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NRL Report 6131

Nuclear Submarine Atmospheres

Part 3 - Aromatic Hydrocarbon Content

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ABSTRACT

A detailed analytical study has been directed to the identification and determination of the amounts of aromatic hydrocarbons present in nuclear submarine atomspheres. Many individual aromatic hydrocarbons have been identified and their occurrence in a number of nuclear submarines has been established. The hydrocarbon oil samples were desorbed from activated carbon which had been exposed in nuclear submarine atmospheres. The aromatic hydrocarbon content of these oils was found to be approximately 25 to 30 percent of the total. The quantitative distribution of individual aromatic hydrocarbons was very similar from submarine to submarine with this distribution strikingly similar to that of typical petroleum distillates in the same boiling range.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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NUCLEAR SUBMARINE ATMOSPHERES

Part 3 - Aromatic Hydrocarbon Content

INTRODUCTION

Starting with the first submerged cruises of USS NAUTILUS, NRL chemists have been sampling and analyzing nuclear submarine atmospheres by every useful, available means. In addition to analyses for the important fixed gases such as oxygen, carbon dioxide, and carbon monoxide, a strong effort was made to establish the magnitude and diversity of organic contaminants. It was soon found that the organic compounds in the atmosphere were present in significant amounts (1), often reaching a total concentration of 150-200 mg/m^3. However, this total was made up of hundreds of individual compounds, many of them hydrocarbons, which together constituted a comples mixture which challenged the analytical techniques and instruments available to the analysts (1,2).

It was important that the identities and concentrations of each organic contaminant or group of contaminants be established so that the possible toxic effects could be evaluated by toxicologists. In addition, it was important in many instances to consider the effect of certain types of materials, in the form of vapors and aerosols, on the effective operation of equipment and instruments. For example, it was necessary to know what compounds were present, so that it could be established experimentally whether or not they were destroyed by the catalytic combustor, and whether deleterious products might be formed in the combustion process (3-5).

Establishing the maximum acceptable concentration (MAC) in the submarine atmosphere for any material is the responsibility of the Bureau of Medicine and Surgery (6). It is the role of the chemist to establish the presence or absence of a particular contaminant in submarine atmospheres so that the work of the toxicologists can be most effective. This is particularly pertinent because for the most part the MAC of such materials had been set previously by industrial medical specialists on the basis of intermittent exposure such as an 8-hour day, 5-day week (7,8). Where exposures are continuous and unalleviated for 24 hours a day for many weeks, new criteria and new limits must be established. In addition to the consideration of long range physiological effects, in several instances acute cases of eye irritation had to be dealt with (9). Since most organic vapors are potential sources of toxicity and other problems, and all organic compounds may be considered to be undesirable contaminants, there has been an urgency to identify them, establish their sources, and eliminate them as much as possible.

It has been of special interest to identify and determine the concentrations of the aromatic hydrocarbons in submarine atmospheres because of their greater toxicities compared to other hydrocarbons. For example, the MAC for industrial exposures to benzene (7) was given as 100 ppm in 1951 and reduced to 25 ppm in 1957. The 8-hour-day exposure limit for benzene set by BuMed (6) in 1963 was 25 ppm. It was recently recommended that the limit for continuous exposure be lowered to 2 ppm based on toxicological studies by the Navy Toxicology Unit (10). They also recommended that other aromatic hydrocarbons be considered to have toxicities comparable to benzene.

HISTORICAL BACKGROUND

It was shown very early in the program for detection and identification of trace contaminants that hydrocarbons make up the bulk of the organic compounds present in nuclear

submarine atmospheres (1). Carbon sampling has been found to be one of the most convenient and effective methods for sampling submarine atmospheres for hydrocarbon content (1,11). Air is drawn through a canister of activated carbon (charcoal) at a given rate for a given period of time, usually 8 to 12 hours. The exposed carbon is sent back to NRL or the Marine Engineering Laboratory where the hydrocarbon sample is removed from the carbon by one of several methods. One desorption method being used regularly is to pass superheated steam through the carbon and collect the hydrocarbon sample by condensation. Similarly, desorption by heating under vacuum followed by condensation in cold traps has been effective for special purposes.

Another source of hydrocarbon samples has been activated carbon taken from the main filter beds used for air purification. For example, vacuum desorption of carbon taken from filters in NAUTILUS in 1956 showed that large amounts of hydrocarbons were being adsorbed from the submarine atmosphere. Hydrocarbon-type analysis of these samples based on mass spectrometer data showed that all types of hydrocarbons were present: aliphatic paraffins, cycloparaffins, olefins, cycloolefins, diolefins, acetylenes, and aromatics (12). Additional analytical work on these samples based on gas chromatography and infrared spectroscopy showed definite traces of benzene, toluene, and xylenes. Infrared spectroscopy was used (2) to identify qualitatively several other aromatic hydrocarbons, including 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1-methyl-4-ethylbenzene, and 1,3-dimethyl-5-ethylbenzene. Additional work with gas chromatography on carbon samples from USS SKATE (13) showed most of the same aromatic hydrocarbons to be present, as well as ethylbenzene, n-propylbenzene, and isopropylbenzene. More recently Kagarise and Saunders reported (14) a technique based on gas chromatography coupled with infrared spectroscopy which has been useful in identification of individual hydrocarbons desorbed from carbon.

The identifications of individual aromatic hydrocarbons were based on samples obtained by desorption of activated carbon which had been exposed in nuclear submarines. On several occasions, however, gas chromatographic analyses of air samples were made directly in submarines. The experimental work under such conditions is much more difficult to perform, but corroboration of the presence of many individual aromatic hydrocarbons in submarine atmospheres was achieved. For example, ten aromatic hydrocarbons of those already listed were identified in the atmosphere of USS SKATE by direct analysis (13,15). Carbon samples taken during the same cruise yielded the same compounds. Comparison of the chromatograms showed that some of the lower molecular weight hydrocarbons (less than six carbon atoms) are not fully retained on carbon, but there is almost complete recovery in the higher molecular weight range based on relative peak areas (15).

During the early work, quantitative measurements were not made of the individual aromatic hydrocarbons due to the complexity of the mixtures in submarine atmospheres, and the specific limitations of the analytical instruments and sampling procedures. In fact, by April 1960, only two hydrocarbons, methane and acetlyene, had been reported in quantitative amounts (16). However, due to the toxicity considerations, it was deemed important to attempt to separate the aromatic hydrocarbons, and estimate their concentrations in nuclear submarine atmospheres.

ANALYTICAL METHODS AND APPARATUS

Collection of Samples by Means of Activated Carbon

Hydrocarbon vapors from the internal atmospheres of nuclear submarines were collected on activated carbon in the main filter units or in analytical carbon samplers (see Fig. 1) (11,17). These samples of carbon were returned to the Laboratory where the hydrocarbons were removed from the activated carbon by steam desorption. In this procedure superheated steam is passed through the carbon charge (80 to 100 grams) while the

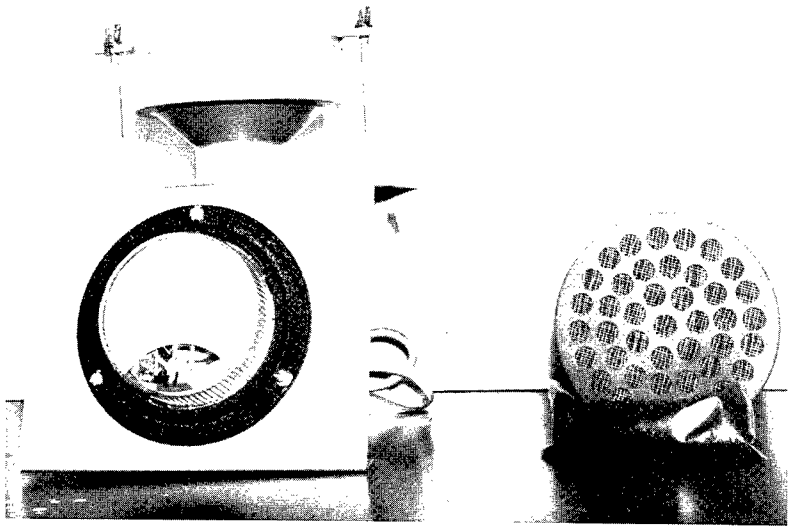

Fig. 1 - NRL Hydrocarbon Sampler with carbon canister shown on right

temperature is slowly raised to about 425°C. The effluent is condensed and the oil layer which contains the hydrocarbons is separated from the water layer. This procedure requires approximately seven hours.

Since most of the data concerning the aromatic content of submarine atmospheres was based on sampling by activated carbon, it was important to establish the soundness of this method and its ability to provide a true picture of the contaminants. A mixture of eight hydrocarbons was prepared with approximately equal volumes of aromatic and aliphatic hydrocarbons having an average molecular weight of 108. This hydrocarbon mixture was sampled with activated carbon from a controlled atmosphere in a large chamber having a volume of approximately 1100 cubic feet with the concentration of hydrocarbons in the chamber maintained at 91 mg/m^3 by controlled metering of the mixture into the air-stream that supplied the chamber.

The atmosphere in the chamber was sampled with a modified commercial carbon canister/blower unit with adsorption and mechanical efficiencies of the carbon canister determined by drawing inlet and effluent air through a catalyst bed, which burned the hydrocarbons completely producing carbon dioxide. The CO_2 was measured with a Beckman nondispersive infrared analyzer. The adsorption efficiency was found to be essentially 100% up to the time of breakthrough, which occurred after 10 hours of sampling. The experiment was terminated after 13 hours of cumulative sampling at which time the adsorption efficiency had dropped to approximately 85%.

After recovery by the standard steam desorption procedure, the adsorbate and the original synthetic mixture were analyzed by the Fluorescent Indicator Adsorption (FIA) method. The synthetic mixture showed 54% aromatic hydrocarbons, whereas the oil recovered from the carbon by steam desorption was 55% aromatic. This was encouraging evidence that the carbon sampling collection method was valid showing no undue distortion of the aromatic content.

Less quantitative, but nonetheless important, corroboration of the carbon sampling method is based on direct analyses by gas chromatography aboard a submarine which could be compared to data from carbon desorbed in the Laboratory (15). This comparison

showed that some of the lower molecular weight hydrocarbons were passing through the carbon. In general, however, the chromatograms indicated good agreement in the recovered oil compared to samples run directly on shipboard.

Analysis by the FIA Method and Separation of Hydrocarbon Oils into Structural Types

The FIA method (18) for structural type analysis of hydrocarbons has been proved to be very useful by the petroleum industry. This method, which is based on an ASTM procedure, was used to determine the proportionate quantities of aromatics, olefins, and saturated hydrocarbons in desorbed submarine oils. It is basically a liquid-solid chromatographic procedure using silica gel. In brief, the method consists of adding to silica gel in a glass column the oil sample to which has been added fluorescent dyes which mark the boundaries of the sections of hydrocarbons separated into compound types in the column. A diagram of the system is shown in Fig. 2. The length of each section is proportional to the volume percent of each hydrocarbon type present in the oil. Isopropyl alcohol is used to displace the hydrocarbons down the column. Nitrogen gas pressure is used to increase the rate of travel through the column of silica gel.

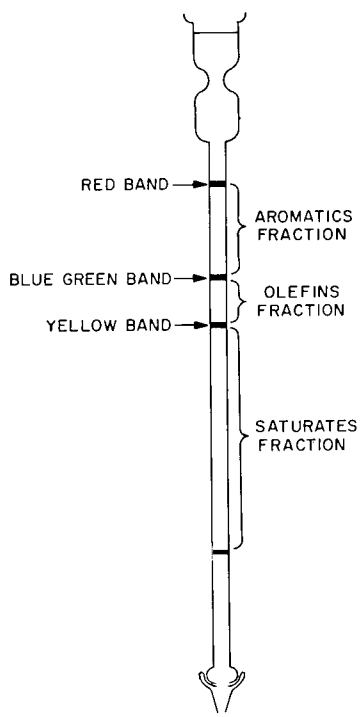

Fig. 2 - Sketch of FIA chromatograph tube depicting separation of hydrocarbon sample into types by molecular structure

However, it was decided to test the method with known mixtures of hydrocarbons because of several modifications which were planned. One modification was based on using silica gel to which 4% water by weight had been added to enhance the separation of hydrocarbon types. This was suggested by Norris, Shively, and Constantin (19) and its efficacy verified at NRL. In addition, it was hoped to collect each hydrocarbon type (e.g., aromatics) separately as it emerged from the column. This sample collection was not part of the standard procedure. Finally, it was planned to use samples larger than prescribed by the standard method to aid in the collection of fractions.

Certain data accumulated in these studies are summarized in Table 1. A mixture (solution A) of eight hydrocarbons was prepared containing 25% aromatics by volume, and 26.4% was found by the FIA method in which dry silica gel is used. In another case (solution B), the standard method using dry gel yielded 37.3% for a mixture containing 33.3% aromatics. Using the wetted gel gave excellent reproducibility of results; the 35.1% aromatics found being nearer the true value. The compositions of these solutions are given in Table 1. The experiments indicated that the partially deactivated silica gel, containing 4% water, improved the separation significantly. Consequently, this gel was used for most of the analytical separations of hydrocarbon types.

Table 1
Determinations of Hydrocarbon Types by FIA Method

Hydrocarbon Mixture Used	Aromatics		Olefins		Saturates	
	Calculated	Found	Calculated	Found	Calculated	Found
	(percent by volume)					
Solution A*‡	25.0	26.4	37.5	40.0	37.5	33.7
Solution B†‡	33.3	37.3	33.3	29.2	33.3	33.8
Solution B†¶	33.3	35.1	33.3	33.2	33.3	31.7
Solution B†¶	33.3	35.1	33.3	32.4	33.3	32.5

*Solution A contained equal volumes of eight hydrocarbons: n-hexane, n-decane, 2,2,5-trimethylpentane, hexene-1, octene-1, dodecene-1, benzene, and p-xylene.
†Solution B contained equal volumes of nine hydrocarbons: 2,2,5-trimethylhexane, n-nonane, n-tridecane, hexene-1, octene-1, 2,2,4-trimethylpentene-1, benzene, o-xylene, and n-butylbenzene.
‡Silica gel used was dried according to ASTM Method 1319 (Ref. 18).
¶Silica gel first dried as above, then moistened with 4% distilled water.

The FIA fractions of solution B which emerged from the column were compared to the original solutions of each type compound by gas chromatography. This comparison showed very little loss of the individual compounds during the FIA process. For example, in the aromatics group, benzene was recovered almost quantitatively. Olefins and saturates were also cleanly separated with excellent recovery (Figs. 3-6). Note particularly that each fraction is not contaminated by the hydrocarbons of another fraction.

Further proof of the essentially quantitative recovery of hydrocarbon types by the FIA method is given in Table 2. The volume percentages read on the chromatograph column by the FIA method check very closely with the weight percents determined by weighing the collected fractions. Also the overall recovery efficiency of 96.8% based on weights of recovered fractions is excellent for this procedure. By infrared spectroscopy, the saturates fraction was found to contain no aromatic hydrocarbons to the IR limit of sensitivity (estimated at less than 0.5%). The gas chromatograms of the aromatics fraction were found to contain no other significant peaks, demonstrating the usual clean separation. Although the FIA method (18) specifies a 0.75 ml sample, samples as large as 3.8 ml have been separated into fractions in this apparatus and gas chromatograms showed excellent separations. This modification allowed the collection of larger samples of each structural type for further analyses.

On the basis of these proofs, it was concluded that the FIA method for estimation of hydrocarbon types is well-suited to hydrocarbon oils recovered from submarine atmospheres. In addition, the separations of the saturates and aromatics fractions have been shown to be quantitative and free of contamination.

Gas Chromatography

Gas chromatography was used to study the individual hydrocarbons in the submarine oil samples and the separated hydrocarbon-type fractions. For much of the work of identification and estimation of the individual aromatic hydrocarbons a model 154C Perkin-Elmer Vapor Fractometer was used. The separation column was a two-meter Perkin-Elmer "A" column which contains diisodecyl phthalate as the stationary phase. In addition, a

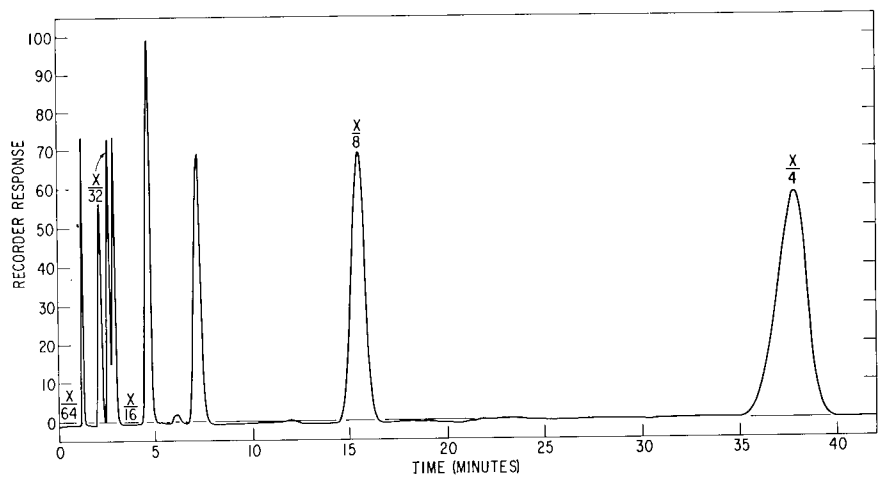

Fig. 3 - Chromatogram of hydrocarbons in solution B (before separation by the FIA method)

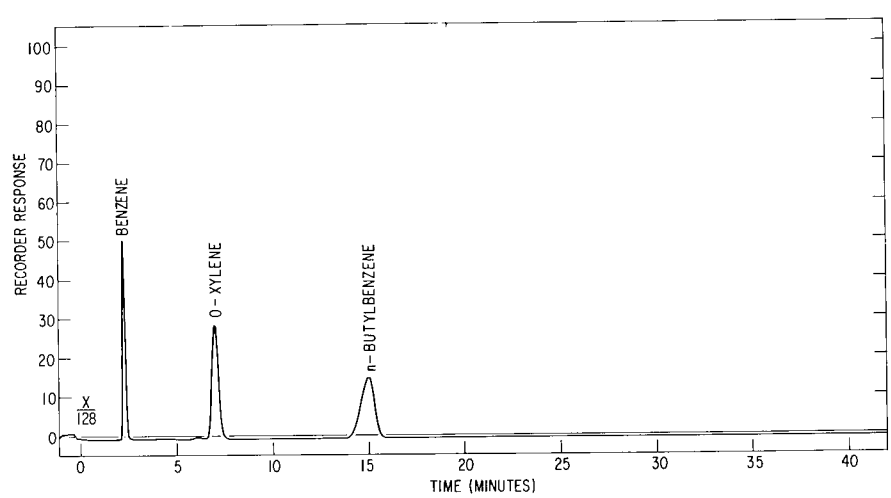

Fig. 4 - Chromatogram of aromatic hydrocarbons separated from solution B by the FIA method

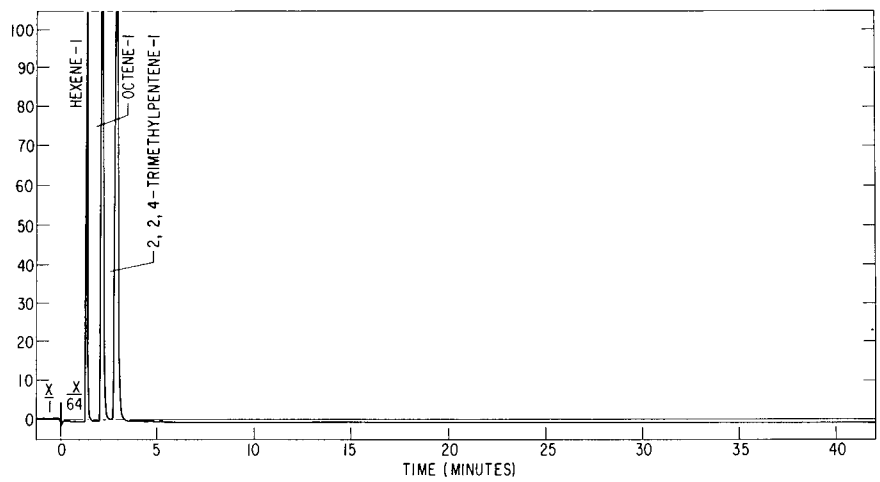

Fig. 5 - Chromatogram of olefins separated from solution B by the FIA method

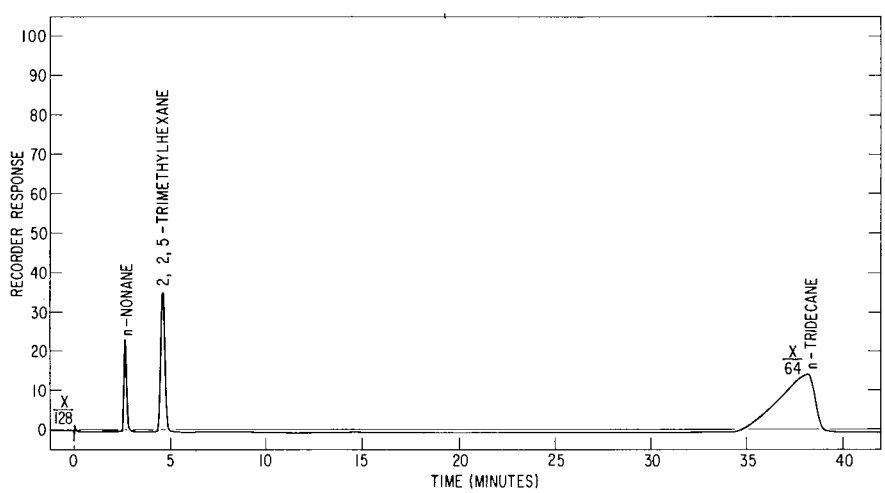

Fig. 6 - Chromatogram of paraffin hydrocarbons separated from solution B by the FIA method

Beckman Model GC-2A chromatograph was used, employing both the thermal conductivity and flame ionization detectors, as well as several different columns.

By establishing relative retention times in these columns with known hydrocarbons, coupled with previous FIA separations, identification of each aromatic hydrocarbon listed in the data has been established. Where separations of two compounds were incomplete, they are listed as pairs of compounds.

The quantitative estimation of each compound is based on area measurements which were made using a 1-millivolt Fisher Integrating Laboratory Recorder or in some cases manually with a planimeter. It has been shown that the areas of alkyl-benzene type hydrocarbons including those in this report do not vary more than 5% with the thermal conductivity detectors used in the chromatographs. Some of the data were taken with a flame ionization detector which gives even less area variation in its response to these compounds.

The two chromatographs were compared by using a synthetic mixture of aromatic hydrocarbons with the results recorded on two different integrating potentiometers and the data given in Table 3. The ratio of flame ionization to thermal conductivity data has an average deviation of ±6%.

Table 2
Recovery of Fractions by Hydrocarbon Types Using FIA Separation Procedure on a Hydrocarbon Oil (C-214) Recovered from Carbon from Submarine

Hydrocarbon Type	FIA Reading (volume percent)	Hydrocarbon Collected	
		Weight (grams)	Weight (percent)
Aromatics*	26.6	0.212	27.2
Olefins	11.1	0.096	12.2
Saturates†	62.4	0.471	60.5
Total weight recovered		0.779	
Original weight of charge		0.805	
Recovery efficiency		96.8%	

*Chromatograph of aromatics fraction shows no significant amount of nonaromatics.
†No aromatics in saturates fraction as shown by infrared analysis.

Table 3
Quantitative Estimation of Aromatic Hydrocarbons by Gas Chromatography

Hydrocarbon	Thermal Conductivity* (weight percent)		Flame Ionization† (weight percent)		Ratio FI/TC
Benzene	8.70		9.31		1.07
Toluene	5.34		6.08		1.14
Ethylbenzene		15.70		14.46	0.93
p-xylene					
o-xylene	8.54	17.06		17.63	1.03
Isopropylbenzene	8.52				
n-propylbenzene	7.68	15.78		15.57	0.98
1-methyl-3-ethylbenzene	8.10				
1,3,5-trimethylbenzene	5.28		5.01		0.95
1,2,4-trimethylbenzene	9.20	22.0		23.22	1.06
1-methyl-4-isopropylbenzene	13.80				
n-butlybenzene	9.08		8.58		0.95

*Perkin-Elmer Vapor Fractometer 154C with "A" column (diisodecyl phthalate).
†Beckman GC-2A with a Ucon 50-HB-2000 column.

AROMATIC CONTENT OF HYDROCARBON OILS RECOVERED FROM NUCLEAR SUBMARINE ATMOSPHERES

The hydrocarbon samples were recovered from activated carbon which had been exposed in nuclear submarines. (This carbon was either analytical carbon exposed for 8 to 24 hours in a carbon sampler or main filter carbon which had been exposed for periods of several days to many weeks.) These samples were examined for types of hydrocarbons by the FIA method with data and other information concerning the samples given in Table 4. The aromatics ranged from 25 to 50 percent of the total.

Table 4
Hydrocarbons from Submarine Atmospheres*
Separated into Types by FIA Method

Sample	Nuclear Submarine	Date Taken	Carbon Type	Exposure (hours)	Hydrocarbon Type (percent)		
					Aromatics	Saturates	Olefins
MS-215	NAUTILUS	Aug. 1958	Analytical	24	36‡	64	ND†
MS-250	SKATE	Oct. 1958	Analytical	24	41‡	59	ND
MS-270	SKATE	Oct. 1958	Analytical	12	54‡	46	ND
C-52X	TRITON	Sept. 1959	Analytical	9	47‡	53	ND
C-53X	TRITON	Sept. 1959	Analytical	9	48‡	52	ND
C-54X	TRITON	Sept. 1959	Analytical	13	50‡	50	ND
C-201	G. WASH.	Sept. 1960	Analytical	24	28	66	6
C-214	A. LINCOLN	Sept. 1961	Main filter	1700	30	63	7
C-221	SNOOK	Sept. 1961	Analytical	12	25	67	8
N-554	P. HENRY	Sept. 1962	Main filter	1100	37	56	7
N-662	R. E. LEE	Sept. 1962	Analytical	8	23	74	3
N-689	NAUTILUS	Sept. 1962	Analytical	12	24	70	6
C-242	SCULPIN	Sept. 1963	Main filter	860	23	73	4

*Recovered by adsorption/desorption of activated carbon.
†Not determined.
‡Obtained by difference, includes olefin fraction.

After separation of the hydrocarbons by the FIA technique, the relative amounts of individual aromatic hydrocarbons in several samples (Table 5) were determined by gas chromatography. Besides the 13 hydrocarbons listed in Table 5, the aromatic fractions contained higher boiling aromatics which were not individually identified and which represented from 12 to 59 percent of the total aromatics in these oils. Representative chromatograms from which the data in Table 5 were obtained are shown in Figs. 7-9 with a standard known mixture of aromatic hydrocarbons in Fig. 10 for comparison.

Total Aromatic Hydrocarbon Content

From the data given in Table 4 it might appear that a chronological factor is present, since the earlier samples showed higher average values for aromatic hydrocarbon content.

Table 5
Composition of Aromatic Fractions of Hydrocarbons
Recovered from Nuclear Submarine Atmospheres

Aromatic Hydrocarbons	C-221 SNOOK	N-554 P. HENRY	N-662 R. E. LEE	C-201 G. WASH.	C-214 A. LINCOLN	N-689 NAUTILUS
	(weight percent)					
Benzene	0.1	1.5	1.6	0.0	0.1	0.6
Toluene	2.7	11.8	9.9	0.2	1.0	5.3
Ethylbenzene	2.6	8.7	10.0	3.8	2.4	3.1
p-xylene, m-xylene	12.0	27.1	33.5	23.9	11.6	13.1
o-xylene	4.3	10.2	9.3	7.7	6.2	4.7
Isopropylbenzene	0.6	1.3	3.2	1.2	0.6	1.6
n-propylbenzene	1.0	1.5	1.9	0.9	0.8	1.6
1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene	4.9	4.3	6.0	4.3	3.4	5.9
1-methyl-2-ethylbenzene, 1,3,5-trimethylbenzene	4.2	3.3	5.1	4.4	4.0	6.1
1,2,4-trimethylbenzene	8.2	6.5	7.2	9.1	12.3	11.7
Subtotal	40.6	76.2	87.7	55.5	42.4	53.7
Higher Boiling Aromatics (by difference)	59.4	23.8	12.3	44.5	57.6	46.3

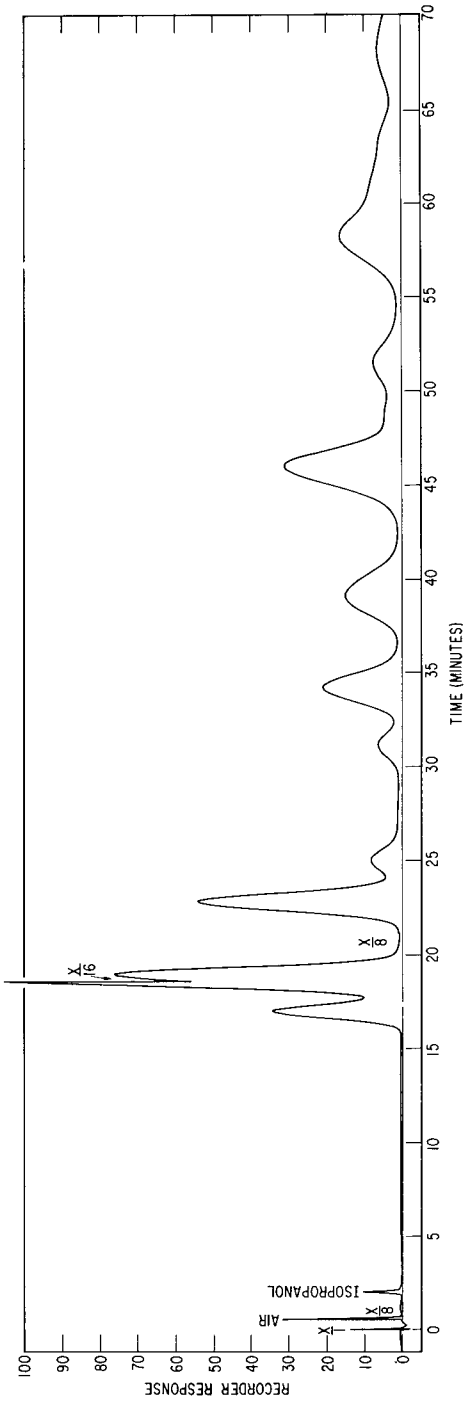

Fig. 7 - Aromatic hydrocarbon fraction from mixture desorbed from analytical carbon (C-201) exposed in USS GEORGE WASHINGTON

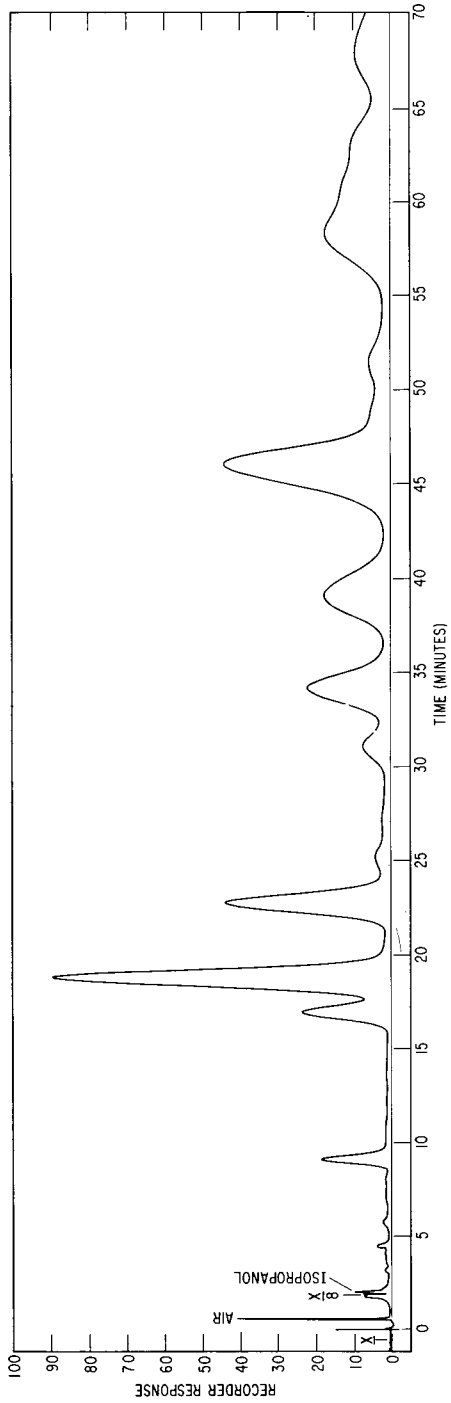

Fig. 8 - Aromatic fraction from hydrocarbon mixture desorbed from main filter carbon (C-214) exposed in USS ABRAHAM LINCOLN

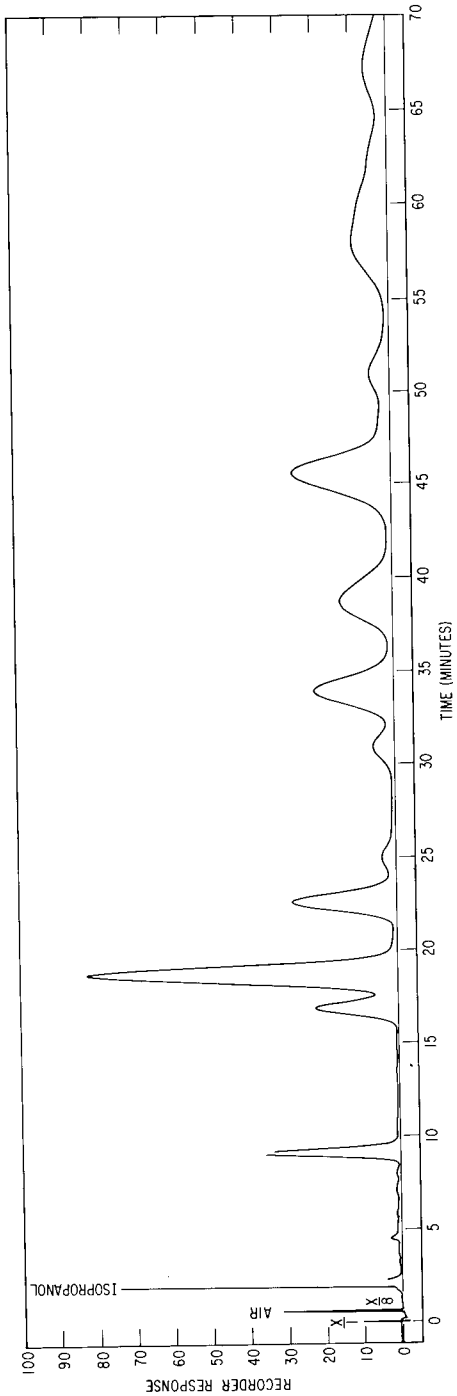

Fig. 9 - Aromatic fraction from hydrocarbon mixture desorbed from analytical carbon (C-221) exposed in USS SNOOK

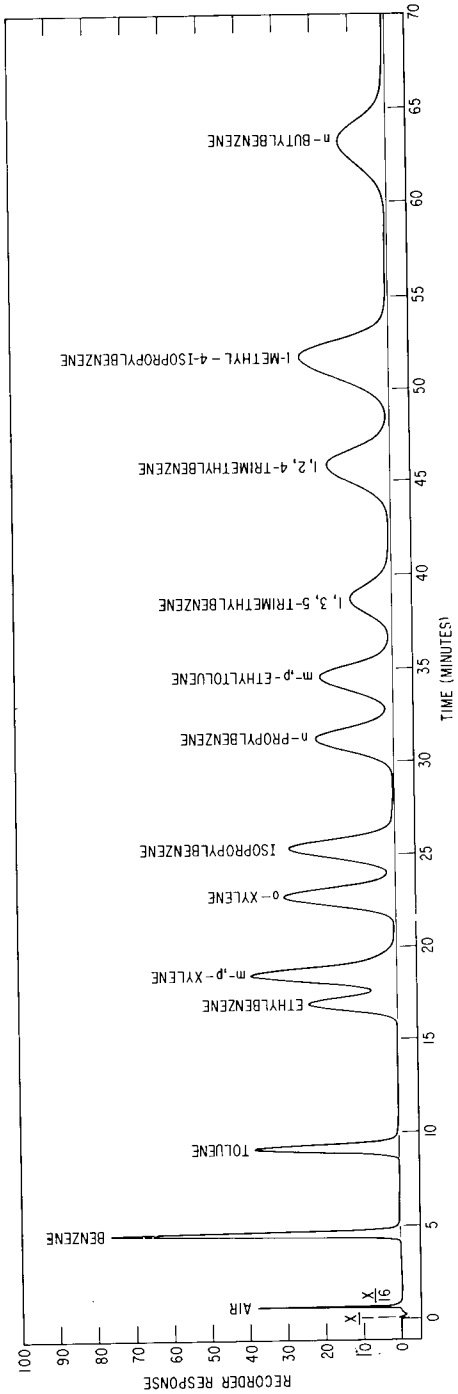

Fig. 10 - Standard mixture of aromatic hydrocarbons

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NAUTILUS, the only submarine with two analyses at different times, showed a drop from 36% to 24%. It is also interesting that all of the samples since 1960 have 26% ± 3% aromatics except the PATRICK HENRY sample, N-554, which analyzed 37%. It seems well established that the aromatic portion of the hydrocarbon content in nuclear submarines has decreased significantly.

It has been suggested from time to time that the aromatic content of the desorbed oils is probably a function of the length of exposure time of the carbon, or perhaps the total loading on the carbon. To examine this point more closely the data for the seven samples more recently collected are brought together in Table 6 showing exposure time, loading, and aromatic content. It is evident from these data that the fairly constant aromatic content of 23% to 30% (except for N-554 with 37%) is independent of exposure time and loading. This seems to confirm the experimental observation made earlier that under the conditions of use, carbon does not appear to selectively adsorb aromatic hydrocarbons.

Table 6
Oils Desorbed from Carbon

Sample	Submarine	Exposure (hours)	Loading (g hydrocarbon per 100 g carbon)	Aromatic Hydrocarbon (percent)
Main Filter Carbon				
C-214	A. LINCOLN	1700	23	30
N-554	P. HENRY	1100	5	37
C-242	SCULPIN	960	19	23
Analytical Carbon				
C-201	G. WASHINGTON	24	10	28
C-221	SNOOK	12	7	25
N-662	R. E. LEE	8	3	23
N-689	NAUTILUS	12	4	24

Distribution of Individual Aromatic Hydrocarbons

The quantitative distribution of individual hydrocarbons shown in Table 5 is also very interesting from several aspects. For purposes of discussion these data will be treated in several ways. For example, in Table 7, the individual hydrocarbons are grouped into three volatility ranges. The two main filter carbon samples show a wide spread in volatility. It is interesting that N-554 has 59% low boiling aromatics even though this carbon was exposed for 1100 hours in PATRICK HENRY. This illustrates the good retentivity of activated carbon for these smaller molecules. The wide spread in volatility of the analytical carbon samples indicates that submarine atmospheres can vary greatly in the types of aromatic hydrocarbons they contain.

In Table 8, only the aromatic hydrocarbons through 1,2,4-trimethylbenzene are considered. The values listed for each sample are normalized for this mixture. For example, the value, 14.6%, given for o-xylene in C-214 means that o-xylene represents 14.6% of the 13 hydrocarbons listed in Table 8. By treating the data in this way, it becomes apparent that there are certain similarities in the composition of these six samples. It is evident that m-xylene and p-xylene represent a substantial fraction of the total in all six samples. It is equally evident that n-propylbenzene represents only a small fraction in all six samples. The greatest variations occur in the two most volatile members, benzene and toluene. A bar graph shown in Fig. 11 illustrates the similarities and trends more clearly.

Table 7
Aromatics in Each Boiling Range

Sample	From Benzene through o-Xylene (percent)	Isopropylbenzene through 1,2,4-Trimethylbenzene (percent)	Above 1,2,4-Trimethylbenzene (percent)
Main Filter Carbon			
C-214	21	21	58
N-554	59	16	24
Analytical Carbon			
C-221	22	19	59
N-689	27	27	46
C-201	36	20	44
N-662	64	23	12

Table 8
Relative Distribution in Submarine Atmospheres of Individual Aromatic Hydrocarbons Boiling from Benzene through 1,2,4-Trimethylbenzene

Aromatic Hydrocarbon	C-214	N-554	C-221	N-689	C-201	N-662	Average
	(percent of total)						
Benzene	0.2	2.0	0.2	1.1	0.0	1.8	0.9
Toluene	2.4	15.5	6.7	9.9	0.4	11.3	7.7
Ethylbenzene	5.7	11.4	6.4	5.7	6.8	11.4	7.9
m-xylene, p-xylene	27.4	35.6	29.6	24.4	43.1	38.2	33.1
o-xylene	14.6	13.4	10.6	8.8	13.9	10.6	12.0
Isopropylbenzene	1.4	1.7	1.5	3.0	2.2	3.6	2.2
n-propylbenzene	1.9	2.0	2.5	3.0	1.6	2.2	2.2
1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene	8.0	5.6	12.1	11.0	7.7	6.8	8.5
1,3,5-trimethylbenzene, 1-methyl-2-ethylbenzene	9.4	4.3	10.3	11.4	7.9	5.8	8.2
1,2,4-trimethylbenzene	29.0	8.5	20.4	21.8	16.4	8.2	17.4

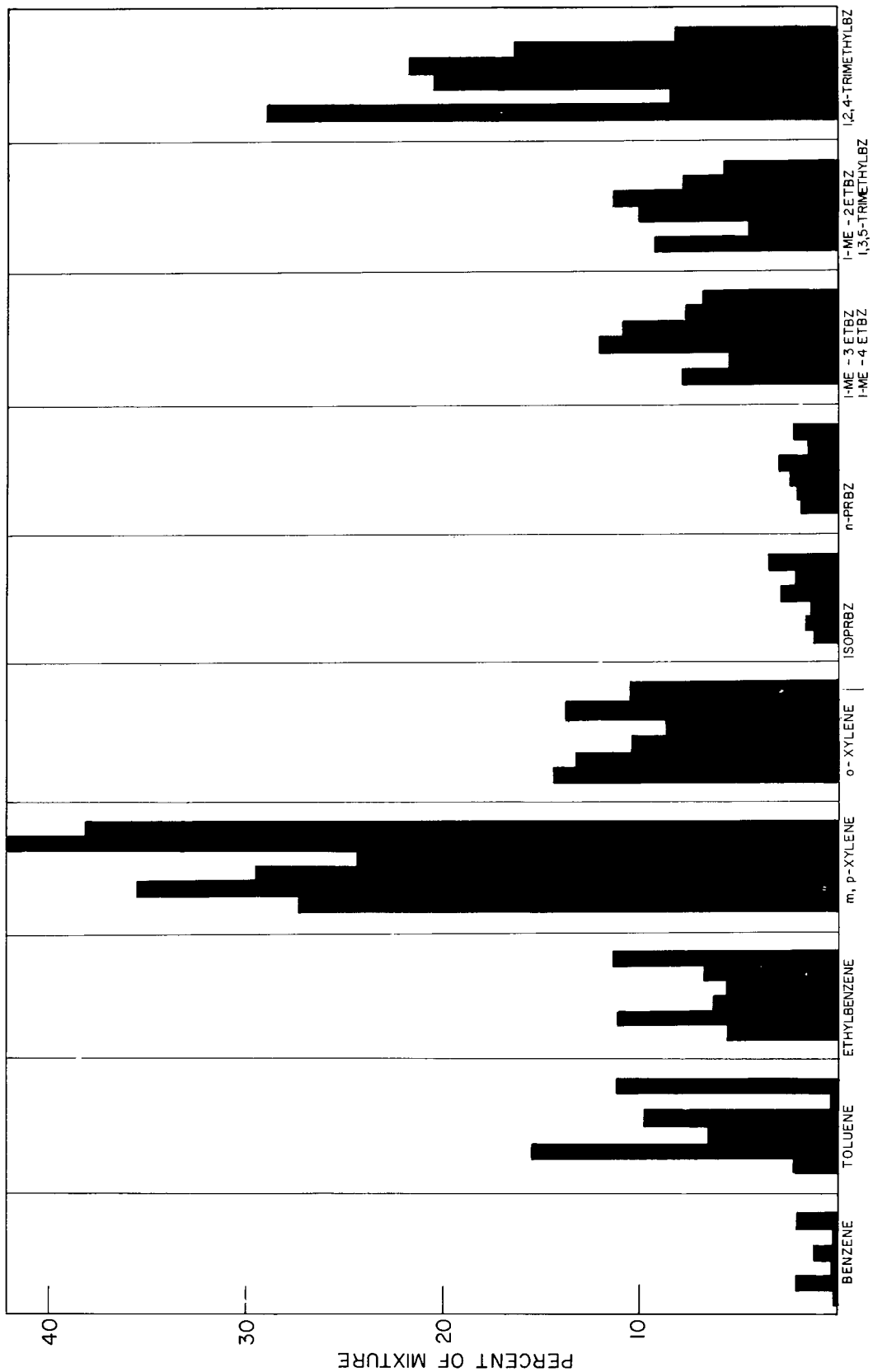

Fig. 11 - Relative distributions of aromatic hydrocarbons boiling from benzene to 1,2,4-trimethylbenzene as recovered from submarine atmospheres (samples in same order as given in Table 8)

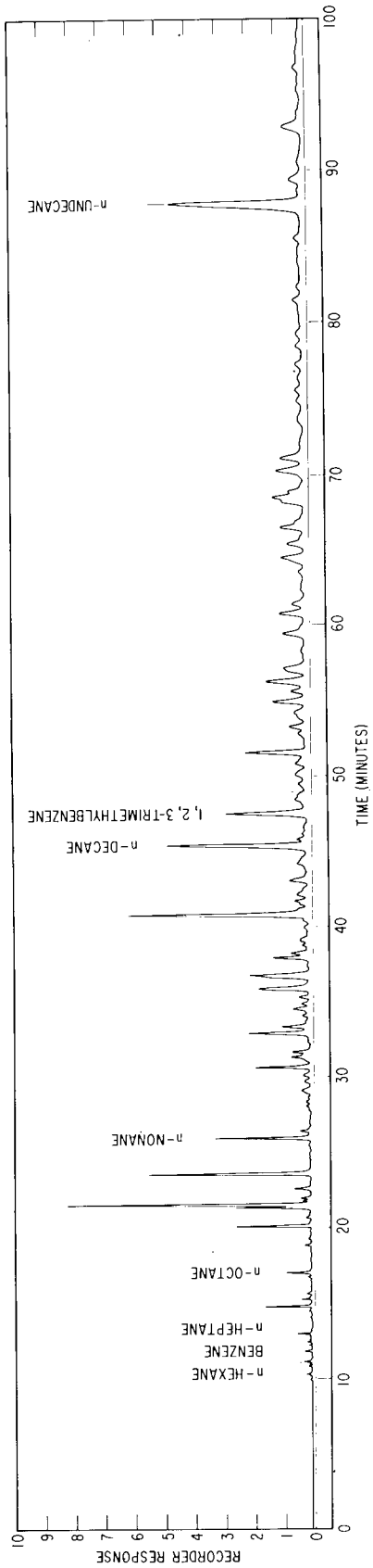

Fig. 12 - Capillary chromatogram of unfractionated oil desorbed from main filter carbon (C-214) from USS ABRAHAM LINCOLN

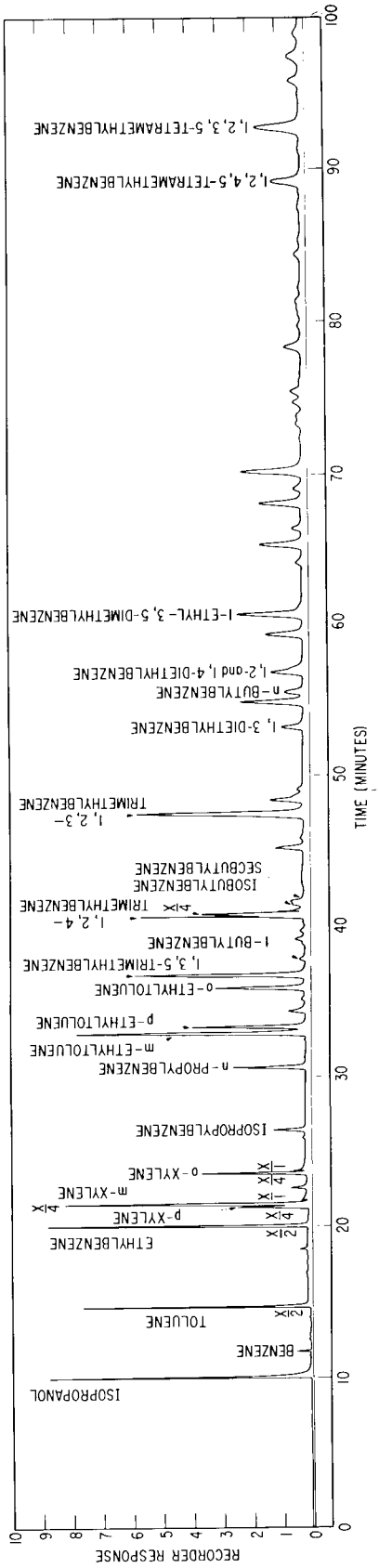

Fig. 13 - Capillary chromatogram of aromatic hydrocarbon fraction obtained from analytical carbon (C-221) exposed in USS SNOOK

Some of the fractions separated by the FIA technique were chromatographed through a 300-ft × 0.01-in. I.D. squalane capillary column at 90°C using a Perkin-Elmer Model 154A Vapor Fractometer equipped with a flame ionization detector. The capillary column gave excellent resolution. All of the C_9 and most of the C_{10} aromatics were resolved. Fig. 12 is a chromatogram of an unfractionated oil desorbed from main filter carbon (C-214) from the USS ABRAHAM LINCOLN. Fig. 13 is an FIA aromatic fraction of an oil obtained from analytical carbon (C-221) exposed aboard USS SNOOK. By combining an integrating potentionmeter with such a capillary column, the concentrations of 14 different aromatic hydrocarbons in the mixture were determined and are given in Table 9. The known exposure time of the carbon was used to calculate the concentration of each hydrocarbon in the atmosphere.

Aromatic hydrocarbons identified by means of the capillary column are included in Table 10. Identification of the higher hydrocarbons listed was by retention time only. In the case of aromatic hydrocarbons of higher molecular weight than C_{10}, identification by means of retention time becomes very difficult because of the large number of isomers

Table 9
Hydrocarbons Recovered from USS SNOOK

Total Hydrocarbons: 133 mg/m³ Aromatic Hydrocarbons: 33.5 mg/m³			
Aromatic Hydrocarbon	Aromatic Distribution (percent)	Atmospheric Concentrations	
		(mg/m³)	(ppm)
Benzene	0.1	0.03	0.01
Toluene	2.0	0.67	0.18
Ethylbenzene	2.1	0.71	0.16
p-xylene	2.0	0.67	0.15
m-xylene	7.3	2.4	0.55
o-xylene	3.5	1.2	0.18
Isopropylbenzene	0.3	0.11	0.02
n-propylbenzene	0.8	0.27	0.06
m-ethyltoluene	2.7	0.90	0.18
p-ethyltoluene	1.3	0.44	0.09
o-ethyltoluene	1.2	0.40	0.08
1,3,5-trimethylbenzene	2.2	0.73	0.15
1,2,4-trimethylbenzene	6.1	2.0	0.41
1,2,3-trimethylbenzene	3.1	1.0	0.20
Subtotal	34.7		
Higher Boiling Aromatics	65.3		

Table 10
Aromatic Hydrocarbons Found in
Nuclear Submarine Atmospheres

Aromatic Hydrocarbon	Boiling Point (°C)
Benzene	80.1
Toluene	110.6
Ethylbenzene	136.2
p-xylene	138.4
m-xylene	139.1
o-xylene	144.4
Isopropylbenzene	152.4
n-propylbenzene	159.2
1-methyl-3-ethylbenzene	161.3
1-methyl-4-ethylbenzene	162.0
1-methyl-2-ethylbenzene	164.7
1,3,5-trimethylbenzene	165.2
1,2,4-trimethylbenzene	169.4
1,2,3-trimethylbenzene	176.1
t-butylbenzene	169.1
Isobutylbenzene	172.8
sec-butylbenzene	173.3
n-butylbenzene	183.3
m-diethylbenzene	181.1
p-diethylbenzene	183.5
3,5-dimethylethylbenzene	183.8
1,2,4,5-tetramethylbenzene	196.0
1,2,3,5-tetramethylbenzene	197.9
Naphthalene	218.0

of each carbon number and because of the dearth of samples of pure hydrocarbon for standards. Although 25 individual aromatic hydrocarbons are given in Table 10, many more aromatic hydrocarbons are represented in Fig. 13. In addition, many others which are higher boiling are not shown in the portion of the chromatogram shown in Fig. 13.

SOURCES OF AROMATIC HYDROCARBONS

A general consideration of the many possible sources of aromatic hydrocarbons (Table 11) in nuclear submarines suggests that some sources are more predominant (12,16). It is noted that the first two sources, diesel fuel and mineral spirits, are distillates from petroleum. Paint thinners frequently are petroleum distillate cuts also. It was of interest to try to estimate the extent of the contribution of petroleum distillates to submarine atmospheric contamination. Consequently a detailed investigation was made of the nature of the aromatic fractions listed in Table 8.

Table 11
Actual or Potential Sources
of Aromatic Hydrocarbons Found in
Nuclear Submarine Atmospheres

Mineral Spirits
Diesel Fuel
Paint Thinners
Paints
Solvents in waxes, cements, glues, adhesives, etc.
Special cleaning solvents
Lighter fluids
Tobacco smoke
Decomposition of lubricating and hydraulic oils
Cooking
Mastics and sealing compounds
Plastic compositions (solvents and plasticizers)
Adhesive sealers (used for lagging)
Rubber compounds
Insulation compositions

The quantitative distributions of aromatic hydrocarbons shown in Table 8 and illustrated in Fig. 11 exhibit similarities in all six samples which suggest common origins. One aspect of the significance of these data can be explored in the following way. Rossini, Mair, and Streiff (20) quantitatively determined the distribution of individual hydrocarbons as they occurred in seven straight-run distillates from petroleum. The data for the aromatic hydrocarbons from petroleum are given in Table 12, expressed in the same manner as the data in Table 8. Study of these two tables reveals strong similarities in distribution between the submarine-derived aromatic hydrocarbons and the same hydrocarbons from the petroleum distillates. A bar graph of the average values for the hydrocarbons from these two sources is given in Fig. 14. The general trends are remarkably similar. It is seen in this graph that benzene and toluene are generally low in the submarine samples compared to the petroleum distillates. This would be expected because most paint thinners and hydrocarbon solvents derived from petroleum are stripped of the lower boiling hydrocarbons in the interests of safety from flammability.

The data shown in Tables 8 and 12, and Figs. 11 and 14 strongly point toward petroleum distillates as being the major sources for the hydrocarbon contamination in nuclear submarine atmospheres. The similarity in the distributions of aromatic hydrocarbons in all six submarine samples with the petroleum-derived distribution is very conclusive.

Paint Thinners

No exhaustive survey of this class of solvents was made, but data on several samples have accumulated and are presented here. In Table 13 are the results of FIA analyses which indicate that the usual paint thinners have relatively low aromatics content (10% to 17%) compared to the hydrocarbons recovered from submarine atmospheres (>23%).

Table 12
Relative Distribution of Individual Hydrocarbons
in Straight-Run Distillates from Crude Petroleum*

Hydrocarbon	Okla.	E. Texas	Penn.	Mich.	Texas	Calif.	W. Texas	Average
	(percent of total)							
Benzene	5.6	2.4	1.3	9.9	3.5	3.3	4.7	4.4
Toluene	18.5	20.0	19.4	27.7	7.0	20.9	28.2	20.2
Ethylbenzene	6.8	7.9	3.3	5.6	6.2	10.7	3.6	4.9
m-xylene, p-xylene	22.0	28.1	29.8	23.2	16.3	24.8	30.2	24.9
o-xylene	9.7	10.2	8.1	8.2	8.9	10.3	7.8	10.5
Isopropylbenzene	2.7	1.4	1.4	2.0	6.0	3.1	1.3	2.6
n-propylbenzene	3.5	3.2	2.3	2.3	3.5	3.4	1.8	2.9
1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene	8.5	9.6	9.1	7.8	11.4	6.8	7.5	8.7
1,3,5-trimethylbenzene, 1-methyl-2-ethylbenzene	4.2	3.7	8.7	3.4	10.8	5.0	5.1	5.9
1,2,4-trimethylbenzene	18.5	13.7	16.8	10.0	26.3	11.7	9.8	15.3

*Taken from Ref. 20.

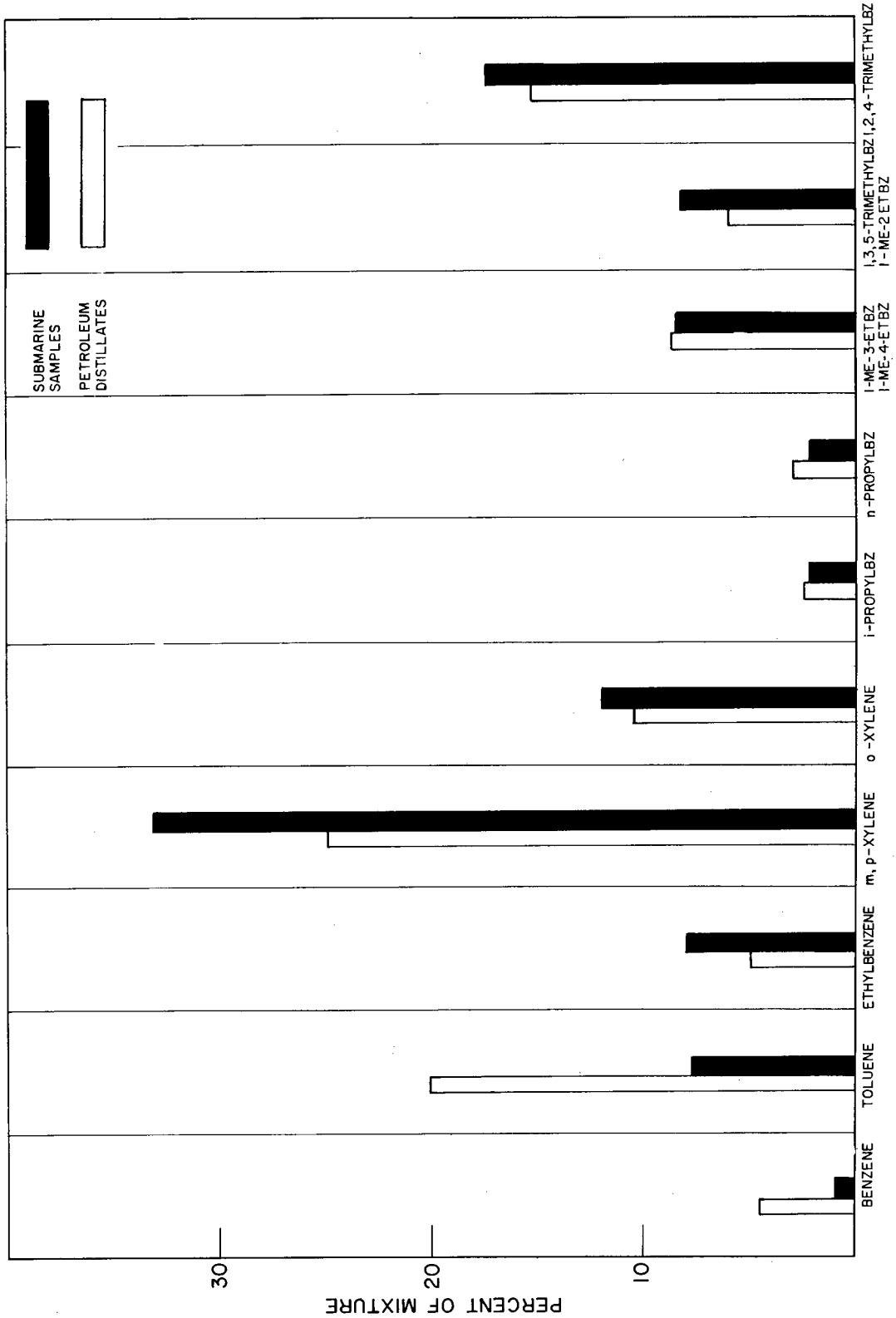

Fig. 14 - Relative distribution of aromatic hydrocarbons recovered from submarine atmospheres (average of six samples) compared with petroleum distillates (average of seven)

Table 13
Analyses of Paint Thinners

Sample	Hydrocarbon Content by Type (percent)		
	Aromatics	Olefins	Saturates
MS200*	10‡	–	90
MS258*	17‡	–	83
PT-1†	13.3	1.2	85.3
PT-2¶	14.6	3.7	81.3

*Given also in Ref. 1. Paint thinner from Federal Spec. TT-T-291a.
†Paint thinner used in toxicology studies at Navy Toxicology Unit, Bethesda, Md.
‡Includes olefins.
¶A paint thinner labelled "British White Spirits" and obtained from Navy Toxicology Unit, Bethesda, Md.

Two of these paint thinners, PT-1 and PT-2, were examined in more detail because they were used in toxicology studies at the Navy Toxicology Unit. As shown by the FIA data, both are made up prodominantly of saturates, which would include aliphatics and alicyclics. Gas chromatographic analyses of the saturates fractions showed a typical straight-run pattern, high in n-paraffins, particularly n-nonane and n-decane, with very little boiling lower than n-octane. The front-end cutoff was very sharp.

The molecular compositions of the aromatic fraction of these two solvents based on gas chromatography are given in Table 14. The similarities in compositions are noteworthy. Neither of these solvents contains benzene. This was confirmed in the case of PT-1 by an internal standard method, which showed that benzene, if present, must be less than 0.01% of the whole solvent. Ethylbenzene is the first aromatic hydrocarbon to appear in a significant amount and the xylenes are also low. The other aromatics determined through 1,2,4-trimethylbenzene show a similar pattern in the two solvents, consistent with that expected of a straight run distillate (Table 12). No detailed analysis was made of individual aromatic hydrocarbons beyond 1,2,4-trimethylbenzene. Data are included, however, which indicate the relative amounts of higher boiling aromatics.

Comparison of the data on paint thinners given in Tables 13 and 14 show significant differences from the submarine hydrocarbons of Tables 4, 5 and 7. The total aromatic content of the paint thinners is considerably lower than in any of the submarine samples given in Table 4. No benzene was found in these thinners, although as much as 1.5% of the submarine aromatic fractions recovered was benzene. Practically no toluene was found, although as much as 10% toluene was found in the submarine fractions. The submarine aromatics were indeed much higher in volatile compounds, the percent through o-xylene being from 21% to 64% (Table 7), as compared to 3.2% and 6.8% in these two paint thinners. The conclusion must be that paint thinners of this type are not major contributors to submarine atmosphere contamination.

Solvents from Paints

Recently two proprietary paints, R-Gray and R-White, were examined to determine the nature of the solvent because they were being used in FBM submarines in the belief

Table 14
Aromatic Composition of Paint Thinners

Aromatic Hydrocarbon	Boiling Point (°C)	Aromatic Distribution (percent)	
		PT-1	PT-2
Benzene	80.1	0.0	0.0
Toluene	110.6	0.0	0.1
Ethylbenzene	136.2	0.5	1.0
p-xylene *	138.4	1.2	4.2
m-xylene *	139.1		
o-xylene	144.4	1.5	1.6
Isopropylbenzene	152.4	2.5	0.9
n-propylbenzene	159.2	3.6	2.3
1-methyl-3-ethylbenzene *	161.4	12.2	12.7
1-methyl-4-ethylbenzene *	162.0		
1,3,5-trimethylbenzene	164.7	6.7	7.0
1-methyl-3-ethylbenzene	165.2	5.3	7.0
1,2,4-trimethylbenzene	169.4	21	20
Aromatics boiling between 1,2,4-trimethylbenzene and n-butylbenzene	169.4 to 183.0	26	25
Aromatics boiling higher than n-butylbenzene	>183.0	20	18

*These meta and para isomers were not resolved and are reported as single values.

that they were thinned with nontoxic solvents (21). The solvents were distilled from these paints and examined by FIA analysis, gas chromatography, and infrared spectroscopy, and found to be preponderantly hydrocarbons.

The R-White paint yielded two fractions on distillation. The first fraction (W-1) was a colorless solution of hydrocarbons, as shown by infrared spectroscopy. The second fraction (W-2) was aqueous with a small layer of yellow oil above it. The infrared spectrum of the yellow oil showed hydrocarbons and some carbonyl compounds which may have been drying oils. As shown in Table 15, the types of hydrocarbons in the W-1 fraction as determined by the FIA method were not very different from those in the solvent from R-Gray paint.

The R-Gray paint yielded a colorless water-insoluble distillate shown by infrared to be hydrocarbons. The FIA analysis (two runs) showed an average of 10.5% aromatics (Table 15). Gas chromatography of the saturates fraction showed the solvent to be a fairly sharp distillation cut, 70% to 75% of the fraction boiling between n-octane and n-decane. The aromatics fractions from both FIA runs were examined quantitatively by gas chromatography, with results given in Table 16. The agreement between the two

Table 15
Analysis of Solvents in Paint

Paint Sample*	Hydrocarbon Content (percent)		
	Aromatics	Olefins	Saturates
R-White (w-1 fraction)	14.1	2.8	83.1
R-Gray, Run 1	12.2	6.0	81.8
Run 2	8.8	5.9	85.3
Average (R-Gray)	10.5	6.0	83.5

*The hydrocarbon solvents were distilled from the paint samples indicated.

Table 16
Composition of Aromatic Hydrocarbon* Fractions Recovered from Paints

Aromatic Hydrocarbon	Aromatic Distribution (weight percent)		
	R-Gray (Run 1)	R-Gray (Run 2)	Average
Benzene	<1.1	<1.3	<1.2
Toluene	0.7	0.6	0.7
Ethylbenzene	9.4	10.0	9.7
m-xylene, p-xylene	24.4	24.9	24.7
o-xylene	5.7	5.7	5.7
Isopropylbenzene	1.1	0.6	0.9
n-propylbenzene	0.6	0.6	0.6
1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene	8.3	8.3	8.3
1,3,5-trimethylbenzene	9.6	9.6	9.6
1,2,4-trimethylbenzene	25.1	25.2	25.2
1-methyl-4-isopropylbenzene	0.1	0.1	0.1
From 1-methyl-4-isopropylbenzene to n-butylbenzene	9.9	8.7	9.3
n-butylbenzene to end	4.0	4.5	4.3

analyses is excellent. The distribution of individual hydrocarbons shows the typical pattern of a petroleum distillate (Table 12). These data show that the solvent stripped from this R-Gray paint contained a much higher percentage of low-boiling aromatics (42.0% through o-xylene) than the paint thinners PT-1 and PT-2, 3.2% and 6.9% respectively. In fact, the resemblance of the data in Table 16 to the submarine samples in Table 5 is readily noticeable. The typically lower total aromatics content and the relative lack of toluene in the paint solvent do not agree well with the hydrocarbon samples from submarines. Nevertheless, it is concluded that the solvents in paints of this type certainly could be significant contributors to contamination in submarine atmospheres.

Data for a number of paints and primers commonly used in nuclear submarines have been tabulated in an earlier report (22). Most of these coatings are known to contain mineral spirits which include aromatic hydrocarbons. In addition, certain coatings contain solvents which are high in aromatic content. For example, MIL-P-18210 Red Deck Paint contains mineral spirits sweetened with xylene and aromatic petroleum naphtha. Such compositions may account at least in part for the relatively high aromatic content of submarine atmosphere samples. It would be desirable to obtain authentic samples of such materials for a closer scrutiny.

Diesel Fuels

The diesel fuel carried for emergency use contributes to the hydrocarbon contamination in the atmospheres of nuclear submarines. Leakage from fuel lines and valves is a constant source. Diesel fuel tanks are customarily vented inboard upon submergence. All of the air vented inboard in this manner is saturated with hydrocarbons vapors from the fuel. In addition, some liquid fuel is vented in the form of aerosol or a stream which has often in the past gone into the bilge to evaporate into the atmosphere. The proportion of the total contamination which comes from diesel fuel has not been established, and it undoubtedly varies from one submarine to another. At any rate, a detailed examination of two diesel fuels taken from nuclear submarine tankage has been made.

The hydrocarbon-type analyses of the diesel fuel samples are given in Table 17. It is noted that these two diesel fuels contained about 20% aromatics which would seem to match the ship's air better than the paint thinners (10% to 15% aromatics). But the issue is not this simple. Gas chromatograms of the aromatics fractions of the diesel fuels show that only about 5% of the total sample is included in the portion boiling below and including n-butylbenzene (183°C). As is usual in all these straight-run distillates, the predominant compounds in this range are m-xylene, p-xylene, and 1,2,4-trimethylbenzene. This means that about 95% of the diesel aromatics boil higher than 183°C, whereas in the submarine atmosphere samples a much smaller percentage (12% to 59%) boils higher than 183°C.

Distillation data for a number of typical Navy diesel fuels (MIL-F-16884(SHIPS)) shows the 5% point to be about 215° to 220°C, the 50% point at 265°C and the 90% point at 305° to 325°C. This indicates the chromatograph data given above is reasonable in that much of the fuel is normally made up of higher boiling hydrocarbons.

Diesel fuel may be a large contributor to vapor contamination in nuclear submarines nevertheless. For example, in blowing down diesel tanks, the air released into the ship will be saturated with vapors which represent primarily the more volatile hydrocarbons. Consequently, the volatility distribution of such a mixture will more nearly correspond to the mixtures adsorbed from submarine air. Testimony to this is given by a chromatogram of the hydrocarbon vapors present in the air over a liquid diesel fuel from USS SKATE (15). Qualitatively this chromatogram shows a great similarity to the hydrocarbons in the submarine air, both in hydrocarbon distribution and the relative quantities of individual aromatic hydrocarbons.

Table 17
Composition of Diesel Fuels by Hydrocarbon Type

Sample	Submarine	Hydrocarbon Content (percent)		
		Aromatics	Olefins	Saturates
D-1	SKATE	21.3	3.3	75.5
D-2	SNOOK (Run I)	20.1	6.3	73.6
	SNOOK (Run II)	19.3	7.3	73.3
D-2	Average	19.7	6.8	73.5

Special Solvents

In the construction and maintenance of nuclear submarines, a large number of compounded materials other than paints are used which employ solvents containing some aromatic hydrocarbons. Some of these materials are treated in reference (22). For example, a MIL-C-3004 adhesive sealer for lagging was found to contain the isomeric xylenes. A cement for securing plastic sheet to bulkheads was found to contain toluene as a constituent (23). Other cements such as epoxy are known to contain xylenes in the solvent formulations. There is no doubt that all of these sources contribute aromatic hydrocarbons to the atmosphere to some extent when they have been used. However, it is typical of these sources that they are made up of selected hydrocarbons such as toluene or xylenes which would not give the typical distribution found in Fig. 14.

Miscellaneous Sources

Several commercial lighter fluids were analyzed by gas chromatography and were found to contain 2% to 20% aromatic hydrocarbons (15). The hydrocarbons found in these fluids were in general the same as the lower boiling hydrocarbons present in submarine air. The contribution from this source is probably small in terms of the total contamination found.

The aromatic contribution from the use of lubricating and hydraulic fluids is probably very limited, although this source has not been studied in detail. It is known that essentially none of the aromatic hydrocarbons such as those listed in Table 5 are found in the fresh fluids. It is possible that some of these compounds are formed in the thermal decomposition of these fluids, although it is estimated that this effect is very small.

Although a great deal has been published on the vapor constituents of tobacco smoke, very little has appeared concerning volatile aromatic hydrocarbons from this source. Most of the published work has been devoted to identification of fused ring aromatics because of the concern regarding the presence of carcinogenic compounds in tobacco smoke. However, three alkylbenzenes and benzene itself have been reported (24). In addition 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene were proved qualitatively to be present (25). The only aromatics for which published quantitative data were found are toluene and benzene (26). To obtain these data Philippe and Hobbs measured these hydrocarbons only in the main stream (that which potentially is drawn into the mouth). No data have been found concerning these products in the side stream (which comes from the lighted end of the cigarette when not being puffed). Bitner and Anderson (27) have shown the side stream to be very important in terms of contamination of atmospheres in closed spaces. Consequently, the calculation of the contribution of tobacco smoking to the aromatic hydrocarbon content of nuclear submarine atmospheres with present

available data must be an approximation. Using the data of Philippe and Hobbs (26) for toluene, an estimate will be made here. The maximum value for toluene of 0.0015 cc/puff corresponds to about 0.015 cc per cigarette. Assuming the consumption of 2000 cigarettes per day in an average submarine, this corresponds to 30 cc of toluene or 0.12 grams per day. At an average of 2% toluene in the total hydrocarbon mixture, and a total of 600 grams/day as found in USS SCULPIN (28), this would amount to about 1% of the total toluene contamination. A contamination of this magnitude from tobacco smoking may be considered more significant as the total contamination decreases, but much more quantitative data of the constituents of tobacco smoke is necessary to establish this

SUMMARY

Based on the data reported in this study, a number of characteristics of the aromatic hydrocarbon content in nuclear submarine atmospheres have been quite well established. The aromatic hydrocarbons constitute about 25% to 30% of the total hydrocarbon content. The quantitative distribution of individual aromatic hydrocarbons is quite similar from one sample to another (Table 5). The striking similarity of this distribution to that in typical distillates derived from petroleum is noteworthy. However, the total aromatic content is quite a bit higher in the hydrocarbons from submarine atmospheres than in petroleum distillates in the same boiling range. This relatively high aromatic content did not appear to be a result of selective removal from the atmosphere by the carbon filter or CO/H_2 burners. The aromatic content was nearly the same whether sampling was done early or late in the cruise.

For example, sample N-689 from NAUTILUS was started 3 hours after submergence and 24% aromatics was recovered. Sample C-201 from GEORGE WASHINGTON was started after 168 hours and yielded 28% aromatics. This implies that the removal systems are not significantly removing nonaromatics selectively.

Nevertheless, it appears quite well proved that for the majority of the aromatic hydrocarbon vapors, we are dealing with petroleum-derived hydrocarbons. The principal sources are known to be paint solvents, mineral spirits, and diesel fuel vapors. Minor sources of aromatic hydrocarbons which have been established are lighter fluids, solvents in formulations such as cements, and tobacco smoking.

REFERENCES

1. Nestler, F. H. M., and Smith, W. D., "Submarine Habitability-Atmosphere Sampling and Analysis," NRL Memo. Rpt. 866, Oct. 1958

2. Saunders, R. A., "The Role of Infrared Spectroscopy in Submarine Habitability," Chapter 5 in "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R. R., and Piatt, V. R., editors, NRL Report 5465, Apr. 21, 1960

3. Johnson, J. E., and Christian, J. G., "A Laboratory Study of the Efficiency of Hopcalite in Catalyzing Hydrocarbon Combustion," Chapter 8 in "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R. R., and Piatt, V. R., editors, NRL Report 5465, Apr. 21, 1960

4. Johnson, J. E., Christian, J. G., and Carhart, H. W., Ind. Eng. Chem. 53:900 (1961)

5. Christian, J. G., and Johnson, J. E., "Catalytic Combustion of Nuclear Submarine Atmospheric Contamination," NRL Report 6040, Mar. 20, 1964

6. "Threshold limit values for toxic materials," BUMED Instruction 6270.3B, March 5, 1963

7. Sax, N. I., "Dangerous Properties of Industrial Chemicals," New York:Reinhold, 1959

8. "Threshold Limit Values for 1961," AMA Archives of Environmental Health, 3:489 (1961)

9. Johnson, J. E., Christian, J. G., Field, D. E., Murphy, C. M., Jr., Smith, J. E., Thomas, F. S., and Umstead, M. E., "Investigation of Eye Irritation in the Atmosphere of USS SNOOK (SS(N)592) – Trip Report," NRL Memo. Rpt. 1248, Nov. 1961

10. NAVTOXU ltr JS/ma 6270 Ser. 15-63 of 24 Sept. 62 with End 2 BUMED-73-cbs of Oct. 25, 62

11. Smith, W. D., and Johnson, J. E., "Contaminations of Hydrocarbon Vapors in Submarine Atmospheres by Carbon Sampling," Chapter 10 in "Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Piatt, V. R., and Ramskill, E. A., editors, NRL Report 5630, July 14, 1961

12. Nestler, F. H. M., "Trace Contaminants, Sampling, and Analysis," Chapter 4 in "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R. R., and Piatt, V. R., editors, NRL Report 5465, Apr. 21, 1960

13. Umstead, M. E., Christian, J. G., and Johnson, J. E., "A Study of the Organic Vapors in the Atmosphere of the USS SKATE," NRL Memo. Rpt. 1057, June 1960

14. Kagarise, R. E., and Saunders, R. A., "Infrared Analysis of Atmospheric Contaminants," Chapter 10 in "Second Annual Progress Report, The Present Status of Chemical

UNCLASSIFIED

Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Piatt, V. R., and White, J. C., editors, NRL Report 5814, Aug. 29, 1962

15. Umstead, M. E., "Gas Chromatography in the Study of Trace Organic Vapor Contaminants," Chapter 8 in "Annual Progress Report, The Present Status of Chemical Research In Atmosphere Purification and Control on Nuclear-Powered Submarines," Piatt, V. R., and Ramskill, E. A., editors, NRL Report 5630, July 14, 1961

16. Piatt, V. R., "Chemical Constituents of Submarine Atmospheres," Chapter 1 of "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R. R., and Piatt, V. R., editors, NRL Report 5465, Apr. 21, 1960

17. Johnson, J. E., "Nuclear Submarine Atmospheres, Analysis and Removal of Organic Contaminants," NRL Report 5800, Sept. 10, 1962

18. American Society for Testing Materials, "Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption," Tentative Method D1319-60T, in "ASTM Standard on Petroleum Products and Lubricants," 37th ed., Philadelphia, Pa.:American Soc. for Testing Materials, Oct. 1960

19. Norris, T. A., Shively, J. H., and Constantin, C. S., Anal. Chem. 33:1556 (1961)

20. Rossini, F. D., Mair, B. J., and Streiff, A. J., "Hydrocarbons from Petroleum," New York:Reinhold Publ. Co. 1953

21. NRL ltr 6100-61:VRP:hlw SER 2012, "Painting during Submergence in Nuclear Submarines," Mar. 4, 1963

22. Johnson, J. E., Christian, J. G., Field, D. E., and Kagarise, R. E., "Nuclear Submarine Atmosphere Contamination by Coatings, Insulations and Other Materials," NRL Memo. Rpt. 1306, Apr. 1962

23. Saunders, R. A., "Volatiles from Bond-Master Contact Adhesive," NRL ltr rpt 6110-159A:RAS:bs, May 21, 1963

24. Johnstone, R. A. W., and Plimmer, J. R., Chem. Rev. 59:885 (1959)

25. Bonnet, J., and Neukomm, S., Helv. Chim. Acta 39:1724 (1956)

26. Philippe, R. J., and Hobbs, M. E., Anal. Chem. 28:2002 (1956)

27. Bitner, J. L., and Anderson, W. L., private communication

28. Umstead, M. E., Smith, W. D., and Johnson, J. E., "Submarine Atmosphere Studies Aboard USS SCULPIN," NRL Report 6074, Feb. 27, 1964