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VAPOR-PHASE SILYLATION OF ALCOHOLS FOR AIR ANALYSIS

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SUMMARY

Vapor-phase oxygenated organics at the parts per billion (10^9) level are difficult to identify or quantify because many are polar or reactive compounds which adsorb or decompose on surfaces within analytical apparatus. The traditional approach to facilitate such analyses has been to reduce the surface activity of collection containers, concentration adsorbents and chromatographic columns through a variety of procedures.

This paper presents a novel concept in air analysis in which reactive trace compounds of interest are derivatized to stable products. A mixture of low-molecular-weight alcohols at sub-parts per million levels were converted into their silyl derivatives upon whole air collection, then these derivatives were concentrated in a freeze-out loop and thermally transferred to a cryogenically controlled gas chromatograph equipped with a glass capillary column for temperature-programmed separation and flame-ionization detection.

Silylated alcohols proved to chromatograph with better resolution and sensitivity than their parent compounds and, unlike the free alcohols, could be stored in stainless-steel canisters without degradation. Of five commercial silylating reagents surveyed, trimethylsilylimidazole and N,O-bis(trimethylsilyl)acetamide showed potential for effective gas-phase derivatization even in the presence of excess moisture. Silyl derivatives were identified by gas chromatography–mass spectrometry techniques.

INTRODUCTION

The vapor-phase content of the atmosphere consists of a complex mixture of hydrocarbons and their oxidation products. Recent improvements in collection, concentration and analytical techniques have made it possible to identify many of these gaseous organic species in urban and rural atmospheres. Using solid adsorbents such as Tenax GC, organic gases can be extracted from large volumes of air while the combined analytical capabilities of gas chromatography and mass spectrometry have

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provided positive identification of the vapor-phase organics collected in this manner[1-5].

Literature reports describing the vapor-phase organic composition of the atmosphere indicate that the major fraction of material consists of true hydrocarbons (containing only C and H atoms). Oxygenated species are seldom reported. The lack of oxygenated hydrocarbons is surprising as significant amounts of these species are directly emitted into the atmosphere by solvent related industries. Along with other anthropogenic emission sources, natural emissions of oxygenated hydrocarbons also contribute to this total. In addition, it is expected that photochemical reactions of hydrocarbons with oxides of nitrogen, ozone and hydroxyl radical will also produce significant amounts of oxygenated products.

The reactivity and adsorptivity of these oxygenated species make their analysis particularly difficult. The adsorptive nature of the surfaces which these compounds contact during analysis and their potential for reaction with other compounds during analysis complicate the processes of quantitative collection, storage, separation and detection.

Traditionally, the approach for analysis of oxygenated and other polar organics has been to decrease adsorption by deactivating the interior surfaces of analytical hardware. Bag collection methods employ inert polymers such as Teflon and Tedlar while other whole air collection methods utilize silylated glass or electropolished stainless-steel containers. For adsorption methods, where organics are collected and concentrated from the air simultaneously, porous organic polymers are replacing inorganics as adsorbent materials. Intensive studies to develop more efficient methods of eliminating active sites on chromatographic packing materials have done much for trace organic analysis of air pollutants. Glass capillary columns have further increased the capacity for high-resolution separation with minimal adsorption. However, for the more reactive compounds surface deactivation is insufficient to eliminate effectively adsorption effects which interfere with quantitative analysis.

In this paper, a novel concept for air analysis is presented in which the reactive compounds of interest are modified rather than the surfaces with which these compounds interact. For many years, derivatization techniques have been used successfully to convert polar, non-volatile organic compounds into non-polar, volatile derivatives for separation by gas chromatography (GC). For alcohols and acids, one of the most successful of these techniques has been silylation in which active hydrogens are replaced with a trimethylsilyl group[6]. The feasibility of applying derivatization techniques to the determination of trace amounts of reactive organics in the atmosphere is demonstrated in this study by converting low-molecular-weight, vapor-phase alcohols at sub-parts per million levels into their silyl derivatives before concentration and chromatography by standard techniques.

EXPERIMENTAL

Reagents

Throughout this study five low-molecular-weight straight-chain alcohols were used as test compounds, namely methanol, ethanol, propanol, butanol and pentanol (Chem Service, West Chester, Pa., U.S.A.). With each of the test alcohols, five silylating reagents were investigated: hexamethyldisilazane (HMDS), trimethylsilyl-

imidazole (TSIM), N,O-bis(trimethylsilyl)acetamide (BSA), trimethylsilyldiethyl-amine (TMSDEA) and trimethylchlorosilane (TMCS) (Pierce, Rockford, Ill., U.S.A.).

Sample preparation

Vapor-phase samples were prepared and derivatized in 5.45-l stainless-steel canisters which had been electropolished using the Molectrics Summa process (Molectrics, Englewood, Calif., U.S.A.). Before use, each canister was baked overnight under a 30 ml/min flow of purified nitrogen or hydrocarbon-free air and tested for cleanness by obtaining a blank chromatogram.

Standards were prepared by injecting pre-determined amounts of each test compound into a canister that had been partially evacuated to insure total vaporization of the standard. Amounts injected were calculated from the following equation[7]:

$$V = \frac{MW}{D} \cdot \frac{5.45 \, l}{22.4 \, l/mole} \cdot \frac{P}{760 \, Torr} \cdot \frac{273°K}{T} \cdot \frac{ppm}{10^6}$$

Where MW is the molecular weight of the compound injected, D is its density in g/ml, 5.45 l is the volume of the canister, 22.4 l is the ideal volume of 1 mole of gas at standard temperature and pressure, P is the gas pressure in the canister in Torr, T is room temperature in °K, ppm is the number of parts per million desired and V is the volume of liquid needed in milliliters.

Free alcohol standards were prepared using the procedure above by injecting 1 μl of each alcohol in the liquid state at room temperature, resulting in a test mixture containing 56 ppm of methanol, 39 ppm of ethanol, 29 ppm of propanol, 25 ppm of butanol and 21 ppm of pentanol. For analysis of free alcohols at sub-parts per million levels, 50 ml of this gas mixture was injected into another evacuated canister which was then pressurized to 2 atm. The resulting mixture contained 250 ppb of methanol, 180 ppb of ethanol, 130 ppb of propanol, 110 ppb of butanol and 100 ppb of pentanol. For all derivatization experiments at sub-parts per million levels, mixing ratios of alcohols were prepared by direct injections of about 0.01 μl* of each alcohol in the liquid state into an evacuated canister. This procedure resulted in an alcohol mixture containing 560 ppb of methanol, 390 ppb of ethanol, 290 ppb of propanol, 250 ppb of butanol and 210 ppb of pentanol. For derivatization, an excess of silylating reagent was injected into the evacuated canister prior to the alcohol injections. When reagents and test compounds were added, canisters were pressurized to 2 atm with purified nitrogen.

Derivatization experiments in air were performed by preparing an initial canister with free alcohols at mixing ratios from 25 to 56 ppm after pressurizing the canister to 2 atm with hydrocarbon-free air. This sample canister was then connected to a second, evacuated canister containing a silylating reagent until the pressures equalized.

Gas chromatography

For each GC analysis, a gaseous sample was drawn from the canister with a

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* 0.01-μl injections were made with a 1-μl Hamilton Series 7001N syringe. The relative standard deviation (determined from direct repetitive injections into a gas chromatograph) was 30%. When the mean of these injections was compared to the mean of an appropriate serial dilution standard, the "*t*-test" indicated no significant differencs.

100-ml glass syringe (Becton-Dickinson, Rutherford, N.J., U.S.A.) and injected into a stainless-steel freeze-out loop packed with silylated glass beads. The loop was cooled with liquid nitrogen to condense volatile components of the sample on to the glass beads. With collection complete, the loop was immersed in hot water and the volatiles were transfered to a gas chromatograph via a heated, six-port valve (Carle Instruments, Fullerton, Calif., U.S.A.) and a 1/16-in. stainless-steel transfer line.

The gas chromatograph was a Hewlett-Packard 5710A equipped with a standard flame-ionization detector and cryogenic oven control. Separation was accomplished by temperature programming the 30-m SE-54 glass capillary column (J & W Scientific, Sacramento, Calif., U.S.A.) from −50°C to 70°C at 4 °C/min. Gas flows were as follows: nitrogen carrier gas 1 ml/min; nitrogen make-up gas 30 ml/min; hydrogen 30 ml/min; and air = 240 ml/min. The injection port temperature and detector temperature were maintained at 200°C and 250°C, respectively. A Sargent-Welch (Skokie, Ill., U.S.A.) SKR strip-chart recorder was used to trace the chromatogram.

Mass spectrometry (MS)

The gas chromatograph–mass spectrometer–data system consisted of a Hewlett-Packard Model 5700 gas chromatograph interfaced to a Hewlett-Packard Model 5930 mass spectrometer and a Model 5934 data system. The mass spectrometer includes separate pumping of the ion source and analyzer tube with two 4-in. diffusion pumps. The addition of a separate diffusion pump for the ion source permits a "direct-coupled" interface between the gas chromatograph and the mass spectrometer. As a result, a molecular separator or enricher is not needed and the entire GC column effluent is transferred into the MS ion source.

For the generation of mass spectral data, the Hewlett-Packard 5934 system includes a 21 MX computer, a 7900 dual disc drive and a Tektronix CRT graphic display terminal together with a Tektronix 4610 hard-copy unit.

Procedure

The sampling and chromatographic system were evaluated for the determination of alcohols at the 20–60 ppm level (*ca.* 4 μg of compound per injection) and at the 0.1–0.3 ppm level (*ca.* 20 ng of compound per injection). Stability studies of the alcohols at the lower level were accomplished by obtaining repetitive chromatograms at selected intervals for 5 h after sample preparation.

A survey of the five silylating reagents indicated which reagents were best suited for gas phase derivatization; 5 μl of each reagent were tested separately with alcohol mixtures at the 0.2–0.6 ppm level. For BSA, reaction products were identified by GC–MS and stability studies were conducted for a period of 5 days.

BSA, HMDS and TSIM were evaluated in the presence of water with alcohols at the 0.3–0.8 ppm level. The silylating reagent was added to an evacuated, clean canister followed by alcohol and water injections. The canister was then pressurized and analyzed. For BSA, 15 μl of reagent were injected with 10 μl (*ca.* 5% relative humidity at 20°C) of water and 50 ml gaseous samples were withdrawn from the canisters for analysis. For HMDS and TSIM, 110 μl of reagent were injected followed by 100 μl of water. Subsequently 10-ml gaseous samples were withdrawn from the canisters for analysis.

Finally, two canisters were doped with alcohols at the parts per million level,
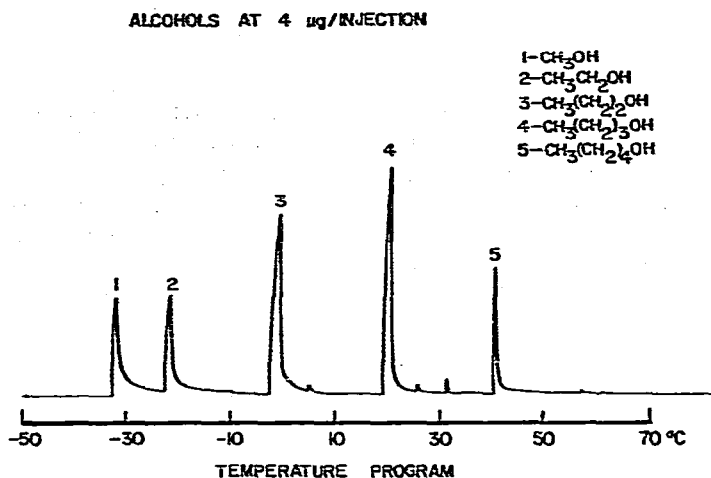
ALCOHOLS AT 4 µg/INJECTION

1-CH₃OH
2-CH₃CH₂OH
3-CH₃(CH₂)₂OH
4-CH₃(CH₂)₃OH
5-CH₃(CH₂)₄OH

Fig. 1. Chromatogram of alcohol mixture at the 20–60 ppm level. Electrometer attenuation = 160. Amount injected = 50 ml.

then filled with hydrocarbon-free air to a pressure of 2 atm. Prior to pressurization water equivalent to 10% humidity was added to one of the canisters. Air from each of these canisters was then allowed to fill a second canister that had been evacuated, then injected with 100 µl of TSIM. Volumes of 10-ml of the resulting air mixtures in the second canisters were analyzed.
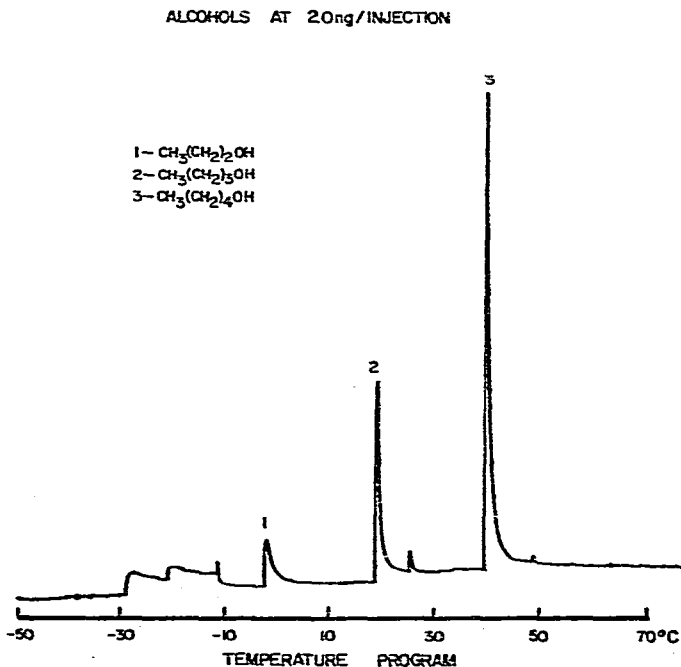
ALCOHOLS AT 2.0ng/INJECTION

1– CH₃(CH₂)₂OH
2– CH₃(CH₂)₃OH
3– CH₃(CH₂)₄OH

Fig. 2. Chromatogram of alcohol mixture at the 0.1–0.3 ppm level. Electrometer attenuation = 16. Amount injected = 50 ml.

RESULTS AND DISCUSSION

Free alcohols

Difficulties associated with direct analysis of vapor-phase alcohols are demonstrated in Figs. 1–3. The chromatogram of alcohols in Fig. 1 was obtained with relatively high mixing ratios compared with those expected in the atmosphere. However, it exemplifies a chromatogram where reversible adsorption has reduced resolution by broadening peaks and creating peak tailing. Irreversible adsorption becomes pronounced as concentrations are reduced. When the concentration of the alcohols in the canisters is reduced to values approaching those expected in the atmosphere, as is the case shown in Fig. 2, compounds with more polar characters such as methanol and ethanol are irreversibly adsorbed by the analytical system, making analysis impossible.
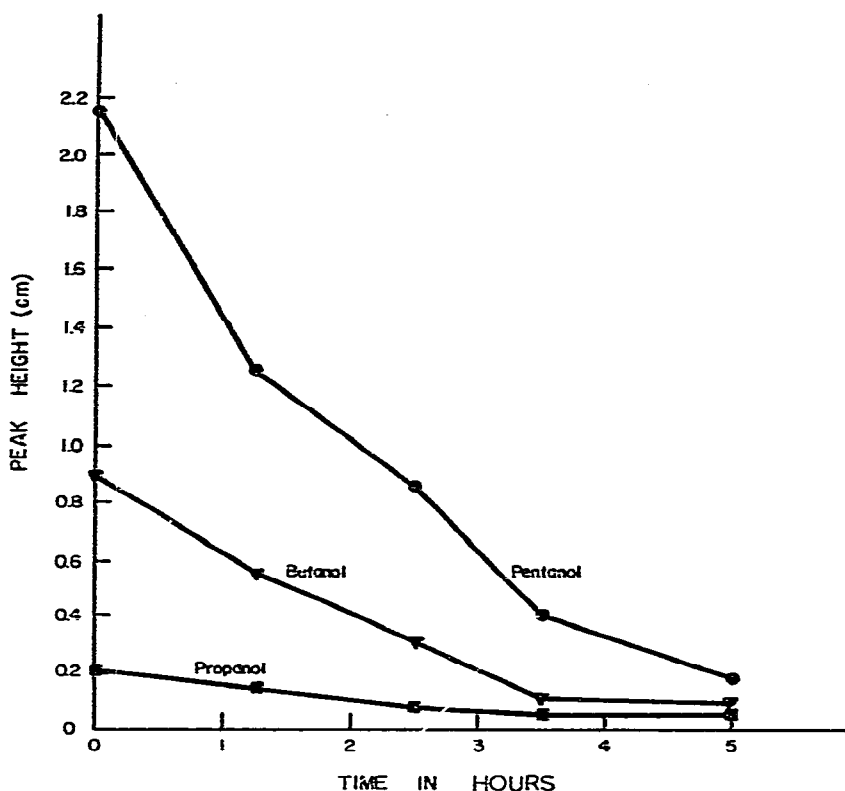

Fig. 3. Stability study of alcohols at the 0.1–0.3 ppm level. Electrometer attenuation = 160. Amount injected = 50 ml.

Stability during storage is another area of concern with trace analysis of reactive compounds. Fig. 3 shows that the concentration of alcohols in the canister decreases as a function of time. Within 5 h after sample preparation, the alcohol response has decreased by more than an order of magnitude as the compounds become irreversibly adsorbed to the walls of the container.

Thus, the combination of reversible and irreversible adsorption during collection, storage and separation of alcohols reduces their analytical sensitivity and resolution while limiting the time of transfer from a sampling site to the laboratory.

Silylated alcohols

Fig. 4 shows a chromatogram of an alcohol mixture at a concentration level about twice that in Fig. 2 but with the alcohols treated with BSA to produce silylated derivatives. Comparing Figs. 2 and 4, a number of observations can be made. The most obvious difference is that for the free alcohols only three peaks are obtained, whereas for the silyl derivatives all five compounds can be detected. Also, the peaks in Fig. 4 are much narrower and more symmetrical than those in Fig. 2, which indicates that adsorption has been greatly reduced, increasing the resolution capabilities of the separation process. Reducing adsorption also increased sensitivity. Silylated compounds produced larger peaks at a higher attenuation than did the free alcohols.

Silylation is expected to alter retention patterns, but silylation procedures used in solutions to decrease the polarity of large molecules normally increase volatility
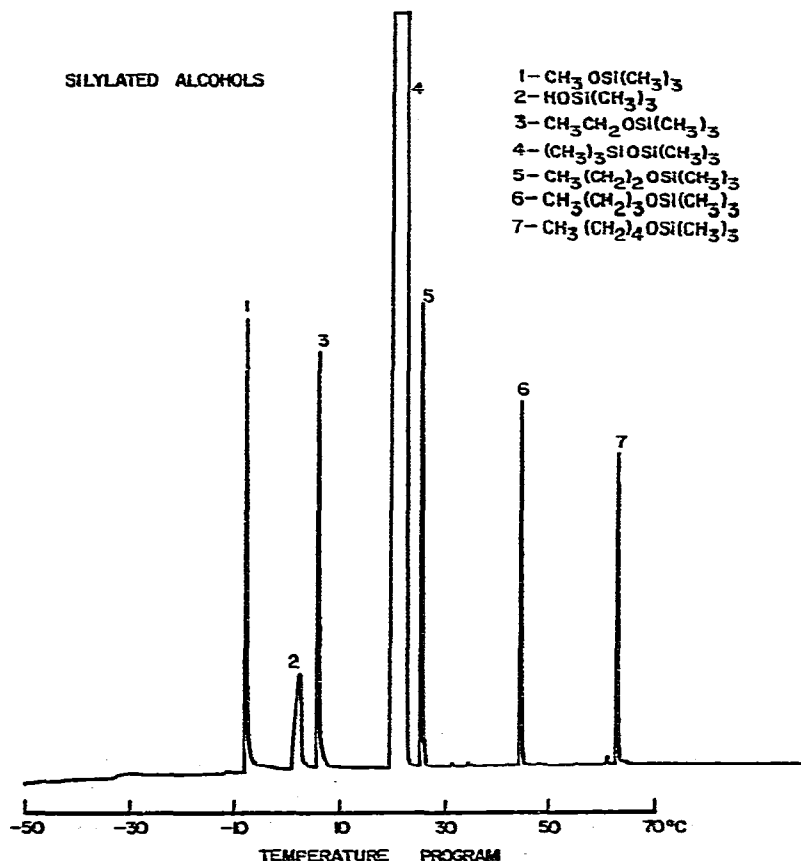

SILYLATED ALCOHOLS

1 - $CH_3 OSi(CH_3)_3$
2 - $HOSi(CH_3)_3$
3 - $CH_3CH_2 OSi(CH_3)_3$
4 - $(CH_3)_3 SiOSi(CH_3)_3$
5 - $CH_3(CH_2)_2 OSi(CH_3)_3$
6 - $CH_3(CH_2)_3 OSi(CH_3)_3$
7 - $CH_3(CH_2)_4 OSi(CH_3)_3$

TEMPERATURE PROGRAM

Fig. 4. Chromatogram of silylated alcohols at the 0.2–0.6 ppm level. Silylating reagent BSA. Electrometer attenuation = 160. Amount injected = 50 ml.

and decrease retention times. When applied to low-molecular-weight polar compounds, as in this study, an increase in molecular weight due to the addition of the trimethylsilyl moiety is sufficient to offset a decrease in polarity and an increase in retention time with respect to the parent compound is observed.

Besides improving sensitivity and resolution, silylation stabilized the alcohols to permit storage for extended periods. Fig. 5 shows the results of a 5-day study in which alcohol derivatives were analyzed periodically. In the first 24 h, concentrations of derivatives increased rapidly but by the fourth day they reached a maximum and remained constant. Such behavior insures quantitative results even when samples are collected far from the analytical laboratory and must be stored several days before analysis.
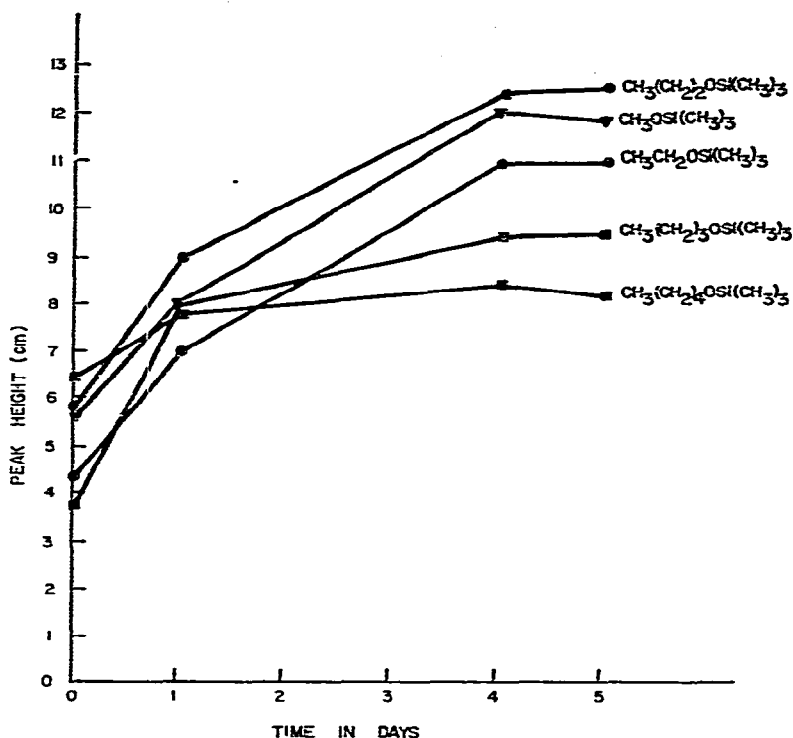

Fig. 5. Stability study of silylated alcohols at the 0.2–0.6 ppm level. Silylating reagent BSA. Electrometer attenuation = 160. Amount injected = 50 ml.

Identification of derivatives

Identity of silyl derivatives was confirmed by GC–MS. Table I lists peaks for which mass spectral data were obtained with number references to peaks shown in Fig. 4. For each peak the four most intense ions are listed, together with their most probable ion structures and the structure of the compound identified. Peaks 1, 3, 5, 6 and 7 were found to be the respective silyl derivatives of methanol, ethanol, propanol, butanol and pentanol. Peaks 2 and 4 were reaction products of water where peak 2 was trimethylsilanol [$(CH_3)_3SiOH$] and peak 4 was hexamethyldisiloxane [$(CH_3)_3Si$ $OSi(CH_3)_3$]. MS patterns and ion structures listed in Table I compare favorably with those reported for silyl compounds in ref. 6.

TABLE I

RESULTS OF GC–MS IDENTIFICATION

Peak number	m/e	Relative response	Ion	Compound
1	89	100	$[CH_2=OSiH(CH_3)_2]^+$	$CH_3OSi(CH_3)_3$
	59	42.6	$[SiH(CH_3)_2]^+$	(MW = 104)
	90	7.7	[89+1 isotope peak]	
	43	5.2	$[SiCH_3]^+$	
2	75	100	$[HOSi(CH_3)_2]^+$	$HOSi(CH_3)_3$
	45	31.4	$[HOSi]^+$, $[CH_3SiH_2]^+$	(MW = 90)
	47	21	$[HOSiH_2]^+$	
	28	20.7	$[Si]^+$, $[N_2]^+$	
	76	6.8	[75+1 isotope peak]	
3	103	100	$[CH_3CH_2OSi(CH_3)_2]^+$	$CH_3CH_2OSi(CH_3)_3$
	75	59.2	$[HOSi(CH_3)_2]^+$	(MW = 118)
	73	21	$[Si(CH_3)_3]^+$	
	59	16.1	$[SiH(CH_3)_2]^+$	
4	147	100	$[(CH_3)_2SiOSi(CH_3)_3]^+$	$(CH_3)_3SiOSi(CH_3)_3$
	148	16.5	[147+1 isotope peak]	(MW = 162)
	73	9.1	$[Si(CH_3)_3]^+$	
	149	8.3	[147+2 isotope peak]	
5	117	100	$[CH_3CH_2CH_2OSi(CH_3)_2]^+$	$CH_3(CH_2)_2OSi(CH_3)_3$
	75	94.6	$[HOSi(CH_3)_2]^+$	(MW = 132)
	73	40.1	$[Si(CH_3)_3]^+$	
	103	20.7	$[CH_2OSi(CH_3)_3]^+$	
6	131	100	$[CH_3(CH_2)_3OSi(CH_3)_2]^+$	$CH_3(CH_2)_3OSi(CH_3)_3$
	75	91.4	$[HOSi(CH_3)_2]^+$	(MW = 146)
	73	33.9	$[Si(CH_3)_3]^+$	
	103	24.5	$[CH_2OSi(CH_3)_3]^+$	
7	145	100	$[CH_3(CH_2)_4OSi(CH_3)_2]^+$	$CH_3(CH_2)_4OSi(CH_3)_3$
	75	84	$[HOSi(CH_3)_2]^+$	(MW = 160)
	73	35.7	$[Si(CH_3)_3]^+$	
	103	24.8	$[CH_2OSi(CH_3)_3]^+$	

Survey of silylating reagents

A number of silylating reagents besides BSA were evaluated for their potential in the derivatization of oxygenated air pollutants. Table II lists the silylating reagents tested and compares the relative responses of individual alcohols with each of these reagents. For all five alcohols, derivatives obtained with HMDS produced the largest response and were assigned an arbitrary value of 100. The response obtained for a specific silylated alcohol is always compared with the response obtained when that silylated alcohol was prepared from HMDS. For example, the peak obtained by silylating methanol with TSIM was 34% as high as the peak obtained for the methanol derivative with HMDS, while the TSIM peak for ethanol was 43% that of the HMDS peak for ethanol. Averages of these relative responses for the five alcohols are listed in the last column in Table II. They indicate that the efficiency of these derivatizing reagents decreases in descending order, with HMDS being the most and TMCS the least efficient.

This survey was conducted as an initial investigation to establish the potential of silylation, not to quantify yields or reaction rates. As standards were prepared by separate injections for each alcohol of 0.01 μl from a 1-μl syringe, sample reproducibility varied as much as 30–40%. Furthermore, data were not obtained at identical times following sample preparation (Table II). Reaction times and rates must be considered if a complete quantitative evaluation is to be accomplished.

TABLE II

SURVEY OF SILYLATING REAGENTS

Reagent	Time (h)	Relative response					
		Methanol	Ethanol	Propanol	Butanol	Pentanol	Average
HMDS	3.5	100	100	100	100	100	100
TSIM	3.0	34	43	56	47	74	51
BSA	3.5	26	48	69	51	41	47
TMSDEA	7.0	4.8	—	3.4	6.3	19	6.7
TMCS	3.0	11	7.5	5.7	1.5	1.3	5.4

However, HMDS, TSIM and BSA produced "clean" chromatograms similar to Fig. 4 with peak heights within a factor of 2 of each other. On the other hand, derivatives for TMSDEA and TMCS produced chromatographic peaks with peak heights that were 15–19 times lower than those from HMDS. Chromatograms of TMCS-treated alcohols were further complicated by a number of unidentified peaks. HCl, a by-product of the silylation reaction of TMCS, may have produced extra peaks by acid degradation of the column.

From these qualitative and semi-quantitative observations, it appears that HMDS, TSIM and BSA have potential as silylating reagents for air analysis and should be investigated further.

Moisture

The presence of moisture in the atmosphere is a primary interference in the determination of oxygenated organics at trace levels. It contributes to inefficient collection by adsorption techniques through displacement chromatography, it limits the amount of air that can be passed through cryogenic traps before lines become plugged with ice, and it increases the rate of column degradation if not removed from the sample before chromatography. Methods for the removal of water before sample collection or chromatography generally require adsorption to or reaction with inorganic materials that may also react with or adsorb many of the polar organic compounds of interest. If silylation of vapor-phase oxygenated organics is to be a practical approch in air analysis, water must not interfere with collection, derivatization or separation processes.

In the mass spectral studies described earlier (see Table I), two peaks are attributed to the presence of water in the sample. Peak 2 (trimethylsilanol) is the result of the addition of one trimethylsilyl group to water, while peak 4 (hexamethyldisiloxane) is the result of the addition of two trimethylsilyl groups to water. In Fig. 4 these two products did not interfere with the analysis of the silylated alcohols, but the gases used to prepare the samples were pre-dried by passing them over a molecular sieve which reduced their water content to about 10 ppm. As the water content of air is normally much higher, an excess of water was injected into the canisters along with the alcohols to evaluate its effect on the silylation process.

Fig. 6 is the chromatogram which resulted when a mixture of 730 ppb of methanol, 520 ppb of ethanol, 380 ppb of propanol, 330 ppb of butanol, 280 ppb of pentanol and 1.3% (ca. 50% relative humidity at 20°C) of water were derivatized by a 110-μl injection of TSIM. Even with this large amount of water present, five sharp peaks for the silylated alcohols are readily observed. The two major peaks in the chromatogram correspond to trimethylsilanol and hexamethyldisiloxane. Although

hexamethyldisiloxane represents by far the major portion of material chromato-graphed, it is well separated from silylated alcohols and would not interfere with analysis. Also, as it is a non-polar stable compound, it would not be expected to de-grade the chromatographic column. Trimethylsilanol, whose retention time is shifted due to the asymmetry of its peak, overlaps the ethanol derivative but is separated from the other four peaks of analytical interest. A similar result was obtained when the derivatization procedure for BSA in the presence of excess of water was investigated. HMDS, however, did not produce a sufficient yield of alcohol derivatives in the pres-ence of water to warrant further investigation. The presence of trimethylsilanol in both Figs. 6 and 4, together with the absence of peaks for unreacted silylating reagents, suggest that the amounts of silylating reagents employed were not sufficient to con-vert all of the water into hexamethyldisiloxane. Total conversion of water into hexa-methyldisiloxane would not only eliminate interference from the trimethylsilanol peak but might also increase the efficiency of alcohol derivatization and reduce deg-radation of the column to make this silylation procedure viable for atmospheric analysis on a routine basis.
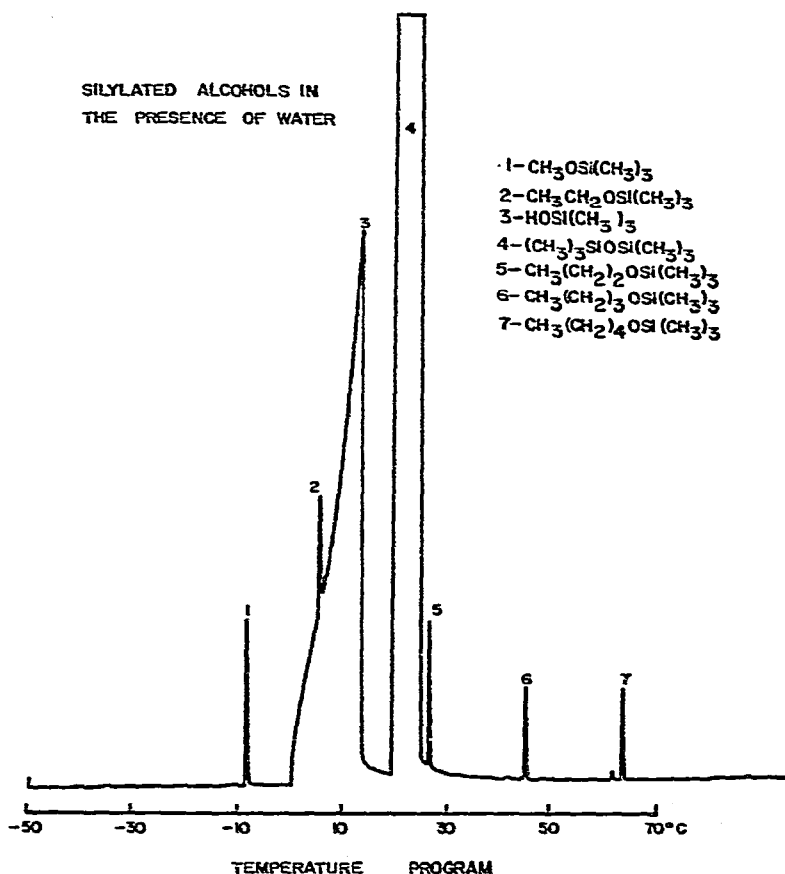

Fig. 6. Chromatogram of silylated alcohols at the 0.3–0.8 ppm level in the presence of 1.3% of water. Silylating reagent TSIM. Electrometer attenuation = 160. Amount injected = 10 ml.

Derivatization in air

Field conditions, in which silylation must occur at atmospheric pressure, were simulated by filling an evacuated canister containing the TSIM with air from another canister that had been doped with appropriate levels of alcohols and water. The resulting chromatograms were essentially identical with those in Fig. 4 for alcohols without added water and Fig. 6 for alcohols with water. The mixing ratio of alcohols used for the standard air was the same as that in Fig. 1. Experiments with lower concentrations were impossible because of excessive adsorption on the walls of the canister during the analysis. Nevertheless, the silylation process described in this paper does occur at atmospheric pressure which, together with other data represented in this paper, indicates that such a method can be successful under actual field conditions.

CONCLUSIONS

This study was primarily a qualitative investigation which demonstrated the potential of silylation as a technique that can be applied to atmospheric analysis of trace levels of oxygenated and other important polar compounds. Quantitative investigations of the technique to determine optimal operating conditions, reproducibility, ultimate sensitivity and reliability under field conditions must be completed before it can be established as a recommended routine operation. However, the results are encouraging in that several silylating reagents were identified which produced detectable derivatives of alcohols at trace levels, even in the presence of an excess of moisture. Further, as these derivatives proved to be stable for several days, samples may be collected in areas where immediate analysis is not possible.

The promise of this derivatization technique for air analysis may be extended from alcohols to other polar compounds with active hydrogens such as organic acids and amines. It may also serve as the basis of a method for determining the trace water content of various technical gases. In addition, through the use of a variety of derivatizing reagents, it may develop into a general analytical procedure for reactive gaseous compounds.

ACKNOWLEDGEMENT

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