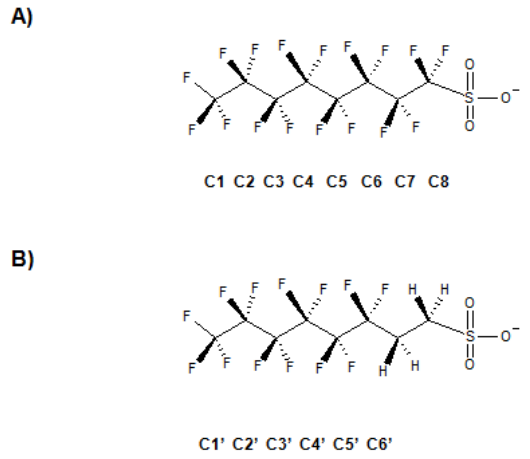

Figure 1: Molecular structure of perfluoroalkyl surfactants. A) PFOS and B) TH-PFOS.

ODS-C_{18}, Agilent Technologies, DE) mounted on a vacuum manifold were conditioned with 5 mL methanol, following by 5 mL of dionized water and then aqueous sample was loaded at 1 mL min^{-1}. SPE cartridges were rinsed with 5 mL of dionized water and then dried under vacuum for 3 h prior elution. Analytes were eluted with 5 mL methanol and collected in clean Nalgene flasks. Standard solutions spiked with known PFOS concentrations were extracted in parallel to determine recovery efficiencies as discussed later.

All ^{19}F NMR spectra were acquired at 22°C on a Varian Unity-300 spectrometer operating at a ^{19}F frequency of 282.208 MHz using a 5mm 4-nucleus (^{31}P, ^{13}C, ^{19}F, ^{1}H) probe. Acquisition involved a relaxation delay of 1.44 s followed by a 90° pulse (16.2 μs) and a Hahn echo with an echo delay of 100 μs, with 16,384 complex data points and a spectral width of 33,333 Hz. The acquisition time for all samples was 32.5 min. A 10 Hz line broadening was applied before zero filling to 32,768 data points and Fourier transform. Baseline correction was performed using a 5^{th} order polynomial, and chemical shifts were referenced to internal standard, 4-TFMeAc at -58.08 ppm [41].

HPLC-suppressed conductivity detection

PFOS and related compounds in aqueous samples were analyzed by a HPLC system with suppressed conductivity detector (ICS-3000 Ion Chromatography System, DIONEX, Sunnyvale, CA). The chromatograph was equipped with an autosampler (injection volume 100 μL), a pump, a degasser, a guard column (Acclaim Polar Advantage II, C_{18}, 4.3 mm i.d., 1 cm length) and a separation column (Acclaim Polar Advantage II, C_{18}, 4.6 mm i.d., 25 cm length) operating at 35°C. A mixture of 20 mM boric acid (pH 9.0) and 95% acetonitrile was used as the mobile phase at a flow rate of 1mL min^{-1}. The amount of boric acid varied with linear gradient program starting with 75% (v/v) at time zero and decreasing to 45% (v/v) in 13.2 min. Blanks were continuously run to assure that the column was clean and

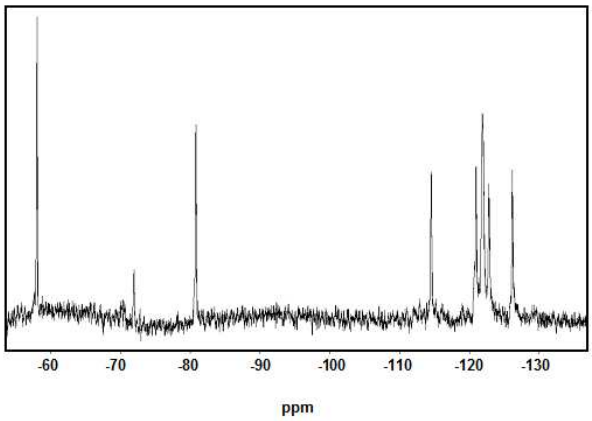

Figure 2: ^{19}F NMR spectrum of an aqueous PFOS sample (31.5 mg L^{-1}) relative to the internal standard, 4'-(trifluoromethoxy)acetanilide, 4-TFMeAc, (-58.08 ppm).

that traces of the analyte were not carried over between samples. Solid phase extraction (SPE) was conducted to preconcentrate analytes when required as described above. Standard solutions spiked with known PFOS concentrations were extracted in parallel to determine recovery efficiencies as discussed later.

TOC analysis

Measurements of PFOS and derivatives in aqueous solution were determined using a Total Organic Carbon analyzer (Shimadzu TOC-V CSH/CSN system, Columbia, MD). All samples, including blanks and standards, were acidified with HCl to pH 2.20-2.50 prior to analysis.

Results and Discussion

^{19}F NMR assignments and quantification of PFOS

The chemical structures of PFOS and TH-PFOS including numerical labels of the carbon chains are depicted in Figure 1. ^{19}F NMR is a very valuable technique for structural studies of fluorinated compounds. Figure 2 illustrates a typical ^{19}F NMR spectrum of aqueous PFOS sample. The spectral window was restricted to -55 ppm to -135 ppm to improve the clarity of the spectrum. Chemical shifts were referenced to the internal standard 4-TFMeAc at -58.08 ppm [41]. Moody and coworkers incorrectly assigned the resonance at -72.0 ppm to 4-TFMeAc [32]. In this study, the mentioned resonance is observed even if 4-TFMeAc is not added, suggesting the presence of fluorinated PFOS impurities. These impurities have been identified as branched PFOS isomers as described by Ochoa-Herrera et al [38]. The peak at about -72 ppm is characteristic of the internal and terminal branched CF_3 of all PFOS isomers [33, 34]. Previous studies on ^{19}F NMR spectroscopy of perfluorinated compounds have clearly identified some of the key peaks in the carbon-fluorine chain [42, 43]. The peak at -80.7 ppm has been assigned to the terminal CF_3 (C1), the peak at -113.1 ppm is shown to arise from fluorine atoms in C8 adjacent to the sulfonate group, and the peak at -125.6 ppm is characteristic of the CF_2 group

(C2) next to the terminal CF_3 [42]. The resonance peaks at -120 ppm, -121.2 ppm, and -122.1 ppm correspond to intermediate CF_2 moieties in carbons atoms C3 to C7.

The spectrum of TH-PFOS, a compound structurally related to PFOS (Figure 1B), was obtained to identify the intermediate CF_2 NMR signals of the perfluorinated compounds. The ^{19}F NMR spectra of aqueous solutions containing PFOS only and a mixture of PFOS:THPFOS in a 1:1 molar fluoride ratio are illustrated in Figure 3. For comparison purposes the spectral window was restricted to -77 ppm to -133 ppm.

As expected, the spectrum of the solution containing the mixture of PFOS and TH-PFOS is different from that of PFOS alone. The intensities of the peaks at -80.7 and -125.6 ppm assigned to the terminal CF_3 (C1) and the CF_2 (C7) moiety next to it, respectively, are higher in the PFOS:THPFOS solution spectrum as compared to the same peaks in the spectrum of the solution that only contains PFOS. These findings suggest that C1' and the C2' in the TH-PFOS molecule are chemically equivalent to the fluorine atoms in C1 and C2 in the PFOS molecule. These two peaks seem to appear in the same place for long chain perfluorinated compounds as suggested by Buchanan *et al.* (2005) [42].

In contrast, the intensities of the peaks assigned to the CF_2 moiety adjacent to the sulfonate group C8 (-113.1 ppm) and that at –120 ppm are reduced approximately by half in the spectrum of the mixture. The decrease in intensity suggests that the resonance at –120 ppm corresponds to the fluorine atoms in C7 in the PFOS molecule.

In the TH-PFOS molecule, the chemical environment of the fluorine atoms that are in the vicinity of the hydrogen atoms is different from that of fluorine atoms in PFOS, a compound that is fully fluorinated. Therefore, the two additional peaks present in the perfluorinated mixture at -112.9 and -122.8 ppm must correspond to fluorine atoms in C3' to C6' in the TH-PFOS compound. So, the peak at -113.4 ppm presumably arises from the CF_2 group (C6') next to the $CH_2CH_2SO_3^-$ group. Under the experimental conditions employed in this study, no further information can be obtained to identify the intermediate fluorine atoms in the PFOS structure.

As shown in Table 1, our ^{19}F NMR assignments are in good agreement with those reported by other research groups [33, 34].

The slight discrepancy with the NMR signals assigned by Arsenault and coworkers [33] can be attributed to the use of a different compound as the internal standard as well as experimental/instrumental errors. The signals referenced to hexafluorobenzene (-169 ppm) are slightly shifted upfiled by 5 ppm, meaning that they were generated at higher external electric magnetic fields. Considering that the shifts were observed in all fluorine assignments, the differences are negligible.

Carbon #	Resonance (ppm)	Literature data (ppm)	
	Our work	Arsenault *et. al.*[a]	Vyas *et al.*[b]
C1	-80.7	-86.0	-82
C2	-125.6	-131.0	-127
C3	–	-127.4	-124
C4	–	-126.6	–
C5	–	-126.4	–
C6	–	-126.3	–
C7	-120	-125.0	-121
C8	-113.1	-117.8	-115

Literature data: [a][33] and [b][34].

Table 1: ^{19}F NMR assignments of the PFOS molecule.

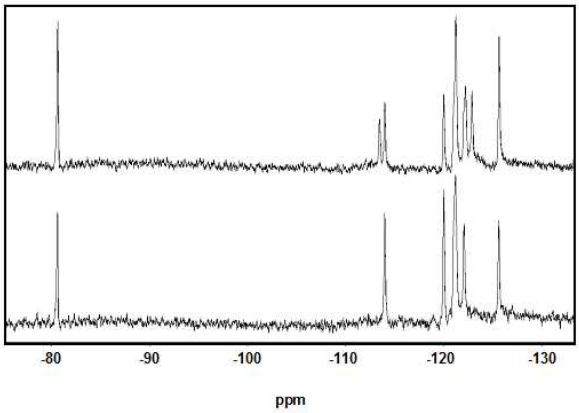

Figure 3: ^{19}F NMR spectra of aqueous solutions containing a mixture of PFOS and TH-PFOS in a 1:1 molar fluoride ratio (100 mg PFOS L^{-1} : 112 mg TH-PFOS L^{-1}) (upper panel) and PFOS only solution (100 mg L^{-1}) (lower panel).

^{19}F NMR quantification of PFOS in aqueous samples was conducted according to the protocol described in the *Materials and Methods* section. A known concentration of the internal standard, 4-TFMeAc, was added to all samples. Quantification was possible by integrating the area of the PFOS signal relative to the area of the internal standard. Although calibration curves were obtained for each PFOS peak in the ^{19}F NMR spectrum, the area of the largest peak, which corresponds to the terminal CF_3, was used for quantification purposes (Figure 4). Linear calibration curves ($r^2 > 0.98$) using known PFOS concentrations ranging from 10 to 140 mg L^{-1} were employed.

The detection limit of ^{19}F NMR based on a signal-to-noise ratio of 3 was found to be 12.5 mg PFOS L^{-1} in aqueous samples. This limit could be significantly improved when a solvent of less polarity-polarizability character is employed. In samples concentrated by SPE procedures based on ODS-C_{18} cartridges using methanol as solvent, PFOS was detected at concentrations as low as 3.6 mg L^{-1}, which is 3.5-fold lower than the detection limit obtained in aqueous samples. This could be attributed to the interactions of the molecule with the solvent. Hence, since H_2O interactions with the fluorine atoms of PFOS are stronger than those with CH_3OH, a higher coupling between the ^{19}F nuclei spins will result in the aqueous solvent, producing an increased diversification of F atoms in the molecule and, thus, higher

detection limits [44]. The recovery efficiency of this procedure was 100.8% $\pm$ 5.4% for triplicate aqueous samples of 100 mg L^{-1} of PFOS standard.

Quantification of PFOS by NMR spectroscopy was accurate and precise. However, the sensitivity of the technique is low and quantification of PFOS will generally require sample preconcentration, e.g., by SPE extraction. Nonetheless, alternative techniques such as LC-MS or LC-MS/MS also often require sample pretreatment by SPE because the concentrations of PFOS in environmental samples are generally in the low ppm range (μg L^{-1}) [45, 23, 24].

Moody *et al.* [32] reported higher detection limits than those obtained in this study by one order of magnitude, 0.25 mg L^{-1} for concentrated samples. However, the acquisition time used in our study was relatively short, 32.5 min, and the sensitivity of the F-NMR sytem used (a Varian Unity-300 spectrometer) was limited compared to that in the study conducted by Moody and coworkers.

^{19}F NMR spectroscopy is a valuable technique to provide structural information of perfluoroalkyl compounds due to its ability to respond to different electronic environments with changes in the chemical shift. Unfortunately, ^{19}F NMR cannot be used for routine monitoring of PFOS because data acquisition and data processing are very time-consuming compared to other analytical methods such as LC-MS and LC-MS/MS.

HPLC-suppressed conductivity detection

A HPLC method that relies on suppressed-conductivity ion chromatography has been developed to separate and detect aqueous PFOS and related perfluoroalkyl compounds in environmental samples. Chromatographic separation was conducted with a C_{18} reverse-phase column and a mobile phase consisting of a mixture of boric acid and acetonitrile with various mixing ratios.

Figure 5 shows a chromatogram obtained for a standard containing 25 mg L^{-1} commercial PFOS. Well-resolved peaks and reproducible results were achieved by this chromatography method. Moreover, various PFOS isomers were separated with this method. The peak at 9.9 min is assigned to the linear PFOS anion and the two little peaks eluting before the major peak at 9.3 and 9.5 min correspond to PFOS isomers. These isomers are structural isomers of PFOS which have the same molecular weight as PFOS but are branched perfluoroalkyl sulfonates [46, 38].

The purity of the PFOS salt was calculated by relating the area of the linear PFOS peak to the sum of the areas of all three peaks, assuming that the response factors for branched and linear isomers are equivalent. The latter assumption cannot be confirmed experimentally due to the lack of authentic isomer standards. Linear PFOS was found to be 75.4% pure [38]. Previous studies have reported the purity of PFOS commercial standards (labeled as > 98%) in the range of 70 to 80% [39, 34, 37].

The quantitative determination of low-ppm concentration of aqueous PFOS was effectively conducted by

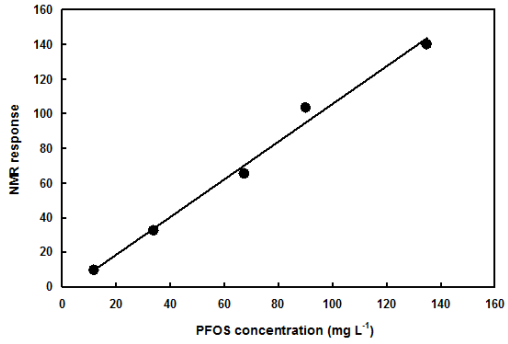

Figure 4: Calibration curve of aqueous PFOS based on the terminal CF_3 peak by ^{19}F NMR (r^2 > 0.98).

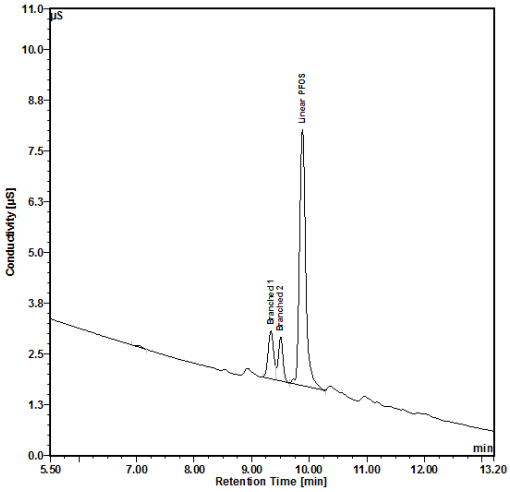

Figure 5: HPLC-suppressed conductivity detection chromatogram of aqueous PFOS (25 mg L^{-1}).

HPLC-suppressed conductivity detection as described in the *Materials and Methods* section. The total concentration of perfluorinated compounds in aqueous samples was obtained by linear calibration curves (r^2 > 0.99) using known concentrations of PFOS, PFBS and PFOA ranging from 0 to 150 mg L^{-1}. The detection limit of PFOS, PFBS and PFOA was 1 mg L^{-1}. A calibration curve for PFOS in aqueous samples is shown in Figure 6. These results are consistent with those obtained by Hori *et al.* [47] by conductimetric detection. A detection limit of 0.66 to 1.0 mg PFOS L^{-1} was reported utilizing a ODS column and a methanol:phosphate gradient with linear calibration graphs up to 100 mg PFOS L^{-1}. The new detection limits for samples pre-concentrated by SPE using ODS-C_{18} cartridges and methanol as solvent increased significantly. PFOS was detected at concentrations as low as 10 μg L^{-1}. Blanks samples spiked with known concentrations of PFOS (25 mg

L^{-1}) were extracted in parallel to determine the recovery efficiency which was 102% ± 9.4% for triplicate samples.

The use of a reverse-phase C_{18} column provided good resolution for the perfluorinated alkyl substances. A mixture of PFBS, PFOA and PFOS in a 1:1:1 ratio was successfully separated as shown in Figure 7. Standard samples of each perfluorinated compound were run in parallel to identify their retention times. The peaks eluted based on number of carbons and molecular weight. PFBS, 4-carbon chain with a molecular weight of 299.08 g mol^{-1}, appeared first followed by PFOA, a 8-carbon chain compound with a molecular weight of 414.07 g mol^{-1}, and finally PFOS, 8-carbon compound with a molecular weight of 499.12 g mol^{-1}. The response factors determined for these perfluorinated compounds differed considerably. The response factor was calculated by dividing the area of analyte by its concentration. The response factors for PFBS, PFOA and linear PFOS were 0.104, 0.067, and 0.039, respectively.

HPLC based on suppressed conductivity detection is a simple, rapid and efficient method for the separation and detection of perfluorinated compounds. Since it does not require sample pretreatment, the analysis times are significantly reduced compared to those required in ^{19}F NMR spectroscopy. Besides, this technique is less expensive and time consuming than LC-MS/MS. The good separation achieved by the reverse phase C_{18} column allows detection of PFOS isomers and calculation of the purity of PFOS commercial standard. This chromatography method can be successfully utilized for monitoring PFAS on a routine basis in aqueous solutions. Moreover, the high sensitivity of the technique makes it appropriate for the determination and quantification of low-ppm amounts of perfluoroalkyl surfactants in real environmental samples. Detection of PFAS concentrations in the ppb-range is feasible if the samples are preconcentrated by solid-phase extraction with cartridges based on ODS-C_{18} columns.

Quantification of PFOS by TOC and COD analysis

The feasibility of utilizing TOC and COD analysis for the quantitative detection of PFOS in aqueous samples was also investigated in this study. Instrument calibration was performed using potassium hydrogen phthalate standards ranging from 0.40 to 25 mg TOC L^{-1}. The coefficient of determination (r^2) for each calibration was > 0.99. Calibration lines obtained using potassium hydrogen phthalate and PFAS standards were nearly identical confirming the suitability of TOC measurements for PFAS quantification.

Figure 8 shows a calibration curve for PFOS in aqueous samples by total organic carbon (TOC) analysis. Linear calibration curves (r^2 > 0.99) using known concentrations of PFOS ranging from 0.5 to 19.2 mg TOC-PFOS L^{-1}, equivalent to 2.5 to 100.0 mg PFOS L^{-1}, were obtained. The detection limit was 2.5 mg PFOS L^{-1} equivalent to 0.5 mg L^{-1} of PFOS as TOC. A significant improve in the detection limit can be obtained by using a high-sensitivity catalyst; PFOS concentrations in the μg L^{-1} range can be detected. Although the TOC analysis provides reliable quantification of PFOS in environmental samples, the lack of selectivity is a drawback of the technique. The method is not compound specific since all organic carbons are detected. PFOS solutions containing 180 and 250 mg L^{-1} were reacted with the dichromate solution for 2 h at 150°C according to the COD protocol described elsewhere [48]. Blank solutions lacking PFOS were also analyzed. No oxidation of PFOS was detected under these experimental conditions. The fact that the dichromate-based COD method was not suitable for the analysis of PFOS was likely due to the

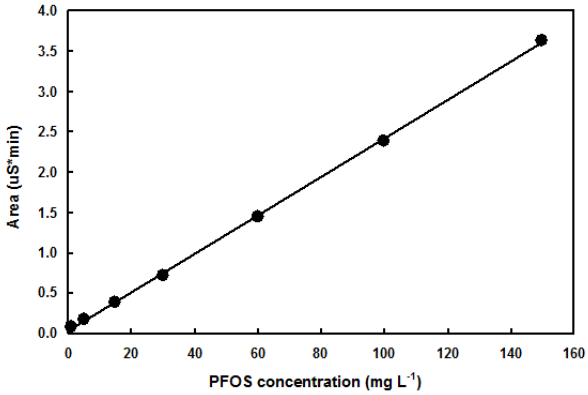

Figure 6: Calibration curve of aqueous PFOS by HPLC suppressed conductivity detection (r^2 > 0.99).

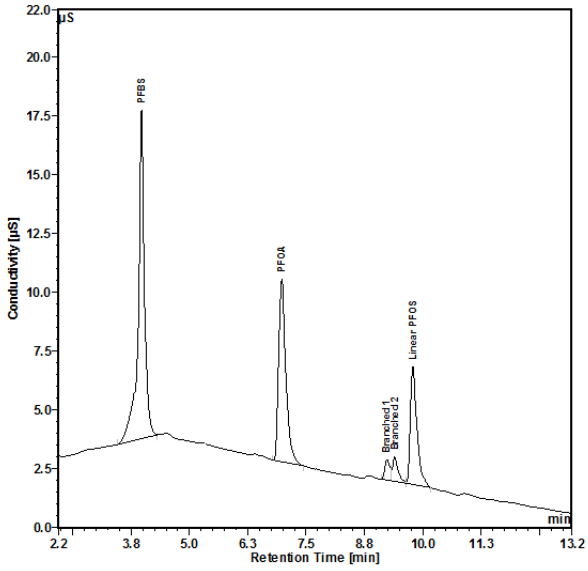

Figure 7: HPLC-suppressed conductivity detection chromatograph of an aqueous solution containing PFBS, PFOA, and PFOS (21 mg L^{-1} each).

well-known chemical stability of perfluorinated compounds. The strength of the carbon-fluorine bond is responsible for the recalcitrant nature of these pollutants [36]. This finding is surprising considering that dichromate is a strong oxidant and the COD assay is the standard method for the analysis of organic matter in wastewaters. However, highly persistent organic compounds such as benzene and pyridines are also not oxidized in the COD test [49].

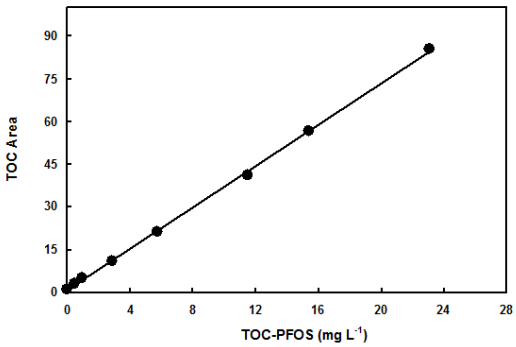

Figure 8: Calibration curve of aqueous PFOS by TOC analysis (r^2 > 0.99).

Conclusions

The detection and quantification of PFOS and related compounds in aqueous samples by two independent methodologies, *i.e.* ^{19}F NMR spectroscopy and HPLC-suppressed conductivity detection, was investigated. In terms of sensitivity and analysis time, the HPLC-suppressed conductivity detection method offers an advantage over ^{19}F NMR as a technique for the quantification of perfluorinated sulfonates and carboxylates. However, ^{19}F NMR spectroscopy is a powerful technique to gain information on the chemical environment of fluorine atoms in the perfluorinated chemicals. The presence of branched PFOS isomers in the PFOS commercial standard was confirmed by these two independent methods. Analysis of PFOS and derivatives can also be conducted by total organic carbon analyzer when no matrix interferences are present, *i.e.*, organic matter. The COD method was not suitable for the analysis of PFOS in aqueous environments; the compound was not oxidized under these conditions, confirming its well-known chemical stability.

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