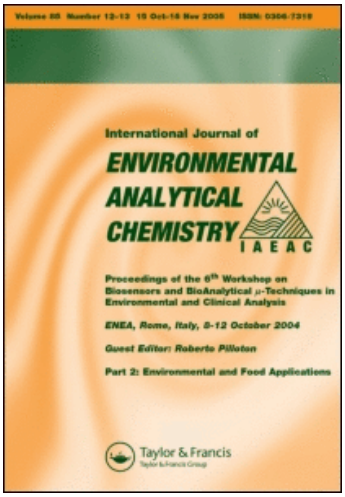

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Esterification of Carboxylic Acids Present on Airborne Particulate Matter During Methanol Extraction and Storage

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Concentrated methanol extracts of airborne particulate matter (APM) collected on glass fiber filters were examined by gas chromatography to document sample composition changes during storage. A major component of the chromatographic profile was observed to decrease in abundance with time while another compound was increasing. These compounds were identified by Gas Chromatography-Mass Spectrometry as myristic acid and methyl myristate, respectively. Although methanol is a common extracting solvent for these samples, this is the first study to document the *in-situ* esterification of acids from APM during storage of the methanol extracts.

KEY WORDS: Air particulates, sample storage, esterification, methanol extraction.

INTRODUCTION

The collection of organics sorbed onto airborne particulate matter (APM) is most often accomplished by filtration using a standard Hi-Vol apparatus.[1] After collection, the organics are usually extracted by Soxhlet apparatus[2,3] or ultrasonic agitation.[4,5] The large number of compounds which have been identified in urban atmospheres using these collection and extraction procedures have recently been reviewed.[6]

A variety of solvents have been employed for the extraction of Hi-vol filters, including cyclohexane,[7] benzene,[8] methylene chloride,[9] chloroform,[10] and methanol.[11] Grosjean has reported that polar solvents such as methanol give high extraction efficiencies for organic compounds sorbed on APM.[12] Hill,[13] Gordon,[14] and Cautreels[15] have also demonstrated the high extraction efficiency of methanol for these samples.

Denney has remarked that the use of methanol as an extracting solvent for APM may result in the esterification of naturally present fatty acids.[11] Carles has reported that when alcohol is used as solvent for extraction of vegetable material, the organic acids which are present always form esters.[16] Because of the difficulty in obtaining good chromatographic peak shape and rapid analysis of fatty acids, the intentional derivatization of these compounds to form their respective esters has been performed.[17-19] Although it seems likely that the esterfication of fatty acids should occur during Soxhlet extraction of these compounds using methanol, no study has yet been reported in which this has been shown to occur. In a previous study, Clement and Karasek have reported losses of organic material from filters containing APM which were stored in a refrigerator for various lengths of time before Soxhlet extraction using methanol.[20] During this study, it was observed that some sample extracts produced different chromatographic profiles when re-analyzed at a later time. These sample changes, caused by esterification of fatty acids which had been extracted from the APM, are reported here.

EXPERIMENTAL

A. Sample collection, extraction, and concentration

Air particulate samples were supplied by the Ontario Ministry of the Environment, Air Resources Branch personnel. Particulates were collected on 8×10 inch glass fiber filters using the standard Hi-Vol technique.[1] Typical volumes of air sampled were 2500 m^3 during a 24 hour period. These samples were from a previously reported study.[20]

Glass fiber filters were cut into approximately 1 cm^2 pieces, placed into a glass-fritted extraction thimble, and extracted overnight (ca 16 h) with 200 mL of distilled-in-glass grade methanol (Burdick and Jackson, Muskegon, MI) using a Soxhlet extraction apparatus. Extracts were reduced to about 10 ml by rotary evaporation under aspirator vacuum. After centrifugation to remove an inorganic precipitate, the extract was further reduced to less than 1 ml and adjusted to 1.0 ml in a volumetric flask. Concentrated methanol extracts were stored in a refrigerator at 0 to 5°C before analysis.

B. Instrumental analysis of data

Concentrated extracts were analyzed by a Hewlett-Packard (HP) 5830A gas chromatograph (GC) equipped with flame ionization detectors and a 6′ or 10′ × 2 mm i.d. glass column packed with a high performance material called Aue Packing.[13] Chromatographic conditions were: initial temperature, 80°C; program rate, 4°/min.; final temperature, 250° held for 20 minutes; injector, 250°; detector, 300°; He carrier flow rate, 32 ml/min. A standard consisting of *n*-alkanes was periodically analyzed for calculation of Kovats retention indices (RI).

Compound identification was performed using a HP5992 GC/Mass Spectrometer/Calculator system equipped with X-Y plotter and floppy disk. Mass spectra were scanned from 500 to 40 amu at a rate of 350 amu per second. Mass scans taken at the top of eluting GC peaks were stored on floppy disk along with a scan taken at the lowest valley between each peak for use in a later background subtraction step to provide corrected mass spectra. The mass spectrometer was tuned using the manufacturer-supplied program AUTOTUNE.

C. Computer analysis of data

Kovats retention indices (RI) were calculated using the Fortran program RICALC. Computer-generated plots were generated using Calcomp plotter by the Fortran program GCPLOT. Both of these programs were developed to run on the University of Waterloo IBM 360/75 computer under the WATFIV complier. Use of these programs has been described previously.[21]

RESULTS AND DISCUSSION

Two concentrated methanol extracts of air particulates on glass fiber-filters were analyzed periodically by gas chromatography (GC) during 100 hours after extraction to examine changes in sample extract composition. Figure 1 is a computer plot of the GC results for one of these samples (Sample A). GC peaks are represented as lines which are proportional to peak areas, and are plotted by RI value. By displaying peak areas as a percent of the total chromatographic area for each run, the major peaks are emphasized in Figure 1 while the chromatographic pattern is retained. The total chromatographic areas shown in the top right-hand corner of each plot are indicative of total organics detected in each analysis.

GC peaks at RI 1790 and 2256 have been identified as methyl myristate ($C_{15}H_{30}O_2$) and myristic acid ($C_{14}H_{28}O_2$), respectively. The mass spectra

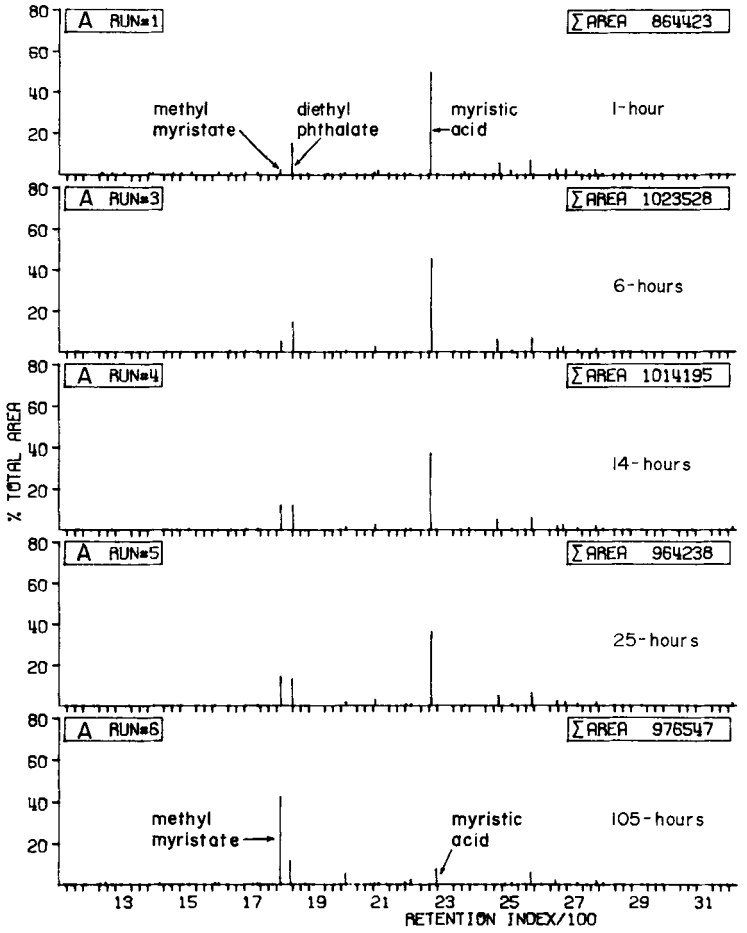

FIGURE 1 GCPLOT Comparison of sample A analyzed during a 105-hour period. Times from extraction in hours are given for each plot. Forty-five components were resolved in this sample; the plotted scale was chosen to emphasize the major peaks which were myristic acid and methyl myristate.

for these two components, shown in Figure 2, match very closely with mass spectra of myristic acid and methyl myristate that are present in the EPA/NIH Mass Spectral Data Base.[22] Figure 1 shows that while the concentration of myristic acid is decreasing from the first run (1 hour from extraction) to the fifth run (105 hours from extraction) the methyl myristate peak is continually increasing. The overall sample does not undergo much change from run-to-run. This is illustrated by the diethyl

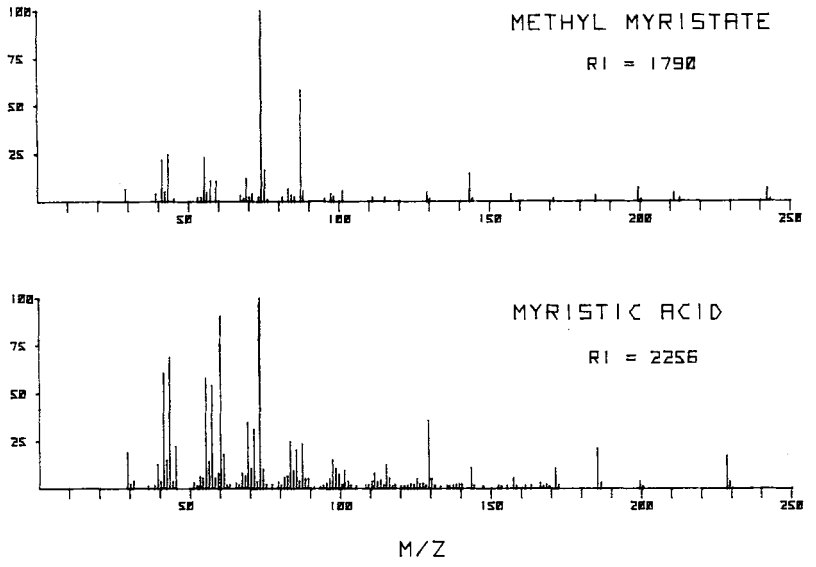

FIGURE 2 Mass spectra of methyl myristate and myristic acid from sample A.

phthalate peak in Figure 1, which remains constant as the ester and acid peaks are changing. All of the GC runs in Figure 1 were performed using the same injection volumes.

The time variation in myristic acid and methyl myristate peaks is further shown in Table I for sample A and for a second sample (sample B). Variations in diethyl phthalate are included in the results for sample A. The relative amount of diethyl phthalate from run to run is almost constant. Phthalate peak areas exhibited a percent relative standard deviation (rsd) of ± 5.3. This compares favourably with variation of total peak areas of $\pm 6.7\%$ rsd for sample A. Injection errors alone are about 5% for the injection procedures employed in this work. Variations of total areas were greater ($\pm 18\%$ rsd) for sample B. The sum of the areas for myristic acid and methyl myristate for each of the GC runs in Table I is approximately 50% of the total chromatographic areas for sample A and 60% of the total area for sample B. The percentages remained about the same for each GC analysis of a particular sample. Therefore, the methyl ester increase is directly associated with the carboxylic acid decrease. No other significant sample changes were noticed during the GC analyses.

Reproducibilities of the RI values for the compounds in Table I are very good, with the exception of the RI for myristic acid in sample A (run 6). The reason for this is the greatly reduced concentration of the acid in

TABLE I
Sample composition changes during storage of aerosol extract condensates

Hours from extraction	Diethyl phthalate		Myristic acid		Methyl myristate		Hours from extraction	Myristic acid		Methyl myristate	
	RI	% Tot. area	RI	% Tot. area	RI	% Tot. area		RI	% Tot. area	RI	% Tot. area
1	1823	14.8	2256	49.9	1787	1.7	1	2253	63.6	1788	1.6
4	1827	14.5	2258	47.7	1790	3.8	6	2256	53.5	1791	5.0
6	1827	14.5	2258	45.5	1790	5.2	12	2256	52.1	1790	10.1
14	1827	12.2	2256	37.1	1790	12.3	25	2254	44.9	1789	11.4
25	1825	13.4	2257	36.3	1789	14.4	100	2262	21.3	1788	38.0
105	1820	11.8	2272	7.5	1787	42.3					

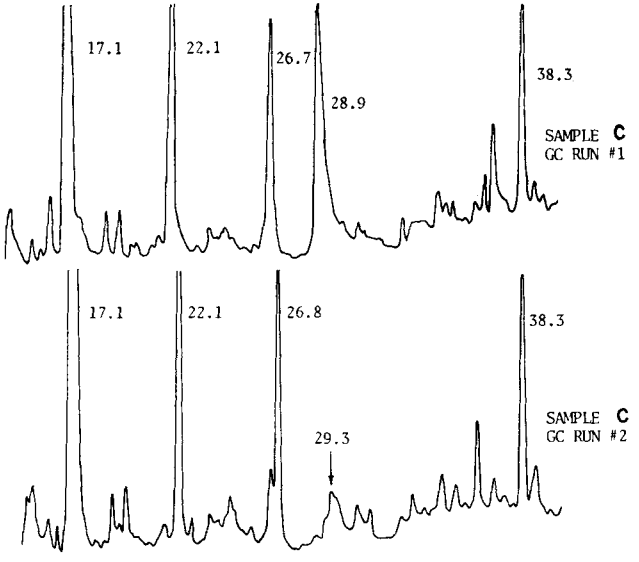

FIGURE 3 Comparison of GC analysis of sample C before and after storage of filter extract condensates. The retention times in minutes of the major peaks are given. The peaks at 28.9 min in GC Run #1 and at 29.3 min in GC Run #2 are myristic acid. The peak at 17.1 minutes is methyl myristate. Similar compounds are present in this sample and sample A. However, the relative concentrations are different.

this analysis, compared to the others. Figure 3 illustrates this by comparing the 17 to 40 minute portion of two chromatograms of a third sample (sample C). The first (top) analysis was performed shortly after extraction and concentration, the second was several days later. Retention time of the major peaks are shown. These times match very closely for both chromatograms, with the exception of the myristic acid peak at retention time 28.9 minutes in the early run and 29.3 minutes in the later analysis. Because of the broad peak shape obtained for this type of compound under the chromatographic conditions employed, an apparent retention time shift is observed in the later analysis due to a greatly reduced acid concentration. Methyl myristate is the peak at retention time 17.1 minutes. The peaks at retention times 22.1 and 26.7 minutes are methyl palmitate and methyl stearate, respectively. No acid precursors of these esters were identified.

This study is the first in which the esterification of carboxylic acids from airborne particulate matter as a consequence of using methanol extraction solvent has been reported. Cautreels and Van Cauwenberghe have reported finding myristic acid and other aliphatic acids on airborne

particulate matter.[8, 15, 23] They derivatized the acids to the methyl esters with diazomethane before analysis, but since these compounds were found in the acid fraction after extraction with methanol and benzene,[23] and with benzene alone,[8] they were assumed to be present on the filters in the acid form. Karasek and co-workers, employing no derivatization step, found the methyl esters of several aliphatic acids in both halves of a Hi-Vol filter sample after one half was extracted with methanol.[11] It appears that both the acids and the methyl esters may be present on airborne particulate matter. Although methanol is an efficient solvent for these types of samples, care must be taken in its use if caboxylic acids are in the specific sample matrix under investigation.

Acknowledgement

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