ELSEVIER

Journal of Chromatography A, 921 (2001) 265–275

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

On-line, inlet-based trimethylsilyl derivatization for gas chromatography of mono- and dicarboxylic acids

Kenneth S. Docherty[a,b], Paul J. Ziemann[a,c,*]

[a]*Air Pollution Research Center, University of California, Riverside, CA 92521, USA*

[b]*Environmental Toxicology Graduate Program, University of California, Riverside, CA 92521, USA*

[c]*Department of Environmental Sciences and Environmental Toxicology Graduate Program, University of California, Riverside, CA 92521, USA*

Received 4 January 2001; received in revised form 2 April 2001; accepted 10 April 2001

Abstract

An on-line, inlet-based trimethylsilyl (TMS) derivatization technique was optimized and evaluated for quantitative analysis of mono- and dicarboxylic acids. The technique involves co-injection of sample and reagent followed by gas-phase formation of TMS derivatives and analysis by gas chromatography with flame ionization detection. Derivatization efficiencies were determined by comparing measured and theoretical effective carbon numbers and used to optimize the technique with respect to experimental parameters. For analysis of C_5–C_{17} monocarboxylic acids and C_2–C_{10} dicarboxylic acids under optimized conditions, average derivatization efficiencies were ≥94%, average measurement uncertainties were ≤5%, and detection limits were ~2 ng. The technique was applied to the analysis of carboxylic acids generated from the ozonolysis of cyclic alkenes in a smog chamber.

Keywords: Derivatization, GC; Carboxylic aids; Alkenes

1. Introduction

Atmospheric aerosols are of current interest due to their environmental and human health effects. Aerosols scatter and absorb radiation causing visibility degradation. They also act as cloud condensation nuclei, impacting the formation of clouds, and thereby influence global climate. In addition, particles affect atmospheric chemistry by providing surface area for heterogeneous chemical reactions. These effects depend on the chemical and physical properties of the aerosol.

The composition of ambient aerosol is a complex mixture of inorganic and organic compounds that depends on particle size. Fine particles, which are those with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$), are especially important in the above atmospheric phenomena [1], and are currently thought to be responsible for the majority of adverse health effects [2,3]. Organic particles in this size range are emitted directly from combustion sources and also result from gas-to-particle conversion of volatile organic compounds (VOCs) emitted from both anthropogenic and biogenic sources. These photochemical processes typically involve OH, O_3, or

*Corresponding author. Tel.: +1-909-787-5127; fax: +1-909-787-5004.

E-mail address: pziemann@ucrac1.ucr.edu (P.J. Ziemann).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)00864-0

NO_3 as an atmospheric oxidizing agent and can lead to the formation of semi-volatile, oxygenated compounds such as mono- and dicarboxylic acids. For example, smog chamber studies of reactions of O_3 with cyclic alkenes [4–6], including biogenic monoterpenes [7,8], have identified dicarboxylic acids among the aerosol products. Furthermore, vapor pressure estimates for the observed products of the monoterpene reactions have found those of dicarboxylic acids to be the lowest [7,8]. Consequently, it has been suggested that dicarboxylic acids are the major species controlling particle nucleation and growth from ozonolysis of monoterpenes [8].

Studies of ambient aerosol have shown dicarboxylic acids to be ubiquitous in the troposphere, although the precise routes of formation remain speculative. Their contribution to ambient aerosol has been measured in polluted urban areas [9–12] as well as remote arctic [13,14] and oceanic regions [15]. The reaction of unsaturated fatty acids of marine origin with O_3 has been proposed as a pathway for the production of dicarboxylic acids in clean, arctic environments [16]. Studies of dicarboxylic acids found in polluted urban areas have attributed their production to smog episodes and automobile exhaust [9,17]. Given the potential importance of carboxylic acids to the formation and growth of atmospheric particles, their accurate and efficient quantitation is crucial to the understanding of many aspects of particle chemistry.

The quantitative analysis of complex organic mixtures is routinely performed via gas chromatography (GC) techniques. However, many semi-volatile, polar organics are not amenable to GC due to the strong dependence of the technique on compound vapor pressure [7]. Additionally, there is evidence that the analysis of organic acids is complicated by an interaction of the acid moiety with the column matrix leading to enhanced column retention and low chromatographic resolution [18]. Due to these problems, the accurate analysis of mono- and dicarboxylic acids by GC requires the use of pre-column derivatization [19]. Derivatization is typically performed by alkylation or reaction of the organic acid with trimethylsilyl (TMS) reagents while silylation is often preferred due to its simplicity, the speed of reaction, and the low eluting temperatures of unreacted reagent [20].

Typical TMS procedures are performed off-line and in the liquid phase, thereby requiring additional sample processing and additional time for sample analysis. Off-line TMS procedures can also lead to experimental errors from sources such as loss of sample through evaporation and re-suspension steps, contamination of samples during work-up, and the interference of water in the reaction system, since TMS reagents and the resulting derivatives are extremely sensitive to the presence of water. On-line derivatization reduces these problems, decreases the amount of reagent required for derivatization, and increases the speed and efficiency with which the analysis can be performed. Automation is another potential benefit of on-line derivatization.

Several on-line derivatization schemes have been shown to be quantitative [20]. Some pseudo on-column techniques have been used in the analysis of ambient air samples. In one study, short-chain alcohols were collected in stainless steel containers and subjected to gas-phase silylation before GC analysis [21]. In another study, short-chain monocarboxylic acids were trapped on sodium hydroxide coated glass beads and silylated in situ, requiring only 20 min for complete derivatization [22]. More successful procedures for on-line derivatization have been developed for the analysis of biological samples. As early as 1976, a TMS reagent was co-injected into a flash heater injection port for the quantitative determination of morphine [23]. Gas-phase TMS was also used as a first step in a double injection derivatization procedure in the GC–flame ionization detection (FID) and GC–MS analysis of phenolalkylamines [24]. To the best of our knowledge, however, no procedure has been evaluated for on-line derivatization of dicarboxylic acids.

Recently, an on-line, inlet-based derivatization procedure utilizing a TMS reagent was developed to analyze fatty acid content in various food oils [25]. This technique involves the co-injection of analyte and reagent, followed by a gas-phase derivatization reaction in the injection port of a GC–MS system. The results of this work were reported to be consistent with previously published results using off-line derivatization. The derivatization of all fatty acids was assumed to proceed to completion due to the absence of underivatized analyte in the mass spectra. However, more convincing evidence is

necessary for the evaluation of a dicarboxylic acid derivatization technique, since interaction of underivatized acid groups with the column matrix can prevent compounds from reaching the mass spectrometer. A similar inlet-based derivatization technique has been used in the quantification of tebufelone and two metabolites from blood plasma by gas chromatography tandem mass spectrometry [26]. In this technique, plasma extracts were dissolved in an *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA)–pyridine (1:1) cocktail, which was then injected into a heated inlet where the hydroxyl and carboxyl moieties of the metabolites were instantly derivatized. An extensive, 8-month evaluation of this technique analyzed over 200 quality control samples and showed the assay to have no bias and relative standard deviations <10% in the quantification of each analyte.

As part of our research on gas-to-particle conversion of VOCs, we are interested in using GC techniques to characterize the photochemical formation and gas-particle partitioning of mono- and dicarboxylic acids. The potential for sample loss, contamination, and time consuming sample preparation detracted us from the use of off-line derivatization methods. Instead, we chose to optimize and evaluate on-line, inlet-based derivatization for quantitative analysis of these compounds. The derivatization efficiencies (DE) of individual acids were determined by comparing measured and theoretical FID effective carbon numbers (ECNs). DE values were then used to optimize the technique with respect to temperature, inlet hold time, and amount of derivatizing reagent. The optimized version of the method was then used to evaluate the efficacy of gas-phase TMS in the quantitative determination of mono- and dicarboxylic acids. As a demonstration, the technique was applied to the analysis of carboxylic acids generated from the ozonolysis of cyclic alkenes in a smog chamber.

2. Experimental

2.1. Chemicals

The following compounds were obtained from Aldrich (Milwaukee, WI, USA) and used without further purification: pentanoic acid (99+%), hexanoic acid (99.5%), heptanoic acid (99%), octanoic acid (99.5%), nonanoic acid (96%), decanoic acid (96%), tridecanoic acid (98%), tetradecanoic acid (95%), pentadecanoic acid (99+%), hexadecanoic acid (99%), heptadecanoic acid (98%), octadecanoic acid (99+%), oxalic acid (99+%), malonic acid (99%), succinic acid (99+%), glutaric acid (99%), adipic acid (99+%), pimelic acid (98%), suberic acid (98%), azelaic acid (98%), sebacic acid (99%), undecandioic acid (97%), cyclopentene (99.5%), cyclohexene (99%), cycloheptene (97%), and cyclooctene (95%), and *n*-hexadecane (99%). Optima grade ethyl acetate and cyclohexane were obtained from Fisher Scientific (Tustin, CA, USA). A dicarboxylic acid test solution was made in ethyl acetate and contained molar equivalents of C_{2-11} dicarboxylic acids and *n*-hexadecane as an internal reference. A similar test solution was prepared containing molar equivalents of C_{5-10} and C_{13-18} monocarboxylic acids as well as *n*-hexadecane internal reference. The size range of carboxylic acids studied in this work was determined by the limitations of the technique and instrumentation. Acids that elute at temperatures lower than unreacted TMS reagent (~55°C) and those that do not elute by 280°C, the upper temperature limit of the GC column, were not studied. Original solutions were diluted to a final concentration of 10 m*M*. Test solutions were used at this concentration while calibration solutions were prepared from this solution by serial dilution. Final concentrations of calibration solutions were 0.01, 0.05, 0.1, 0.2 and 0.5 m*M*. These solutions were used to generate calibration plots for quantitation of smog chamber reaction products. Calibration curves for all studied mono- and dicarboxylic acids were linear over the tested concentration ranges. BSTFA was purchased from Supelco (Bellefonte, PA, USA) and used as the TMS reagent in all analyses.

2.2. Equipment

A Hewlett-Packard (Palo Alto, CA, USA) 6890 GC system with an FID was used for on-line derivatization and quantitative analysis. The column used was a HP-1701 fused-silica capillary (30 m× 0.53 mm), with 1.0 μm film thickness. The GC was

modified by the addition of a 4P4T plug valve obtained from Nupro (Willoughby, CA, USA) in the carrier gas supply line in order to stop the gas flow and allow prolonged retention of injections in the inlet. A Hewlett-Packard 5890 GC system with a similar column and a 5971A mass-selective detector was used to verify the presence and identity of individual acids by mass spectrometry. Analytical methods and columns for both instruments were identical. A split/splitless injection inlet set at 220°C was used in splitless mode. An initial column temperature of 50°C was maintained for 8 min and was subsequently ramped at 10°C/min to a final temperature of 280°C. The FID and the GC–MS transfer line were maintained at 280°C.

2.3. Smog chamber ozonolysis of cyclic alkenes

Secondary organic aerosol was formed in a series of smog chamber experiments from reactions of O_3 with cyclopentene, cyclohexene, cycloheptene, and cyclooctene in humid air. Aerosol was generated by reacting 20 ppm (v/v) (ppmv) of each cyclic alkene with 13–19 ppmv O_3 in a 6800 l PFTE bag at room temperature (~23°C). The chamber was filled with clean, dry air [<5 ppbv hydrocarbons, ~0.1% relative humidity (RH)] from an Aadco pure air generator (Clearwater, FL, USA) and humidified to an RH of ~10% by adding water vapor. The RH was measured using a Vaisala HMP230 probe. In all experiments, 1000 ppmv of cyclohexane was added to scavenge OH radicals formed in the alkene–O_3 reaction [27]. The cyclic alkenes, water, and cyclohexane were added to the chamber by evaporating the heated liquids from a glass bulb into a clean air stream. Ozone was added by flowing clean air through a 5 l bulb containing ~2% O_3/O_2 from a Welsbach T-408 ozone generator. During all chemical additions a PFTE-coated fan was run to mix the chamber contents. For the O_3 concentrations used here the alkene–O_3 reaction was complete within a few minutes. Aerosol formed by homogeneous nucleation, usually a few minutes after adding O_3, and then continued to grow by vapor condensation. Post-reaction sampling commenced 45 min after addition of O_3. Chamber air was sampled through stainless steel tubing at a rate of 1 l min^{-1} into a 47 mm I.D. filter cartridge containing a Millipore (Bedford, MA, USA) Fluoropore 47 mm diameter filter with a 0.5 μm pore size. An Ace 25 ml midget bubbler obtained from Aldrich was filled with 10–15 ml ethyl acetate and placed immediately downstream of the filter in order to collect gas-phase components and to trap any compounds that may have evaporated from the filter. Post-reaction samples were collected for 30 min. Immediately after collection, the bubbler solvent volume was determined gravimetrically, filters were removed and suspended in 4 ml ethyl acetate for extraction of collected compounds, and both filter and bubbler samples were analyzed by on-line derivatization.

3. Results and discussion

Prior efforts in this laboratory to quantify carboxylic acids by GC–FID, in both standard solutions and in alkene–O_3 reaction products, without pre-column derivatization were unsuccessful. The results of these analyses often failed to indicate the presence of any acids in the solutions and, in the event that acids were detected, the results were highly variable. These results were attributed to the low vapor pressures of carboxylic acids and to interaction of these compounds with the column matrix, which prohibited the acids from reaching the detector. We sought a derivatization technique that was fairly rapid with a low eluting temperature of unreacted reagent and were, therefore, attracted to the use of trimethylsilylation reagents. However, the possibility of introducing artifacts into the analysis from a lengthy derivatization procedure and the need for fast quantitative results led us to consider the use of an on-line TMS derivatization procedure using the inlet of the GC to form the TMS derivatives. Fig. 1 demonstrates the efficacy of the on-line TMS procedure and also shows the nature of the difficulties inherent in the analysis of carboxylic acids. Fig. 1A is a GC–FID chromatogram of a 0.2 m*M* dicarboxylic acid test solution that was not subjected to on-line TMS derivatization. Fig. 1B is the same test solution subjected to our on-line TMS derivatization procedure. As these figures show, the underivatized dicarboxylic acids were not detected. The presence of the *n*-hexadecane internal reference (IR) in Fig. 1A verifies that the injected solution reached the

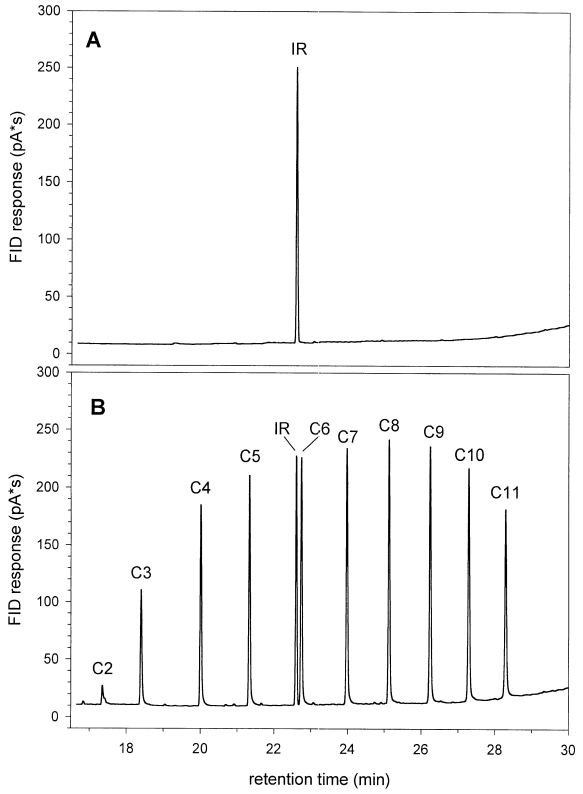

Fig. 1. Sample chromatograms of 0.2 m*M* dicarboxylic acid test solution in presence and absence of derivatizing reagent. (A) is from injection of the dicarboxylic acid test solution alone while (B) is from the co-injection of the same solution and BSTFA. The peak labeled IR is the internal reference compound, *n*-hexadecane.

column and that the detection failure is specific to the acids within the solution.

Injections of both carboxylic acid test solutions using on-line TMS derivatization–GC–MS confirm the identity of each peak as the TMS derivative of the corresponding carboxylic acid. A prominent M^+-15 peak characterized each derivatized carboxylic acid mass spectra, which is typical of TMS derivatives, and, for each acid, corresponded to fully derivatized compounds: singly-derivatized monocarboxylic acids and doubly-derivatized dicarboxylic acids. Similar to the GC–FID chromatograms, no mass spectral evidence was found for the presence of underivatized acids. We chose to use FID ECN calculations in order to evaluate the performance of this technique in achieving complete derivatization of a range of both mono- and dicarboxylic acids.

3.1. Effective carbon number (ECN)

The ECN concept was first introduced to explain observed FID responses obtained from a homologous series of organic compounds [28]. Since then, this concept has been used for column evaluation, for the calculation of response factors for compounds that cannot be obtained in pure form, and as a check on experimentally determined response factors for neat and derivatized compounds [29]. The ECN concept is used here to determine the efficiency of on-line derivatization by comparing the measured FID response of each derivatized mono- or dicarboxylic acid with the calculated theoretical response.

3.1.1. Experimental ECN calculation

The basis of the ECN concept is that maximum FID response is achieved for the detection of alkanes and diminishes as the oxygen content of an organic compound increases. Alkanes are, therefore, used as an internal reference compound due to predictable FID response. Ideally, an internal reference alkane should be equal or similar in carbon number to the non-alkane compound. However, the two critical qualifications of an internal reference are that it has a predictable response and that it not co-elute with the compound of interest. The latter requirement limits the choice for the internal reference compound. In this study, *n*-hexadecane was found to meet both criteria and was chosen as the single internal reference alkane. For ECN calculations, FID response to non-alkane compounds is measured relative to that of the internal reference alkane, for which the weight response factor is considered to be 1.

Detailed equations for calculating response factors and experimental ECN values are presented by Scanlon and Willis [29]. To simplify the calculations for our solutions, we used equi-molar concentrations of carboxylic acids and reference alkane. This simplifies the experimental ECN calculation to:

$$\mathrm{ECN}_{\mathrm{comp}} = (\text{FID area counts}_{\mathrm{comp}} / \text{FID area counts}_{\mathrm{ref}}) \cdot \mathrm{ECN}_{\mathrm{ref}}$$

where $\mathrm{ECN}_{\mathrm{ref}}$ is the theoretical ECN of the internal reference compound, in this case *n*-hexadecane, the calculation of which is described below.

3.1.2. Theoretical ECN calculation

There is general agreement regarding the contribution of different functional groups to the ECN of a compound [29]. The theoretical ECN is the sum of the contributions made by each carbon atom in the molecule with corrections made for the presence of specific functional groups. Normal alkyl carbons contribute 1.0 to the theoretical ECN while carbonyl or carboxyl carbons have zero contribution. Therefore, where n is the number of carbons in the compound, the theoretical ECN of an underivatized monocarboxylic acid is $n-1$, and that of an underivatized dicarboxylic acid is $n-2$, relative to its corresponding alkane. The theoretical ECN of derivatized compounds can also be calculated using experimentally determined contributions for the added functional groups. TMS groups have been found to have a contribution of 3.0 [28].

Using the theoretical ECN for derivatized compounds and the reference alkane, along with the experimental ECN for each acid, the efficiency of a particular derivatization technique can be evaluated using standard solutions. The calculated derivatization efficiency, DE, is

$$\mathrm{DE} = (\text{experimental ECN}_{\mathrm{comp}} / \text{theoretical ECN}_{\mathrm{comp}})$$

3.2. Optimization of derivatization parameters

This on-line derivatization procedure utilizes the GC inlet as a gas-phase reactor for TMS derivatization of carboxylic acids. The derivatization efficiency of the technique was optimized with respect to three parameters: the inlet temperature, the inlet-hold time for sample and reagent, and the amount of BSTFA co-injected with the sample. An average derivatization efficiency ($\mathrm{DE_{avg}}$) was used for the optimization procedure. $\mathrm{DE_{avg}}$ was determined at a particular parameter setting by calculating each compound's experimental ECN value and then averaging over the entire homologous series. Using $\mathrm{DE_{avg}}$ ensured that each parameter setting in the final procedure would produce a maximum response over the entire range of acids and would not weight the response from any one subset. Efficiency maxima were obtained by varying one parameter at a time while monitoring the effect on $\mathrm{DE_{avg}}$.

3.2.1. Inlet temperature

The optimal inlet temperature was determined by injecting test solutions at inlet temperatures ranging from 160 to 260°C while co-injecting excess BSTFA. The in-line toggle valve was not used and therefore the inlet hold time was a minimum. The minimum hold time was used in order to get a true baseline of injector temperature effect. Fig. 2 shows the effect of inlet temperature on the $\mathrm{DE_{avg}}$ of the dicarboxylic acid series. The optimal temperature was determined to be 220°C, with a slight decrease in efficiency at lower and higher temperatures.

3.2.2. Inlet hold time

The effect of inlet hold time on the derivatization efficiency was determined by placing a Nupro plug valve in the carrier-gas supply line, which allowed the gas flow to be shut off temporarily. The reagent and sample were co-injected when this valve was closed and the inlet pressure was zero. In this manner, the reaction mixture could be held above the column for any length of time ≤ 1 min. After the desired period of time had elapsed, the valve was opened and normal inlet pressure was restored in under 5 s. During characterization, the inlet hold time was varied from 0 to 40 s while the inlet was maintained at 220°C and excess BSTFA was injected. As Fig. 3 shows, there is only a slight variation in $\mathrm{DE_{avg}}$ within this time range. Because an

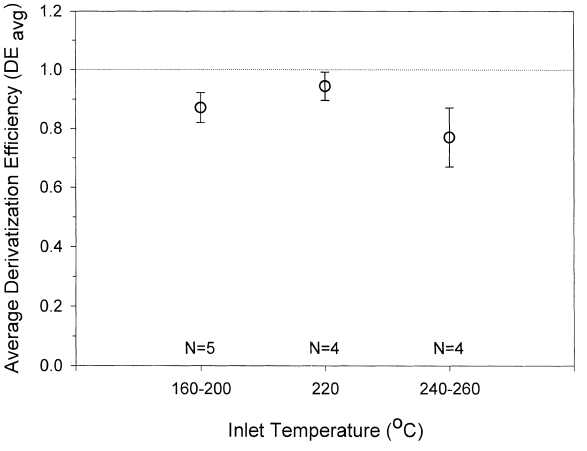

Fig. 2. Effect of inlet temperature on average derivatization efficiency ($\mathrm{DE_{avg}}$) for $\mathrm{C_2}$–$\mathrm{C_{11}}$ dicarboxylic acids. Error bars represent one standard deviation of $\mathrm{DE_{avg}}$.

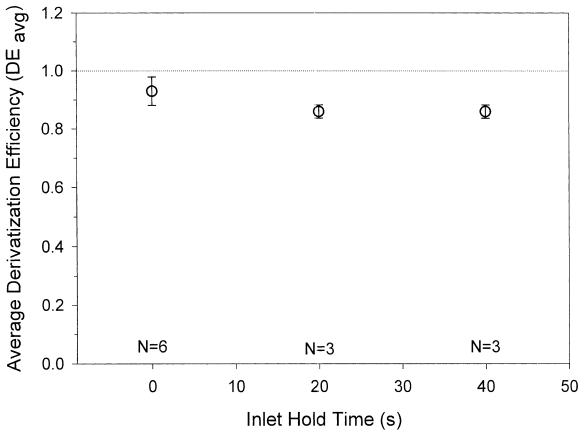

Fig. 3. Effect of inlet hold time on average derivatization efficiency (DE_{avg}) for C_2–C_{11} dicarboxylic acids. Error bars represent one standard deviation of DE_{avg}.

increase in reaction time did not improve the on-line DE, our final procedure did not employ an inlet hold time.

3.2.3. Amount of reagent co-injected with sample

In order to determine the effect of BSTFA:sample ratio on DE_{avg}, different ratios of BSTFA:sample were co-injected while the inlet temperature was maintained at 220°C and the hold time was constant at 0 s. Molar ratios were varied from 0:1 to 10:1 BSTFA:–C(O)OH. The results are shown in Fig. 4. The BSTFA derivatization of an acidic functional group has 1:1 stoichiometry. The derivatization efficiency is ~80% at this ratio, and does not reach a maximum until BSTFA:–C(O)OH≥2:1. This may be due to water contamination in the reaction system or test solutions. However, for a 180 m*M* –C(O)OH solution (i.e., 10 m*M* for each dicarboxylic acid×9 acids×2 –C(O)OH per acid), the volume of neat BSTFA required to be in excess of acidic functional groups remains in the sub-μl range.

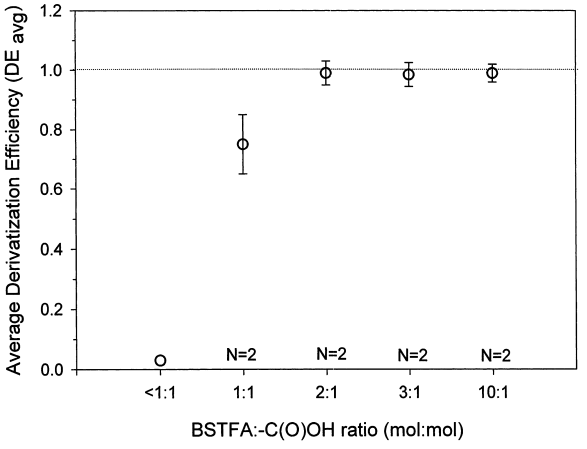

Fig. 4. Effect of BSTFA:–C(O)OH ratio on average derivatization efficiency (DE_{avg}) for C_2–C_{11} dicarboxylic acids. Error bars represent one standard deviation of DE_{avg}.

The optimized parameters determined for this technique are therefore: inlet temperature = 220°C, inlet hold time = 0, and BSTFA:–C(O)OH≥2:1. It is possible that by investigating other regions of parameter space, additional sets of parameters could be found that give comparable performance. For example, it may be that some combination of lower inlet temperature and longer hold time would also give satisfactory performance. Such a mode could be useful, for instance, if one were trying to simultaneously analyze carboxylic acids and thermally labile compounds present in the same sample. We have not performed such studies, and so the optimized parameters that work for our application should be viewed as possibly being only a local maximum in parameter space.

3.3. Individual compound ECN values and derivatization efficiencies

The experimental ECN values and corresponding DEs for each mono- and dicarboxylic acid were determined using the optimized parameters. Fig. 5 shows a plot of experimental and theoretical ECN values for monocarboxylic acids (Fig. 5A) and dicarboxylic acids (Fig. 5B). Fig. 6 is a plot of the corresponding DEs. The error bars in Fig. 5 represent one standard deviation of the experimental ECN values while those in Fig. 6 are one relative standard deviation (i.e., standard deviation/mean value) of DE.

The plots for mono- and dicarboxylic acids are similar, indicating similar derivatization behavior for the two classes of compounds. A notable trend is lower DE at the extremes of the measured size ranges. In the case of monocarboxylic acids, experimental efficiencies are greater than 90%, with the exception of pentanoic, heptadecanoic and octadecanoic acids, which had values of ~80%. The

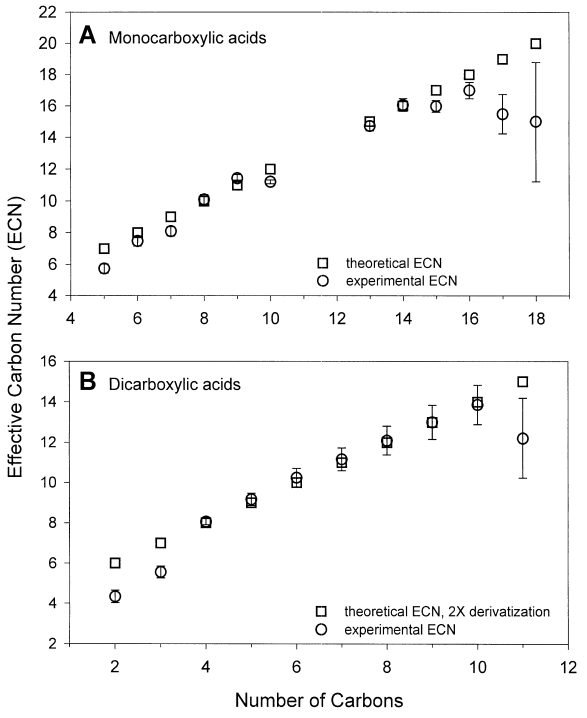

Fig. 5. Experimental ECN vs. theoretical ECN values for (A) C_5–C_{18} monocarboxylic acids and (B) C_2–C_{11} dicarboxylic acids, measured relative to *n*-hexadecane internal reference. Error bars represent one standard deviation of experimental ECN measurements.

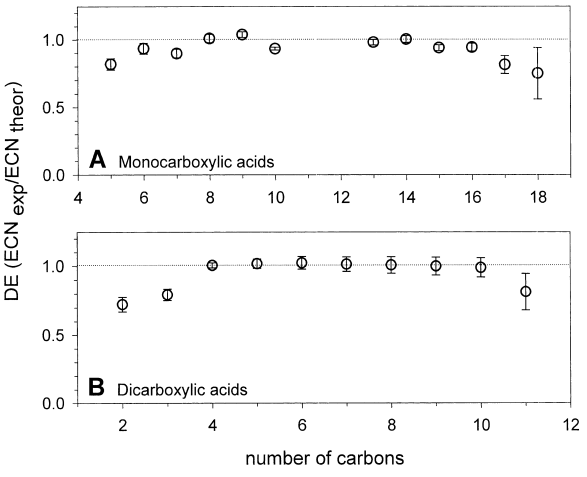

Fig. 6. Derivatization efficiencies (DEs) of (A) C_5–C_{18} monocarboxylic and (B) C_2–C_{11} dicarboxylic acids. Error bars represent one relative standard deviation of DE.

dicarboxylic acids also had efficiencies greater than 90%, with the exception of oxalic, malonic, and undecandioic acids, which were ~70–80%. Factors that could reduce derivatization efficiency include reduced stability of the smaller derivatized acids and lower volatility or steric effects in the larger acids. The precision of the ECN measurements, as represented by the standard deviation of absolute FID response, was approximately ±3% and ±5% for C_5–C_{17} mono- and C_2–C_{10} dicarboxylic acids, respectively. The precision decreased dramatically for monocarboxylic acids $>C_{17}$ and dicarboxylic acids $>C_{10}$, which is also the size where the DEs drop, indicating that the technique is not as suitable for acids of this size.

3.4. Detection limit and sampling requirements for laboratory and ambient aerosol analysis

Calibration plots for each acid were generated using serial dilutions of the 10 m*M* test solutions. The calibrations were used to quantify carboxylic acids produced in a series of cyclic alkene–O_3 reactions, as described below. Calibration plots were also used to determine the detection limit associated with the technique. The detection limit is taken to be the amount of acid necessary to achieve an FID response of 3×background, which, in this case, is ~3×10 pA s=30 pA s. From the calibration plots, this corresponds to a minimum solution concentration of ~0.01 m*M* for a compound with MW= 100 g mol^{-1}. Assuming a 2 μl injection volume, this corresponds to a required injection mass of ~2 ng. A demonstration of the stated detection limit is provided in Fig. 7, which shows chromatograms from the analysis of a 0.01 m*M* dicarboxylic acid solution in the presence and absence of co-injected BSTFA. This corresponds to an injected mass increasing from 1.8 ng for oxalic acid to 4.3 ng for undecandioic acid. Also shown is a chromatogram from the on-line derivatization of a 0.1 m*M* solution in order to clearly identify each acid peak. As this figure shows, with the exception of oxalic and malonic acids (C2 and C3), each acid can be differentiated from background at a 0.01 m*M* concentration. The detection limits for oxalic and malonic acids are significantly higher, at ~40 and ~20 ng, respectively.

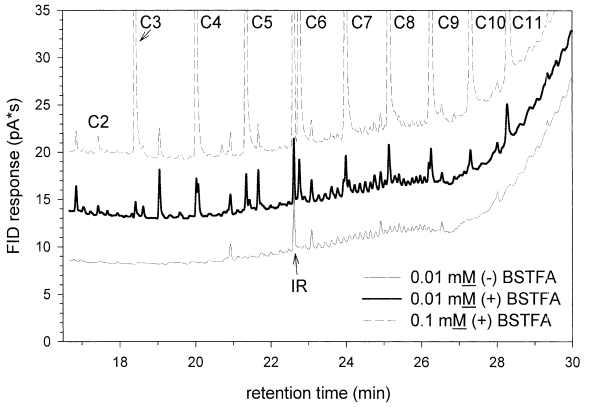

Fig. 7. Chromatograms of derivatized dicarboxylic acid standards near the detection limit. The two lower chromatograms are for a 0.01 m*M* dicarboxylic acid solution in the presence (+) and absence (−) of BSTFA. The upper chromatogram is a 0.1 m*M* test solution and was added to clearly identify each acid derivative. The derivatized acid chromatograms have been adjusted upward for clarity. The peak labeled IR is the internal reference compound, *n*-hexadecane.

The amount of aerosol needed for analysis of smog chamber compounds, which we collect into a final solution volume of 4 ml, depends on the organic reactant concentrations and the product yields. Typical reactant concentrations of 1 ppmv (~4000 μg m^{-3}) and aerosol product yields of a few percent [7,8] produce ~100 μg m^{-3} of an aerosol compound, requiring a chamber sample of ~100 l. Analysis of ambient air, which has organic acid aerosol concentrations of ~1–10 ng m^{-3} [1], requires sample volumes of ~10^3–10^4 m^3.

3.5. Yields of carboxylic acids from chamber reactions of O_3 with cyclic alkenes

The ozonolysis of cyclopentene, cyclohexene, cycloheptene, and cyclooctene was carried out in a series of smog chamber experiments to demonstrate the application of the on-line derivatization technique to the analysis of carboxylic acids. Since the products of these reactions can exist in both the gas and particle phases, both phases were sampled using a two-stage collection technique that has been employed previously to sample dual-phase cyanide compounds [30,31]. The technique uses a particle filter to trap aerosol immediately upstream of an all-glass bubbler that is used to trap gas-phase species. Although the efficiency of bubblers for collecting 0.1–2 μm diameter particles has been found to be as small as 20% [32,33], their use in conjunction with an upstream particle filter has several advantages when sampling semi-volatile products. The bubbler allows for liquid-phase extraction of gaseous compounds in a solvent suitable for injection into a GC system, thereby requiring no additional work-up before analysis. Using a filter to collect particles before the air stream enters the bubbler eliminates particle losses while retaining the ease of liquid-phase extraction. In addition, this technique minimizes evaporative losses of particle-associated compounds from the filter as placement of a bubbler downstream of the filter allows for their recovery.

The measured yields of dicarboxylic acids (as molar percentages of reacted alkene) from the chamber experiments are presented in Table 1. The values were determined using individual calibration curves for each carboxylic acid. The lowest reported yield is close to our ~2 ng detection limit. Fig. 8 shows sample chromatograms from the cyclooctene–O_3 reaction. Fig. 8A is the full chromatogram for the filter sample, and Fig. 8B is a magnified view of the C6–C8 region. As Fig. 8B shows, on-line derivatization of the filter sample provides adequate selectivity and sensitivity to quantify dicarboxylic acid contributions at the ~2 ng level, as was the case for $C_6H_{10}O_4$ in this chromatogram. The yields

Table 1
Total gas and particle yield of dicarboxylic acids from the ozonolysis of C_5–C_8 cyclic alkenes

Product	Dicarboxylic acid yields (mol%)[a]			
	Cyclo-pentene	Cyclo-hexene	Cyclo-heptene	Cyclo-octene
$C_2H_2O_4$	0	0	0	0
$C_3H_4O_4$	0	0	0	0
$C_4H_6O_4$	0.71	0	0.11	0.25
$C_5H_8O_4$	1.07	1.38	0.17	0.32
$C_6H_{10}O_4$	0	2.38	2.61	0.16
$C_7H_{12}O_4$	0	0	6.85	2.70
$C_8H_{14}O_4$	0	0	0	6.90
Total yield	1.78	3.76	9.74	10.30

[a] The value in each cell is calculated relative to the amount of reacted cyclic alkene.

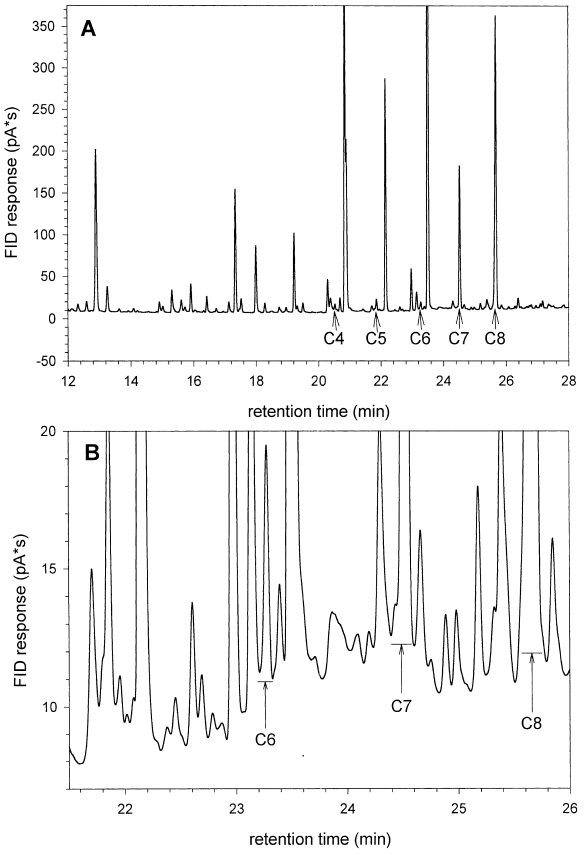

Fig. 8. Chromatograms from cyclooctene + O_3 reaction filter sample analyzed by on-line derivatization. (A) Full chromatogram with $C_8H_{14}O_4$, the largest contribution to dicarboxylic acid content, as the base peak. (B) Magnified view of the C_6–C_8 dicarboxylic acid region demonstrating the detection limit of the technique for analysis of the least abundant dicarboxylic acid, $C_6H_{10}O_4$.

observed here are on the order of a few percent and, for dicarboxylic acids other than oxalic and malonic acids, are similar to those measured previously using off-line derivatization with diazomethane [4,5] and BSTFA [6] to analyze products of cyclohexene [5,6] and cyclopentene and cycloheptene [4] ozonolysis. The relative amounts of individual dicarboxylic acids differ among the various studies and probably reflects differences in experimental conditions such as reactant concentrations and the presence or absence of an OH scavenger as well as sample collection, extraction, derivatization, and analysis procedures.

4. Conclusions

In this study we evaluated an on-line, gas-phase trimethylsilylation technique for the quantitative analysis of mono- and dicarboxylic acids by gas chromatography. The derivatization efficiency of the technique was optimized with respect to inlet temperature, inlet hold time, and the amount of TMS reagent used. The most important parameter is the amount of reagent, particularly for dicarboxylic acids, due to the stoichiometry of the derivatization reaction. However, inlet temperature and inlet hold time also have slight effects on efficiency. The optimized version of the technique provides a rapid, sensitive, accurate and precise means for quantifying carboxylic acids. Derivatization is nearly complete for a wide range of mono- (C_5–C_{17}) and dicarboxylic (C_2–C_{10}) acids, as indicated by experimental ECN that were 94% (±9%) and 95% (±12%), respectively, of theoretical ECN values. The measurements are highly reproducible, with an average precision of ±3% and ±5% for C_5–C_{17} mono- and C_2–C_{10} dicarboxylic acids, respectively. The detection limit is estimated to be ~2 ng for both mono- and dicarboxylic acids. The utility of the technique has been demonstrated for the analysis of secondary organic aerosol resulting from smog chamber reactions of O_3 with cyclopentene, cyclohexene, cycloheptene, and cyclooctene. The results are in general agreement with earlier studies that used off-line derivatization. This technique will be a valuable tool in our future studies of atmospheric aerosol chemistry.

Acknowledgements

This material is based upon work supported by the National Science Foundation under grant ATM-9816610. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation (NSF). We would also like to thank Dr. Janet Arey and Dr. Roger Atkinson of the Air Pollution Research Center for technical assistance regarding GC, GC–MS and ECN calculations and for their discussions relating to the subject of this research.

References

[1] J. Seinfeld, S. Pandis, Atmospheric Chemistry and Physics, Wiley, New York, 1998.
[2] J. Schwartz, D.W. Dockery, L.M. Neas, JA&WMA 46 (1996) 927.
[3] P. Pagano, T. De Zaiacomo, E. Scarcella, S. Bruni, M. Calamosca, Environ. Sci. Technol. 30 (1996) 3512.
[4] S. Hatakeyama, T. Tanonaka, J. Weng, H. Bandow, H. Takagi, H. Akimoto, Environ. Sci. Technol. 19 (1985) 935.
[5] S. Hatakeyama, M. Ohno, J. Weng, H. Takagi, H. Akimoto, Environ. Sci. Technol. 21 (1987) 52.
[6] M. Kalberer, J. Yu, D.R. Cocker, R.C. Flagan, J.H. Seinfeld, Environ. Sci. Technol. 34 (2000) 4894.
[7] J. Yu, D.R. Cocker III, R.J. Griffin, R.C. Flagan, J.H. Seinfeld, J. Atmos. Chem. 34 (1999) 207.
[8] S. Koch, R. Winterhalter, E. Uherek, A. Kolloff, P. Neeb, G.K. Moortgat, Atmos. Environ. 34 (2000) 4031.
[9] D. Grosjean, K. Van Cauwenberge, J.P. Schmid, P.E. Kelley, J. Pitts, Environ. Sci. Technol. 12 (1978) 313.
[10] H. Satsumabayashi, H. Kurita, Y. Yokouchi, H. Ueda, Atmos. Environ. Part A Gen. Top. 24 (1990) 1443.
[11] K. Kawamura, K. Ikushima, Environ. Sci. Technol. 27 (1993) 2227.
[12] K. Kawamura, S. Steinberg, I.R. Kaplan, Atmos. Environ. 30 (1996) 1035.
[13] K. Kawamura, H. Kasukabe, L.A. Barrie, Atmos. Environ. 30 (1996) 1709.
[14] V. Kerminen, K. Teinila, R. Hollamo, T. Makela, Atmos. Environ. 33 (1999) 2089.
[15] E.D. Baboukas, M. Kanakidou, N. Mihalopoulos, J. Geophys. Res. 105 (2000) 14459.
[16] K. Kawamura, R. Semere, Y. Imai, Y. Fujii, M. Hayashi, J. Geophys. Res. 101 (1996) 18721.
[17] K. Kawamura, I.R. Kaplan, Environ. Sci. Technol. 21 (1987) 105.
[18] V.G. Pastushenko, S.S. Krivolapov, J. Anal. Chem. USSR 44 (1989) 536.
[19] E. Dabek-Zlotorzynska, M. McGrath, Fresenius. J. Anal. Chem. 367 (2000) 507.
[20] R. Evershed, in: K. Blau, J. Halket (Eds.), Handbook of Derivatives for Chromatography, Wiley, New York, 1993, p. 53.
[21] M. Osman, H.H.J. Hill, M. Holdren, H. Westberg, J. Chromatogr. 186 (1979) 273.
[22] T. Aoyama, T. Yashiro, J. Chromatogr. 265 (1983) 57.
[23] K.E. Rasmussen, J. Chromatogr. 120 (1976) 491.
[24] A.S. Christophersen, E. Hovland, K.E. Rasmussen, J. Chromatogr. 234 (1982) 107.
[25] E.L. Nimz, S.L. Morgan, J. Chromatogr. Sci. 31 (1993) 145.
[26] L.M.R. Dobson, M.K. Dirr, B.L. Merkt, J. Mass Spec. 32 (1997) 1290.
[27] R. Atkinson, S.M. Aschmann, J. Arey, B. Shorees, J. Geophys. Res. 97 (1992) 6065.
[28] J.C. Sternberg, W.E. Gallaway, D.T.L. Jones, in: N. Brenner, J.E. Callen, M.D. Weiss (Eds.), Gas Chromatography, Academic Press, New York, 1962, p. 207.
[29] J.T. Scanlon, D.E. Willis, J. Chromatogr. Sci. 23 (1985) 333.
[30] NIOSH Method 7904, Cyanides: Aerosol and Gas, issue 2, in: P.M. Eller, M.E. Cassinelli (Eds.), NIOSH Manual of Analytical Methods, 4th ed., DHHS (NIOSH) Publication NO. 94-113, US Dept. of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute of Occupational Safety and Hazards, Cincinnati, 1994.
[31] R.P. Streicher, E.R. Kennedy, C.D. Lorberau, Analyst 119 (1994) 89.
[32] S.A. Grinshpun, K. Willeke, V. Ulevicius, A. Juozaitis, S. Terzieva, J. Donnelly, G.N. Stelma, K.P. Brenner, Aerosol.. Sci. Technol. 26 (1997) 326.
[33] M. Spanne, P. Grzybowski, M. Bohgard, AIHAJ 60 (1999) 540.