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Determination of Trifluoroacetate by Ion Chromatography for Snow and Ice Analysis

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ABSTRACT

Trifluoroacetic acid (TFA) is a product of the atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). HCFCs and HFCs are widely used substitutes for chlorofluorocarbons (CFCs) that have been found to contribute to the loss of stratospheric ozone. Deposits of TFA with precipitation (rain and snow) can lead to its presence and accumulation in the aquatic and cryosphere environments, with unknown long-term environmental consequences. Investigation on TFA impact and its fate in the environment requires sensitive, accurate, and fast analytical methods. The determination of trace concentrations of TFA using the technique of ion chromatography (IC) is investigated in this study, with a potential application of the technique for TFA in Antarctic snow samples. It was found that the IC detection and quantification of TFA as an anion is free from chromatographic interference by major anions in Antarctic snow. The detection limit using a procedure without preconcentration was found to be 0.2 ppb TFA, while the limit of quantification is as low as 0.5 ppb. Keywords: trifluoroacetic acid, trifluoroacetate, ion chromatography, snow, ice.

INTRODUCTION

The stratosphere is a part of the atmosphere at the altitude range of approximately 12 to 50 km. The stratosphere contains a relatively large amount of ozone (O_3) that absorbs short-wavelength ultra-violet (UV-B) radiation from the sun. The high-energy UV-B photons, if allowed to reach Earth's surface, can damage biological molecules and cells in plants and animals (1). Therefore the stratospheric ozone layer provides important protection for life on Earth.

The emission and atmospheric accumulation of chlorofluorocarbons (CFCs), a class of compounds commonly used as propellants in aerosols and refrigeration gases prior to the 1990s, has been found to cause severe losses of stratospheric O_3 , especially O_3 over Antarctica during the austral spring (i.e., the Antarctica ozone hole). CFC molecules are chemically inert under ground level atmospheric conditions, a property that made CFCs popular in commercial products that required the use of stable gases. Due to the inert

chemistry of the CFC molecules, once in the atmosphere, they are able to resist chemical reactions that would normally remove pollutants from the atmosphere. The stability of these molecules results in long atmospheric residence times and allows significant amounts to drift into the stratosphere. The high-energy solar radiation in the stratosphere breaks down the CFC molecule and releases chlorine radicals that serve as a catalyst in reactions that destroy O₃ molecules. As a result of the chlorine-catalyzed destruction of ozone, a severe loss of the ozone layer has been observed over the poles of the earth.

Efforts to stop the destruction of the ozone layer have led to a ban on CFCs and the introduction of substitutes such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). HCFCs and HFCs were designed to break down in the troposphere (0-12 km), so that they do not pose a threat to the stratosphere.

The long-term effect of HCFCs and HFCs on the environment as a result of their degradation is relatively unknown. One of the products from the degradation of HCFCs and HFCs, trifluoroacetic acid (TFA), is of particular concern because it tends to accumulate in the environment. The majority of TFA found in the environment is formed as a product of the atmospheric degradation of HCFCs and HFCs (2).

The CFC substitutes, HCFC-134a, HCFC-123 and HCFC-124, are considered to be the primary source of TFA. One of the products from the initial degradation of these compounds is trifluoroacetyl fluoride (CF₃COF) which is taken up by clouds, subsequently hydrolyzed to TFA (3) and deposited on Earth's surface through precipitation. TFA is a very persistent chemical in aqueous environment and may have the potential to accumulate in lakes, rivers, and in glaciers and ice sheets (4). The accumulation of TFA in these ecosystems is an environmental concern because of the unknown long-term consequences. The amount of TFA occurring naturally in the environment is known to be very small so most TFA found in the environment is likely to be man-made. There is evidence suggesting that >95% of TFA found in surface water comes from precipitation (4).

TFA concentration in precipitation was found to be very low (5). However, TFA concentrations in surface water in Europe were found to be significantly higher (4). This may indicate that surface waters could be accumulating TFA and other degradation products of air pollutants such as HCFCs and HFCs. Industrial operations are thought to be another source of environmental TFA, because high concentration levels were reported in river waters near industrialized areas (2).

The current method for the determination of TFA in precipitation and surface waters relies on the technique of gas chromatography and mass spectrometry (GC-MS). GC-MS requires a water soluble analyte to be converted to a volatile compound, usually through derivatization, followed by extraction using an organic solvent prior to quantitative determination by GC-MS (2). The technique is usually very sensitive but requires a complex sample preparation process that results in long analysis time. The typical efficiency of TFA extraction for GC-MS determination is found to be 92 ±3% (2).

The objective of this work is to determine whether TFA can be measured using an alternative technique, ion chromatography (IC) and to investigate if IC would be suitable to measure TFA in Antarctic snow and ice core samples where the concentration of TFA is believed to be very low. Since only ionic analytes are detectable in IC, TFA must be a

relatively strong acid (i.e., with a large acid dissociation constant, K_a), in order to be detected by IC. The K_a of trichloroacetic acid, a structural analog of TFA, is 3.2×10^{-1} . Since TFA is a stronger acid than trichloroacetic acid because of the higher electronegativity of fluorine than chlorine, this suggests that TFA is nearly a strong acid and would be expected to completely ionize in aqueous solutions to TFA⁻ (6).

Ion chromatography is well suited to the analytical measurement of ionic analytes in aqueous solutions at sub-ppb concentrations without preconcentration. Using ion chromatography for TFA determination would allow for very minimal sample preparation and consequently shorten the analysis time of GC/MS. This technique has been used for the detection of low concentrations of commonly found anions (Cl⁻, NO₃⁻, SO₄²⁻, formate and acetate) in Antarctic snow and ice core samples.

This study is aimed at determining the ability of IC to quantitatively measure TFA, with the ultimate goal of applying this technique to the determination of low concentrations of TFA in Antarctic snow and ice core samples. The analysis of Antarctic snow and ice samples for TFA may yield insight into the annual amount of TFA being deposited on the Earth's surface and a timeline of the trend in TFA deposition.

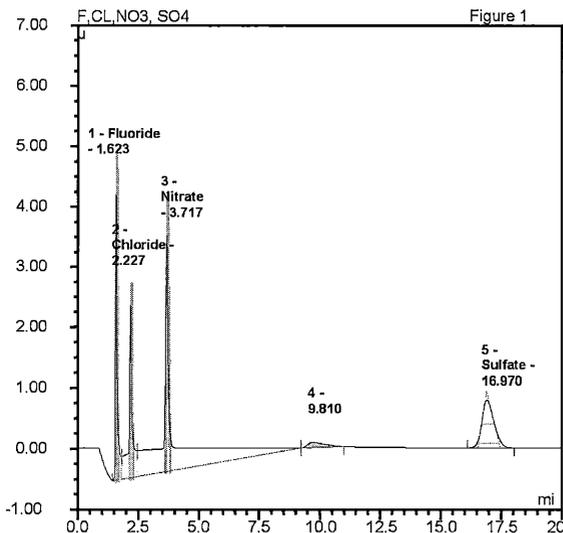
METHODS

A Dionex (Sunnyvale, California) DX600 ion chromatograph with an AS11 column with suppressed conductivity detection was used for the analysis of TFA⁻ and other common anions. A Dionex AS40 autosampler with 5 mL plastic vials was used to hold samples and transfer them to a 500 μ L sample injection loop. The relatively large 500 μ L injection volume was used to obtain sufficiently large peaks for very low (a few ppb) concentrations of TFA⁻ and other common anions. A dilute solution of NaOH was used as the eluent at a flow rate of 1.00 mL/min for the isocratic elution of the anions. The eluent and all calibration standards were prepared using deionized water with resistivity > 18 M Ω cm at 25 $^{\circ}$ C. The concentrations of anions measured in this study are very low and susceptible to contamination. As a precaution against contamination, all glassware and other containers were thoroughly cleaned before being used.

Standard solutions of TFA were prepared from concentrated (99%) TFA, supplied by Aldrich Chemicals. An initial solution of 1000 ppm TFA was made by volumetrically diluting the concentrated TFA and then storing in 100 mL plastic containers that had been thoroughly washed with deionized water. Further dilutions were made from this stock solution to prepare test samples and calibration standards. For example, a test solution of 250 ppb TFA was prepared to determine and optimize the retention time of TFA⁻ vs. other common anions. A typical calibration curve for TFA was created using a blank and four standards at 0.5, 1.5, 2.5, and 5 ppb. All calibration standards were freshly prepared for each day of analysis. The common anions that could interfere with the TFA⁻ peak in a chromatogram include F⁻, Cl⁻, NO₃⁻ and SO₄²⁻. Standard 1000 ppm solutions of these anions were prepared and stored in 1000 mL plastic containers. Solutions of individual anions and a mixed standard containing F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ were analyzed separately to determine the retention time of each anion. The strength of the eluent or

NaOH concentration was then adjusted to optimize chromatographic separation of the anions and to avoid any overlap between peaks of the four anions and the TFA peak.

To investigate a pre-concentration technique to lower the TFA detection limit, standard solutions of 0.1 to 1.0 ppb TFA⁻ were prepared in clean 1 L volumetric flasks and transferred to clean 1 L glass beakers. The solutions were then heated on a hot plate



and allowed to evaporate without boiling. The evaporation was done in a Laminar flow hood to ensure that the laboratory air would not contaminate the solutions. The volume of each solution was first reduced to about 25 mL and then transferred quantitatively into a clean 50 mL beaker which was heated again to reduce the volume to less than 10 mL. At this point, the solution was immediately transferred to an autosampler vial and analyzed using the IC.

Figure 1. Chromatogram of 37.5 ppb F⁻ and Cl⁻ and 150 ppb NO₃⁻ and SO₄²⁻.

RESULTS AND DISCUSSION

An initial eluent solution of 7 mM NaOH eluded the chloride on the shoulder of the negative peak (water dip), making it difficult to accurately measure the concentration of chloride. The eluent strength was gradually weakened to delay the elution of chloride until its retention time was approximately 3 minutes, where it would be separated from the water dip. This occurred when the eluent strength was about 3 mM. The retention time of TFA⁻ was found to be in the range of 3.9–4.1 minutes using a 3 mM NaOH eluent.

The retention times of common anions found in snow and ice samples were determined to ensure no peak overlap would occur involving the TFA⁻ peak. Peak overlap must be prevented so that each peak represents only one anion and therefore can be measured separately and quantitatively. Figure 1 shows a chromatogram of a test solution to find the retention times of F⁻, Cl⁻, NO₃⁻, and SO₄²⁻ and to determine the proximity of their peaks to each other and the TFA⁻ peak shown in Figure 2 using the 3 mM NaOH eluent. The F⁻ and SO₄²⁻ peaks elude before the Cl⁻ peak and after the NO₃⁻ peak respectively and therefore posed no threat to overlap with the TFA⁻ peak.

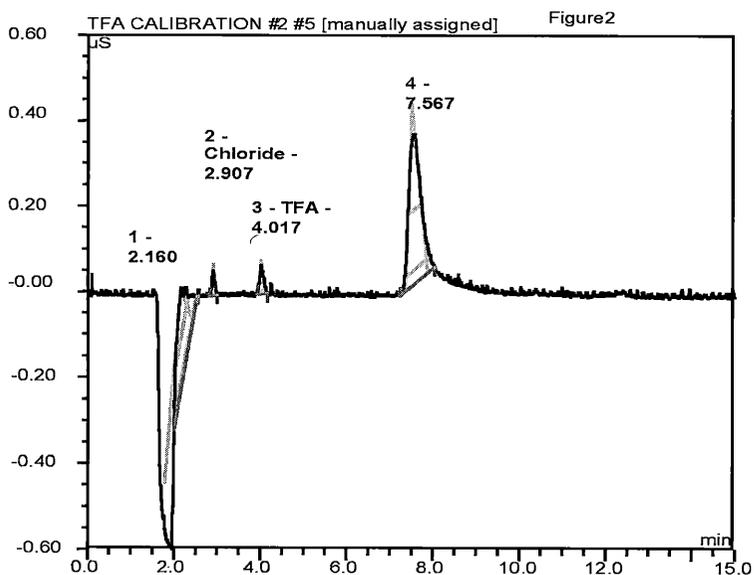


Figure 2. Chromatogram of 6 ppb TFA⁻ with retention time of 4.017 minutes.

The retention time for TFA⁻ is shown in Figure 2. The nitrate and chloride peaks were the most likely peaks from Figure 1 to overlap the TFA⁻ peak in Figure 2 due to the similar retention times. The chromatogram in Figure 3 shows NO₃⁻ and Cl⁻ concentrations of 200 ppb and 100 ppb respectively which are greater than the average NO₃⁻ and Cl⁻ concentrations of 100 and 30 ppb respectively, in Antarctic snow and ice samples (7,8). Figure 3 shows that even at extremely high NO₃⁻ and Cl⁻ concentrations the peaks do not overlap the TFA⁻ peak.

The TFA calibration curve shown in Figure 4 was used to determine the detection limit of the IC for TFA⁻. The calibration curve is composed of TFA concentrations of 0.5, 1.5, 2.5, and 5 ppb and shows a correlation coefficient of 0.9998. The detection limit is defined as the TFA concentration that gives a peak height 3 times average noise level of the chromatogram and is the lowest detectable concentration of the analyte. The noise level is determined by taking an average of the heights of the random peaks in the baseline.

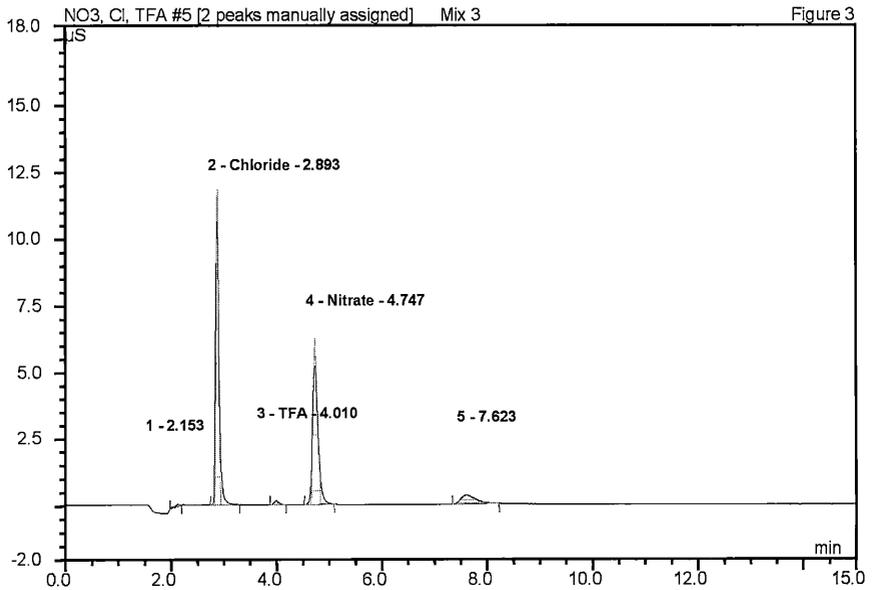


Figure 3. Chromatogram showing retention times of analytes in a solution of 100 ppb chloride, 10 ppb TFA⁻ and 200 ppb NO₃⁻.

Using the above approach and an average baseline noise level of 0.001 μS , the detection limit of IC for TFA⁻ was determined to be 0.2 ppb. The limit of quantification of IC for TFA⁻ was 0.5 ppb, which is the lowest concentration of TFA⁻ that can be accurately quantitatively measured.

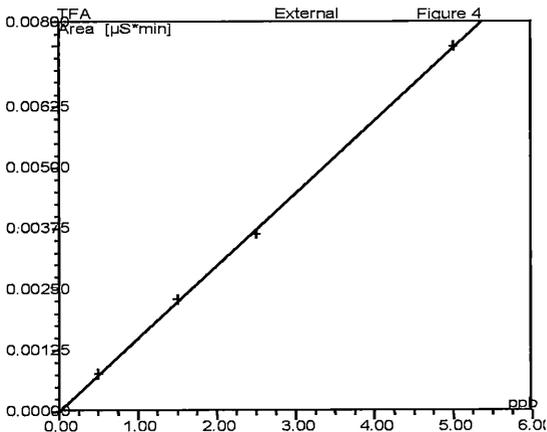


Figure 4. TFA⁻ calibration curve of 0.5, 1.5, 2.5 and 5.0 ppb.

The analysis of TFA by GC-MS on Antarctic snow by Von Sydow et al. detected a mean TFA concentration of 0.04 ppb or 40 ppt in layers that were formed in the 19th century (9). That same study found that the concentration of TFA in individual rainfalls over Mace Head, Ireland varied from 2 to 92 ppt.

This detection limit of the IC method for TFA is not low enough to measure TFA in Antarctic snow and ice samples directly by ion chromatography because the expected TFA concentration is about 0.04 ppb (9).

The results from the pre-concentration investigation did not yield useful data. Due to high baseline noise resulting from the concentrated impurities in the evaporated solutions, it was impossible to quantify the TFA⁻ peak accurately. Estimates of the TFA⁻ peak concentration were much smaller than would be expected after concentrating the samples to one hundredth of the original volume. More work would be needed to find the cause of this problem or to determine whether the evaporation technique will be applicable to the TFA⁻ analysis on snow and ice samples.

CONCLUSION

The analysis of TFA through the use of ion chromatography found that it was possible to detect and accurately measure concentrations of TFA as low as 0.5 ppb with a detection limit of 0.2 ppb. Ion chromatography will offer less sample preparation and shorter analysis time than GC-MS. However, snow and ice samples will need to be pre-concentrated in order to measure the expected low concentrations of TFA. Ion chromatography would be a better technique (more accurate and faster) than GC-MS to measure TFA in surface waters and in snow and ice core samples where the concentrations of TFA are above 0.5 ppb.

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