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NUCLEAR SUBMARINE ATMOSPHERES

ANALYSIS AND REMOVAL
OF ORGANIC CONTAMINANTS

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ABSTRACT

This Laboratory has carried out a program of sampling and analysis of the atmospheres of nuclear submarines for the identification and estimation of organic contaminants. Most of these organic compounds have been found to be hydrocarbons. The total hydrocarbon content of submarine atmospheres was initially very high (100 to 200 mg/m$^3$) but has decreased to very low values in many cases (<10 mg/m$^3$) by means of careful control measures. Individual aromatic hydrocarbons have been isolated with an estimation of their concentrations.

The principal sampling method is based on the exposure of activated carbon on shipboard followed by desorption of the carbon in the laboratory.

The most useful means of removing organic contaminants from the submarine atmospheres are combustion by means of a catalyst and adsorption by activated carbon contained in large filter beds. Calculations of the effectiveness of these measures under various conditions of use were made based on typical analytical data.

PROBLEM STATUS

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

AUTHORIZATION

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CARBON SAMPLING AND ANALYSIS PROGRAM

Beginning with the first long submergence of the NAUTILUS in the spring of 1956, a fairly continuous atmosphere analysis program for organic constituents has been carried on by NRL in the nuclear submarine fleet. The mainstay of this program has been the carbon sampler, which has gone through several modifications (1,2). Supporting data have been obtained by several methods including gas chromatography and catalytic combustion analysis on shipboard (3,4) and by various techniques in the laboratory (5,6). Useful samples have also been obtained on shipboard in pressurized steel bottles.

The carbon sampling technique has proved to be very useful as a collection device for sampling submarine atmospheres in spite of several known limitations (1,3,7). It has provided the principal data upon which is based the present knowledge of the organic content of the atmospheres of nuclear submarines (1,2,5-8). A routine sampling and analysis program was established by the Bureau of Ships (9) on a recommendation by NRL. This program is based on the exposure of carbon canisters by the ship's force and subsequent recovery of hydrocarbons by steam desorption at the Materials Laboratory of the New York Naval Shipyard. The equipment presently being used on shipboard includes a carbon sampler based on an NRL design, and a flat "pancake" type carbon canister, both shown in Fig. 1. Although it has been in full effect only since last summer, this sampling program has already provided significant data (10) and food for thought. In a recent visit to the Materials Laboratory (11), it was possible to suggest a decrease in the number of samples selected for analysis based on data already obtained. The present data also indicate the feasibility of reducing the sampling frequency during long submergences in order to cut the analytical load without a significant loss of information.

HYDROCARBON CONTENT OF SUBMARINE ATMOSPHERES

Early in the submarine atmosphere analysis program it became clear that the composition of the organic mixture in the atmosphere was very complex and was predominantly hydrocarbon in nature (7). For several years the total hydrocarbon content* in nuclear boats was found to be very high, often exceeding 100 mg/m³,† indicating a remarkably high rate of contamination. Then the first carbon samples were received from the SARGO (1), taken during the October 1959 submergence. The SARGO had used water-thinned paints in its interior (with liberal use of formica and stainless steel) for many months prior to this cruise. The first five samples averaged only 12 mg/m³, the last sample was 184 mg/m³. Extensive oil-based painting had been done during this submergence just before the last sample was taken. This incident underlined the already known fact that paint solvents could contribute significantly to hydrocarbon contamination, and provided a powerful stimulus to the water-thinned paint program which was already underway (12).

* Methane is not included in this category of hydrocarbons. Methane often runs as high as 100-200 mg/m³. However, for the purpose of this discussion, it is excluded from the total hydrocarbon figures.
† 16 ppm based on an average molecular weight of 150.
Fig. 1 - Improved hydrocarbon sampler with pancake-type carbon canister (on right)

Table 1
Total Hydrocarbon Concentrations Found by Analytical Carbon Sampling

<table>
<thead>
<tr>
<th>Ship</th>
<th>Exposure Dates</th>
<th>Concentration Range (mg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKIPJACK</td>
<td>9-1 to 9-7, 1959</td>
<td>31-90</td>
</tr>
<tr>
<td>SARGO</td>
<td>9-21 to 9-29, 1959</td>
<td>6-184</td>
</tr>
<tr>
<td>SKATE</td>
<td>10-19 to 10-31, 1959</td>
<td>39-82</td>
</tr>
<tr>
<td>SWORDFISH</td>
<td>2-11 to 3-10, 1960</td>
<td>6-25</td>
</tr>
<tr>
<td>TRITON</td>
<td>4-11 to 5-9, 1960</td>
<td>1-12</td>
</tr>
<tr>
<td>SKATE</td>
<td>3-25 to 4-1, 1960</td>
<td>17-47</td>
</tr>
<tr>
<td>SKATE</td>
<td>4-1 to 4-6, 1960</td>
<td>20-43</td>
</tr>
<tr>
<td>G. WASHINGTON</td>
<td>2-19 to 3-31, 1961</td>
<td>9-93</td>
</tr>
<tr>
<td>TRITON</td>
<td>7-7 to 7-8, 1961*</td>
<td>3-6</td>
</tr>
<tr>
<td>R. E. LEE</td>
<td>5-9 to 7-9, 1961</td>
<td>21-77*</td>
</tr>
<tr>
<td>PATRICK HENRY</td>
<td>7-5 to 8-26, 1961</td>
<td>0-3</td>
</tr>
<tr>
<td>R. E. LEE</td>
<td>8-10 to 9-30, 1961</td>
<td>2-5</td>
</tr>
<tr>
<td>G. WASHINGTON</td>
<td>9-6 to 11-7, 1961</td>
<td>0-3</td>
</tr>
</tbody>
</table>

\*Data reported beyond this date were obtained with new NRL Sampler (flat pancake-type canisters).
\*After 1260 hours, the indicated concentration fell to 0.0 (see Fig. 1).

For the next several years as shown in Table 1, it was normal for the hydrocarbon content in nuclear submarines to average from 30-60 mg/m$^3$ or higher, with few exceptions (1,10). Then early in 1962, reports from the carbon sampling program indicated atmospheric concentrations of hydrocarbons of less than 5 mg/m$^3$ (10). Most of these samples had been received from Squadron 14. This drop in the reported hydrocarbon content was very encouraging, although at the same time the suddenness with which it occurred is somewhat puzzling.
An example of the puzzling aspect of the recently reported low hydrocarbon values is that of the ROBERT E. LEE (SSB(N)601). In this instance, during the first 1200 hours of submergence, the carbon sampling method showed hydrocarbon concentrations of 21 to 77 mg/m³ with a generally rising trend as shown in Fig. 2. After 1200 hours had passed, the hydrocarbon content of the samples dropped to nothing. Since this event, however, the ROBERT E. LEE as well as several other boats, including the PATRICK HENRY and GEORGE WASHINGTON, have reported very low values for hydrocarbon content.

The case of the ROBERT E. LEE, cited here, was cause for a reappraisal of the carbon sampling program. Although the low values recently reported from other boats show that this is probably not an isolated case, it was feared that there may have been some fault in procedure or deficiency in equipment. For example, it is known that the first pancake-type canisters supplied by the manufacturer for use with the NRL-designed samplers were loosely filled. This loose fill was noted at NRL and reported to the Bureau (13). This deficiency is being corrected and properly filled canisters should soon be in use. However, it is conceivable that bypass through the loosely filled canisters may have given low results. This would be particularly true if canisters were not held horizontally during exposure. At any rate, several alternate methods of sampling submarine atmospheres are being readied in the laboratory to be used to check the hydrocarbon content in nuclear submarines.
It is certainly possible for nuclear submarines to reach and maintain relatively low hydrocarbon levels in the atmosphere by strict control of sources of contamination, as in the case of the SARGO cited earlier. Another example of good contaminant control is the TRITON, which, since the spring of 1960 (2), has had consistently low hydrocarbon concentrations, averaging 5 mg/m³ or lower. This, of course, is the aim for all the nuclear submarines. But, in order to provide reliable information on the trend of hydrocarbon contamination in each nuclear boat, it is important to know that the analytical results are dependable.

Unfortunately, the hydrocarbon concentrations in the atmospheres of newly activated nuclear boats are still very high. For example, data obtained in the late summer and fall of 1961 in the ABRAHAM LINCOLN and SNOOK (16) ran as high as 100 to 150 mg/m³. Main filter carbon exposed during the same periods confirmed these findings. It is hoped that concerted efforts by the shipbuilders and the Bureau of Ships can substantially improve this situation.

ANALYSIS OF MAIN FILTER CARBON

A number of samples taken from main carbon beds have been analyzed over the years at NRL, and more recently, at the Materials Laboratory. Some of this data is given in Table 2. These data also have indicated the trends in hydrocarbon content of submarine atmospheres. For example, it was estimated from early data (7) that a main carbon bed of 125 pounds was essentially saturated within 24 to 48 hours, i.e., the carbon had adsorbed hydrocarbons equivalent to as much as 20 to 30 percent of its own weight.

<table>
<thead>
<tr>
<th>Ship</th>
<th>Approximate Exposure Dates</th>
<th>Length of Exposure (days)</th>
<th>Percentage of Hydrocarbon Desorbed Carbon Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWORDFISH</td>
<td>Fall 1959</td>
<td>11</td>
<td>23.4</td>
</tr>
<tr>
<td>HALIBUT</td>
<td>Fall 1960</td>
<td>About 30</td>
<td>14.4</td>
</tr>
<tr>
<td>HALIBUT</td>
<td>Fall 1960</td>
<td>5</td>
<td>1.2</td>
</tr>
<tr>
<td>ABRAHAM LINCOLN</td>
<td>Summer 1961</td>
<td>28</td>
<td>21.6</td>
</tr>
<tr>
<td>PATRICK HENRY</td>
<td>Summer 1961</td>
<td>–</td>
<td>19.3</td>
</tr>
<tr>
<td>HALIBUT</td>
<td>Summer 1961</td>
<td>120</td>
<td>22.4</td>
</tr>
<tr>
<td>G. WASHINGTON</td>
<td>Summer 1961</td>
<td>14</td>
<td>1.7</td>
</tr>
<tr>
<td>PATRICK HENRY</td>
<td>Fall 1961</td>
<td>30</td>
<td>1.7</td>
</tr>
<tr>
<td>R. E. LEE</td>
<td>Fall 1961</td>
<td>14</td>
<td>0.8</td>
</tr>
<tr>
<td>SNOOK</td>
<td>Fall 1961</td>
<td>25</td>
<td>22.4</td>
</tr>
</tbody>
</table>

Several years ago, a main carbon bed configuration was designed in which approximately 500 pounds of activated carbon was charged into the bed in 5-pound muslin bags rather than in loose form. About a year ago it was requested by NRL that sample bags of carbon exposed in this manner be sent by the ships to NRL for experimental purposes. The Bureau of Ships arranged this as part of the Fleet Assist Program (14). Such samples were received at NRL and the Materials Laboratory, although the exposure data supplied by the boats were sometimes incomplete or not precise. Nevertheless, it appears evident that the data on hydrocarbon concentrations found by steam desorption of this carbon confirm the analytical carbon data. For example, carbon which had been exposed in the main filter of the ROBERT E. LEE for 14 days during the patrol immediately following that of
Fig. 1, yielded only 0.8 g of hydrocarbon oil per 100 g sample of carbon. Carbon exposed for 14 days in the GEORGE WASHINGTON yielded 1.7 g per 100 g carbon. Several other data obtained in this way average only 1-2 g hydrocarbon per 100 g of carbon after exposures of up to 30 days. However, the exposure information in the latter cases is not always known accurately.

The data which resulted from analyses of main filter carbon are important in several respects. These data tend to confirm the data from analytical carbon in that the hydrocarbon content of some nuclear submarines is shown to be very low. Also, it is indicated that, contrary to current practice, the main carbon beds on certain Polaris patrol boats may not need to be recharged with new carbon during patrols of 60 days or even longer.

Because of the useful information which has been demonstrated by this approach, it is urged that the main filter sampling program of Ref. 14 be revised and reactivated or a similar one begun. It seems clear that valuable information would be obtained from the analysis of at least one bag of carbon taken from an appropriate location in the bed whenever the latter is recharged. Similar-sized samples from boats with bulk carbon beds should be taken. Such a program would provide data in a reasonably short time, which would be especially valuable in supplementing the analytical carbon sampling program.

Incidentally, up to now no feasible method has been devised for determining on shipboard the degree of usefulness remaining in partially spent activated carbon. This is due in part to the lack of definition for this degree of usefulness. With relatively clean boats, it appears appropriate to consider a method which would require removal of a sample to a dockside facility for test. This implies the possibility that the carbon may remain useful for more than one patrol or cruise.

AROMATIC HYDROCARBONS IN SUBMARINE ATMOSPHERES

It has been of special interest to identify the aromatic hydrocarbons in submarine atmosphere because of their reputedly greater toxicity. A number of them have been shown to be present (3,5,15), and some time ago it was established by a liquid chromatographic procedure that the oils recovered from carbon exposed on four different submarines contained from 36 to 54 percent aromatics (1). Since then several additional samples have been shown to have 25 to 30 percent aromatics. This relatively high aromatic content has been verified recently by a gas chromatographic method.

It is of interest in regard to sources of contamination that four samples of paint thinners from different sources contained only 10 to 17 percent aromatics. It has been observed again (16) that the venting of diesel fuel tanks inboard can be a significant hydrocarbon source. It is planned to check the aromatic content of the volatiles from several diesel fuels. Further work on the influence of various other sources of hydrocarbon contamination is in progress. For example, calculations based on analysis of cigarette smoke indicate this to be a significant source of hydrocarbons as well as many other organic compounds.

The identification and estimation of individual aromatic hydrocarbons in oils recovered from submarines has been attacked recently with new tools. In general, the techniques are similar to those applied to a recent analysis of paint thinners (17). The hydrocarbon sample is separated by liquid chromatography on silica gel into three hydrocarbon type fractions: saturates, olefins, and aromatics. Controlled gas chromatography on several partition columns has been used successfully in the quantitative estimation of a number of individual hydrocarbons.
REMOVAL OF ORGANIC VAPOR CONTAMINANTS FROM SUBMARINE ATMOSPHERES

The major removal agents for organic vapors in nuclear submarines are the CO/H\textsubscript{2} burners and the main carbon beds. Some minor removal capacity is contributed by the monoethanolamine scrubbers for acid materials such as acetic acid. The cooler condensates have been shown to contain some organic compounds, especially oxygenated ones such as alcohols and aldehydes.

The hopcalite used in the CO/H\textsubscript{2} burners has been demonstrated to be an effective catalyst for the combustion of hydrocarbons of different types as well as oxygenated organic compounds (18). At the operating conditions of the CO/H\textsubscript{2} burner on submarines, the burner is an effective incinerator for the large majority of organic compounds. In passing, it is noteworthy that the CO/H\textsubscript{2} burner is effective also in the combustion of organic aerosols and in their consequent removal from the atmosphere (19).

Of the organic compounds known to be in submarine atmosphere, methane and the Freons pass through the burner essentially untouched. Incidentally, these compounds are not normally included in the material reported by carbon sampling. The main filter carbon is also ineffective in their removal of methane and relatively poor in the removal of Freons. Freons might be removed by carbon in significant quantities if some method of frequent desorption were used.

The hopcalite catalyst appears to have an indefinite life for effectiveness against organic compounds. Also, the evidence is that combustion of hydrocarbons on the catalyst is complete, yielding carbon dioxide and water, with no partially oxidized products (18). In contrast, carbon will tend to desorb adsorbed materials upon continued passage of air. One of the attributes of activated carbon, however, is its selectively greater effectiveness for larger molecules which tend perhaps toward enhanced physiological activity. The removal of such large molecules is of undoubted benefit to atmospheric habitability.

The concurrent effect of the CO/H\textsubscript{2} burner and the carbon bed on data which have been reported for the organic content of submarine atmospheres can be explained by resorting to an idealized model. It must be assumed that a constant source of contaminant exists, and that the CO/H\textsubscript{2} burner is 100 percent effective for removal of the contaminant. If we disregard the carbon bed, and depend only on one 250-cfm CO/H\textsubscript{2} burner, it can be shown that the following holds:

| Equilibrium Concentration Rate of Supply of |   |
| of Combustible Organics, | Combustible Organics, |
| mg/m\textsuperscript{3} | grams/day |
| 100 | 1080 |
| 30 | 325 |
| 5 | 50 |

This means that over 2 pounds per day of combustible organic contaminants is supplied to the atmosphere of a nuclear submarine under these conditions when the equilibrium concentration is 100 mg/m\textsuperscript{3}.

To determine the effect of a fresh bed of carbon on this situation, let us assume that a 500-pound bed of activated carbon has been installed with an air flow of 2000 cfm. It is evident that the concentration of organic contaminants will show a pronounced drop if the reasonable assumption is made that fresh carbon is essentially 100 percent effective in their removal. Under these circumstances, the concentration could drop temporarily from 100 mg/m\textsuperscript{3} to about 15 mg/m\textsuperscript{3}. In practice we can expect leakages through the carbon bed which will result in a somewhat higher concentration. As the carbon adsorbs the
contaminant, its effectiveness will drop, and the equilibrium concentration will gradually rise until the carbon is saturated (or rather reaches an equilibrium with the atmosphere). At this point we are again completely dependent on the CO/H₂ burner and the equilibrium concentration in the atmosphere is again 100 mg/m³. Although this is an ideal model, data are available which fit it qualitatively (7,10).

To emphasize the value of the CO/H₂ burners and carbon beds it is interesting to speculate on the situation which would obtain should both of these removal agents be inoperative. Under this condition, the hydrocarbon content of the atmosphere would increase at the rate of 300 mg/m³ per day. At the end of 20 days, the concentration would have reached the incredible figure of 6000 mg/m³.

ADDITIONAL DISCUSSION

It has been known and emphasized that the carbon sampling method is reasonably quantitative within broad limits at about 100 mg/m³ and higher, but not at very low concentrations. This is primarily because of the difficulty of desorbing organic materials from carbon. A "heel" always remains in the carbon after steaming or other desorption methods have been applied. This residue is much more significant at lower concentrations, and may even represent a major part of the total adsorbed material. As a relative matter, however, the low values such as those cited earlier are useful, although far from quantitative.

Because of these limitations, it is necessary to develop new methods of sampling to make the results meaningful at low concentrations. The current goal is to devise a method suitable for operation by shipboard personnel. Research on several promising methods is in progress and, although the prospects are encouraging, it seems premature to describe them at this time.

In addition to the hydrocarbon analyses, some progress has been made in developing sampling techniques and procedures suitable for the identification and estimation of non-hydrocarbon compounds. Certain alcohols, ketones, and aldehydes have been identified and in some instances estimated. Currently, some emphasis is on the assessment of analytical methods for aldehydes, particularly formaldehyde and acrolein. With the exception of the simple alcohols, concentrations of these oxygenated compounds in nuclear submarines are usually less than a part per million.

Research is underway concerning the ignition and flammability characteristics of activated carbon, especially when loaded with hydrocarbons. Synthetic samples as well as carbon obtained from the main filters of nuclear submarines have been studied. Flash points on samples of carbons which have been exposed on shipboard have thus far been found to be above 165°F. The results to date indicate that the flash point may be as low as that of the oil itself, but no lower. Spontaneous ignition temperatures of these carbon samples have been found to be as low as 500°F, which is about the same as that for a JP-5 jet fuel or diesel fuel. Thus far there has been no indication of any effect of activated carbon to catalyze the spontaneous ignition of the adsorbed hydrocarbons. Nevertheless, a 500-pound bed of carbon containing 15 to 30 percent by weight of hydrocarbons is a potent amount of flammable material which must be treated with all the respect due such a hazard.

RECOMMENDATIONS

Upon the basis of the data on organic contaminants discussed in this report, the following recommendations are made:

1. The frequency of carbon sampling on shipboard should be substantially reduced, especially for long submergences.
2. The nuclear submarines should be requested to furnish for analysis two bags of carbon or the equivalent of loose carbon which has been exposed in the main filter beds, whenever the latter are recharged.

3. Consideration should be given to lengthening the interval between changes of main filter carbon, particularly in those submarines which have demonstrated a consistently low level of contamination.
REFERENCES


### 1. Nuclear submarines - Habitability

This Laboratory has carried out a program of sampling and analysis of the atmospheres of nuclear submarines for the identification and estimation of organic contaminants. Most of these organic compounds have been found to be hydrocarbons. The total hydrocarbon content of submarine atmospheres was initially very high (100 to 200 mg/m³) but has decreased to very low values in many cases (<10 mg/m³) by means of careful control measures. Individual aromatic hydrocarbons have been isolated with an estimation of their concentrations.

(over)

### 2. Air - Decontamination

(over)

### 3. Air - Sampling

(over)
The principal sampling method is based on the exposure of activated carbon on shipboard followed by desorption of the carbon in the laboratory. The most useful means of removing organic contaminants from the submarine atmospheres are combustion by means of a catalyst and adsorption by activated carbon contained in large filter beds. Calculations of the effectiveness of these measures under various conditions of use were made based on typical analytical data.