

Feasibility of the Total Hydrocarbon Analyzer for Evaluating the Life of Charcoal Beds

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was a sensitive indicator of the degree of depletion of adsorptive capacity of the charcoal, even for a bed with substantial bypass leakage. The ratio of effluent to influent concentration constitutes a *performance ratio* for the bed. Periodic monitoring of this ratio and its trends is proposed as a means of assessing useful bed life.

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FEASIBILITY OF THE TOTAL HYDROCARBON ANALYZER FOR EVALUATING THE LIFE OF CHARCOAL BEDS

INTRODUCTION

Prior to 1955, submarines could stay totally submerged for only a day or two, and essentially the only special provisions on board for controlling the atmosphere were those designed for use in emergencies. Of necessity, the routine method of freshening the air was frequent ventilating to the outside. However, with the advent of nuclear submarines, which can stay submerged for many weeks, the detection and control of atmospheric contaminants became a problem of major concern to the Navy.

A principal element for controlling atmospheric contaminants in the nuclear submarines is an adsorbent bed of activated carbon, or charcoal. Charcoal purifies the air by adsorbing and holding vapors on its surface. At room temperature charcoal is quite effective for adsorbing the less volatile hydrocarbons and other organic compounds whose molecular sizes correspond to six or more carbon atoms. However, it is relatively ineffective for removing lower molecular weight compounds of higher volatility, such as methane and the common refrigerant gases.

As the charcoal adsorbs contaminants from the submarine atmosphere, its capacity decreases. When enough material has been adsorbed to be in equilibrium with the influent air stream, the charcoal has no more capacity and its continued use would serve no useful purpose. Heretofore, there has been no method available on board the submarine to determine when the charcoal has lost its effectiveness. Consequently, the charcoal beds have been replaced routinely on a fixed schedule of every 20 or 21 days, even though the charcoal in many instances might still retain considerable life.

At the beginning of the nuclear submarine program, it was not uncommon to find atmospheric concentrations of hydrocarbon-type contaminants, other than methane and refrigerants, sufficient to load up the charcoal beds completely in a few days. For example, Johnson [1] in 1959 used a desorption technique [2] to analyze contaminants adsorbed on charcoal exposed for only 11 days on board USS *Swordfish* (SSN 579). The charcoal was found to have a contaminant loading of 23.4% by weight. This was essentially complete saturation of the charcoal. Subsequent stringent control of the sources of these contaminants markedly reduced the atmospheric concentrations. A similar study was made on charcoal from USS *Patrick Henry* (SSBN 599) in 1961, after the above-mentioned controls had been instituted. This charcoal, exposed for 30 days, had a total contaminant loading of only 1.7% by weight [1].

In a related study in 1967, Lakin [3] with an NRL-built Total Hydrocarbon Analyzer [4] monitored the submarine atmosphere, rather than the carbon bed, aboard USS *Francis Scott Key* (SSBN 657). Lakin's data (Fig. 1) showed that the total-hydrocarbon concentration fluctuated between 15 and 25 mg per cubic meter throughout the

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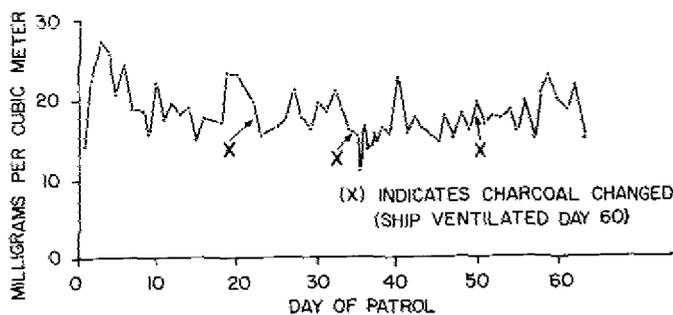


Fig. 1 — Concentration of "total hydrocarbons" in the atmosphere of USS *Francis Scott Key* (SSBN 657) during a 60-day patrol

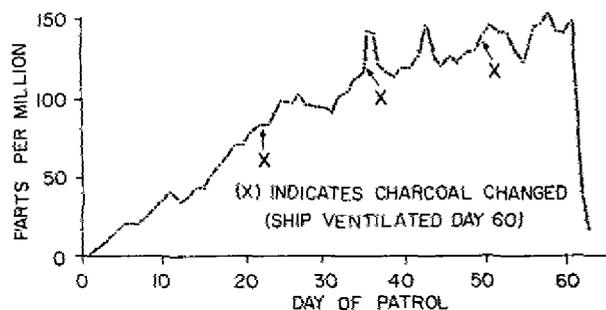


Fig. 2 — Concentration of methane in the atmosphere of USS *Francis Scott Key* (SSBN 657) during a 60-day patrol

60-day patrol. His data (Fig. 2) also show that the methane concentration had increased almost continuously from 0 to 150 parts per million during the same period. The points marked by crosses show when the charcoal bed was replaced. It is seen that replacement of the charcoal had no apparent immediate significant effect on the hydrocarbon concentration in the atmosphere. One reason for this is that only a portion of the ship's air goes through the charcoal bed in any one pass. A second is that there is a considerable amount of bypass leakage through the bed itself [5], since the charcoal bed consists of small bags of charcoal stacked sandbag fashion in a plenum in the ventilating system. Also it is reasonable to assume that the old charcoal still retained much of its capacity and was thus removing vapors efficiently. Thus, replacement with fresh charcoal would not have increased this efficiency markedly.

To assure that there is adequate protection of the atmosphere and yet avoid the cost of material and manpower resulting from unnecessary changes, it is desirable to be able to monitor directly the capacity or efficiency of the charcoal bed from time to time. The NRL-developed Total Hydrocarbon Analyzer (THA) appears to offer one means of doing this. This report describes the results of laboratory experiments in which the THA was used to assess the performance of charcoal beds representing various degrees of depleted capacity.

The laboratory charcoal beds were preloaded with different amounts of n-decane, a low-volatility hydrocarbon. n-Decane was chosen because it is held quite firmly by the charcoal and as such would represent loading of the charcoal with the less volatile hydrocarbons found in submarines. The beds were then challenged with controlled concentrations of n-hexane vapor to represent the more volatile hydrocarbons found in submarines which could be expected to penetrate the beds more easily. The THA was used to monitor the n-hexane concentration in both the influent and the effluent air streams and for n-decane in the effluent only.

EXPERIMENTAL PROCEDURE

The apparatus for conducting the experiments is shown schematically in Fig. 3. Dry air was metered through a fritted glass bubbler (A) containing n-hexane. A water bath around the bubbler stabilized the vapor pressure of the hexane. This hexane-laden air stream was then diluted with clean air in the dilution chamber (B). Depending on the particular experiment, the final concentration was 150 to 200 parts per million. The hexane-containing air was then passed through the charcoal bed (C) at 800 to 900 cc per minute. Samples of the influent and the effluent air streams were withdrawn at intervals with a syringe and injected into the THA for analysis.

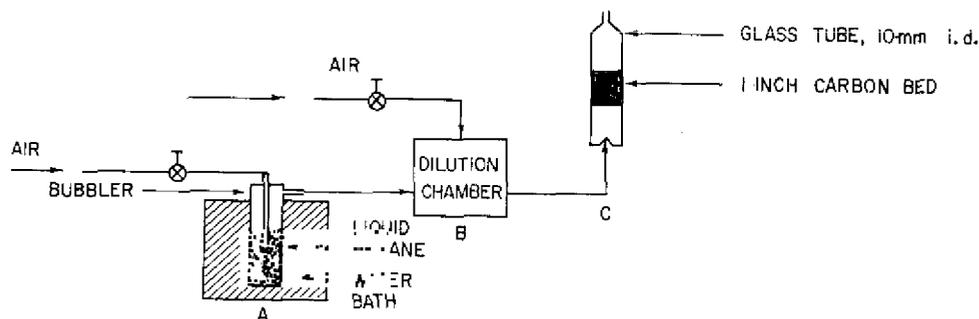


Fig. 3 — Apparatus for exposing charcoal beds to concentrations of n-hexane vapor

The THA has previously been described in detail [4,5]. It is a specialized gas chromatograph which can give both cumulative and resolved analyses of the concentration of hydrocarbons and certain other organic compounds to be found in the air. The sensitivity of the instrument is less than 1 ppm for the more volatile components.

The charcoal beds consisted of coconut-shell charcoal, approximately 10-20 mesh size, packed in glass tubes. The beds were 10 mm in diameter by 25 mm (1 inch) deep. In one bed a capillary tube was extended through to simulate the bypass leakage due to imperfect packing of the small bags of charcoal which make up the adsorbent bed on board a submarine.

The charcoal beds were preloaded with n-decane by allowing vapor from a liquid-containing bulb to diffuse into one end of the tube while a vacuum pump pulled from the other end. The orientation of the tube was noted and preserved so that in later exposures the hexane-laden air stream passed through in the same direction as the decane vapor. The amount of n-decane adsorbed per gram of dry charcoal was determined by weighing.

The total amount of n-hexane adsorbed by the charcoal during exposure was determined by weighing at the end of a run. The runs were continued well past the hexane breakpoint in order to get substantial concentrations in the effluent air stream. The amount of hexane adsorbed at intermediate stages during a run could be calculated by appropriate integration of the concentration-vs-time data for both the influent and the effluent air streams.

RESULTS

In the experiments reported here, only the hydrocarbon n-hexane appeared in the effluent gas stream for all the charcoal beds except the one preloaded to 23% with n-decane. This bed was completely saturated. Hence, the n-decane preload as well as the influent hexane vapor bled through immediately on starting the run.

The results of the n-hexane exposure studies are summarized in Table 1. The amount of n-decane preloading on the charcoal is expressed in Column 1 as percent by weight of dry charcoal. The influent concentration of n-hexane in air is shown in Column 2, and the flow rate through the charcoal bed is given in Column 3. The exposure time and the corresponding effluent concentration of n-hexane in air are shown in Columns 4 and 5, respectively. The amount of n-hexane adsorbed by the charcoal is given in Column 6, expressed as percent by weight of dry charcoal. The sum of Columns 1 and 6 is shown in Column 7. Thus, Column 7 gives the total amount of hydrocarbon adsorbed by the charcoal — whether it is decane or hexane or both.* The table includes some intermediate values of hydrocarbon loading calculated from integrated concentration-vs-time data. All other values are based on actual weights.

* Adding the weight percent of n-decane to the weight percent of n-hexane (Columns 1 and 6) to get a total is an approximation and a simplification that is sufficient for the practical purpose of this report. Because of the difference in density of these hydrocarbons, it would have been more nearly correct to normalize and express the amount of each adsorbed hydrocarbon in terms of space occupied (cc liquid per gram of charcoal).

Table 1
Penetration of Charcoal Beds by n-Hexane Vapor:
Effect of Adsorbed Hydrocarbon on Effluent Concentration

1 Charcoal Bed Preload with n-Decane (wt-%)	2 Influent Concentration of n-Hexane in Air (ppm)	3 Flow Rate Through Bed (cc/min)	4 Exposure Time (min)	5 Effluent Concentration of n-Hexane in Air (ppm)	6 Adsorbed n-Hexane by Charcoal (wt-%)	7 Total Hydrocarbons Adsorbed by Charcoal (wt-%)
0	175	834	90	0.1*	—	—
0	175	834	100	0.29	4.0†	4.0†
0	175	834	226	4.58	9.0†	9.0†
0	175	834	265	9.7	11.5	11.5
4.3	200	882	5	0.49	≈0‡	4.3†
4.3	200	882	100	4.8	5.7	10.0
7.6	200	882	2	0.28	≈0‡	7.6†
7.6	200	882	100	4.58	6.0	13.6
11.2	200	882	0	4.2	≈0‡	11.2†
11.2	200	882	22	9.7	1.0†	12.2†
11.2	200	882	50	16.0	2.3†	13.5†
11.2	200	882	100	29.0	5.1	16.3
14.0	200	882	0	10.8	≈0‡	14.0†
14.0	200	882	50	29.0	2.6†	16.6†
14.0	200	882	100	59.0	6.0	20.0
23.0	210	882	0	195.0	≈0‡	23.0†
0‡	150	882	0-200	≈32.0¶	—	—
0‡	150	882	200	32.0¶	6.3†	6.3†
0‡	150	882	280	38.0	8.7†	8.7†
0‡	150	882	500	74.0	15.3	15.3

* Limit of detection: 0.1 ppm.

† Intermediate value calculated from integrated concentration-vs-time data.

‡ With leak.

¶ Leak level.

The n-hexane effluent concentration is shown in Fig. 4 as a function of exposure time for all the intact nonloaded and preloaded charcoal beds. As would be expected, the samples with previously adsorbed n-decane showed proportionately shorter lives than ones without preloading. As was mentioned before, the 23% preloaded sample showed zero life to n-hexane.

In Fig. 5 n-hexane effluent concentration versus exposure time is shown for the charcoal bed which had a built-in leak. For comparison the performance of the nonloaded intact bed is plotted again (from Fig. 4). One can see from the figure and from Table 1 that the charcoal bed with the leak gave an initial constant penetration of about 20% of the influent n-hexane concentration. This means that the net flow rate through the charcoal itself was about 80% of the total amount going through the system.

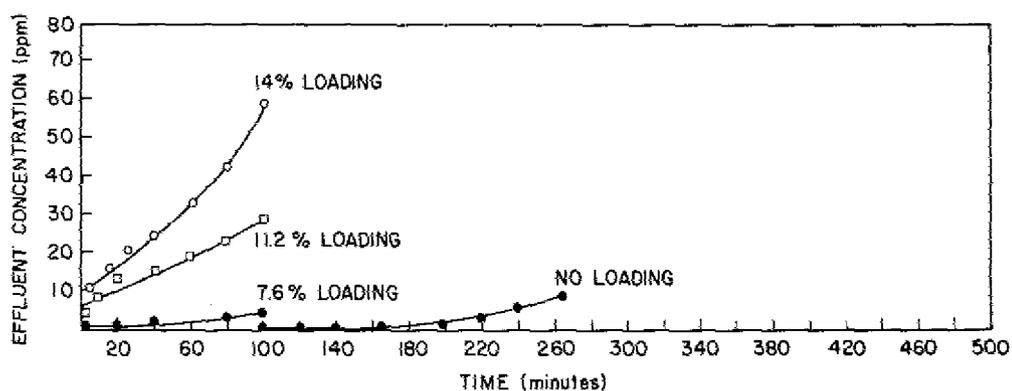


Fig. 4 -- Effluent concentration (parts per million in air) as a function of time for charcoal beds exposed to n-hexane vapor. Preloading with n-decane is expressed as percent by weight of dry charcoal

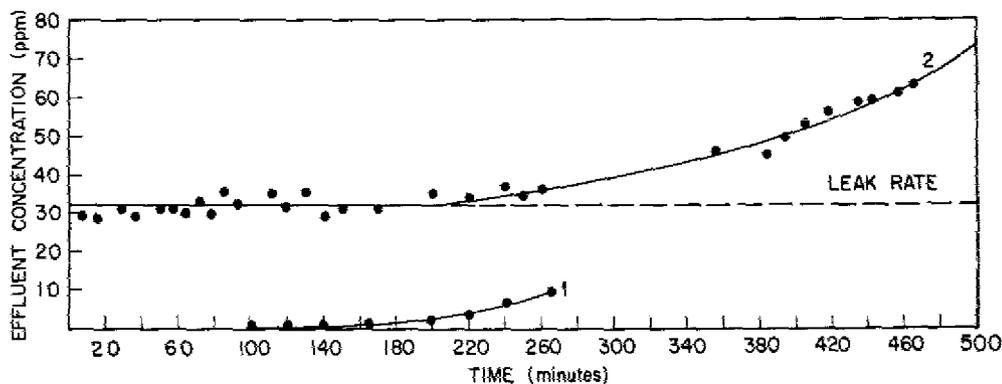


Fig. 5 -- Effluent concentration (parts per million in air) as a function of time for nonloaded charcoal beds exposed to n-hexane vapor: (1) intact bed; (2) bed with approximately 20% bypass

When the charcoal was finally penetrated by the n-hexane, the effluent concentration rose above the initial leakage level. Because of this leakage and the slightly lower influent concentration, the time to this penetration was somewhat longer than the life for the intact charcoal bed. Total loading of the charcoal however was essentially the same.

The performance results for all the charcoal beds are combined in Fig. 6, which shows the effluent concentration of n-hexane as a function of the total amount of hydrocarbon adsorbed (Table 1, Columns 5 and 7). The concentration for the charcoal bed with the leak is plotted as the amount above the initial leakage value. It is to be seen here that the concentration in the effluent air stream appears to depend on the total hydrocarbon loading — whether it is n-decane, n-hexane, or both. At a total loading of about 7% by weight of dry charcoal, the n-hexane breakpoint occurs. Beyond this loading, the effluent concentration rises markedly.

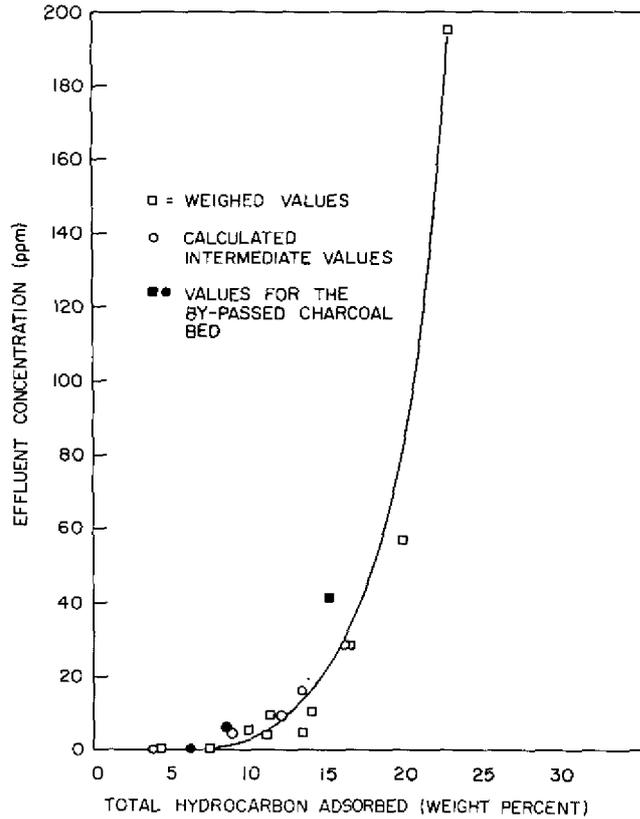


Fig. 6 — Effluent concentration (parts per million in air) of n-hexane as a function of total amount of hydrocarbon adsorbed. Total adsorbed hydrocarbon is expressed as percent by weight of dry charcoal

DISCUSSION

It appears from these experiments that the Total Hydrocarbon Analyzer (THA) was indeed sensitive and capable of assessing the condition of the charcoal beds by measuring the influent and effluent hydrocarbon concentrations. The effluent hydrocarbon concentration is sensitive indicator of the extent of depletion of the charcoal bed capacity. This was true even for the charcoal bed which had a substantial leakage rate.

It is postulated that by making approximately simultaneous determinations of the hydrocarbon concentrations in both the effluent and influent air streams, one can establish a ratio of effluent concentration to influent concentration for a given clean charcoal bed. This would be a *performance ratio*. By repeating these determinations periodically, one can then detect changes in this performance ratio as the capacity of the charcoal bed becomes depleted. For example, a newly installed charcoal bed with a considerable amount of bypass leakage might give an initial effluent/influent performance ratio of 50%. (Short-term variations in atmospheric hydrocarbon concentrations such as were shown in Fig. 1 should not affect this ratio appreciably; the influent and effluent leakage concentrations should vary together.) As the capacity of the charcoal becomes depleted, this ratio would be expected to increase toward unity. By the time the performance ratio reached some predetermined limit, 75%, for example, the charcoal bed could be replaced.

These laboratory results indicate that the THA should be a feasible means for determining and monitoring the condition of submarine charcoal beds. However, before any final conclusions can be drawn, it will be necessary to relate these laboratory experiments to actual field conditions. For example, these 10-mm by 1-inch charcoal beds were exposed to hydrocarbon concentrations of 150 to 200 parts per million at flow rates of 800 to 900 cc per minute. This corresponds to a linear flow rate of 33 to 38 feet per minute. In a submarine the hydrocarbon concentration may be quite variable, but the linear flow rate through the charcoal beds is typically about 103 feet per minute. Other matters which can be answered only by field experience are: (a) sensitivity and precision of the method, (b) accessibility for sampling, and (c) logistics of equipment and manpower for performing the necessary tests.

To obtain some of this field experience, NRL has designed and recommended to the Naval Ship Engineering Center (NavSEC) a series of experiments to be conducted on board representative submarines of the nuclear-attack and fleet-ballistic-missile types [6].

These experiments are to be conducted by the ship's company, following procedures delineated by NRL. The THA will be used daily to determine the hydrocarbon concentrations upstream and downstream of the charcoal bed. In addition, whole gas samples are to be collected in evacuated bottles at the beginning, the middle, and the end of the test period for confirmatory analyses back at the laboratory.

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