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Development of an ^{19}F NMR Method for the Analysis of Fluorinated Acids in Environmental Water Samples

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This investigation was carried out to evaluate ^{19}F NMR as an analytical tool for the measurement of trifluoroacetic acid (TFA) and other fluorinated acids in the aquatic environment. A method based upon strong anionic exchange (SAX) chromatography was also optimized for the concentration of the fluoro acids prior to NMR analysis. Extraction of the analyte from the SAX column was carried out directly in the NMR solvent in the presence of the strong organic base, DBU. The method allowed the analysis of the acid without any prior cleanup steps being involved. Optimal NMR sensitivity based upon T1 relaxation times was investigated for seven fluorinated compounds in four different NMR solvents. The use of the relaxation agent chromium acetylacetonate, $Cr(acac)_3$, within these solvent systems was also evaluated. Results show that the optimal NMR solvent differs for each fluorinated analyte. $Cr(acac)_3$ was shown to have pronounced effects on the limits of detection of the analyte. Generally, the optimal sensitivity condition appears to be methanol-d_4/2M DBU in the presence of 4 mg/mL of $Cr(acac)_3$. The method was validated through spike and recovery for five fluoro acids from environmentally relevant waters. Results are presented for the analysis of TFA in Toronto rainwater, which ranged from <16 to 850 ng/L. The NMR results were confirmed by GC-MS selected-ion monitoring of the fluoroanalide derivative.

The number of anthropogenically produced fluorinated compounds has increased dramatically over the past few years. For example, the sales of fluoropolymers were projected to rise from $1.35 to $1.76 billion dollars over the past 5 years.[1] Since the Montreal protocol of 1987, which called for a worldwide reduction of chlorofluorocarbons (CFCs), the use of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) has become more prevalent. Both HCFCs and HFCs are more "ozone friendly" because they undergo tropospheric oxidative degradation processes, which are believed to be the major sink for these compounds.[2]

Much of the degradation of fluoroorganics in the atmosphere has yet to be investigated; however, it is known that HCFCs 123 and 124, along with HFC 134a, degrade to produce TFA.[3−5] A large number of studies have shown TFA to be ubiquitous in surface and rainwaters, ranging in concentration from 40 to 630 ng/L.[6] It has been observed that TFA concentrations were 4−13 times higher in terminal lake systems, suggesting that TFA may accumulate over time.[7] More recently, chlorodifluoroacetic acid has also been observed in Ontario rainwaters, using GC-MS in selected-ion mode (SIM).[8] Although not fully established, it is believed that the primary source of this acid is through the degradation of HCFC-142b and CFC-113. It has been suggested that the combustion of fluorinated polymers may also lead to the production of TFA.[9] Other fluorinated acids have also been detected in aqueous environments, including monofluoroacetic acid[10] and the trifluoromethylated acids, which are produced through the degradation of bifenthrin and tefluthrin.[11−13]

Several methods exist for the measurement of TFA, such as GC-ECD or ion chromatography.[14−17] These methods generally require arduous concentration steps, the use of deleterious derivatizing agents, or are only appropriate for TFA. In this study, a novel method for the detection of fluorinated acids using ^{19}F

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NMR was developed to avoid these impediments. ^{19}F NMR has been previously used to investigate the production of TFA from the metabolism of 1,1,1,2-tetrafluoroethane,[18] to measure TFA cell membrane potential,[19] and to monitor the uptake of TFA in stems and leaves of the plant *Lycopersicon esculentum*.[20] The use of SAX extraction has been employed by several groups for the concentration of haloacetic acids.[21,22] These methods typically involve elution of TFA under strongly acidic conditions and esterification with a small amount of alcohol to yield a suitably volatile derivative for GC analysis. The presence of species competing for active sites on the SAX column can often lead to reduced recoveries in the analyte. [23] These species include sulfate and DOC, which can be successfully removed using IC-Ba and C-18 cartridges, respectively. Our objective was to remove deleterious sample-cleanup steps, to have the analyte in an organic solvent system that would allow direct measurement, and to have a method of detection and quantification of the fluoro acids irrespective of the plethora of other chemicals present in the rainwater samples. Because of the limited quantity of fluorinated compounds observed in rainwater, it was decided that a method which was specific to only fluorine and transparent to all other compounds should be employed.

^{19}F NMR spectroscopy has a large spectral window associated with it. Typically organofluorine nuclei lie within a window of 300 ppm, resulting in a small probability of peak overlap between molecules. Furthermore, the spin $^1/_2$ ^{19}F isotope is 100% abundant and has a sensitivity which is 81% of a ^{1}H nucleus. The technique can be used for spectral identification of an analyte and for quantification, when an internal standard of known concentration is included.[24−26] One drawback of the NMR technique is that, relative to other techniques, it is an inherently low sensitivity form of spectroscopy as a result of a small population difference between ground and excited states. Thus, for the low concentrations of fluorinated acids seen in the aqueous environment, key factors influencing the sensitivity of the experiment must be optimized. One of the parameters which is routinely open to the spectroscopist for optimizing sensitivity is the recycling delay time (D1) which is related to the spin lattice relaxation time (T1) of the nuclei. Prior to the measurement of the T1 time, the exact 90° pulse must be established. The optimal spectrometer conditions will vary depending on the specific analyte. A precise measurement of the T1 duration allows for the maximum number of transients to be obtained in a given time. The T1 relaxation time for chemically different fluorines is dependent upon such factors as the solvent, temperature, and the presence of paramagnetic materials in the solution. Through the purposeful inclusion of a paramagnetic material, such as $Cr(acac)_3$, within the sample, relaxation times can be reduced.[27] However, this can be to the detriment of observed line widths. By optimizing each of these parameters a maximum signal-to-noise ratio can be established. Since the overall relaxation time is dependent upon a multivariant system, predicting the optimal conditions for an analyte becomes a complex operation. Mapping out the effect of each of these parameters for a suite of compounds provides a useful tool for predicting a starting point for a new target analyte. The apparent sensitivity of the NMR experiment can be further enhanced by post free-induction decay (FID) manipulations. An example of this is the mathematical manipulation by the multiplication of the FID with an exponential factor.

Here we report the development and evaluation of ^{19}F NMR spectroscopy for the analysis of fluorinated acids at environmentally significant concentrations and its application to measuring TFA in rainwater samples.

Table 1. Comparison of T1 Relaxation Times (s) for Seven Fluorinated Compounds in the Solvents Dimethyl Sulfoxide, Acetone, Chloroform, and Methanol

DMSO							
$[Cr(acac)_3]$	MFA	DFA	TFA	CDFA	TEF	HFB	TFMAA
				T_1 Relaxation Time[a]			
0	2.97	1.37	1.73	2.16	0.64	1.56	1.04
1	0.72	0.51	0.59	1.21	0.44	0.45	0.38
2	0.31	0.27	0.32	0.50	0.23	0.30	0.19
4	0.18	0.15	0.19	0.38	0.14	0.21	0.12
line width[b]	8.50	10.16	9.12	10.53	15.55	10.36	15.72
Acetone							
$[Cr(acac)_3]$	MFA	DFA	TFA	CDFA	TEF	HFB	TFMAA
				T_1 Relaxation Time			
0	1.51	2.05	1.27	1.71	0.85	1.98	1.30
1	1.88	1.04	0.98	1.24	0.73	1.25	0.86
2	0.72	0.48	0.61	0.47	0.44	0.63	0.43
4	0.40	0.32	0.46	0.37	0.27	0.40	0.25
line width	8.50	8.49	6.96	8.57	9.91	7.17	10.00
Chloroform							
$[Cr(acac)_3]$	MFA	DFA	TFA	CDFA	TEF	HFB	TFMAA
				T_1 Relaxation Time			
0	1.49	1.18	1.49	1.21	0.90	2.23	1.51
1	N/A	0.58	0.66	0.71	0.43	0.70	0.49
2	N/A	0.51	0.41	0.55	0.28	0.52	0.28
4	N/A	0.19	0.23	0.31	0.21	0.34	0.16
line width	5.24	6.23	6.85	6.32	6.69	5.60	6.84
Methanol							
$[Cr(acac)_3]$	MFA	DFA	TFA	CDFA	TEF	HFB	TFMAA
				T_1 Relaxation Time			
0	1.51	2.05	1.27	1.71	0.85	1.98	1.30
1	0.73	1.49	0.59	0.77	0.67	0.87	0.44
2	0.68	0.53	0.34	0.41	0.47	0.57	0.25
4	0.22	0.35	0.13	0.36	0.26	0.34	0.15
line width	4.98	5.41	4.71	6.85	11.86	5.89	4.74

[a] T1 relaxation times are given for varied concentrations of the relaxation agent $Cr(acac)_3$. [b] The effect of $Cr(acac)_3$ on peak resolution (line width, Hz) is given for all of the compounds at a $Cr(acac)_3$ concentration of 4 mg/mL.

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Table 2. NMR Experiment Time Restraints as Based upon T1 Values, and MDL for Fluorinated Compounds in Methanol-d_4/2M DBU and 4 mg/mL $Cr(acac)_3$

compound	T1 (s)	total acquisition time (min)	MDL (ng/L)
MFA	0.220	100	84
DFA	0.353	120	66
TFA	0.134	60	16
CDFA	0.362	150	42
TEF	0.261	120	56
TFMAA	0.153	N/A[a]	N/A
HFB	0.335	N/A	N/A

[a] N/A = not applicable.

EXPERIMENTAL SECTION

Chemicals Used. Sodium monofluroacetate (MFA), difluoroacetic acid (DFA), chlorodifluoroacetic acid (CDFA), 4′-(trifluoromethoxy)acetanalide (TFMAA), hexafluorobenzene (HFB), $Cr(acac)_3$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) which were purchased from Aldrich Chemical Co. (Mississauga, Canada). Trifluoroacetic acid (TFA) was purchased from Caledon (Georgetown, Canada). 3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylic acid (TEF) was prepared through the hydrolysis of Tefluthrin, which was kindly given to us by Dr. Joel Coats. The NMR solvents used were chloroform-*d*, dimethyl-d_6 sulfoxide (DMSO), acetone-d_6 from Cambridge Isotope Laboratories, Inc. (Andover, MA), and methyl-d_4 alcohol from Isotech Inc. (Miamisburg, OH).

NMR Spectrometer Parameters. An overview of the generic parameters used in individual experiments is given in Tables 1 and 2. All spectra were obtained at 25 °C on a Varian Unity 500, 3-channel spectrometer operating at 470.297 MHz and equipped with a 5-mm Nalorac ^{19}F proton decoupling probe. Free induction decays (FID) were zero filled by making the Fourier number equal to twice the number of data points. Chemical shifts were recorded relative to $CFCl_3$ (0.000 ppm). For individual experiments, the operating parameters associated with the spectrometer can be found in the Supporting Information for this article.

SAX Extraction of Fluorinated Acids. For the analysis of aqueous environmental samples with low concentrations of the fluoro acids (<1 μg/L), a preconcentration step was employed.[24] Aqueous samples (≤ 1 L) were filtered using a 0.45 μm filter paper. They were then passed sequentially through a C-18 and an IC-Ba cartridge (Alltech, Geulph, Canada) and two 500-mg SAX columns (Varian, Mississauga, Canada). The SAX columns were centrifuged at 3400 rpm for 10 min, to remove any residual water, and then eluted using 800 μL of the deuterated solvent/2M DBU mixture. This solution was transferred to a 1-mL volumetric cylinder, which included 4 mg of $Cr(acac)_3$. To this was added 50 μL of the deuterated solvent containing the internal standards TFMAA and HFB. The solution was then diluted to the mark, using deuterated solvent, and sonicated until all of the $Cr(acac)_3$ had dissolved. The NMR spectra were recorded using the appropriate established parameters (in particular D1 = 5T1) for the analyte and the internal standards. The minimum D1 value was set to the maximum T1 for either the analyte or for the internal standard. External calibration was performed using standards of known concentration in both the analyte and the internal standard, in the same matrix as for the samples. Care was taken to ensure that all the NMR parameters were the same for the samples as they were for the standards.

Spin−Lattice Relaxation Time as a Function of Solvent. All T1 relaxation times were recorded using an inversion recovery method.[28] All samples were made using the following procedure. A stock solution of deuterated solvent (chloroform, methanol, DMSO, and acetone) containing 2 M DBU was prepared. This solution was degassed to remove as much molecular oxygen as possible for 5 min using a diffusion vacuum pump operating at −600.04 mmHg. One milligram of the analyte was dissolved in 1 mL of this solution in a 528-PP NMR tube (Willmad Glass Co., Buena, NJ). The 90° pulse was established for the fluorine nuclei and then the T1 time recorded. It should be noted that the minimal spectral window required for each analyte was used.

Spin−Lattice Relaxation Time as a Function of $Cr(acac)_3$ and Solvent. Separate deuterated solvent/2M DBU solutions containing 1, 2, and 4 mg/mL of $Cr(acac)_3$ were prepared. The solutions were then sonicated until the $Cr(acac)_3$ had completely dissolved. The seven fluorinated compounds were individually dissolved in four separate solvent mixtures, to avoid relaxation due to analyte interaction. Each of these experiments was repeated at the three $Cr(acac)_3$ concentrations. The T1 values for the fluorine were then recorded and compared.

Effect of $Cr(acac)_3$ on Peak Resolution. Solutions were prepared for all of the analytes (1 mg/mL) in the four solvent systems which were 4 mg/mL in $Cr(acac)_3$. The NMR spectra were then recorded and the peak width noted.

Optimal NMR Solvent for Spike and Recovery of Fluorinated Acids from Lake Huron Water and Toronto Rainwater. To establish the optimal NMR solvent for the extraction of the fluoro acids from the SAX column, all of the analytes were spiked into Lake Huron water (120 μg/L), passed through the SAX extraction procedure, and eluted with the four NMR solvents containing 2M DBU. The NMR spectra were then recorded using the appropriate parameters for the analyte in question, the internal standard pertaining to that analyte, and the solvent matrix. The experiment also provided information on the overall performance of the procedure. A spike and recovery of TFA from Toronto rainwater was also conducted at environmentally relevant concentrations. Five-hundred-milliliter aliquots of Toronto rainwater were spiked with 50, 250, and 300 ng/L of TFA ($n = 3$). The solutions were passed through the SAX system and analyzed by ^{19}F NMR. The concentration of TFA, which was naturally present in the rainwater sample used in the spike and recovery, was recorded and subtracted from the total concentration.

NMR Time limits and Determination of MDL. The S/N ratio for a peak in the NMR experiment increases with time as the $\sqrt{S/N}$. A limitation was therefore placed on the time frame of the NMR experiment depending on the analyte of interest. The time limit was set to 1 h for TFA, and the time limit for other analytes was based on their comparative relaxation times with TFA. For example, the T1 time for CDFA was found to be approximately twice that of TFA; therefore, CDFA acquisition times were 2 h. Employing these time constraints, the MDL for each of the analytes was established on the basis of the minimum

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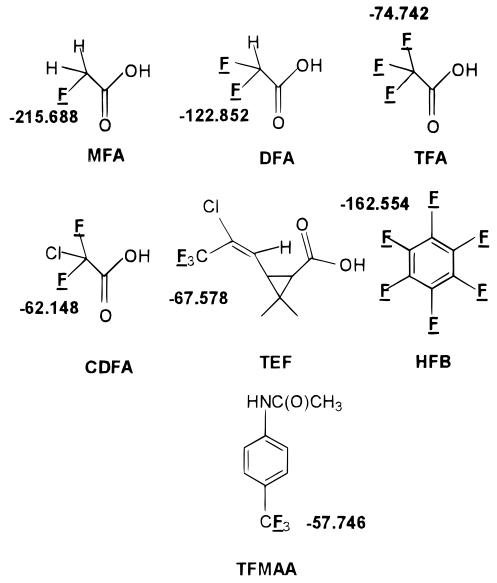

Figure 1. Chemical structures and acronyms of fluorinated acids used in ^{19}F NMR studies. The chemical shift of the fluorinated moiety is given in ppm, relative to $CFCl_3$ (0.000 ppm), in methanol-d_4/2M DBU. Chemical shifts of multiplets are given as the central line.

concentration that would allow a signal to be observed that was ≥3S/N.

Measurement of TFA in Toronto Rainwater using ^{19}F NMR. Toronto rainwater samples were collected on the roof of the Gauge Institute (University of Toronto, 223 College Street), a four story building, in downtown Toronto. Samples were collected using an automated (wet only) rain collector (MCI Company, Thornhill, Ontario). On an event basis, sample volumes ranged from 0.5−4 L. Nine sampling dates were used, spanning all four seasons. The SAX extraction and concentration method was applied to a 500-mL aliquot of the rainwater collected; SAX columns were eluted using the 2M DBU/methanol-d_4 solvent system. NMR samples were prepared with the inclusion of the internal standard TFMAA and 4 mg/mL of $Cr(acac)_3$. Calibration was performed using external standards that were matrix-matched. The NMR conditions were held constant for each of the samples and standards. The smallest possible spectral window and relaxation time that would allow quantitative detection of TFMAA and TFA was employed.

Measurement of TFA in Toronto Rainwater using GC-MS-SIM. Rainwaters were passed through glass microfiber filters (Whatman GF/C). To the aqueous phase was added ethyl acetate containing 2,4-difluoroaniline and dicyclohexycarbodiimide to produce the acid anilide of TFA as described by Scott and Alaee.[29] Analysis was performed on a gas chromatograph (HP Model 5890 Series II) interfaced to a quadrupole mass selective detector (HP Model 5971A) operating in single-ion mode and equipped with a 70 eV electron ionization source. GC separation was performed on a fused silica capillary column coated with cross-linked 5% phenyl methyl siloxane (HP-5MS, 30 m × 0.25 mm, film thickness 0.25 μm), using helium as a carrier gas. The injector temperature was 220 °C, and the initial oven temperature was 50 °C for 2 min, increasing at a rate of 5 °C min^{-1} to 250 °C. A procedural blank was run with each sample set.

RESULTS AND DISCUSSION

Spin−Lattice Relaxation Time as a Function of Solvent. The T1 relaxation time for a fluorine atom contained within a molecule can be affected by multiple parameters. Since the relaxation of the nuclei involves the transfer of excess energy to the surrounding lattice, one of these parameters is the deuterated NMR solvent. TEF had the overall shortest relaxation time of all seven fluorinated compounds investigated in all solvents (Table 1). The reduction or gain in T1 times for each analyte, in shifting from one solvent system to another, was not comparable. In other words, the optimal solvent for analysis for a given analyte was dependent on the nature of the analyte itself and not the solvent. Furthermore, the optimal solvent system for the analysis of MFA is acetone, while for DFA it is chloroform. The sensitivity of the NMR experiment for an analyte is dependent upon the total number of acquired transients, and the number of transients acquired is dependent upon the T1 relaxation time. It is apparent that, for an analysis that requires optimal spectrometer sensitivity, the choice of solvent is imperative and would have to be made after the careful screening of several solvents. It should also be noted that, for quantitative analysis, the time of the NMR experiment, and hence sensitivity, is restricted by the T1 relaxation time of the internal standard in that solvent when it is higher in value than the analyte.

Spin−Lattice Relaxation Time as a Function of $Cr(acac)_3$ and Solvent. The T1 relaxation times for each of the fluorinated compounds were measured as a function of the concentration of the relaxation agent $Cr(acac)_3$. Measurements were made for three different concentrations of $Cr(acac)_3$, for each of the compounds, in four different solvents (Table 1). The overall trend in the reduction of T1 for each compound is a $1/x$ function with increasing $Cr(acac)_3$ concentration, applicable for each of the solvents investigated. However, the value assigned to x differs for each compound and differs between solvents for that compound; the enhancement in T1 is not as pronounced for particular compounds. For example, the T1 relaxation time of MFA in acetone, in going from 1 to 2 mg/mL $Cr(acac)_3$, shows a decrease in T1 by a factor of 0.6, while under the same conditions the T1 of TFA is only decreased by a factor of 0.4. The sensitivity of all compounds investigated in the NMR experiment can be enhanced by the inclusion of $Cr(acac)_3$ in each solvent system, for which the optimal concentration is 4 mg/mL. All T1 measurements showed <1% standard deviation.

Effect of $Cr(acac)_3$ on Peak Resolution. Interference in the ^{19}F NMR experiment due to peak overlap may present a problem. This is especially true for analytes that are very similar in structure. In these cases, careful selection of the NMR solvent system must be made on the basis of lowest peak line width. $Cr(acac)_3$, along with the solvent, can have a marked effect on the resolution. It should be noted that the concentration, the NMR tube, and magnetic inhomogeneities can also have detrimental effects on the line width, and thus, every effort was made to minimize these problems. A comparison of the effect of $Cr(acac)_3$ on line width for each compound in the four solvent systems is given in Table 1. As can be seen, there is a general trend of increasing line widths with the following solvent series; DMSO > acetone > chloroform > methanol. This is, in part, due to the

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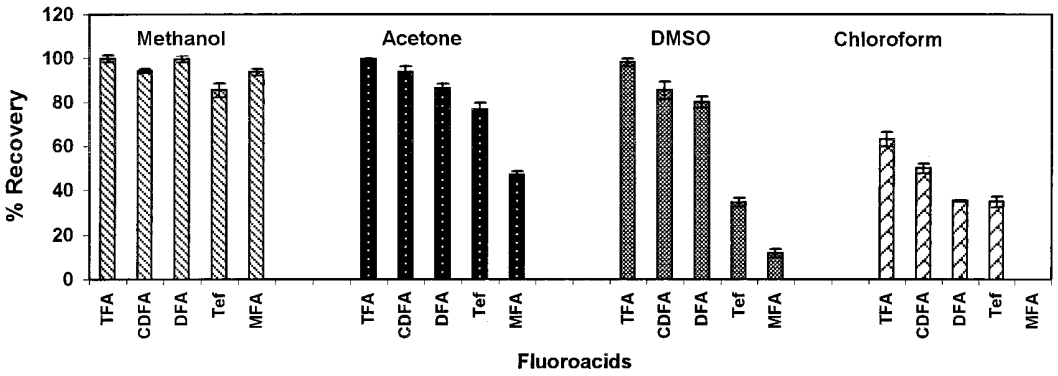

Figure 2. Spike and recovery of five fluorinated acids from Lake Huron waters. Optimization of NMR solvent for extraction of each of the acids from a SAX column was determined.

Table 3. Concentration of TFA in Toronto Rain Water; A Comparison of the Results Obtained by ^{19}F NMR and by GC-MS-SIM

date	[TFA][b] ^{19}F NMR	[TFA] GC-MS-SIM	rain volume[c] (approx)
June 11, 1998	635	N/A	0.5
July 17, 1998	74	99	2
Sept 8, 1998	80	83	2
Sept 16, 1998	185	200	2
Oct 1, 1998	850	810	2
Nov 11, 1998	ND	N/A	4
Jan 26, 1999	343	N/A	1
Feb 3, 1999	ND	N/A	4
May 20, 1999	149	N/A	1

[a] ND = not detected. N/A = not applicable. [b] The concentrations are expressed in parts per trillion (ng/L). [c] Volumes are in liters.

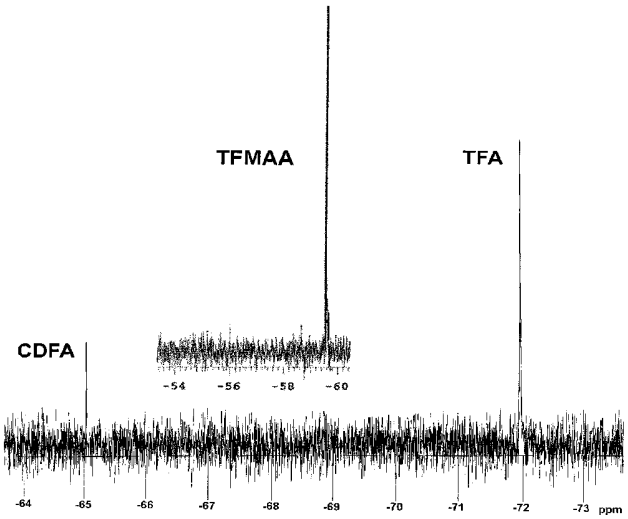

Figure 3. ^{19}F NMR spectra showing TFA relative to the internal standard TFMAA, shown in the inset. The measured concentration of TFA was 343 ng/L. The results are obtained from Toronto rainwater, dated January 26, 1999. The fluoroacetic acid CDFA, also observed in rainwater, is shown.

ability of the nuclei to transfer excess energy to the surrounding lattice. The most pronounced deviation from this is for TEF, which shows a similar trend excluding methanol. In general, the optimal solvent system for peak resolution is methanol-d_4/2M DBU.

NMR Time Limits and Determination of MDL. The method detection limit for each of the fluoro acids in methanol-d_4/2M DBU, for a defined total NMR acquisition time (based upon their T1 values), is shown in Table 2. The length of the NMR experiment required to obtain comparable sensitivity between analytes was quite variable. Furthermore, the sensitivity of the experiment was dependent upon the total number of equivalent fluorine atoms giving rise to the signal.

SAX Extraction of Fluorinated Acids. All five acids studied could be analyzed from the same sample due to their differing chemical shift values (Figure 1). The results for the spike and recovery of the five fluoro acids, MFA, DFA, TFA, CDFA, and TEF, from Lake Huron water are shown in Figure 2. The optimal solvent system for all the acids was methanol-d_4/2M DBU. The general order of solvent suitability for extraction is methanol > acetone > DMSO > chloroform. Quantitative recovery of all the acids was observed when methanol-d_4/2M DBU was used as the eluting solvent. Recoveries were 94.3 ± 6.2% (n = 8). Quantitative recovery of TFA can also be obtained using the acetone-d_6 and DMSO-d_6 solvent systems. The general order of recovery with respect to the acids is TFA > CDFA > DFA > TEF ≫ MFA. The elution of MFA was not observed in chloroform. It is believed that this may be due to a combination of the acid pK_a and the solvation power of the eluting solvent. DBU, being a soft base, would have a higher affinity toward soft acids; thus, MFA, being the hardest acid, would have the least affinity. It appears that the percentage recovery decreases as the pK_a decreases—MFA having the lowest recovery and TFA the largest. There is also a direct correlation between the percentage recovery and the polarity of the solvent. The mechanism for the elution of the acid, which is bound to the quaternary amine within the SAX stationary phase, may occur by complexation with the protonated form of DBU. This hypothesis is further supported by the solvent elution series, that is, DBU would be protonated to a smaller degree in chloroform than it would be in methanol. Furthermore, the methanol would thermodynamically support an ion pair such as analyte$^-$ $^+$DBU more effectively than chloroform would. Presumably the percentage recovery could be further enhanced for each of the analytes by increasing the concentration of the DBU. This would, however, result in a decrease in the ability to obtain magnetic homogeneity (shimming) because of a decrease in deuterated solvent concentration for the sample, ultimately resulting in a decrease in the sensitivity of the experiment. This method of elution and analysis of fluoro acids from SAX columns enhances

the currently available techniques,[21,22] as the analyte is contained within an organic matrix and further derivatization is not required.

Spike and recovery of TFA from Toronto Rainwater. The recovery of TFA from Toronto rainwater ($n = 3$) using the SAX method, employing methanol-d_4/2M DBU as the eluent, was 104.3 ± 6.2% for 50 ng/L, 100.9 ± 3.7% for 250 ng/L, and 100.7 ± 3.7% for 300 ng/L. These results indicate good accuracy and precision for the method compared with the currently available methods, which involve several additional steps.

Measurement TFA in Toronto Rainwater using ^{19}F NMR and GC-MS-SIM. The concentration of TFA was measured in Toronto rainwater using ^{19}F NMR. Four time points were also measured using GC-MS-SIM. As can be seen through comparison of the data (Table 3), the ^{19}F NMR data are in close agreement with results obtained from the accepted published procedure. A typical ^{19}F NMR spectrum is shown in Figure 3 indicating the presence of TFA and CDFA in Toronto rainwater. There are no indications of interferences observed. This results in short sample preparation times for the NMR.

The results show that there was considerable variance in the measured amount of TFA in Toronto rainfall (74−850 ng/L). These results suggest that the degradation of HCFCs 123 and 124, along with HFC 134a, is not solely responsible for the production of TFA. This is in accord with results for the concentration of CDFA in Toronto rainwater which shows an inverse relationship with the sample volume of the rain event.[8]

CONCLUSIONS

A method based upon SAX extraction and ^{19}F NMR has been developed which permits the determination of TFA and other fluorinated acids at nanogram per liter levels. Fluorinated acids can be concentrated from natural waters using SAX column chromatography at environmentally realistic concentrations. The acids can then be quantitatively eluted using an appropriate NMR solvent in the presence of the strong organic base DBU. Given the large chemical shift range, all of the fluoroacids could be analyzed from the same sample. The choice of NMR solvent used can have a significant effect on the sensitivity of the NMR experiment. The inclusion of $Cr(acac)_3$ in the NMR solvent allows the sensitivity to be increased by as much as 80%. Of the four solvents used in the present study, methanol was the optimal solvent for elution and for peak resolution in the presence of $Cr(acac)_3$. The limits for quantification using ^{19}F NMR spectroscopy are strongly influenced by the T1 relaxation times of the nuclei, which, in turn, are affected by the choice of solvent matrix.

SUPPORTING INFORMATION AVAILABLE

Overview of NMR parameters used in solvent and $Cr(acac)_3$T1 experiments and the spike and recovery experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

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