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Nuclear Submarine Atmospheres

Part 2 - Development of a Total Hydrocarbon Analyzer

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ABSTRACT

An instrument has been developed for the shipboard monitoring of total hydrocarbons in nuclear submarine atmospheres. In addition to hydrocarbons, the instrument also measures methane and Freon-12 and, with a slight modification in operating procedure, Freon-11. The system is based upon a chromatographic technique coupled with a highly sensitive flame ionization detector. An air sample is injected into a chromatographic column and chromatographed in the usual manner until the methane and Freon-12 peaks emerge. At this point, the flow of carrier gas is reversed and the higher hydrocarbons are backflushed from the column through the detector as a single peak. The area under the backflushed peak provides a measure of the total hydrocarbon content of the atmosphere. The principles on which the instrument is based have been successfully tested at sea aboard the U.S.S. SCULPIN.

PROBLEM STATUS

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

AUTHORIZATION

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NUCLEAR SUBMARINE ATMOSPHERES

PART 2 - DEVELOPMENT OF A TOTAL HYDROCARBON ANALYZER

INTRODUCTION

For many years there has been a need, which recently has become more acute, for a method of analysis which can be used on shipboard to determine the total hydrocarbon content in the atmospheres of nuclear submarines. It is important for optimum atmosphere control, from the standpoint of both personnel and equipment, to be able to establish the hydrocarbon content in any compartment of the submarine while it is underway. This report briefly describes the development at this Laboratory of an analyzer which is suitable for this purpose.

HISTORICAL BACKGROUND

Beginning in the spring of 1956 with USS NAUTILUS, an analysis program has been carried on by this Laboratory to determine the organic constituents in the atmospheres of the nuclear submarines. It was soon found that the composition of the mixture of organic atmospheric contaminants was very complex (1,2). In addition, it was established that this mixture was predominantly hydrocarbon in character. In these atmosphere analyses, some of the most useful data were obtained by adsorption of organic molecules on activated carbon in the submarine, return of the exposed carbon to the laboratory, followed by desorption and analysis of the desorbant. A semiroutine sampling and analysis program based on this carbon sampling scheme was instituted in 1961 (3-5) and is still in operation. In successive years, as new and more sensitive instruments and methods of analysis were devised, these were applied to the determination of the concentrations of hydrocarbons and other organic compounds, both in the laboratory and on shipboard. Many methods were tried to satisfy the urgent need for shipboard analysis of total hydrocarbon content but none of these methods were suitable for such use except by trained analysts for special analyses.

A new principle in chemical analysis, called gas chromatography, has been developing very rapidly in recent years and has become one of the most versatile and useful analytical tools available. New developments in gas chromatography have been exploited quickly in the NRL program (6) for use in many varied applications such as determining the identity or type of organic compounds found in closed atmospheres, as well as the concentrations of many of these compounds. In several instances, gas chromatographs have been used on shipboard (7-10). Generally speaking, these analyses in the submarines have confirmed the analytical data obtained by carbon sampling.

The earlier chromatographs did not have detectors sensitive enough to run direct analysis on submarine atmospheres without using a concentration step (6). The earliest detector with a sensitivity sufficiently high to make direct analyses was the argon ionization detector. It was sensitive enough, and was very useful in skilled hands, but it was temperamental in many ways which made it unsuitable for routine shipboard use. Particularly troublesome was its sensitivity to traces of water vapor. As each new detector became available, it was evaluated for its suitability for the determination of the total hydrocarbon content of submarine atmospheres. With the invention of the flame ionization detector, a very promising lead was uncovered in the search for a suitable detector for this use (11-12).

DEVELOPMENT OF THE HYDROCARBON ANALYZER

As soon as more technical information and suitable instrumentation for the flame ionization detector became available, especially in regard to stable electrometer systems, development of a hydrocarbon analyzer (Total Hydrocarbon Analyzer) based on this detector was started at NRL. The flame ionization detector has a very high potential sensitivity to hydrocarbons which is essential for this application. It is sensitive also to most other organic compounds but insensitive to such common atmospheric gases as oxygen, carbon dioxide and water. Unfortunately, the presence of relatively large concentrations of methane and Freon in nuclear submarine atmospheres complicates the situation because the flame ionization detector also responds to these two organic compounds. It is often the case that either methane or Freon, always present in these atmospheres, will more than equal in concentration the combined concentrations of all the other hydrocarbons in nuclear submarines. Consequently, some provision must be made to eliminate the interference of methane and Freons in order to get a good analysis for total hydrocarbons.

The solution to the methane/Freon problem was based on a gas chromatographic approach known as the "backflush" technique. The approximate description of the method as it was developed is as follows: A sample of submarine air (about 5 cc) is injected into the system either by means of a hypodermic syringe or a sampling loop. The sample is swept into a chromatographic column and the column flushed by the stream of carrier gas until the peaks for methane and Freon-12 emerge. The column is then backflushed and the total hydrocarbon content, exclusive of methane and Freon-12, is measured as a single peak (Fig. 1). The area represented by this peak is measured by a suitable means and the total hydrocarbon content is calculated based on area calibrations with air samples of known hydrocarbon content.

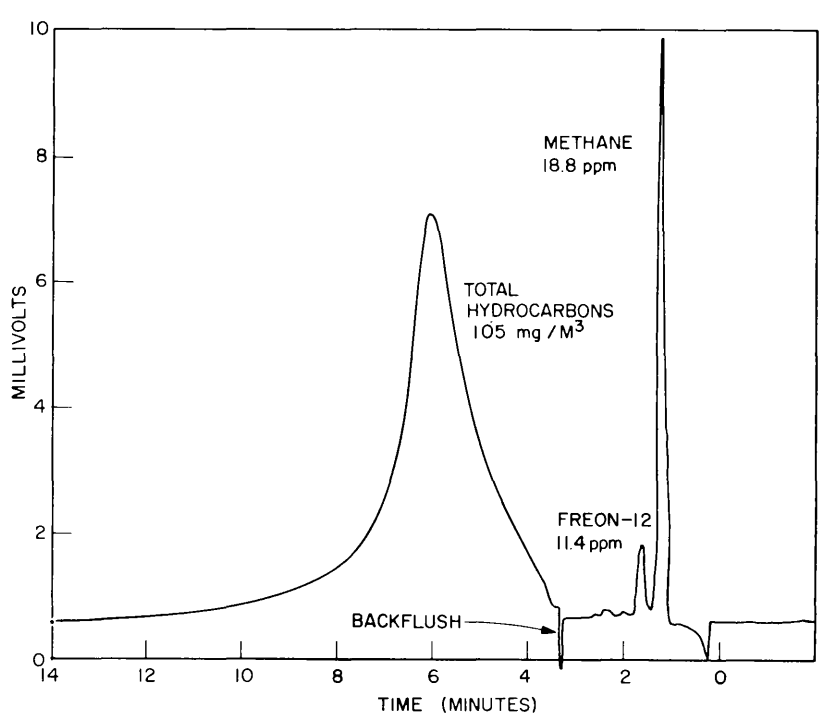

Fig. 1 - Backflush chromatogram of air sample from USS SCULPIN

An interesting bonus feature of this development is that it provides an excellent determination for both methane and Freon-12, while at the same time removing them from interference in the total hydrocarbon analysis (Fig. 1). This is important because at present there is no backup method for the analysis of Freon-12 by the Mark III or Mark IV Atmosphere Analyzers. In addition, Freon-11, which is being used in some submarines, can be determined by the Total Hydrocarbon Analyzer by a minor change in its mode of operation.

An important aspect in the development of the Total Hydrocarbon Analyzer at NRL was the simplification of the carrier gas system. In most flame ionization chromatographic systems, an inert carrier gas such as helium is used to move the sample being analyzed through the system. In the present design, air is substituted for the inert gas, making it possible to measure methane without separating it from oxygen as would be required with another carrier gas. Since air or oxygen is needed for burning the hydrogen to produce the flame in any case, this modification means that a two-gas system is provided instead of the usual three-gas system. This change, therefore, not only provided for better analytical results but simplifies the logistics of the compressed gases used.

A more recent corollary development has to do with the air supply for the Total Hydrocarbon Analyzer. The compressed gases presently required for its operation are a modest supply of hydrogen, and somewhat larger amounts of clean air. To avoid the necessity of providing bottled air, a scheme has been devised successfully which would permit the use of compressed air from the ship's supply. This development is based on passing the air through a heated catalyst to oxidize all the organic compounds. A scrubber is provided to scrub out any acids formed during the oxidation.

APPLICATION TO SHIPBOARD USE

A model of the flame ionization analyzer for total hydrocarbon content was used by NRL chemists during a 12-day submerged cruise (10) in USS SCULPIN from Feb. 18 to Mar. 1, 1963. The operation was very successful and by means of this instrument, a number of studies were carried out which had not been previously possible. The hydrocarbon content was determined for air samples taken at points throughout the submarine. The removal efficiency of the main carbon bed for hydrocarbons and Freon-12 was studied in detail. Included also was a detailed investigation of the effect of catalyst temperatures between 500°-600°F in the CO/H_2 burners on the removal of hydrocarbons and the decomposition of Freon-12. These studies illustrate the versatility and usefulness of this analyzer in the submarine. It performed efficiently with no serious problems and caused no interference with the ships electronic or other systems.

Two minor disadvantages of the Total Hydrocarbon Analyzer which should be mentioned are its need for a supply of hydrogen gas, and the presence of the pilot flame when the analyzer is in operation. However, the analyzer can be in standby condition (flame off and hydrogen secured) and be put into operation within a few minutes. This would minimize the disadvantage of the flame and conserve hydrogen so that a modest supply of this gas would suffice, even for a long patrol. For example, the current model if in operation for a total of two hours a day would consume only about 12 cu. ft. of hydrogen in a 60-day period. It is not visualized that the analyzer would be in use more than a few hours a day. Consequently, it is believed that these disadvantages are minor and not limiting.

An exhaustive search has not revealed another analytical system which has all the characteristics required for this application. A number of candidate systems, e.g. several methods based on catalytic combustion, have been studied in detail in the laboratory and in several instances, they have been tried on shipboard. The Total Hydrocarbon

Analyzer appears to be eminently more suited to this job than any other scheme considered or tested experimentally.

SUMMARY AND CONCLUSIONS

A summary of the advantages and usefulness of the Total Hydrocarbon Analyzer follows:

1. It will provide an analysis for the total hydrocarbon content in nuclear submarine atmospheres within a few minutes.

2. The analyzer is characterized by a high sensitivity to hydrocarbons, excellent stability, linearity of response, and relative insensitivity to and lack of interference by water, CO_2, and other inorganic gases.

3. It provides an excellent analytical method for methane.

4. It provides an excellent analytical method for Freon-12.

5. It can be readily adapted for the analysis of Freon-11 and certain other organic compounds which might occur in more than a few parts per million.

6. It should be especially suitable for special uses such as determining the useful life remaining in carbon filter beds by means of input and output readings.

7. It can produce a record from which chemists may deduce the presence of certain organic compounds which might appear unexpectedly in submarine atmospheres.

8. The present design lends itself to substitution of components. For example, if at a later date another detector is found which is judged to be superior to the flame ionization detector, it may be substituted readily. A possible competitive detector is the breakdown voltage ionization detector (Karmen detector) which needs considerably more study. The substitution of this detector would require only minor modifications.

RECOMMENDATION

In view of the current need for an analyzer that can give the total hydrocarbon content in nuclear submarine atmospheres within a few minutes, it is recommended that the Total Hydrocarbon Analyzer developed at NRL be adopted for this use. This analyzer has few disadvantages and many advantages, including several plus features attested to by its demonstrated versatility. A model of this instrument was used on shipboard during a 12-day submergence. During this time several hundred individual analyses were performed successfully.

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