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EXTRACTION OF ORGANIC COMPOUNDS FROM AIRBORNE PARTICULATE MATTER FOR GAS CHROMATOGRAPHIC ANALYSIS

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SUMMARY

Airborne particulate matter was collected on high-volume glass fiber filters for analysis of the organic fraction by gas chromatography-flame ionisation detection and gas chromatography-mass spectrometry techniques. Exhaustive solvent extraction followed by concentration through condensation results in a sample suitable for gas chromatographic analysis. Although cyclohexane is the solvent most commonly used for extracting organic compounds from atmospheric particulate matter, methanol was found to be more effective for this extraction. It extracted more components in larger quantities and in less time than did cyclohexane. The methanol extraction from particulates collected on glass fiber filters appears to be effective for collections of both aliphatic and polycyclic aromatic compounds and organic acids. An inorganic precipitate which forms during the condensation of the methanol extract from 200 ml to 1 ml is removed by centrifugation.

INTRODUCTION

The presence in air of polycyclic aromatic compounds, some of which are highly carcinogenic, has generated interest in the development of improved and more rapid analytical techniques for identification and quantification of the organic compounds adsorbed onto airborne particles. The conventional procedure of analysis for polycyclic aromatic compounds consists of the collection of particulate matter on inert filters, the Soxhlet extraction of these filters with an organic solvent such as benzene or cyclohexane, the isolation of the desired portion of the extract by various fractionation methods such as thin-layer chromatography and column chromatography and, finally, the detection of the components of interest with UV and fluorescence techniques¹⁻³. Benzene has been used frequently as the extracting solvent because of its ability to easily dissolve polycyclic aromatic compounds. More recently, cyclohexane has become preferred since it is less toxic than benzene and does not absorb UV radiation associated with spectroscopic detection methods³.

Because UV and fluorescence methods detect only selected aromatic com-

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pounds and often experience interference from compounds with absorption and emission spectra similar to that of the compounds being analyzed, other analytical approaches have been investigated. High-resolution gas chromatographic (GC) techniques appear to be the most suitable. Combined gas chromatography/mass spectrometry (GC-MS) methods have been used to identify a number of polycyclic aromatic compounds⁴ and by gas chromatographic separation with flame ionization detection (GC-FID) many aromatic and non-aromatic components have been detected⁵⁻⁹.

The principal advantage of GC techniques rests in the ease and efficiency with which a number of components can be separated and accurately analyzed. High-resolution columns allow the analysis of the major components in a sample without lengthy pre-separation steps. As the efficiency of packed columns improves and the technology for preparing glass capillary columns becomes available, GC promises to provide the most precise and complete analysis of airborne organic particulate matter.

A second advantage to GC is that it obviates the need for selecting extraction solvents on the basis of their compatibility with detection methods or pre-separation techniques. Since GC identification is normally by retention time or through mass spectral data, solvent selection can be made solely with respect to extraction efficiency.

In our work on the development of rapid methods for the qualitative and quantitative analysis of major volatile organic compounds contained in air particulate extracts, the basic procedure involves high-resolution GC-FID analysis. An efficient extraction step is crucial. This study was undertaken to determine whether methanol, rather than the more commonly used cyclohexane, should be selected as the extraction medium. This choice of method initially was suggested by studies by Grosjean¹⁰ and Gordon¹¹, in which a number of solvents were compared and methanol was found to be the most efficient for extracting organic compounds from glass fiber filters. Grosjean found methanol to be 1.35 times more efficient than benzene, and 1.61 times more efficient than cyclohexane. Gordon's respective ratios were 2.73 and 4.40. The disparity of these results, coupled with the fact that their values do not necessarily reflect efficiency in extracting chromatographable organic material, suggested a need for further studies of methanol as an extracting agent before GC.

Appraisals of the extraction abilities of methanol and cyclohexane were made after separating individual compounds in the extracts on a GC column. By comparing the total area of the chromatograms, the effectiveness of the two solvents in extracting chromatographable material was determined. By comparing the areas of individual peaks in the chromatograms, the extraction selectivity of the solvents was evaluated.

Efficiency and selectivity are not the only considerations to be made when selecting a viable solvent for extraction. Other considerations, such as the time required for complete extraction and the quantitative problems presented by insoluble inorganics, also need examination. This paper presents data on the comparative advantages of using methanol rather than cyclohexane for the extraction of organic compounds on airborne particulate matter for GC analysis.

EXPERIMENTAL

Collection of particulate matter

The airborne particles were collected from the atmosphere by passing air

through high-volume glass fiber filters for a 24-h period at flow-rates ranging from 46–125 m³/h. The total weight of the particulate matter collected and the total volume of air passed through the filters were recorded. The concentration of particles in the air studied ranged from 15–650 µg/m³.

Extraction of the particulate matter

One half of a glass fiber filter was cut into cm² pieces, placed into a glass extraction thimble, and extracted in a soxhlet apparatus by 200 ml of either methanol or cyclohexane for 16 h. The solvent was then condensed from 200–20 ml and the 20-ml condensate centrifuged to separate a precipitate which appeared during the concentration step. After decanting the solvent, the precipitate was washed with two 1-ml aliquots which were added to the decanted solution. The extract was then further condensed to 1 ml from which 3 µl were injected into the gas chromatograph.

Both the methanol and cyclohexane were high-purity "Distilled in Glass" solvents (Burdick & Jackson Labs., Muskegan, Mich., U.S.A.). Blanks run on methanol showed no detectable compounds in 1 ml of solvent which had been condensed from 200 ml. Although several contaminants of the cyclohexane solvent were found in blank runs, these compounds were more volatile than any of the sample components and did not interfere with the GC analysis.

Chromatography of the condensed extract

A Hewlett-Packard Model 5830A gas chromatograph with a flame ionization detector using both a 6 ft. × 2 mm I.D. and a 10 ft. × 2 mm I.D. glass column containing a packing coated with an ultrathin polymer of Carbowax 20M having low bleed characteristics and high selectivity was used in the separation and detection of the sample components¹². The chromatograph is digitally controlled and gives GC retention times with a better than ±1% reproducibility. The column was run isothermally at 100° for 4 min after injection and then programmed to 240° at 4°/min. The detector temperature was 300° and the injection port was held at 240°; gas flow-rates for helium, air, and hydrogen were kept constant at 28, 250, and 42 ml/min, respectively.

RESULTS AND DISCUSSION

Cyclohexane has long been the solvent of choice for extracting organic compounds from airborne particulate matter. It remains extensively used even though several studies have indicated that other solvents are more efficient. The widespread employment of cyclohexane can be attributed to its lack of interference with various pre-separation and detection methods. However, when GC-MS or GC-FID techniques are used for separation and detection, the advantages of more effective extraction solvents can be realized. The purpose of this study was to compare the extraction properties of methanol and cyclohexane with respect to GC analysis.

Airborne particulate matter was collected on glass fiber filters in Welland (Ontario, Canada) on eight different days during 1974. One half of each filter was extracted with cyclohexane and the other half with methanol. Fig. 1 compares the total area of the peaks obtained from each chromatogram of the eight cyclohexane extracts to the respective total peak areas obtained from the methanol extracts. A line

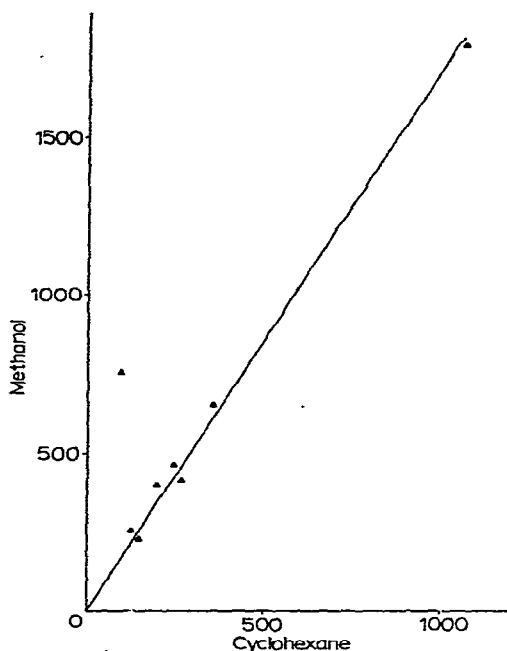


Fig. 1. Comparison of total response from chromatograms of cyclohexane extracts and methanol extracts. The slope of the line is 1.69, indicating that methanol more efficiently extracts organic material from glass fiber filters.

drawn roughly through the centers of the data points has a slope of 1.69. This is in good agreement with Grosjean's ratio of 1.61 for the extraction efficiency of methanol with respect to cyclohexane.

Gordon's ratio of 4.40 for the extraction efficiency of methanol compared to cyclohexane was much larger than that obtained by either us or Grosjean. This discrepancy is explained by the different detection methods used in obtaining the data. We measured the FID ionization response as the chromatographed components of the extracts burned individually in the flame. Grosjean measured flame ionization response as he burned the total extracted material without separation. Gordon simply weighed the residue after the extracts had been evaporated to dryness. Since inorganic compounds give little or no conductivity response in a hydrogen/air diffusion flame, use of the GC-FID apparatus primarily measured the organic compounds extracted, while Gordon weighed both the organic and inorganic components of the extracts. Gordon's results suggest that methanol is not only more efficient for extracting the organic components but that it also extracts a larger amount of inorganic components than does the cyclohexane.

A precipitate is formed in the methanol extract as it is concentrated from 200 to 1 ml. Cyclohexane-extracted samples also occasionally contained small amounts of precipitate. To determine if the precipitate was caused by saturation of the methanol with chromatographic organic material, chromatograms of samples which had been concentrated to 2 ml and then to 1 ml were compared. The chromatograms from the 1-ml concentrates were always twice as intense as those from the 2-ml solutions,

indicating that the methanol had not been saturated by any of the organic compounds. The precipitate was therefore assumed to be inorganic salts which are slightly soluble in methanol. This inorganic material most probably originated from both the particulate matter and the glass fiber filters, since smaller amounts of the precipitate appeared even when blank filters were extracted.

The quantity of the precipitate varied from sample to sample and condensing the extracted solution to small volumes resulted in concentration fluctuations of the organic compounds in solution. Fig. 2 shows two chromatograms: one which was obtained from a 1-ml sample containing about 0.1 ml of precipitate, and the other from a 1-ml volume of this same sample after the precipitate had been centrifuged, removed, and washed with several 1-ml aliquots of methanol. The comparative chromatograms illustrate the difference in response caused by the presence of the precipitate and that none of the components are lost during removal of the precipitate. To avoid minor concentration errors from fluctuations in precipitate content, all the precipitates were removed from the sample by centrifugation prior to adjusting the sample volume to 1 ml.

For judging the effectiveness of cyclohexane and methanol for use as extracting solvents before GC, a better criterion than total area response is individual peak response. Fig. 3 shows example chromatograms where one half of a filter has been extracted with methanol and the other half with cyclohexane. These chromatograms are typical of ones obtained from the eight filters analyzed and represent a day when the pollution was moderate to heavy. The patterns of peaks for components with longer retention times were similar for both chromatograms although the intensities of the peaks were generally stronger for the methanol extract. However, the chromatographic patterns of the components which were eluted in the first half of the chromatograms are noticeably different. In this portion of the chromatogram methanol not only extracted larger quantities of a given component but also extracted many more components than did the cyclohexane.

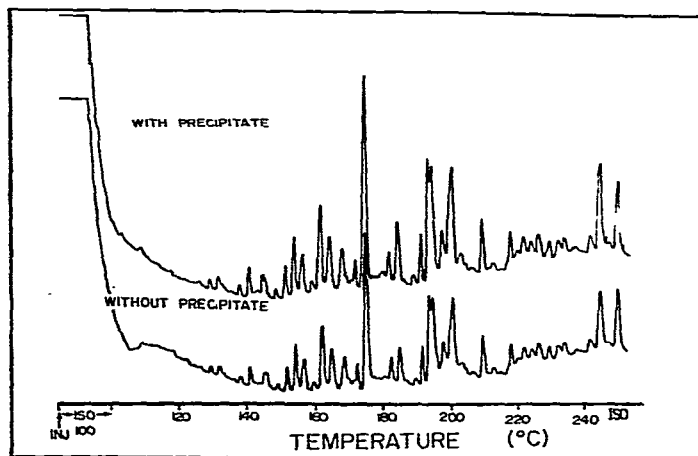


Fig. 2. The upper chromatogram is a 3- μ l injection of a methanol extract which had been adjusted to a total volume of 1 ml including precipitated matter. The lower chromatogram is a 3- μ l injection of the same extract which had been adjusted to a total volume of 1 ml after the precipitate had been removed. The column length was 6 ft. Other operating conditions are given in Experimental.

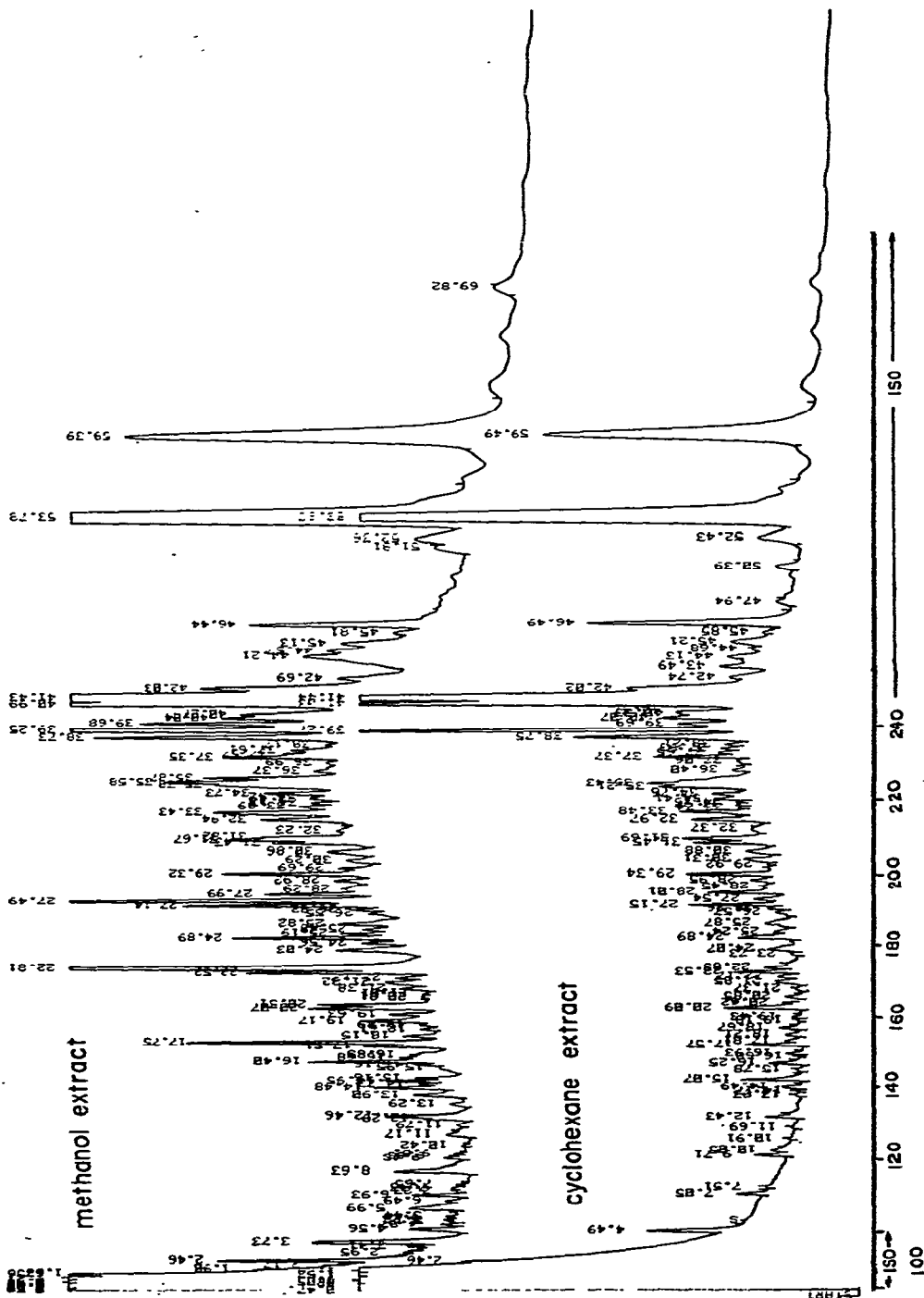


Fig. 3. Comparative chromatograms of organic compounds extracted from different halves of the same glass fiber filter. Methanol was used as the extraction solvent for the upper chromatogram while cyclohexane was used for the lower chromatogram. The column length was 10 ft. Other operating conditions are given in Experimental.

TABLE I
 LISTED RETENTION TIMES AND COMPARATIVE AREA RESPONSE VALUES (IN ARBITRARY UNITS) FOR INDIVIDUAL PEAKS SHOWN IN FIG. 3

Retention time		Area response		Retention time		Area response	
Cyclohexane	Methanol	Cyclohexane	Methanol	Cyclohexane	Methanol	Cyclohexane	Methanol
	3.73	—	16.1	28.01	27.99	6.0	7.3
9	4.56	7.3	4.9	28.95	28.92	1.5	2.2
	4.87	—	1.2	29.34	29.32	6.7	12.7
	5.99	—	7.6	—	29.69	—	3.3
	6.49	—	1.2	30.31	30.29	3.5	3.7
05	6.93	1.9	3.5	30.88	30.86	3.4	5.4
	8.63	—	12.8	31.45	31.43	5.6	7.4
	9.48	—	1.8	31.69	31.67	8.5	13.2
1	9.63	2.3	1.1	—	31.82	—	6.7
05	—	1.6	—	32.37	32.23	1.0	2.4
	11.17	—	1.9	32.97	32.94	8.3	10.5
	12.29	—	3.1	33.48	33.43	9.8	18.4
43	12.46	2.1	8.5	33.74	—	2.3	—
	13.29	—	2.0	33.97	33.89	2.6	7.7
	13.90	—	7.7	34.15	34.13	2.3	3.5
49	14.48	1.7	10.5	34.41	34.42	5.7	4.3
	14.73	—	4.1	34.76	34.73	5.3	9.6
07	14.95	5.4	6.0	35.21	35.38	9.9	20.9
	15.16	—	5.3	35.43	35.58	21.7	23.2
	15.95	—	5.4	—	35.87	—	16.1
25	16.16	2.2	4.5	36.40	36.37	1.4	6.7
	16.40	—	16.0	37.37	37.35	7.4	13.3
	16.68	—	5.9	37.65	37.57	2.8	5.6
	16.85	—	9.4	37.93	37.81	2.1	7.2
57	17.51	4.1	10.5	38.21	38.17	1.5	2.4
81	17.75	1.7	25.9	38.75	38.73	23.1	38.2
21	18.15	1.4	9.9	39.27	39.25	44.3	69.2
67	18.61	1.3	4.7	39.69	39.68	8.5	24.1
	18.89	—	4.1	40.07	40.04	9.8	16.1
	19.17	—	14.4	40.33	40.27	5.7	17.3
	19.63	—	5.6	40.47	—	6.9	—
09	20.07	7.5	12.4	41.03	40.99	60.7	71.0
42	20.31	1.5	9.6	41.44	41.43	241.7	352.3
85	—	1.5	—	42.02	42.03	24.6	32.5
	21.38	—	2.6	42.74	42.69	5.9	10.1
85	21.82	2.6	6.5	43.49	—	5.7	—
17	22.12	1.6	3.4	44.13	44.21	6.7	33.7
53	22.52	4.5	15.2	44.68	44.57	<1	15.3
83	22.81	2.0	82.8	45.21	45.13	5.4	19.1
07	24.03	3.4	17.9	45.85	45.81	<1	4.7
	24.56	—	7.4	46.49	46.44	35.4	35.9
89	24.89	6.5	21.0	47.94	—	1.5	—
24	25.19	2.5	8.3	50.39	—	3.2	—
	25.48	—	9.0	—	51.81	—	2.2
87	25.82	5.4	17.4	52.43	52.36	12.4	7.2
57	26.55	1.9	8.6	53.83	53.78	245.9	323.0
86	26.82	1.9	5.7	59.49	59.39	109.4	161.3
15	27.14	8.6	20.1	—	69.82	—	2.2
54	27.49	3.1	47.1	—	—	—	—

In Table I retention times have been matched to compare the area response of each peak in Fig. 3. The methanol extract produced 90 peaks while the cyclohexane solution produced only 70. Of the 63 components that were extracted by both solvents, 57 were extracted more efficiently with methanol. Many of the extra peaks from the methanol extract were only minor, but seven, those at retention times 3.73, 8.63, 16.40, 16.85, 19.17, 25.48, and 35.87 min, had areas larger than 57% of all the compounds responding. Cyclohexane extracted seven components that methanol did not extract, but in each case these were only minor components of the mixture.

It is beyond the scope of this paper to identify all of the components extracted and detected. The peak occurring at 22.81 min, however, is of special interest, since it was a very minor peak in the cyclohexane extract but one of the major components of the methanol extract. GC-MS methods identified the peak as methyl hexadecanoate¹³, indicating that this compound and possibly other organic acids or their salts or esters are more efficiently removed by methanol. Esterification of acid salts might be involved in the extraction step.

The time required for an analysis is often as important a consideration as any other when choosing analytical procedures. Eight to twenty-four hours are often the times of extraction when cyclohexane or benzene are used as solvents. Extraction times of 16 h were used in this study because the sample could conveniently be left extracting overnight and because this length allowed a fair comparison of cyclohexane with methanol. The optimum time for a methanol extraction had not been established but subsequent 16-h extractions of previously extracted filters implied that the initial methanol extractions had been complete.

A time vs. extraction efficiency study of methanol was made by shredding and mixing one and a half filter papers and then dividing them evenly into three separate samples. One sample was extracted for 2 h, another for 4 h, and a third for 8 h. Following the first extraction each sample was subjected to an exhaustive 16-h methanol extraction. No difference was observed in the chromatograms produced from extracts of the 2-, 4-, and 8-h periods. The 16-h exhaustive extractions showed no residual compounds present. These data indicated that the 2-h extraction had been sufficient to completely remove the organic compounds from the filter.

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