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Submarine Atmosphere Studies Aboard USS SCULPIN

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ABSTRACT

Studies of the organic contaminants in the atmosphere of USS SCULPIN were made during a submerged cruise. Detailed analyses were made of the concentrations of methane, Freon-12, and "total hydrocarbons" by means of a backflush gas chromatograph of new design. The effectiveness of the CO/H_2 burners and main carbon bed as removal agents for organic contaminants was included in the studies. The CO/H_2 burners satisfactorily burned organic contaminants at temperatures as low as 500°F. The active carbon in the main filter bed removed the higher hydrocarbons, but was not very effective for the removal of lower hydrocarbons and Freon-12. Based on experimental data obtained on shipboard, it was calculated that the rate of generation of organic vapor contaminants was about 1.5 pounds per day throughout the cruise.

PROBLEM STATUS

This is an interim report. Work on this problem is continuing.

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SUBMARINE ATMOSPHERE STUDIES ABOARD USS SCULPIN

INTRODUCTION

The atmospheres in nuclear submarines have been the subject of a continuing study by NRL for many years. Although for the most part research in this field is carried on in the laboratory, from time to time it is advisable, and indeed necessary, to pursue atmospheric studies in a submarine while underway. It is not possible in the laboratory to duplicate the complex atmosphere of a nuclear submarine, or the operating variables which affect the atmosphere. Accordingly, J. E. Johnson, F. S. Thomas and M. E. Umstead of NRL and R. O. Bullock of Code 649B, Bureau of Ships, accompanied USS SCULPIN, SSN 590 while operating in Pacific waters from 18 February through 2 March 1963.

Studies made on this trip included the determination of the concentrations of several components of the atmosphere and the effectiveness of the purification systems, with particular attention to organic contaminants. A detailed investigation was made of the operation of the CO/H_2 burners at temperatures from 500-600°F. Of primary interest here was the effect of temperature on combustion of CO, removal of hydrocarbons and decomposition of Freon-12. The performance of the main carbon bed for removal of hydrocarbons and Freon-12 from the atmosphere was studied in detail also. For the first time, it was possible to get accurate and immediate shipboard determinations of the "total hydrocarbon" content of the atmosphere by means of a newly devised apparatus.

In addition, correlative activities included the operation and study of several other instruments, including a gas chromatograph using a flame ionization detector for the determination of individual hydrocarbons. During the cruise, discussions were held with the officers and members of the crew concerning details of operation of equipment, maintenance problems, etc.

In addition to the studies reported herein, Dr. F. S. Thomas, Code 6160, of NRL, conducted studies based primarily on data obtained with a special infrared analyzer for CO, and a versatile ultraviolet analyzer, the results of which will be reported separately.

Appendix I contains a chronological table of the events which are believed to be the most pertinent to the data and observations made during this cruise.

INSTRUMENTATION AND PROCEDURES

"Total Hydrocarbon" Analysis

"Total hydrocarbons", methane, and Freon-12 were measured by a chromatographic procedure involving back-flushing using a hydrogen flame as a detector. The term "total hydrocarbons" as used in this report includes all organic vapors with the exception of methane and Freon-12. Hydrocarbon derivations such as alcohols, ketones, etc., would be included although past experience has indicated that the preponderance of the organic vapor contaminants in submarine atmospheres consists of hydrocarbons. Methane is measured separately because it often runs as high as 100-200 ppm.

The hydrogen flame detection system used was part of a commercial unit, a Beckman Hydrocarbon Analyzer. Although this commercial unit was designed for measuring hydrocarbons in air, it was not suitable for use with submarine air because of its inability to discriminate among methane, Freon-12 and other hydrocarbons. In principle, a stream of air containing the hydrocarbons to be measured is mixed with hydrogen and burned at a jet. The ion current in the flame is measured and provides a quantitative measure of the hydrocarbons passing through the flame. If this method is applied to submarine air, there is no way of measuring the relative contributions of methane, Freon-12, and higher hydrocarbons to the ion current, especially since the response of Freon-12 is quite different from the others.

In order to measure methane and Freon-12 individually and "total hydrocarbons" as one group, a chromatograph was constructed that operated at ambient temperature and used the Beckman Hydrocarbon Analyzer burner assembly as a detector. The system was valved so that the column could be backflushed through the detector. The column consisted of a six foot length of 1/4-in. O.D. copper tubing packed with DC-200 silicone oil, 23% on Chromosorb-P. This column was not the ideal for this separation; it was chosen in view of the short time available for preparation for the shipboard studies because it was on hand and well-purged of volatile materials. Compressed breathing air was used for the carrier gas to eliminate the necessity of separating methane from oxygen. If another carrier gas had been used, the oxygen in the sample would have given a response due to changes in the flame on the same order of magnitude as the signal from the methane at the low concentrations encountered. With air as the carrier, the oxygen concentration passing through the flame remained essentially constant at all times.

The operation of the hydrocarbon detector was as follows: A 5-cc sample of submarine air was injected into the system by means of a gas sampling valve and was carried through the chromatographic column in a stream of carrier gas (air) in the usual fashion. After methane and Freon-12 had emerged from the column and had been detected as separate peaks, the direction of flow of carrier gas in the column was reversed by turning a four-way valve. At the moment of reversing the carrier flow, components of the sample less volatile than Freon-12 were still in the column, partially separated and distributed throughout the column in the order of their volatilities. Reversing the carrier gas flow, or backflushing, as this is commonly known, moves these components back through the column and tends to regroup them so that they emerge as a single peak. Figure 1 represents a typical chromatogram obtained aboard SCULPIN.

The methane and Freon-12 concentrations were determined by peak height measurements after calibration with standard mixtures of known composition. In the case of methane, a slight correction had to be applied due to the presence of a low concentration of methane in the carrier gas. Peak height could not be used as a measure of "total hydrocarbons." Values for these substances were obtained by measuring the area under the backflushed peak with a planimeter and comparing this area with that obtained from a standard sample (5 ppm of n-hexane) backflushed in the same manner.

During these shipboard studies certain observations were made which indicated that better results in estimating "total hydrocarbons" could be obtained by minimizing baseline shifts and avoiding the broadening of the back-flushed peaks. Based on these observations, further work was planned for the laboratory in these directions.

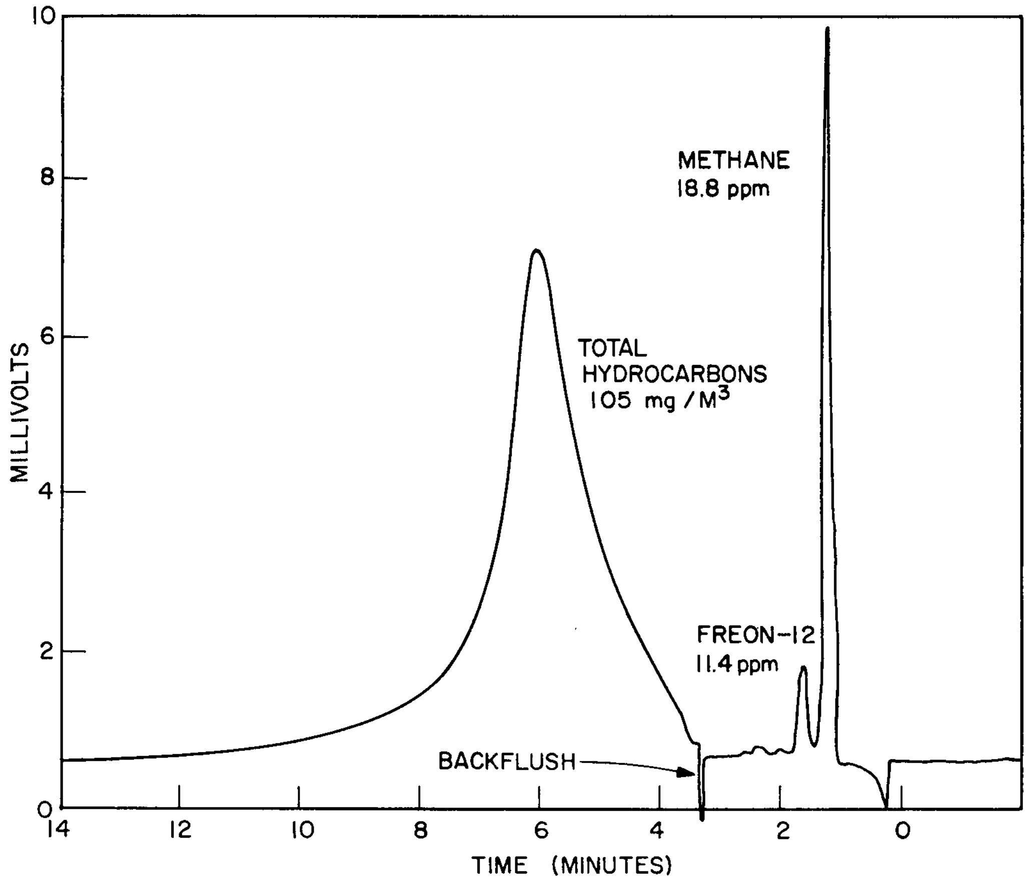

Fig. 1 – Chromatography of atmospheric methane, Freon-12 and total hydrocarbons (blackflushed)

Analysis by Standard Gas Chromatography

A standard gas chromatograph was used to study the nature of the hydrocarbons found in the SCULPIN atmosphere. The total hydrocarbon analyzer provided quantitative values for their total concentrations; the gas chromatograph provided quantitative information as to the distribution of individual hydrocarbons in the samples. The latter method was particularly useful in detecting changes in composition of the hydrocarbon contaminants upon passing through the main carbon bed and the CO/H_2 burner.

The chromatograph used was a Beckman GC-2a equipped with a flame ionization detector. Because of the relatively high hydrocarbon levels present in the atmosphere, the sensitivity of the instrument was adequate to chromatograph directly the contaminants in a 5-cc air sample without a prior concentrating step. The chromatographic column used principally was a 12-ft x 1/4-in. O.D. column of DC-550 silicone oil, 15% on Chromosorb-P, and was operated at temperatures ranging from 40° to 130°C. A 16 ft. x 1/4 in. O.D. bis(2-ethoxyethyl) sebacate column, 30% on C-22 Firebrick, saw limited use at 40°C for investigating low molecular weight hydrocarbons. Helium was the carrier gas.

Carbon Samplers

The carbon sampling equipment used consisted of two blower/canister assemblies based on an NRL design (1) using flat "pancake" type carbon canisters. One of the samplers was operated by the medical department of SCULPIN, and the other by NRL personnel. The samples were entered into the carbon desorption program at the USN Marine Engineering Laboratory, Annapolis, Md.

Compressed Atmosphere Samples

Some samples of ship's atmosphere were obtained in 1.7 liter stainless steel bottles by means of a portable oilless compressor. Analysis of these samples in the laboratory showed good agreement of the methane and Freon-12 concentrations with those obtained during the cruise. The "total hydrocarbon" results were somewhat lower in the bottle samples than on shipboard. This method of sampling is still under investigation.

EXPERIMENTAL STUDIES

Variation in Hydrocarbon, Methane, and Freon-12 Concentrations with Submergence Time

Periodically throughout the cruise, readings were taken of methane, Freon-12, and "total hydrocarbons" in the air entering the Missile Guidance Compartment from an overhead duct to serve as a reference as to the overall levels in the ship. These readings were obtained with the total hydrocarbon analyzer. The concentrations found for methane and Freon-12 are shown in Figure 2. Also indicated in Figure 2 is the CO/H_2 burner on the line and its operating temperature, the status of the main carbon bed, and the outboard ventilation periods. Figure 3 is a similar plot for "total hydrocarbons."

Undoubtedly the values given for hydrocarbons also include some substituted compounds such as ethyl alcohol. It is believed that much of the scatter of points on the hydrocarbon plot in Figure 3 is real, especially among the higher values. At one point when readings jumped suddenly in the AMS, it was noted by the ship's force that alcohol was used in the vicinity at that time for cleaning purposes.

Studies of CO/H_2 Burners

(a) Methane

Methane concentration in the CO/H_2 burner influent and effluent were measured with the total hydrocarbon analyzer. Precise values for the amount of methane burned could not be obtained since the amount disappearing amounted to only one or two parts per million. Roughly though, about 15-20% appeared to burn at 600°F, 10% at 550°F and 3% at 500°F.

In Figure 2, the effect of the burners on the overall methane level in the ship can be seen. For example, with one burner at 550°F and the other at 600°, a plateau appeared on the methane curve. With two at 600°F, the methane concentration dropped.

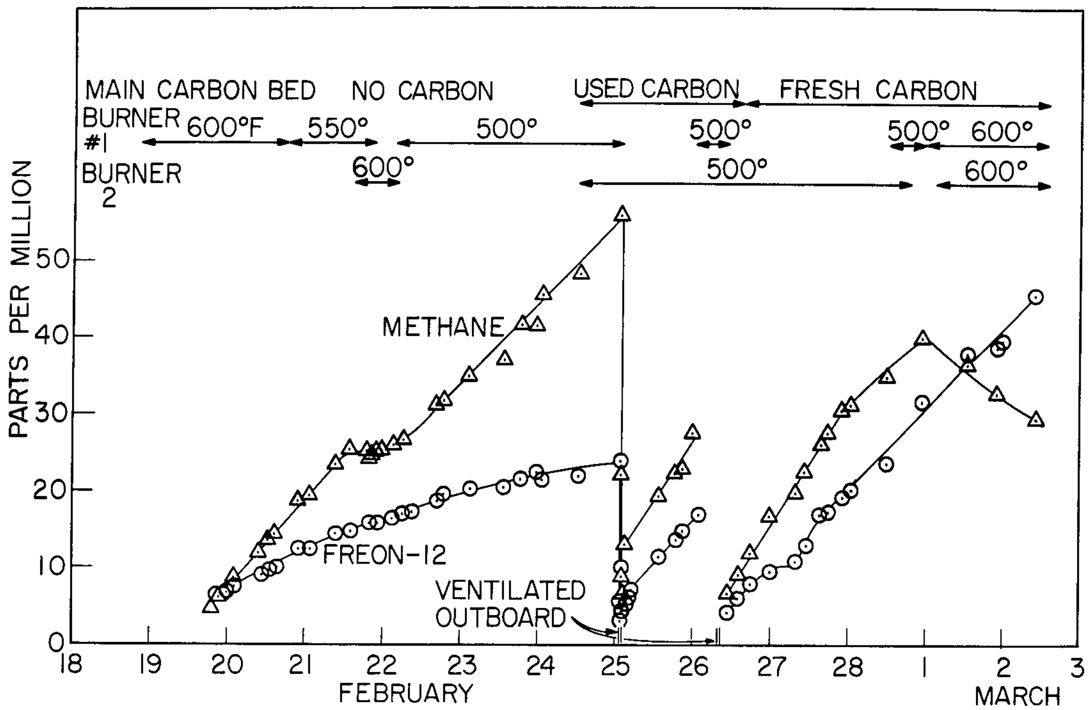

Fig. 2 – Atmospheric concentrations of methane and Freon-12

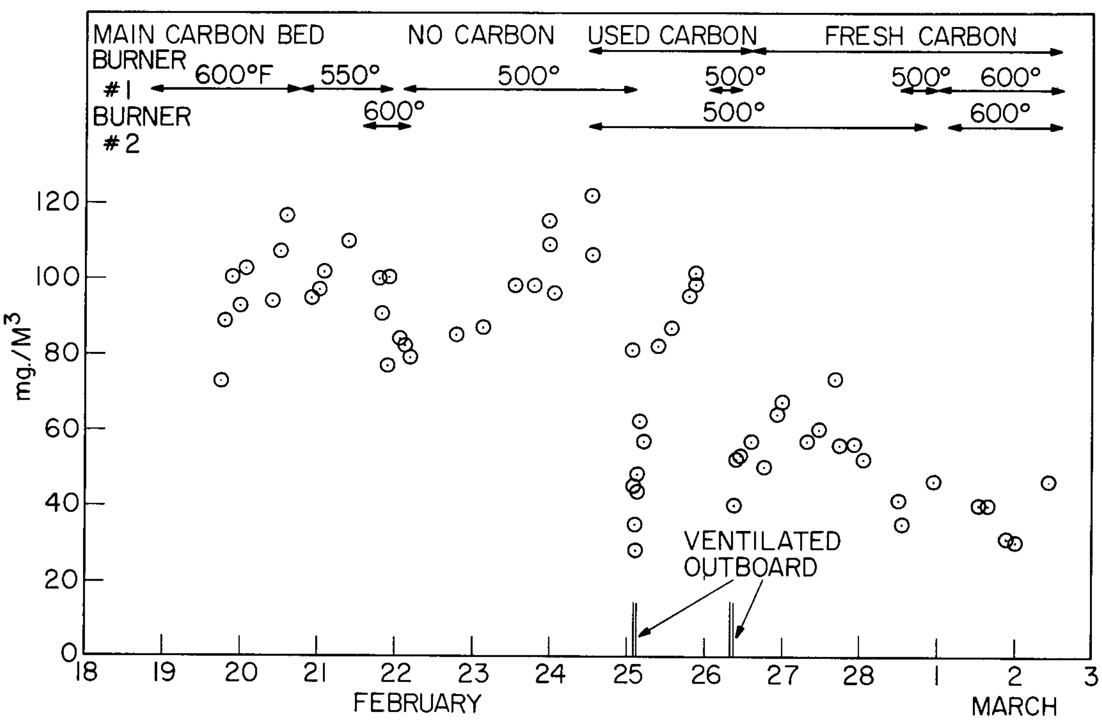

Fig. 3 – Atmospheric concentrations of total hydrocarbons

(b) Freon-12

A slight decrease in the height of the Freon-12 peak in the burner effluent was noted. It is probable that this decrease was only an apparent one and was due to the burning of trace hydrocarbons such as propane that have the same retention time as Freon. Figure 2 shows no significant changes in the Freon-12 level as a result of varying burner conditions. The Freon-12 readings on the Mk III Atmosphere Analyzer agreed very well with the readings obtained with the total Hydrocarbon Analyzer

(c) "Total Hydrocarbons"

Measurement of "total hydrocarbon" levels across the burner indicated that about 80% burned at all three temperatures used, 500°, 550°, and 600°F. The accuracy of measurement of "total hydrocarbons" in the burner effluent was low, however, because of the low levels found in the effluent. Readings in the effluent ranged from 9 to 30 mg/m^3. Figure 3 shows the effect of burner operation on the overall hydrocarbon content of the air, although the ventilation and carbon bed must also be taken into consideration.

Some chromatograms were obtained of the burner influent and effluent when the burner was operating at 500°F. A selectivity in the burning efficiency with molecular weight was noted. Hydrocarbons in the decane range and higher burned about 60% while lower molecular weights burned more efficiently. Those in the pentane and hexane range burned 90-95%. The fraction burning decreased progressively from hexane to decane. Hydrocarbons more volatile than pentane could not be measured under the conditions used.

Further shipboard study of this selectivity of combustion is needed to confirm these observations.

Main Carbon Bed Studies

A study was carried out aboard SCULPIN to determine the efficiency of the main carbon filter for the removal of volatile organic contaminants. The carbon bed in this ship held about fifty pounds of carbon. The intake air to the bed was drawn from the battery tank and exhausted into the supply system fore and aft.

Taps were placed on the ducts leading to and from the bed so that the influent and effluent air could be sampled. Measurements were made of methane, Freon-12 and "total hydrocarbon" concentrations. Samples also were chromatographed for individual hydrocarbons to determine if any changes took place in the composition of the hydrocarbon contaminants in passing through the carbon.

Shortly after getting underway, the used carbon (in place since 21 Jan 1963) was removed from the bed and stored. The ship was operated with no carbon in place until 24 Feb at 1200 when the used carbon was reinstalled in the filter and used until 1500 hours, 26 Feb. A sample of this carbon returned to the Laboratory was steam desorbed and found to be loaded to the extent of 19.6 g hydrocarbon per 100 g carbon (See Table 1), which means the carbon was essentially saturated. At 1500 on 26 Feb., the carbon filter was refilled with fresh carbon which was used for the remainder of the cruise. Its loading after this use period was 2.4 g hydrocarbon per 100 g carbon.

Table 1

HYDROCARBON CONTENT OF MAIN FILTER CARBON
USS SCULPIN, SSN 590

NRL No.	Exposure Dates	Total Exposure Days	Hydrocarbons Desorbed g/100 g carbon
C-242	1/21/63 to 2/26/63	ca. 30	19.6
C-241	2/26/63 to 3/3/63	5	2.4

(a) Methane and Freon-12

As should be expected, no change was detected in methane concentrations across either the new or used carbon bed.

No significant change could be seen in the Freon-12 concentration in passing through the used carbon. After fresh carbon was placed in the bed, a decrease in Freon-12 concentrations could be detected for several hours. A sample taken about two hours after the bed had been changed showed that about 11.5% of the influent Freon was adsorbed. Subsequent samples showed a decreasing efficiency for its removal.. A small effect due to the new carbon on the over-all Freon-12 level in the ship can be seen in Figure 2. Shortly after the point of installation of fresh carbon, a break is present in the Freon curve indicating a temporary reduced rate of build-up in the atmosphere. The adsorbed Freon undoubtedly is soon desorbed by heavier hydrocarbons.

(b) "Total Hydrocarbons"

"Total hydrocarbon" measurements on the used carbon influent and effluent air indicated that about 90% of the influent hydrocarbons were passing through the bed without being adsorbed. Gas chromatograms of the effluent hydrocarbons were essentially identical to those of the influent.

With fresh carbon in the filter, about 50% of the influent hydrocarbons were adsorbed during the first three days. During the next and final two days of the trip, the efficiency of the bed for hydrocarbon removal appeared to drop to about 30%. However, the concentration of atmospheric hydrocarbons in the ship was considerably lower during these last two days.

A comparison of chromatograms of the influent and effluent air obtained a few hours after the new carbon was installed showed that hydrocarbons in the butane range and lighter were not adsorbed by the bed and that higher molecular weight hydrocarbons were adsorbed to the extent of about 50%. On the last day of the cruise, hydrocarbons through hexane were passing through the bed completely and the higher ones appeared to be adsorbed to about the same extent as initially. The fact that the fraction of the hydrocarbons passing through the fresh carbon bed was the same over a wide range of molecular weights indicated that much of the inefficiency of the bed for hydrocarbons removal was due to bypass of air in the system. If good contact were made between the air and the carbon, the fraction of the influent hydrocarbon adsorbed should increase progressively with decreasing volatility.

Effect of Outboard Ventilation on Organic Contaminants

Two periods of outboard ventilation took place, the first at 0135, 25 Feb and the second at 0807, 26 Feb. Each period was about one hour in duration.

During the first ventilation period, the atmospheric concentrations of methane, Freon-12, and "total hydrocarbons" in the Missle Guidance Compartment were followed with the total hydrocarbon analyzer. At the end of this period, methane and Freon-12 had dropped to 10% of their original levels in this compartment. After the ship was sealed up and air recirculation resumed, the methane and Freon concentrations rose rapidly to 25% of their original concentrations. This was undoubtedly due to mixing of the cleaner air with that from compartments which were less efficiently ventilated than Missile Guidance. It was concluded that the overall efficiency of the ventilation was 75%. The second ventilation period was unexpected and no data were obtained during this time. Extrapolation of the methane and Freon curves before and after the second ventilation period indicated that about 85% of the air was changed.

The "total hydrocarbon" concentration also dropped swiftly during ventilation but recovered rapidly to about 60% of the initial value after the ship was closed up. It seemed as if some reservoir of hydrocarbons existed aboard the ship to recontaminanate the air so rapidly. Desorption of adsorbed hydrocarbons by painted or oily surfaces, the bilge, and the loaded carbon bed are likely contributors. At any rate, ventilation was much less effective for decreasing hydrocarbon concentrations in the atmosphere than for Freon-12 and methane.

Carbon Sampler Studies

For years carbon sampling has been a very useful source of information in regard to the organic contaminants in the atmospheres of nuclear submarines (1). By this means samples of the contaminants are collected on activated carbon in the submarine and then are sent to the laboratory for analysis. The amount of "hydrocarbon oil" recovered, together with the total volume of air sampled permits an estimate of the concentration in the submarine air during sampling. Although it has been very helpful in atmosphere studies, it is known that the carbon sampler is not 100% efficient (2). Tests were made in SCULPIN comparing influent and effluent air with two such samplers. It was found that an average of 15-20% of the organic content, as measured by the total hydrocarbon analyzer, passed through the sampler. Part of this throughput is doubtless due to passage of low-molecular weight compounds. An additional amount is apparently due to bypass in the blower.

Table 2 contains the data from the carbon canisters exposed by the ship's force and returned to USN Marine Engineering Laboratory for analysis (3). Curiously enough this carbon sampling data indicated somewhat of an increase during a period when the total hydrocarbon analyzer showed an average decrease. In any case, the carbon data is at best, about 50% of the shipboard analyzer data for "total hydrocarbons". This difference is due to the loss during adsorption, the loss upon desorption in the laboratory, and the compounds such as methyl and ethyl alcohols which are included in the shipboard data, but not in the carbon sampling data.

Table 2

ANALYTICAL CARBON SAMPLES
USS SCULPIN (SSN 590)

MEL No.	Location	Exposure Period			No. hrs. Subm. at Start of Sampling	Hydro-carbons mg/m^3
		From	To	Hrs.		
141	OPS Compt 3rd level	0400-2/20/63	1600-2/20/63	12	32	24.9
142	OPS Compt 3rd level	1630-2/20/63	0425-2/21/63	11.9	45	35.9
143	OPS Compt 3rd level	1610-2/21/63	0405-2/22/63	11.9	68	35.9
144	OPS Compt 3rd level	1555-2/22/63	0353-2/23/63	11.9	92	39.3
145	ERUL	0400-2/23/63	1600-2/23/63	12	104	39.9

A carbon sample exposed in the NRL sampler from 0105 to 2400 on 2-22-63 (total time, 23 hours) contained 6.1 g per 100 g of carbon (total weight, 182.7 g). This calculated to represent 53.8 mg/m^3 of hydrocarbon in the atmosphere. The total hydrocarbon analyzer indicated about 80 mg/m^3 at this time, indicating about 68% recovery by the carbon sampling method.

MISCELLANEOUS OBSERVATIONS

Carbon Dioxide Scrubber Operation

USS SCULPIN has had a long history of difficulties with the CO_2 scrubbers which are due primarily to very high maintenance requirements and very poor availability of spare parts. During a typical submergence one scrubber is started when the two-hour analyzer reading reaches 0.8%. One scrubber is sufficient to keep the concentration below 1.0%, and it need not run continuously. In fact, the experience is that at lower concentrations of CO_2, there is insufficient gas being scrubbed out to permit the scrubber to run under load. The compressor then begins to chatter and overheat. Operation under these conditions leads to early compressor failures. Thus it was found important to secure the scrubber at low CO_2 ($<0.8\%$). It was not uncommon to maintain a watch full-time outside the scrubber room to detect the noisy operation of the compressor at the earliest moment.

The high frequency of mechanical failures coupled with the difficulty of obtaining spare parts made the CO_2 scrubber operation a weak point in overall atmosphere control, despite the high removal efficiency when in operation.

Several samples directly relating to scrubber operation were obtained on SCULPIN and brought back to the Laboratory. These samples were analyzed by C. H. Blachly and H. Ravner of Code 6170. The following results are abstracted from their report (4):

(a) A sample labelled unused MEA was found to be sea water with only a trace of MEA.

(b) A sample of lean MEA from the scrubber was found to be 4.1 N MEA, well within the specified normality range. It contained no sea water.

(c) A sample of the titration acid from SCULPIN was 0.50 Normal, precisely the rated concentration.

(d) A sample of make-up water appeared to be a satisfactory grade of distilled water.

(e) A sample of titration indicator from SCULPIN appeared to be the normal specified Methyl Purple. It gave a very poor performance in a titration of the used MEA from SCULPIN, the end point could not be seen. This type of experience had been observed previously with Methyl Purple. It was therefore again recommended (4) that Brom Phenol Blue be specified for this use, because it has been proved to perform satisfactorily with used MEA.

Electrostatic Precipitator Operation

USS SCULPIN had seven electrostatic precipitators in operation. Generally, the recommended maintenance schedule provided relatively trouble-free operation. Some difficulties had been experienced with the transformers, but the incidence of these troubles had decreased in the past year. The galley precipitator was a constant source of trouble. It was hard to clean and was very difficult to take down for cleaning because it was wedged in position very tightly due to its location and construction. This particular precipitator had been cleaned 4-5 times in a year's time, requiring disassembly each time.

It was the consensus of the operators that a portable ozone analyzer would be helpful in attaining proper adjustment of the operating voltages of the precipitators.

DISCUSSION OF RESULTS

Sources of Organic Contamination

It has been shown repeatedly (1,2,5) that the composition of the organic mixture in the atmospheres of nuclear submarines is very complex, consisting largely of hydrocarbons. It is also certain that solvents from oil-based paints can be a major contributor to the hydrocarbon contamination unless such painting is controlled carefully. Other sources of specific organic contamination have been found. Because of the analytical capability for hydrocarbons available during this cruise, an effort was made to learn more about sources of organic contaminants.

A lengthwise survey of SCULPIN in terms of methane, Freon-12, and "total hydrocarbon" is given in Table 3. This survey took about 3-1/2 hours to accomplish. The data for methane and Freon-12 show no significant difference from one compartment to another in terms of local build-up. The data for "total hydrocarbons" also show no important differences, except that the lower level of the auxiliary machinery space (LLAMS) did show the somewhat lower concentration often found there. This is attributed to the fact that the CO/H_2 burner effluent air is dumped into this space, tending to maintain a lower overall hydrocarbon level.

Table 3

COMPARTMENT SURVEY, USS SCULPIN
22-23 FEBRUARY 1963

Sample	Time	Space	Concentrations of Contaminants: Methane ppm	Freon-12 ppm	"Total Hydrocarbons" mg/m^3
22-22	2317	ERUL	34.2	20.4	98
22-24	2355	Maneuvering	34.2	20.2	106
23-1	0010	Maneuvering	34.2	-	108
23-2	0035	AMS-UL	34.0	21.0	101
23-3	0100	Intake to Scrubber room	34.2	21.8	103
23-4	0115	Galley Hood	34.7	21.3	101
23-5	0135	FWD RM	34.7	21.5	101
23-7	0220	AMS-LL	34.7	21.0	80
23-8	0250	Missile Guidance	35.0	22.3	87

Approximately 5 days later a similar survey was made (See Table 4). On this occasion the bilge below the deck plates in several compartments was sampled also. Again it was established that no local build-up of methane, Freon-12, or "total hydrocarbon" had occurred. As in the previous survey, both methane and Freon-12 showed a small but definite concentration increase with time.

Table 4

COMPARTMENT SURVEY, USS SCULPIN
27 FEBRUARY 1963

Sample	Time	Space	Concentration of Contaminants: Methane ppm	Freon-12 ppm	"Total Hydrocarbons" mg/m^3
27-4	0744	Missile Guidance	19.8	10.6	57
27-6	0835	Carbon Bed, In	-	11.4	52
27-7	0842	AMS, FWD BILGE	20.3	11.6	62
27-8	0853	AMS, Burner In	20.3	-	63
27-9	0904	FWD RM BILGE	20.9	11.6	60
27-10	0920	FWD RM	20.9	11.6	60
27-11	0933	3rd Level, Crew Berthing	21.3	12.4	63
27-12	0948	Battery Well, Port	21.0	11.6	60
27-13	1004	Tunnel	21.3	12.4	62
27-14	1030	ERUL	22.4	13.4	62
27-15	1042	ER, BILGE	22.4	13.2	65
27-16	1057	Missile Guidance	22.5	12.8	60

On an earlier occasion, a sampling of the atmosphere in the AMS bilge under the deck plates showed a "total hydrocarbon" concentration of 195 mg/m^3 versus 110 mg/m^3 in the AMS itself. It is believed that this was due to diesel fuel which had accumulated in the bilge when the fuel tanks were vented. Unfortunately, the total hydrocarbon analyzer was not yet in operation at the time the fuel tanks were vented so that the vapor content of the tank air was not obtained. There is considerable circumstantial evidence, however, that the diesel fuel tanks contribute sizably to the organic contaminants in the atmosphere.

A sampling of air from the forward sanitary tank showed the following: methane, 88.0 ppm; Freon-12, 43.8 ppm; "total hydrocarbon", 61.3 mg/m^3. The general ship atmosphere at this time contained: methane, 34.0; Freon-12, 45.0; and "total hydrocarbon", 30 mg/m^3. This confirms the sanitary tanks as a major source of methane, as was expected. In addition, these tanks contribute to the total organic concentration.

There was essentially no painting on board SCULPIN during this cruise. However, a considerable amount had been done in the previous several weeks at Mare Island. This fresh paint coating was probably one source of the hydrocarbon vapors found during the cruise. The data on hydrocarbon content as affected by outboard ventilation suggests that older paint coatings and similar materials may absorb solvents during periods of high concentration and release them to the atmosphere again as the equilibrium concentration drops.

It was observed that for the limited touchup painting while underway a proprietary paint product known generically as Rustoleum was used mostly. It was established at NRL (6) that these proprietary paint products are thinned with solvents which are mostly hydrocarbons. Therefore they should be treated as oil-based paints.

Alcohol vapors, both ethanol and methanol, were found to some extent. Both of these solvents were detected strongly in the area of the Yeoman's office when duplicating fluid was used. Ethanol was used also for cleaning equipment in the engine room.

Generation of Organic Vapors

(a) "Total Hydrocarbons"

It was of interest to attempt calculations which would give some idea of the rate of generation of organic contaminants during the cruise. The results of these calculations are given in Table 5. The equilibrium concentrations for organic contaminants were estimated from the graphical data shown in Figure 3. The removal rates for the CO/H_2 burners were calculated using an average efficiency of 75%. The removal by the carbon bed is based on the steam desorption analysis of the main filter carbon (See Table 1). The generation rates were taken as equal to the combined removal rates shown in Table 5. It was surprising to find that the generation rate throughout the cruise ranged from 600-700 grams (about 1.5 lb.) per day.

Table 5

GENERATION AND REMOVAL RATES OF ORGANIC CONTAMINANTS IN USS SCULPIN

			"Total Hydrocarbon" Content		
Phase	Date	Removal Agent	Equil. conc. Mg/m^3	Removal Rate, grams/day	Generation Rate, grams/day
I	2-21-63	Burner 1	100	700	700
II	2-27-63	Burner 2	60	420	600
		Carbon Bed		180	
III	3-2-63	Burner 1	40	280	680
		Burner 2		280	
		Carbon Bed		120	

The data support the surprising conclusion that there was no significant change in the generation rate during the twelve-day cruise. There were undoubtedly some fluctuations in the generation rates of hydrocarbon contamination, but these average calculated figures are reasonably certain. It would be of considerable interest to pursue this type of study on other submarines.

(b) Freon-12

Calculations based on the Freon concentration changes shown in Figure 2 indicate that during the first five days Freon-12 was being added to the atmosphere at a rate of about 35 grams per day. During the latter part of the cruise the input rate for Freon-12 varied between 80-120 grams per day.

(c) Methane

The data obtained on methane were of interest because there had been little opportunity to learn much about it in the nuclear submarines earlier. It was known that the sanitary tanks and human sources would produce methane. In addition, methane has been found in breathing oxygen (7), in cigarette smoke, and it has been surmised that cracking of lubricating oils would contribute an unknown but probably minor amount. From the data in Figure 2, it was calculated that the buildup over a 30-hour period (during Feb 20-21) was 0.5 ppm/hour with one CO/H_2 burner operating at 600°F. In a submarine of 62,000 cu. ft., this is equivalent to an increase in methane concentration of 0.53 grams per hour in excess of that burned. Based on the observation that at 600°F about 20% of the methane was burned, it is concluded that approximately 1.2 grams per hour of methane was being contributed to the submarine atmosphere.

To compute the possible contribution of methane from the compressed oxygen, it was assumed from reference (7) that the oxygen banks contained the relatively high concentration of 60 ppm of methane. On this basis it was calculated that 0.1 grams per hour of methane might come from this source. This is only about 8% of the calculated total rate of generation of methane in SCULPIN. Therefore, it is indicated that the oxygen banks are only a minor source of methane.

Removal of Organic Contaminants

(a) Methane

Analyses of the concentrations of methane in the influent and effluent air streams of the main carbon filter proved that no measurable amount of methane was adsorbed by the carbon. Studies of the CO/H_2 burner indicated that 15-20% methane was burned at 600°F, 10% at 550°F, and 3% at 500°F. The outboard ventilation studies showed that about 80% of the methane in the atmosphere of SCULPIN was removed in one hour by this means.

(b) Freon-12

The main filter carbon studies showed that removal by this means was not very effective. Any advantage gained in using fresh carbon was soon lost, apparently by desorption of any adsorbed Freon by heavier hydrocarbons. The evidence obtained during the CO/H_2 burner studies was that no appreciable Freon-12 is destroyed by this means even at 600°F. Again, as for methane, the most effective means of removing Freon-12 from the atmosphere of SCULPIN was outboard ventilation.

(c) "Total Hydrocarbons"

The CO/H_2 burner is an effective means of removal of organic contaminants, including hydrocarbons, as shown in Table 5. In these studies, no pronounced difference in removal efficiency was observed between 500-600°F. The principal reason for checking the effect of catalyst temperature is the possibility that temperatures below 600°F might be used to reduce Freon decomposition. Otherwise it probably would be preferable to operate at 600°F.

The main carbon filter is also an effective removal agency for hydrocarbons as shown by these studies in SCULPIN. It is apparent from Table 5, however, that the CO/H_2 burner is the major contributor to removal. A big factor here is that only 50 pounds of activated carbon was used to charge the filter in this installation.

As shown in the EXPERIMENTAL STUDIES, ventilation was not nearly as effective for decreasing hydrocarbon concentrations as for Freon-12 and methane. One explanation for this fact is that painted surfaces, plastic materials, and oily surfaces such as in the bilges, all act as reservoirs of volatile hydrocarbons. It is suggested that after a ventilation period, these sources then tend to contribute hydrocarbons to the atmosphere at a higher rate until a new equilibrium concentration is reached. It would be of great interest to make a similar study on another submarine to test the validity of this hypothesis.

SUMMARY AND CONCLUSIONS

1. The successful use of a new total hydrocarbon analyzer based on a backflush gas chromatographic principle was demonstrated. This instrument was shown also to be an excellent method for the analysis of methane and Freon-12.

2. In keeping with earlier laboratory studies, it was found that the CO/H_2 burner on board ship satisfactorily burned organic contaminants at 500°F. Based on these findings, it is concluded that consideration might be given

to lowering the operating temperature of the burners on shipboard. This would reduce the extent of decomposition of Freons, thus minimizing the formation of halogen acids.

3. It was found that the activated carbon in the main filter bed removed the higher hydrocarbons, but was not particularly effective for the removal of lower hydrocarbons and Freon-12.

4. Based on experimental data obtained on shipboard, it was calculated that the rate of generation of organic vapor contaminants was about 1.5 pounds per day throughout the cruise.

5. The concentrations of methane, Freon-12, and "total hydrocarbons" throughout the submarine were reasonably constant at any one time. No significant buildup in any one compartment was found.

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REFERENCES

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

2. 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 Report 1057, June 1960.

3. USMEL Evaluation Report 73-111G; Fleet Assist Project "Atmosphere Monitoring in Nuclear Powered Submarines," S-F013-08-03, Task 4097; "Liquid Hydrocarbon Content of Activated Carbon Canisters Exposed Aboard USS SCULPIN (SSN590)," 26 August 1963

4. Blachly, C. H., and Ravner, H., NRL Letter Report 6170-105a:HR:eb, "Analysis of scrubber samples for USS SCULPIN, SSN590," 3 April 1963.

5. 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., NRL Report 5465, April 21, 1960.

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

7. Kagarise, R. E. and Saunders, R. A., "The Analysis of Contaminants in Aviation Breathing Oxygen," NRL Report 5554, 19 October 1960.

APPENDIX I

CHRONOLOGY OF EVENTS PERTINENT TO
ATMOSPHERE STUDIES IN USS SCULPIN
18 Feb to 2 Mar 1963

18 Feb 1963

1730 Got underway
2000 Vented fuel tanks
2022 Submerged - #1 Burner at 600°F
2300 Removed carbon bed (main) from Battery Exhaust System

19 Feb 1963

20 Feb 1963

0955 Collison drill (BHD valves closed)
1745 Patrol quiet commenced
1800 #1 Burner temperature lowered to 550°F

21 Feb 1963

1500 #2 Burner on line at 600°F
1655 Commenced battery charge
2100 #1 Burner secured (catalyst sample taken)
2100 Battery charge secured

22 Feb 1963

0300 #1 Burner on line at 500°F
0400 #2 Burner secured
1427 Torpedo drill (BHD valves closed)
1442 Torpedo drill secured

23 Feb 1963

24 Feb 1963

1200 #2 Burner on line at 500°F
1200 Reinstalled main carbon filter (containing used carbon dating from 1-21-63)

25 Feb 1963

0135 Ventilated outboard
0200 #1 Burner secured
0234 Secured ventilation outboard
1430 R. A. drill (all ventilation secured)
1450 Secured drill

26 Feb 1963

0100 #1 Burner on line at 500°F
0807 Ventilated outboard
0908 Secured outboard ventilation
1000 Secured #1 Burner
1500 Replace carbon in main filter with fresh carbon

27 Feb 1963

1455 Drill (secured all ventilation)
1535 Secured drill, ventilation restored

28 Feb 1963

1200 #1 Burner on line at 500°F
1900 #2 Burner secured
2400 #1 Burner temperature raised to 600°F

1 Mar 1963

0030 #2 Burner on line at 600°F
1510 Commenced battery charge (normal)
1713 Finishing charge rate reached
1859 Smoking lamp out
2110 Battery charge completed and secured
2129 Smoking lamp lit

2 Mar 1963

1118 Commence ventilating outboard
1120 Ventilation secured
1340 Surfaced, outboard ventilation