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HYDROCARBONS IDENTIFIED IN EXTRACTS FROM ESTUARINE
WATER ACCOMMODATED NO. 2 FUEL OIL BY
GAS CHROMATOGRAPHY-MASS SPECTROMETRY

by Beverley W. Lewis, Ann L. Walker, and Rudolf H. Bieri

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GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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SUMMARY

This data report presents the results of a computerized gas chromatograph-mass spectrometer analysis of methylene chloride and n-heptane extracts of a No. 2 fuel oil accommodated estuarine water sample. The analytical method is briefly described and the limitations on the identifications are categorized. Major and trace constituents in the water accommodate were determined.

Altogether 66 hydrocarbon compounds were identified specifically and 75 compounds were partially identified. Seven compounds could be recognized as major constituents of the water accommodated oil and ten were present only as traces. The aromatic compounds found were alkyl benzenes, naphthalene, tetralin, indane, biphenyl, fluorene, anthracene, and some of their alkyl substituted isomers in the range of carbon numbers C_7 to C_{15} . Four n-alkanes, C_{10} to C_{13} , were found along with four other assorted hydrocarbons.

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INTRODUCTION

The detailed analyses of petroleum hydrocarbon compounds which dissolve in or are accommodated by estuarine water systems are needed for ecological studies of the fate and effect of oil spills. Until recently, the available analytical techniques and instruments limited the progress in analyzing these extremely complex samples, each of which contain hundreds of compounds. The development of computerized gas chromatograph mass spectrometer (GC-MS) systems has now placed a much more detailed analysis of these types of samples within reach. This report presents these data resulting from the investigation of the use of a low resolution GC-MS system to analyze extracts of York River water which had accommodated a No. 2 fuel oil in a laboratory equilibration process. Several GC, support coated open tubular (SCOT) columns were evaluated in the GC-MS. Two columns were selected to separate the aromatic fractions of oil for the MS analysis. They were Didecyl phthalate (DDP) and OV-25, the DDP giving better separation of the alkyl benzenes and the OV-25 giving better separations for the substituted naphthalenes.

This work was the preliminary phase of a continuing program to develop analytical capabilities for identifying the major hydrocarbon compounds in estuarine environmental samples due to oil pollution. One objective was to identify as many of the gas chromatographically separated compounds as possible, and to indicate which ones were the most abundant. The results of this phase have shown that the techniques and equipment are capable of a rather detailed analysis of this type of sample, and with further refinements will be satisfactory for ecological studies of the fate and effect of oil in estuaries. The purpose of this report is to make these data obtained available rather than to evaluate the method, since the methods are still being developed and refined.

APPARATUS AND PROCEDURES

A System/150 computerized data acquisition unit was used to obtain data from a Finnigan 1015 quadrupole mass spectrometer interfaced to a Varian Aerograph gas chromatograph oven. Support coated open tubular (SCOT) GC columns with either DDP or OV-25 were used under isothermal and temperature-programed conditions to separate sample components.

The oil-accommodated water was extracted with either n-heptane or methylene chloride. In the case of n-heptane, the extract was concentrated at low temperature to a volume on the order of 0.3 ml and injected as the n-heptane solution. However, the methylene chloride was evaporated completely and the hydrocarbons were then dissolved in a small amount of n-heptane to provide the sample for injection.

Table I gives the GC parameters for the three pertinent runs.

The entire effluent from the column was fed directly into the ionization chamber of the mass spectrometer. The filament in the ion source was turned off just prior to solvent elution and remained off three-four minutes until the pressure on the manifold had returned to its normal operating level of $<5 \times 10^{-5}$ torr. A real time total ion current chromatogram was obtained on a Houston Instruments digital plotter, and at the completion of a run, a reconstructed chromatogram, normalized to the highest peak, was also produced. Generally several series of mass searches were then made to detect compound classes having specific molecular weights and to determine if any components had been partially or completely obscured by simultaneous elution of other material. Mass spectral data in the form of ion current intensities and m/e for each ion fragment were printed out numerically on the teletype for each GC peak of interest.

Whenever possible, identifications were made by comparing the actual GC retention time and the mass spectral data of standard compounds with that of the sample. These compounds are listed in the a sections of tables II, III and IV. When standard compounds were not available, the mass spectral data were compared with literature data for compound classification, and further identification by isomers was made from boiling point data and GC retention times. Such compounds are listed in the b sections of the tables. In cases where neither standards nor boiling point data were available, partial identifications were made on the basis of literature mass spectral data alone. The similarity of mass spectral fragmentation patterns of aromatic isomers, often coupled with the large number of isomers (e.g. C₅-substituted benzenes), made it extremely difficult to identify the nature and position of the alkyl substituents. Partially classified compounds are found in the c sections of the tables. All identifications were made by manual comparisons with mass spectra given in the Aldermaston collection or obtained by running standards on our Finnigan GC-MS system.

RESULTS AND DISCUSSION

Tables II, III, and IV list the compounds identified along with the mode of identification (a, b, or c) and an indication of whether the compound was a major (M) or trace (T) constituent.

Table II lists the benzene compounds found in the methylene chloride extract of the No. 2 fuel oil accommodated York River water. It is noted that all isomers of dimethyl-, diethyl-, methyl-ethyl-, methyl-isopropyl-, trimethyl-, and tetramethyl-benzenes were found. All dimethyl-ethyl benzenes were found except the 1, 3-5-isomer. Altogether 30 substituted benzenes were identified and 16 more were separated and partially identified.

Table III shows the naphthalenes and tetralins (1, 2, 3, 4-tetrahydronaphthalenes) found in the methylene chloride and a n-heptane extract of the accommodate. The monoalkyl naphthalenes containing either a methyl or ethyl group are complete. Four of the ten possible isomers of dimethylnaphthalene are not identified with respect to their structure, but two of these were separated. The missing two isomers were either not present above the detection limits or were co-eluted with a relatively abundant compound. Only two of the 15 possible trimethylnaphthalenes could be specifically identified. Others may be among the seven separated C₃-substituted naphthalenes. All naphthalenes of either higher substitution or molecular weight remain of unknown specific structure because their mass spectra do not allow further distinction. All of the possible methyltetralins were identified and, together with tetralin itself, they were among the most abundant compounds found in the water extracts. Ethyl-, dimethyl-, and trimethyl-tetralins were separated and identified by their mass spectra but no specific isomers could be assigned. Thus, 18 naphthalenes and tetralins could be identified completely, while 30 more were separated and partially identified.

Table IV contains the indanes, biphenyls, and a few polyaromatic compounds and some of their alkylated forms which were found in the methylene chloride extract. Only a few of the compounds in this group were specifically identified, among which were two methyl indanes, biphenyl (a major constituent), three methyl biphenyls, acenaphthene, fluorene, anthracene, four n-alkanes and dibenzofuran (the only heterocompound found). A total of 18 compounds were specifically identified with 28 others separated and partially identified.

CONCLUDING REMARKS

This work has demonstrated the capabilities of the computerized GC-MS to separate and analyze many of the compounds in a complex environmental sample and has indicated some areas where improvements or refinements in techniques are needed to optimize the utility of the method. These data are presented as a guide to the compounds found in a water accommodate of a No. 2 fuel oil for use in related research.

Altogether 66 hydrocarbon compounds were identified specifically and 75 compounds were partially identified. Some seven compounds could be recognized as major constituents of the water accommodated oil and ten were present only as traces.

TABLE I

GC PARAMETERS FOR PERTINENT RUNS

Run	<u>GULF 3</u>	<u>GULF 7</u>	<u>GULF 8</u>
Column	DDP	OV-25	OV-25
Length	100 ft	50 ft	50 ft
Diameter	0.02 in	0.02 in	0.02 in
Temperature			
Injection Port	208° C	205° C	205° C
Oven-Isothermal	140° C for 121 min 120° C for 210 min	108° C for 45 min	108° C for 45 min
Oven-Programed	---	1°/min to 220° C	1°/min to 220° C
Sample Size	1.50 μ l	0.45 ml	1.05 μ l
Sample Solvent	n-heptane	n-heptane	n-heptane
Carrier Gas	1.5 cc/min He	1.5 cc/min He	1.5 cc/min He
Extraction Solvent	methylene chloride	methylene chloride	methylene chloride

TABLE II

BENZENE COMPOUNDS FOUND IN A METHYLENE CHLORIDE EXTRACT OF AN ESTUARINE
WATER ACCOMMODATE OF A NO. 2 FUEL OIL BY GC - MS

MONOSUBSTITUTED BENZENES, C ₇ to C ₁₀		TRISUBSTITUTED BENZENES, C ₉ & C ₁₀	
a	ETHYLBENZENE	T	
	n-PROPYLBENZENE	T	
	ISOPROPYLBENZENE	T	
	SEC-BUTYLBENZENE	T	
	ISOBUTYLBENZENE	T	
BISUBSTITUTED BENZENES, C₈ to C₁₀			
a	o - XYLENE		
	m - XYLENE		
	p - XYLENE		
	o - DIETHYLBENZENE		
	m - DIETHYLBENZENE	T	
	p - DIETHYLBENZENE		
	o - ETHYLTOLUENE		
	m - ETHYLTOLUENE		
	p - ETHYLTOLUENE		
	b	o-n- PROPYLTOLUENE	
		p-n-PROPYLTOLUENE	
		o - ISOPROPYLTOLUENE	T
		m - ISOPROPYLTOLUENE	
		p - ISOPROPYLTOLUENE	T
TETRASUBSTITUTED BENZENES, C₁₀			
a	1,2,4,5 - TETRAMETHYLBENZENE		
	b	1,2,3,4 - TETRAMETHYLBENZENE	
		1,2,3,5 - TETRAMETHYLBENZENE	
C₁₁ & C₁₂ ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED			
			NO.
	c	C ₅ - SUBSTITUTED BENZENES	16
		C ₆ - SUBSTITUTED BENZENE	T 1
T = TRACE, M = MAJOR CONSTITUENT			
a - INDICATES IDENTIFICATION BY COMPARISON WITH STANDARDS RUN ON SAME GC - MS			
b - IDENTIFIED BY B.P. & GC RETENTION TIME DATA AND COMPARISON WITH M.S. DATA IN LITERATURE			
c - CORRELATED WITH M.S. LITERATURE DATA			

TABLE III

NAPHTHALENE COMPOUNDS FOUND IN A METHYLENECHLORIDE OR HEPTANE EXTRACT
OF AN ESTUARINE WATER ACCOMMODATE OF A NO. 2 FUEL OIL BY GC-MS

a NAPHTHALENE, C ₁₀ H ₈			
MONOSUBSTITUTED NAPHTHALENES, C ₁₁ & C ₁₂			
a	1- METHYLNAPHTHALENE	M	
	2- METHYLNAPHTHALENE		
	1- ETHYLNAPHTHALENE		
	2- ETHYLNAPHTHALENE		
BISUBSTITUTED NAPHTHALENES, C ₁₂			
a	1,6, & 1,3 - DIMETHYLNAPHTHALENE	M	
	1,5 - DIMETHYLNAPHTHALENE		
	2,6 - DIMETHYLNAPHTHALENE		
	2,3 - DIMETHYLNAPHTHALENE		
	1,4 - DIMETHYLNAPHTHALENE		
TRISUBSTITUTED NAPHTHALENES, C ₁₃			
a	2,3,5 - TRIMETHYLNAPHTHALENE		
	2,3,6 - TRIMETHYLNAPHTHALENE		
C ₁₂ to C ₁₅ ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED			NO.
c	DIMETHYLNAPHTHALENES		2
	C ₃ -SUBST'D. NAPHTHALENES		7
	C ₄ -SUBST'D. NAPHTHALENES		8
	C ₅ -SUBST'D. NAPHTHALENE		1
1,2,3,4-TETRAHYDRONAPHTHALENES (TETRALINS)			
b	1,2,3,4-TETRAHYDRONAPHTHALENE, C ₁₀ H ₁₂	M	
MONOSUBSTITUTED TETRALINS, C ₁₁			
b	1 - METHYLTETRALIN	M	
	2 - METHYLTETRALIN	M	
	5 - METHYLTETRALIN	M	
	6 - METHYLTETRALIN	M	
C ₁₂ & C ₁₃ ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED			
c	ETHYLTETRALIN		1
	DIMETHYLTETRALINS		9
	TRIMETHYLTETRALIN		1
	C ₃ -SUBST'D TETRALIN		1

TABLE IV

INDANES, BIPHENYLS, AND OTHER ORGANICS FOUND IN A METHYLENECHLORIDE EXTRACT OF AN ESTUARINE WATER ACCOMMODATE OF A NO. 2 FUEL OIL BY GC-MS

INDANES, C ₉ to C ₁₁		HIGHER CONDENSED RING HYDROCARBONS, C ₁₂ to C ₁₅	
b	INDANE, C ₉ H ₁₀ 1- METHYLINDANE 2- METHYLINDANE	a	ACENAPHTHENE C ₁₂ H ₁₀ FLUORENE, C ₁₃ H ₁₀ ANTHRACENE, C ₁₄ H ₁₀
ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED		ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED	
c	METHYLINDANES ETHYLINDANE DIMETHYLINDANES		c METHYLFLUORENES C ₂ -SUBST'D FLUORENES METHYLANTHRACENES
	NO. 2 1 6		NO. 4 3 4
BIPHENYLS, C ₁₂ to C ₁₅		SATURATED ALIPHATIC HYDROCARBONS, C ₁₀ to C ₁₃	
a	BIPHENYL, C ₁₂ H ₁₀ M	a	n - DECANE, C ₁₀ H ₂₂ n - UNDECANE, C ₁₁ H ₂₄ n - DODECANE, C ₁₂ H ₂₆ b n - TRIDECANE, C ₁₃ H ₂₈
b	2 - METHYLBIPHENYL 3 - METHYLBIPHENYL 4 - METHYLBIPHENYL		OTHER ORGANICS, C ₁₂ to C ₁₄
	NO. 3 2 3	a	DIBENZOFURAN, C ₁₂ H ₈ O DIPHENYLMETHANE, C ₁₃ H ₁₂ c PHENYLCYCLOHEXANE, C ₁₂ H ₁₆ 1,1 - DIPHENYLETHENE, C ₁₄ H ₁₂
ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED		ISOMERS SEPARATED, NOT SPECIFICALLY IDENTIFIED	
c	DIMETHYLBIPHENYLS C ₂ -SUBST'D BIPHENYLS C ₃ -SUBST'D BIPHENYLS		
	NO. 3 2 3		