

**NRL Report 6053**

**Third Annual Progress Report**

**The Present Status of Chemical Research  
In Atmosphere Purification and Control on  
Nuclear Powered Submarines**

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## Contents

Foreword	ii
Problem Status	ii
Authorization	ii
Summary of Progress	1
Chapter 1 - The Sulfate-Cycle System	6
Chapter 2 - Algae as a Source of Oxygen for Nuclear Submarines	10
Chapter 3 - Monoethanolamine Stability Studies	25
Chapter 4 - Comparison of Carbon Dioxide Removal Systems	31
Chapter 5 - The Mark IV Atmosphere Analyzer	37
Chapter 6 - Gas Chromatography as a Submarine Atmosphere Monitor	41
Chapter 7 - Organic Contaminants, Sampling and Analysis	46
Chapter 8 - Chemical Constituents of Nuclear-Submarine Atmospheres	53
Chapter 9 - Hopcalite-Catalyzed Combustion	60
Recommendations	65

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## Foreword

The Fleet Ballistic Missile nuclear submarine continues as one of the mightiest components of the deterrent system of the United States. The tragic loss of the USS THRESHER early in 1963 has affected neither this deterrent capability, nor the capability of the FBM submarine to stay submerged almost indefinitely. However, the THRESHER incident did underline the constant need to ensure that all submarine equipment functions perfectly all the time. This necessary insurance adds to the current motivating factors for the continuance of research, development, and engineering on atmospheric habitability by the U.S. Naval Research Laboratory, the Bureau of Ships, the Special Projects Office, and others.

NRL Report 5465, "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," April 1960, summarized the development of an adequate atmospheric system for submarines and covered in some detail the research at NRL through calendar year 1959. In July 1961, and August 1962, NRL Reports 5630 and 5814, respectively, were issued as subsequent annual progress reports.

The present report is essentially a summary of the progress made in submarine-atmosphere control by NRL during calendar year 1962, but it also covers some of the early work of 1963. Research-and-development studies by other Naval laboratories or contractors are not discussed in any detail.

The Bureau of Ships Fleet Assist Project, although now discontinued for administrative purposes, nevertheless has continued in fact, with considerable cooperation by the fleet in permitting research and experimentation aboard the nuclear submarines. Overall during the year, fleet experience indicated continued favorable trends in reduction of contamination and in improvements in monitoring and control equipment. However, there was as yet no operational evaluation of the new Mark IV Atmosphere Analyzer and Mark III CO/H<sub>2</sub> burner.

The total atmospheric-habitability research-and-development effort by NRL during 1962 decreased, as expected, with about 20 man-years of direct effort at a cost of approximately \$500,000.

### PROBLEM STATUS

This is an interim report; work is continuing on all phases of the program.

### AUTHORIZATION

NRL Problems C08-05, C08-18, C08-30  
Project SF 013-08-03, Tasks 4092, 4093, 4094, 4095

NRL Problems C08-32 and C08-33  
BuWeps SP89422

NRL Problem R05-24  
SPO WW 041

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Third Annual Progress Report  
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Summary of Progress

INTRODUCTION

Although there were many significant accomplishments in 1962 in the nuclear-submarine fleet, there was in general only a gradual improvement in the atmospheric habitability of these ships. This lag in the fleet application of the Navy program of air-purification research and development had no apparent direct effect on operations; nevertheless it is obvious that a much greater effort will be necessary to obtain satisfactory atmospheric conditions to guarantee the required wartime capability.

The preceding annual reports (1,2,3) provided historical, status, and progress accounts on submarine air-replenishment equipment and research. The present is the third supplementary annual progress report, and although representing generally the events in 1962, it contains much of the early research during 1963.

OXYGEN SOURCES

The Treadwell high-pressure "monopolar" oxygen generator (2,4) has continued to be the workhorse for the Polaris submarines despite an increasingly large number of maintenance problems attributable to the increased age of the equipment. Among the earlier problems were damage to controls by sea water backing into the ship's 100-psig air system via the ship's whistle during a deep dive, pressurization of generators with nitrogen containing oil or Cellulube, unequal dilution of the electrolyte in cells, failures of the distilled-water-pump bypass valve and pressure transmitter, etc. (4). With an apparently decreasing oxygen requirement per man (close to 0.9 cu ft per hour), these generators have often been able to supply all of the oxygen required when fully functioning at their capacity of 120 cu ft per hour. Development work by the contractor on the Treadwell bipolar oxygen generator has continued.

The NRL - originated "split-cell" generator being built at the Electric Boat Company has encountered construction difficulties, which, however, are not caused by weakness of the principles involved. Such difficulties must be resolved before considering this unit for installation on a submarine now under construction.

Research on the sulfate-cycle system (1,2,3,5) at NRL has been completed, and a final report is in preparation (Chapter 1). In this system, both oxygen and sodium hydroxide are generated from an aqueous sodium sulfate solution in an electrolytic cell, the hydroxide then being used to absorb the carbon dioxide; the sodium sulfate is subsequently

regenerated. The system worked satisfactorily in the NRL pilot model, using the microporous rubber found by NRL to be superior in diaphragms for the electrolytic cell during 125-day runs in miniature test cells. Operational difficulties with the microporous rubber in the pilot model were solved by leaching the commercial product of excess silica used as a pore former. The results fully warrant construction of a prototype model for installation in a submarine, particularly in view of the backup needed for other developmental items still requiring a long lead time.

The feasibility study by Ionics, Inc., on an ion-exchange system for oxygen generation and carbon dioxide absorption proved very promising, and the Bureau of Ships has continued the contract work to include construction of a ten-man prototype model (Chapter 4). Although reservations are still necessary on the durability and electrical properties of the ion-exchange resins, this system still appears to be the best candidate to supersede the high-pressure, Treadwell "monopolar" oxygen generator.

The feasibility study on the use of algae in nuclear submarines for oxygen generation and carbon dioxide absorption has been completed (Chapter 2). The conclusion was that the power requirement was much too high to permit utilization on nuclear submarines in the near future, and would undoubtedly remain too high for the long-term future unless a much more efficient light source could be obtained. Since the study had developed a considerable body of knowledge, equipment, techniques, and ideas, the longer-term study of algal systems is being continued under Office of Naval Research sponsorship rather than that of the Special Projects office.

Continued evaluation of commercial and experimental chlorate candles and their burner filters has continued, although not in an amount warranting a special chapter in this report. The NRL-developed glass blanket filter appears particularly advantageous for service use.

Although considerable research is being done elsewhere at the present time on the use of superoxides as oxygen sources for spacecraft cabins, none appears to be extending the information level acquired before and during World War II (Chapter 4).

#### CARBON DIOXIDE REMOVAL

As repeatedly discussed elsewhere and in the earlier progress reports, the most attractive carbon dioxide removal techniques are those combined with oxygen generation. These techniques are adequately described in Chapters 1, 2, and 4. The appeal of such systems is based on the hope of achieving more simplicity and economy in space, less maintenance, decreased manpower, and lower cost. However, not all of these advantages would necessarily result from a dual system, and obviously the advantages of a new system must be balanced against the advantages of continuing the use of the current MEA (monoethanolamine) scrubber.

At present the MEA scrubber is the best available continuous method for removing  $\text{CO}_2$  from nuclear submarines. There are various problems associated with its use, but few that adequate improved design and construction cannot eliminate. The stability of MEA obviously leaves something to be desired, but MEA is better in this regard than most candidate absorbents. The addition of Versene- $\text{Fe}_3$  Specific, as recommended by the Mare Island Naval Shipyard and as reported earlier (3), does much to stabilize MEA. A recent study (Chapter 3) shows that this stabilizing action is due to reasons other than presumed by the originators, and indicates that there are better stabilizing agents. Furthermore, it was shown that one of the chief contributors to MEA deterioration is an excess of copper ions in the solution as the result of using the ship's system for distilling sea water; this excess is avoidable if battery-quality distilled water is used in making up the solution.

All CO<sub>2</sub> removal systems of current interest are reviewed in Chapter 4. It is concluded that the MEA system is still the most efficient and most practical for a nuclear submarine pending development of a system which would also include oxygen removal.

#### ATMOSPHERE SAMPLING AND ANALYSIS

With the advent of the Mark IV Atmosphere Analyzer and its installation on nuclear submarines, the associated problems have required sufficient attention to cause essentially the discontinuance of research on the Mark III analyzer. Difficulties with the radiation detectors were encountered in the early production models of the Mark IV, and deliveries were postponed pending their solution (Chapter 5). Special tests were performed at the Mare Island Naval Shipyard on subsequent models until necessary modifications were made by the manufacturer. An NRL research advisory committee established that there was no fundamental reason why the Mark IV should not be an excellent replacement for the Mark III. However, mechanically and electrically stable radiation detectors needed to be consistently produced (6). Furthermore, better quality control by the manufacturer was clearly required.

In the meantime, substitute systems continue to be considered. Gas chromatography is one of the leading candidates as such a substitute (Chapter 6). Although progress has been made in the development of two commercial instruments procured by NRL in its research program, the inherent difficulty in obtaining sufficient sensitivity and reliability in the carbon monoxide measurement has postponed what might otherwise have been a rapid and happy ending to the chromatography story. Present indications are that any early solution of the analytical problem using chromatography on submarines must exclude carbon monoxide detection, and the same obstacle appears to face all competitive analytical systems.

The above-mentioned atmosphere-analyzer systems are concerned only with the predominant gases in the submarine atmospheres; analysis of the trace contaminants requires even more elaborate techniques. Sampling the atmosphere with carbon adsorbents has been used as one of the major techniques, primarily for the identification of hydrocarbons (Chapter 7). Although the total quantity of hydrocarbons in most nuclear-submarine atmospheres has been diminishing, either the aromatic portion of the hydrocarbons (the most toxic) appears to be increasing, or the improved analytical techniques are changing the concepts. Commendable hydrocarbon cleanup is proceeding, but there is no warrant for a letup in the campaign to curtail unnecessary painting while submerged. It must be remembered that the carbon-sampling technique inherently gives low values for total hydrocarbons, the error being larger the lower the atmospheric concentration. The chromatographic techniques under study give promise of more accurate and more successful monitoring of hydrocarbons aboardship in the future.

Due to the steady increase in the number of new compounds identified in the nuclear-submarine atmosphere, it has been necessary to bring earlier data (7) up to date (Chapter 8). Quantitative data on these trace contaminants are difficult to obtain, and it is even more difficult to assess the effect of these compounds on submarine crews, particularly when toxicity data are so meager even for an eight-hour-day exposure. It is notable that most of the compounds earlier reported as having been found in all cigarette smoke have now been identified in the submarines.

The thermistor-bridge gas-leak detector developed by the Radar Division at NRL (from the earlier Chemistry Division model) has received additional operational experience on Polaris submarines (8). Comments from the submarine crews have been uniform both in their praise and in their scarcity. Two different manufacturers have built the instrument satisfactorily, so the logistical position is good. Additional improvements by NRL are expected by the time the instrument becomes a standard item of issue.

### ELIMINATION OF CONTAMINANTS

The Mark III carbon monoxide/hydrogen burner (500 cfm) has now been installed on several nuclear submarines but has not received sufficient operational evaluation to warrant any prediction other than that it will serve as planned. There is no doubt but that the CO will be maintained adequately at less than the 25-ppm limit.

Catalytic-combustion studies in the laboratory (Chapter 9) lead to the conclusion that much of the CO indication in the Mark III analyzer, when it is above 25 ppm, is due to the  $N_2O$  present as the result of amine or ammonia oxidation. It is expected that the Mark IV analyzer when in successful operation will not give this false indication. The quantities of other combustion products found when Freons were passed through the laboratory burner indicate, in conjunction with the hydrocarbon problems of Chapter 7, that a delicate temperature balance is required with the shipboard burner to minimize corrosive products and yet maximize destruction of toxic and other undesirable compounds.

### OTHER AREAS

The Intra-Navy Committee for Submarine Habitability Research and Development has been disestablished (9), since its purpose in assuring a broad naval program in habitability had been accomplished. Its essential functions are continuing via the Polaris Human Factors Committee of the Special Projects Office and the quarterly meetings on submarine atmospheric habitability at NRL.

The habitability program at the Marine Engineering Laboratory (formerly Engineering Experiment Station) has been expanded to assume some of the engineering responsibilities abdicated by NRL in favor of the remaining fundamental research tasks still necessary in the submarine program.

The advent of the British nuclear submarine DREADNOUGHT, with essentially all-American air purification equipment, and the launching of the VALIANT, with British-modified equipment, make more meaningful the British research on air purification, and may contribute more in the future to our own development of an integrated system. The British modification of the MEA scrubber to include a foam absorption bed, and their prototype molecular sieve plant, may in particular provide considerable information of use in the U.S. program (10).

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# Chapter 1

## The Sulfate-Cycle System

S. T. Gadomski and A. L. Pitman

### INTRODUCTION

The sulfate cycle is a system for the production of oxygen and the elimination of carbon dioxide; this system has been proposed as a means of solving these two major problems in submarine air purification. As described in the earlier reports of this series, the system is based on the electrolysis of an aqueous solution of sodium sulfate, yielding oxygen and hydrogen as gases and sodium hydroxide and sulfuric acid as liquids. The oxygen would be used for breathing purposes, and the hydrogen would be pumped overboard. The caustic (sodium hydroxide) would be used to absorb the carbon dioxide from the submarine atmosphere, forming sodium carbonate, which would then be neutralized by the acid, releasing the carbon dioxide in a concentrated form to be compressed and pumped overboard. In the same neutralization reaction, sodium sulfate would be re-formed, and additional sodium sulfate would be regenerated by the reaction of excess acid and caustic, thus completing the cycle. Only electrical power and a small amount of water are required as input to the system.

The corresponding chapter in the last annual progress report (1) was concluded with a brief mention of several runs with microporous rubber diaphragms in the electrolytic cell. Difficulties mentioned were primarily a rapid increase in catholyte flow caused by the leaching action of sodium hydroxide on silica gel, a pore former, in the microporous rubber, and the slow but continuously increasing cell voltages observed in run number J.O. 17 (J.O. to distinguish the runs in joint operation of the principal components of the pilot plant from the separate runs of these components. Data for these runs are given in Ref. 1).

### THE POROSITY PROBLEM

The quickly appearing instability in catholyte (NaOH) flow through the microporous rubber diaphragms was unexpected in view of the miniature-cell tests, which showed only a gradual increase in flow for cathode and anode diaphragms in the 125-day runs. The shape of the pilot-plant cell, tall and narrow, with the usable diaphragm dimensions being about 20 × 4 in., may have contributed to the problem by introducing sizable variations in pressure and flow over the length of the diaphragm. In comparison, the diaphragm dimensions of the miniature cells were 3 × 3 in. The miniature cells were also operated at higher hydrostatic pressures, but it is believed that the most important distinction can be found in catholyte normality. The miniature test cells produced 0.5 to 0.7 normal sodium hydroxide solutions, but much higher concentrations were desired in the pilot-plant cell, of the same order (about 1.6 normal) as found in the anolyte (H<sub>2</sub>SO<sub>4</sub>). It was subsequently discovered (2) that a hot two-normal sodium hydroxide solution is a very effective leaching agent for the silica gel. In fact, all of the accessible silica (30 percent) in a totally immersed sample of microporous rubber can be removed by such a solution of 70°C in about four hours.

With all accessible silica removed, the preleached cathode diaphragms were stable. Since a two-normal sulfuric acid solution as well as an 18 weight percent solution of sodium sulfate have a leaching effect on the silica gel, although to a lesser extent (2), the diaphragms intended for anode service were similarly treated with hot caustic to obtain matched sets.

With two sheets of the preleached microporous rubber at all electrodes and using distilled water at room temperature to obtain flow information, it was found that the anolyte and catholyte flow rates were about 450 cc/min at a mean hydrostatic pressure of 31 in. It was calculated that a run under these conditions with sodium sulfate solution and a current density of 50 amp/sq ft would result in caustic and acid normalities of only 0.1.

The next step was to try two sheets of the microporous rubber on the anode with a preleached sheet interposed between the electrode and a silica-bearing sheet. The preleached sheet was to maintain the flow control of the inner sheet by minimizing any leaching action through separation from the bulk of the anolyte. For the catholyte, however, such a step did not seem feasible in view of the more vigorous leaching action of the caustic. It was therefore decided to substitute asbestos with a perforated Lucite sheet on the feed-frame side to keep the asbestos in close contact with the cathode, as well as to prevent shredding into the feed-frame space. The perforated cathode had always furnished enough support to the asbestos so that asbestos fragments were never found in the catholyte. Unfortunately, the perforated Lucite sheet and the diaphragm thickness required to fill in the step of the gasket with four 25-mil sheets of asbestos made the electrical resistance of such a cell much too high.

In the next trial the perforated Lucite sheet and two sheets of asbestos were discarded and replaced by a sheet of preleached rubber. The rubber placed on the feed-frame side provided a suitable support for the remaining two sheets of asbestos. In this case the voltage per cell was nine volts.

Because the combination of preleached and silica-bearing rubber was providing the desired flow rates at the anode, it was decided to try the same arrangement at the cathode. A partial solution to the flow problem was thus realized in run number J.O. 19 as the catholyte flow in the cell with normal ohmic resistance was stable over 31 hours of continuous operation.

#### CELL VOLTAGE PROBLEM

Another problem soon appeared with the use of two sheets of rubber. In comparison with the experience gained in using microporous rubber in the miniature cells, the rubber in the pilot-plant cell was susceptible to swelling or bulging. The swelling seemed to be the result of gas entrapment between sheets, so that one sheet would bow out into the feed frame space while the other sheet remained flat against the electrode. Gas entrapment is possible, because a sheet of microporous rubber when wet will not permit the passage of gases below a pressure of 200 in. The gases involved would probably be dissolved CO<sub>2</sub> or air that remained in solution in passing through the first sheet, but which were then released, forming a gas pocket which could not pass through either sheet. Although swelling was more apt to develop on the cathode side, it was also seen on the anode. The swelling occurred with electrolyzer temperatures below 50°C, and the swelling seemed to increase with higher temperatures and lower hydrostatic pressures. Pressures of 45 to 100 in. above the top of the diaphragm did not prevent swelling, and the rubber, once deformed, took a permanent set.

Swelling, if not observed directly, can be detected by an increase in cell potential without a corresponding increase in current. The discontinuity in flow between the separated diaphragm sheets also decreased the percolation rate.

In run J.O. 17 Lucite spacers or restrainers were placed in all of the feed frames to prevent swelling. Each spacer assembly consisted of eight rectangles perpendicular to the diaphragms, with the thin beveled edges bearing against the rubber on either side. These rectangles were supported by two plastic rods on which they were mounted in a staggered fashion to permit the flow of feed solution through the feed frame.

The results were not satisfactory, with cell voltages still unequal and higher than normal. Examination of the diaphragms after disassembly revealed only one location with a light imprint of a contact mark from the spacers. The spacers therefore did not confine the diaphragms as intended. Since the tolerance requirements for the width of the spacers were difficult to determine, spacers were considered impractical.

Acquisition of thin sheets of corrugated and perforated polyvinylchloride (PVC) material, which had been used as battery separators, brought about a renewal of interest in the plastic spacers of J.O. 17. It was found that one sheet of the PVC material used with the spacers firmly wedged the diaphragms into place every two inches of their height for about 80 percent of their width at these locations. Cathode diaphragms supported in this manner did not bulge in 800 minutes of intermittent operation in which the anode diaphragms consisted of single sheets. This cell assembly, with another sheet of rubber added to the anode, made the anode similar to the cathode diaphragm, which consisted of a sheet each of preleached and silica-bearing rubber; this assembly was then used in J.O. 19. This run, a two-cell operation, had the cell voltages differing 0.25 volt from each other for the first three hours. Then, as the diaphragms in one cell bulged between the Lucite support strips, that cell voltage increased until it was 7.7 volts in excess of the voltage required for the other cell. If power had not been cut off, the bulged diaphragms would have cracked shortly; subsequent examination revealed incipient fissures at the support locations. Most of the swelling, as usual, occurred in the upper half of the cell.

After disassembly, the good cell was restored to service within a few hours by itself. With an initial hydrostatic pressure of 100 in., this cell failed at the start as its diaphragms quickly bulged.

#### MICRONIZED CARBON IMPREGNANT

The obvious way to eliminate the swelling problem was to use single sheets of microporous rubber as cathode and anode diaphragms. This still would leave engineering problems relating to the desired percolation rates through the diaphragms. Since microporous sheets of the desired thickness and porosity were not readily available, an expedient solution to these problems appeared to be in the use of preleached sheets of rubber, which would have their porosity reduced by the controlled addition of micronized carbon. This was accomplished in the assembled cell by feeding a water suspension of the carbon into the feed frame and filtering out the carbon. While some of the carbon was undoubtedly forced into the pores of the rubber, the desired flow rates could be obtained only with a substantial coating of carbon on the rubber surfaces. Such a solution to the porosity problem was obviously never intended to be used outside of the laboratory.

In preliminary trials this assembly operated successfully in three two-hour runs. At a current density of 89 amp/sq ft, the voltage across a cell was 5.5 volts, and with a catholyte flow of about 45 cc/min per diaphragm, the caustic normality was 0.67.

Preparations for a fourth run, however, revealed that the carbon coating had collapsed and that the diaphragms were free-flowing again with flow rates almost back to the values

before the plugging operation. Although this coating was replaced, it did not duplicate the first application with regard to flow rate or voltage. The catholyte flow rate at approximately the same conditions was 83 cc/min per diaphragm. At a current density of 97 amp/sq ft, the cell voltage was 6.7 and the caustic normality was 0.40.

Run J.O. 20 was halted when the flow rates suddenly increased to 200 cc/min per diaphragm when the carbon again failed to stay in place. When power was switched off, however, the two cells were still operating satisfactorily from an electrical viewpoint. The cell voltages were stable and practically identical (within 0.15 volt) over 38 hours of continuous operation, which included 22 hours of feed regeneration. This was considered sufficient evidence to confirm the belief that single sheets of microporous rubber were the answer to the swelling problem. There is also no reason to doubt that the manufacturer of the rubber could provide sheets of the required porosity and stability.

## CONCLUSIONS

On the basis of the sulfate-cycle-plant experience and the 125-day runs of the miniature electrolytic cells, the sulfate cycle is considered feasible for oxygen generation and carbon dioxide absorption aboard nuclear-powered submarines. The major obstacle to this system, the diaphragm problem, can be resolved by using single sheets of microporous rubber, silica-free and of the correct porosity, as anodic and cathodic diaphragms. While these diaphragms are not on hand, they can be made available if the material were ordered on specification.

A current density of 100 amp/sq ft appears to be a reasonable operating condition in regard to current efficiency, electrode areas, and cell voltage. Voltage per cell should be five volts or less if the distance between electrodes is reduced (as it can be if a filter-press assembly is used), and if the cell temperature is increased. Thus the power required to generate one cubic foot of oxygen at standard conditions should be less than the 0.75 kw-hr found in J.O. 13 with single sheets of microporous rubber at a cell temperature slightly below 50°C.

To permit higher operating temperatures the lead anode should be replaced with platinized titanium or platinized tantalum. A platinized nickel screen may be best for cathode service, although stainless steel, despite its higher electrical resistance, may also be considered as a cathode material in view of its corrosion resistance during and between times of miniature-cell operation.

No further laboratory studies of the conventional diaphragm cell and sulfate-cycle pilot plant are planned. The Ionics, Inc. electrolytic cell, including an ion-exchange membrane, has recently been evaluated, and a separate report is in preparation.

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## Chapter 2

### Algae as a Source of Oxygen for Nuclear Submarines

P. J. Hannan, R. L. Shuler, and C. Patouillet

#### INTRODUCTION

Five years ago, NRL began a feasibility study on the use of algae as a source of oxygen on nuclear submarines, as well as the removal agent for the carbon dioxide exhaled by the crew (1). Such a use would solve in one system the two problems currently requiring separate treatment. An incidental, but perhaps important, advantage of algae is their ability to absorb certain "exotic" vapors or odors from the air (2), the removal of which now requires catalytic burners on submarines. Another advantage of algae, in comparison with the production of oxygen by electrolyzing water, is that hydrogen, which poses a disposal problem, is not produced.

In earlier reports of this series, studies with test-tube experiments and with small pilot-plant gas exchangers have been described (3,4,5). Each succeeding model of gas exchanger marked an improvement in design, but there was considerable difficulty in reproducing results to the desired degree. Our more recent research has led to improvements in the equipment which have provided a high degree of reproducibility, permitting us to form some valuable conclusions.

During this feasibility study only one algal species has been used, the Sorokin strain of Chlorella pyrenoidosa, 7-11-05 (6). This organism has a temperature optimum of 37 to 39°C, and its growth rate is greater than any other species known at this time; it was decided early to use this organism exclusively unless it exhibited characteristics which would remove it from consideration.

Two small gas exchangers have been operated during the past year; one, hereafter referred to as the six-lamp unit, includes features which were found to be desirable in previous units, and it represents a "best-guess" design (Fig. 1). The second unit (Fig. 2) consisted of concentric glass tubes around a single light source, the tubes being held in Lucite plates at top and bottom. By using glass tubes of various diameters the annulus containing the algal culture could be varied, thereby providing a choice of light paths of different lengths through the suspension. In this way it was possible to study the effect of the light-path variable on oxygen production.

In each of these units light energy was provided by G.E. Quartzline lamps. These are compact light sources 3/8 in. in diameter and 10 in. long which are rated at 1500 watts when operated at 277 volts.

#### SIX-LAMP UNIT

##### Experimental

The six-lamp unit was designed to provide intense illumination and rapid stirring for the culture. Two purposes were served by the turbulence achieved in rapid stirring.

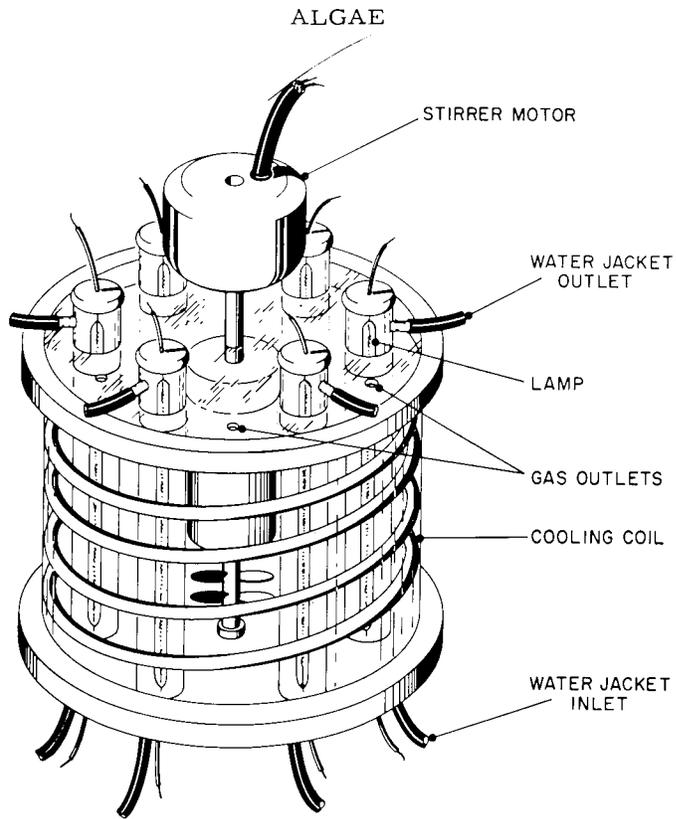


Fig. 1 - Schematic diagram of six-lamp unit

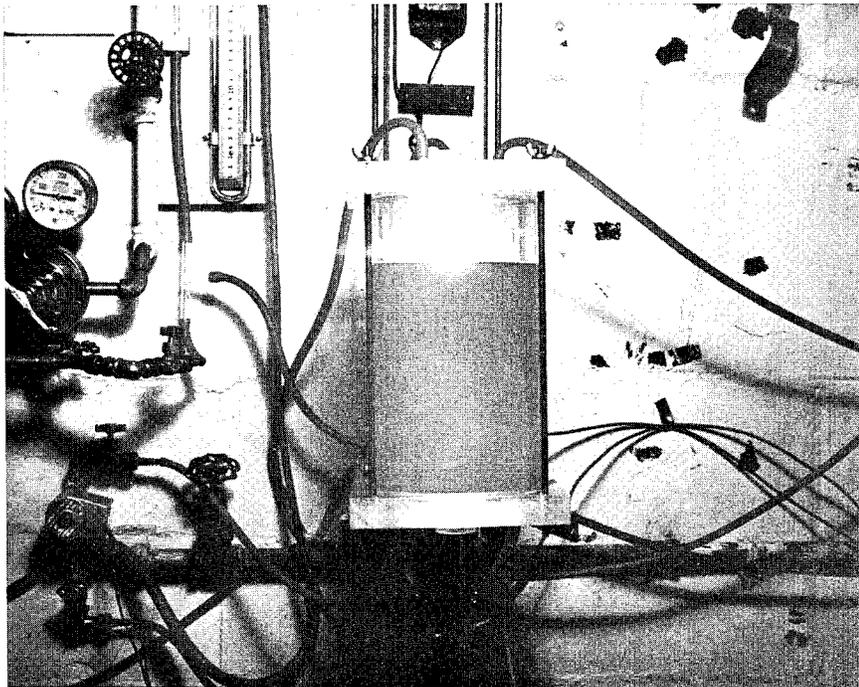


Fig. 2 - The unit which provides choice of light paths

1. The cells were prevented from settling to the bottom or sticking to the walls.
2. They were whisked into and out of the bright light quickly; consequently high light intensities could be used.

Other features provided for the operation of this unit were a dependable constant-dilution device and a simple gas-sampling system for the continuous analysis of the exit gas for  $\text{CO}_2$  and  $\text{O}_2$  content.

The unit consisted of a glass cylinder 10 in. I.D. and 10 in. high which was held by O-rings in grooved Lucite plates. Each of six Quartzline lamps was surrounded by a 50-mm O.D. cooling jacket which extended through the unit, being held in place at the bottom by O-ring seals. The distance between cooling jackets was 1-1/4 in., and the distance from the jacket to the wall of the container was 1/2 in. Stirring was provided by a 1/3-hp variable-speed dc motor which rotated a stainless steel shaft, 5/8 in. diameter, at 1450 rpm. Two 3-in. propellers were attached to the lower portion of the shaft, and a Lucite collar, 3 in. diameter and 4 in. long, was also attached to the shaft to exclude the algae from the center portion of the chamber. The distance from the cooling jackets to this Lucite collar was 1/2 in., the same distance as the jacket to the wall.

Mixtures of  $\text{CO}_2$  and air were provided by the method described previously (5), the incoming gas being forced into the suspension through two fritted glass spargers in the base of the unit. The propellers forced the suspension downward and across the gas inlets, carrying bubbles outward and then upward through the suspension. Temperature equilibrium was maintained by two complementary systems, the first a preset flow of cooling water through the jackets surrounding the lamps, and the second a thermoregulator which activated a solenoid valve, permitting cooling water to flow through the stainless steel coil within the cylinder. Temperature was easily maintained within  $\pm 0.2^\circ\text{C}$ .

Fresh culture medium was allowed to flow continuously into the vessel through a flowmeter, and the corresponding volume of algal suspension passed out of the vessel through an overflow tube. Several openings in the top plate allowed the air- $\text{CO}_2$  mixture to escape freely after passing through the suspension; the vent gas was sampled and pumped through several drying columns, then through a Mine Safety Appliances  $\text{CO}_2$  analyzer and a Beckman  $\text{O}_2$  analyzer.

The volume of suspension contained in the vessel was 6200 ml under normal conditions of use. If the speed of the stirrer was increased, a significant portion of the suspension was forced out through the overflow tube.

#### Effects of $\text{CO}_2$ Input Rate and Light Intensity

During the early gas-exchange studies with this unit there appeared to be a correlation, at a given light intensity, between the oxygen production per hour and the percentage of  $\text{CO}_2$  remaining in the gas stream after passage through the suspension. Prior to these studies a residue of several tenths of a percent  $\text{CO}_2$  in the effluent gas was regarded as evidence of an excess supply.

The effect of changes in the rate of  $\text{CO}_2$  input on oxygen production was determined in a week-long study. During this experiment the light intensity was maintained at 9,000 foot-candles, but the  $\text{CO}_2$  supply rate was varied in two ways; at constant flow rate by adjusting the  $\text{CO}_2$  concentration of the gas, and at constant concentration by adjusting the flow rate. Within the limits of the conditions imposed, the oxygen production varied directly with the rate of  $\text{CO}_2$  addition (the product of  $\text{CO}_2$  concentration times the flow rate).

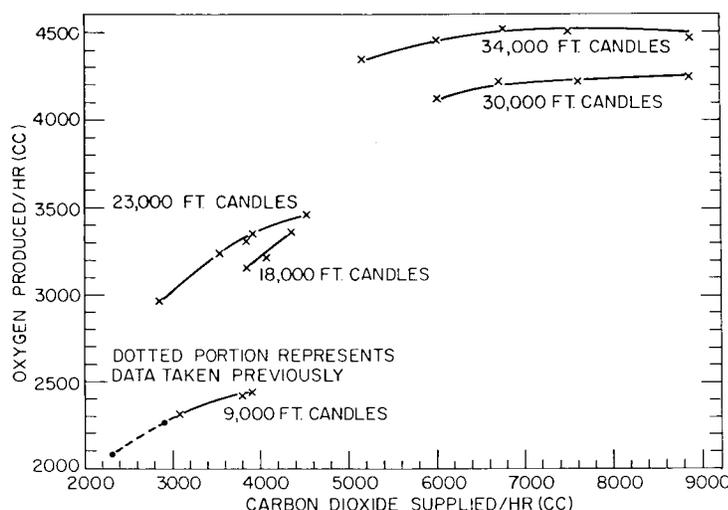


Fig. 3 - Effects of rate of CO<sub>2</sub> supplied and light intensity on oxygen production by six-lamp unit

The study was extended to a number of other light intensities, the results being shown in Fig. 3. In each case the oxygen production increased with an increase in CO<sub>2</sub> made available to the algae, until a plateau was reached beyond which no additional oxygen production resulted. This graph represents in a concise manner the performance of the six-lamp unit; its maximum oxygen production is 4500 cc/hr when measured at ambient temperatures, which amounts to 726 cc/hr per liter of suspension at STP.

The light intensity marked on each curve represents the intensity at the surface of each cooling jacket. At each light intensity a different dilution rate with fresh medium was maintained, the rates varying from 13 to 19 percent per hour. These dilution rates were arbitrarily chosen to maintain the suspension density at approximately 1.5 percent by wet volume of cells. Suspension density is not a matter of vital interest here, because the growth rate of cells in the linear phase of growth is independent of the concentration of cells.

#### Uniformity During a Given Run

It is common to maintain a suspicious attitude about the reliability of biological systems. However, we have premised that constant results should be obtainable with constant conditions, even in biological systems; and the results cited appear to substantiate this hypothesis.

Once the general performance of the unit was known, and once there was reason to believe that long-term stability was obtainable, the unit was operated during the week from Monday morning through Friday afternoon under constant conditions of light intensity, gas-flow rate, dilution rate, and temperature. Oxygen-production measurements and cell-density determinations were taken hourly from 8:30 to 4:30 each day. The spread in these values for each day is shown in Table 1. It should be emphasized that for 16 hours out of each 24 the operating unit was totally unattended, and yet consistent results were obtained.

On the first day, of course, the system had not come to a steady state, but once this was established the unit gave reproducible results. The spread in the O<sub>2</sub> production

Table 1  
Summary of Week-Long Performance of Six-Lamp Unit

Light Intensity 23,000 Foot-Candles      Dilution Rate 15.6% per hour  
Electrical Power 7040 Watts      Gas Flow Rate 4000 cc/minute,  
air containing 1.9% CO<sub>2</sub>

Day	Suspension Density, Percent Wet-Cell Volume	Oxygen Production		Dilution Rate, cc/hr for 24 hr
		Volume per hour (cc)	Standard Deviation	
Monday	1.27 - 1.37	3432	145	Not measured
Tuesday	1.44 - 1.50	3565	30	964
Wednesday	1.43 - 1.47	3606	29	969
Thursday	1.41 - 1.44	3584	25	966
Friday	1.41 - 1.43	3638	24	950

results on each of the days when steady-state conditions prevailed was less than 100 cc per hour, or less than 3 percent deviation. A large proportion of this minor variability can be attributed to precision in reading the oxygen analyzer.

#### Reproducibility from One Run to Another

The results described in the preceding paragraph indicated the stability of the gas exchanger's performance during a five-day test in which conditions were maintained uniformly. It is interesting to compare the performance of the unit at other times under these same conditions of light intensity, dilution rate, and CO<sub>2</sub> input rate. These observations extend over a three-month period and are summarized in Table 2.

In making this survey, the data selected were obtained under the general conditions listed at the heading of Table 2, but individual dilution rates were not computed. The dilution represented a given flowmeter reading which usually amounts to 15.6 percent per hour, but because of the lack of sensitivity of the flowmeter a variation of 0.3 percent might be expected.

Another factor in the selection of data listed in Table 2 was that results in the first days of a given run were excluded because the time necessary to attain a steady-state condition was usually more than eight hours. Otherwise the data represent a random selection; the agreement is much better than had been expected.

#### Effect of Stirring Rate

In test-tube experiments conducted here, which did not include gas-exchange studies, there was an increase in density of suspensions when stirred rapidly compared to those in which gas bubbles provided the only turbulence (5). Similar beneficial results were noted by Davis, et al. (7) and by other investigators. At the time the six-lamp unit used in the studies reported here was designed, provision was made for variations in the stirring rate. The 1/3-hp motor was connected to a voltage divider and, for all the experiments except the one described here, the speed was maintained at a constant value.

At a time when the unit had been operating uniformly for 13 hours the speed of the stirring motor was increased from its normal rotation of 1450 to 2450 rpm, causing an

Table 2  
Variation in Oxygen Production at Different Times

Light Intensity 23,000 Foot-Candles, Power 7040 Watts, Dilution 15.6%/Hr

Date	CO <sub>2</sub> Input (Percent)	Gas Flow Rate (cc per min)	CO <sub>2</sub> Supplied (cc per hr)	O <sub>2</sub> Production (cc per hr)
Oct. 12 1962	1.83	4000	4390	3468
Oct. 16 1962	1.79	4000	4300	3456
Oct. 18 1962	1.86	4000	4470	3492
Oct. 19 1962	1.87	4000	4490	3620
Oct. 26 1962	1.88	4000	4510	3490
Jan. 15 1963	1.95	3500	4100	3505
				Average 3505
				Standard Deviation 50

almost immediate expulsion of a significant fraction of the suspension through the overflow tube. Gas-exchange measurements showed a consequent decrease in oxygen production from 3624 cc/hr to 3360 cc/hr. However, on the basis of oxygen evolution per liter of suspension, the additional stirring provided an increase from 585 cc/hr to 680 cc/hr. In a system of this type, therefore, it is advisable to determine the optimum stirring rate in order to realize the full potential of the unit.

#### ONE-LAMP UNIT

As stated earlier, the present unit was designed and built primarily to determine the relationship between oxygen production and culture thickness (culture thickness as used in this report refers to the thickness of the annulus containing the culture through which the light has to penetrate). However, only three culture thicknesses have been used to date, so this relationship cannot be well defined at this time. Nevertheless, the results obtained so far show that oxygen production is profoundly affected by culture thickness, and that definite statements can be made on the relationship between oxygen production and power input, or voltage applied to the lamp. In addition, the experimental data have supported an earlier finding at NRL that oxygen production is a logarithmic function of incident light intensity (8).

#### Design and Operation

The basic design and operation of the one-lamp culture unit is very similar to the one described previously (5). The main difference is that the first unit had a fixed culture annulus (approximately 1.9 cm), whereas the thickness of the culture annulus in the present unit can be changed. As shown in Fig. 4, several culture annuli were possible in the range of 1.0 to 2.9 centimeters. In addition to the culture annulus, two other annular spaces

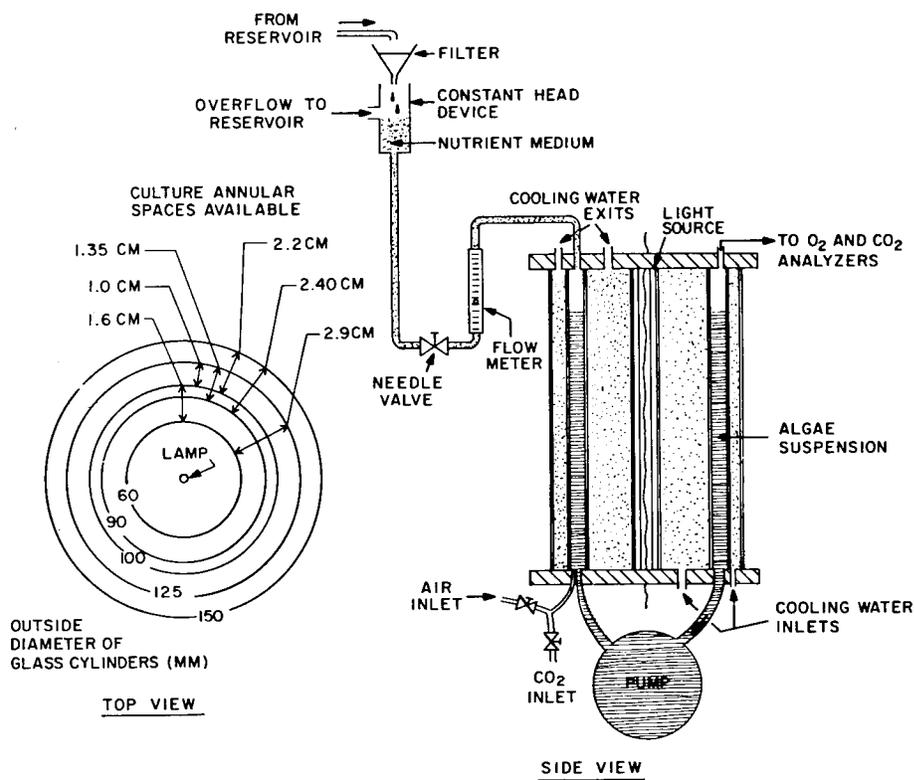


Fig. 4 - Schematic diagram of one-lamp unit

ordinarily were required for operation of the unit. Water was continuously passed through the inner annulus surrounding the light source to dissipate some of the heat emitted by the lamp. The third annulus was used to thermostat the culture; when the temperature reached 39°C, a relay opened a solenoid valve, allowing water to flow through this annulus, cooling the culture. This method was very effective in controlling the temperature to within  $\pm 0.2^\circ\text{C}$ .

The suspension was stirred by means of a centrifugal pump placed beneath the unit. Suspension was withdrawn from the bottom of the culture annulus and returned to the chamber through a right-angle tube positioned in the base plate. The force of the liquid coming from this tube imparted a rapid swirling motion to the suspension. Stirring was less vigorous when the smallest (1-cm) culture annulus was used; consequently more cells adhered to the culture-chamber walls.

A mixture of carbon dioxide and air was introduced to the culture through a small tube placed immediately in front of the tube coming from the circulating pump. The exact concentration of carbon dioxide in the mixture was not known, since the concentration exceeded the upper limit of the carbon dioxide analyzer (2 percent), but in most cases was about 3.5 percent, based on the rate of oxygen evolution and the normal photosynthetic quotient. With the concentration of  $\text{CO}_2$  and the gas-flow rate used, growth was not limited by a deficiency of carbon dioxide.

The culture was diluted continuously with fresh medium at a constant rate of about 10 percent of the culture volume per hour. To assure an adequate supply of nitrogen, the concentration of the nitrogen source, either urea or nitrate, was increased to five times the amount of nitrogen normally found in Burk's medium (9).

### Suspension Density

The cell concentrations of the cultures used varied from about 0.5 to 1.75 percent (wet-packed cell volume). In this concentration range, under the conditions employed, the cells would be expected to be in the linear phase of growth when zero-order kinetics are obeyed. In accord with theory, the oxygen production of all the cultures described in this report was found to be independent of cell concentration.

### Oxygen Production as a Function of Light Intensity at Three Culture Depths

The effect of light intensity on the rate of oxygen evolution for three culture depths is shown in Fig. 5. Since the volumes of the three cultures differed, oxygen production was computed on the basis of a liter of suspension to show the relative outputs.

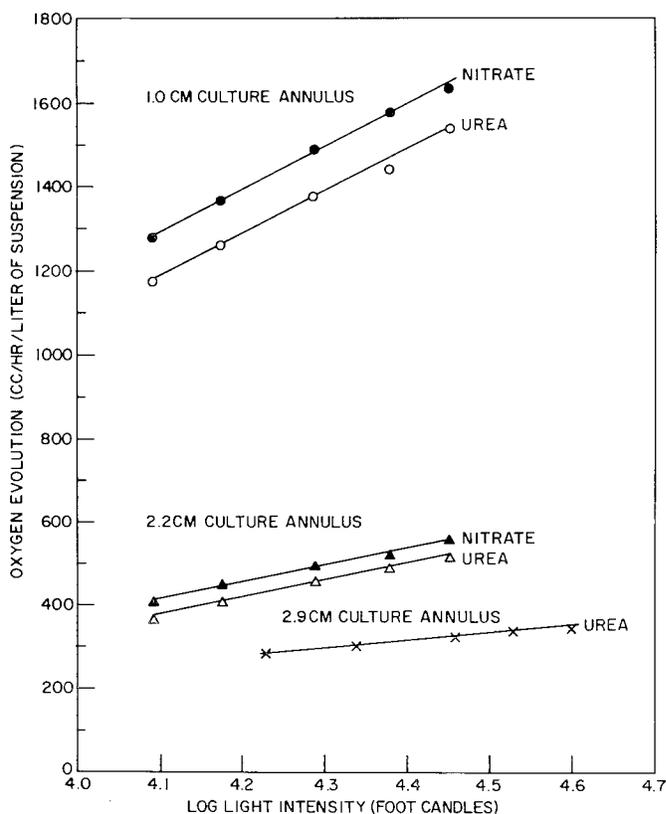


Fig. 5 - Effects of light intensity and light path on oxygen production.

Confirming earlier observations, Fig. 5 clearly shows that the rate of oxygen production is a logarithmic function of light intensity (8). The results of the experiments with the 1.0- and 2.2-centimeter culture chambers were checked by using nitrate as the nitrogen source instead of urea. As expected from earlier work, more oxygen was produced by the cells growing in the nitrate medium, although the increase (about 8 percent) was considerably lower than the 20 percent obtained previously (8).

### Light Intensity

Light-intensity measurements were made at the surface of the glass cylinder surrounding the light source. The incident-light intensities were the same in the 1.0- and 2.2-cm culture annuli, since the same inner glass cylinder (100 mm O.D.) was used in both cases. A smaller inner cylinder (60 mm O.D.) was used for the 2.9-centimeter culture annulus; the culture was therefore closer to the lamp, and as a result higher light intensities were obtained in the 2.9-cm culture annulus than in the other two annuli for comparable voltages.

### Oxygen Production and Power Input

The variation of oxygen production with power supplied the lamp is shown in Fig. 6. The data were obtained in the foregoing experiments, with the wattage values representing the power required for the light intensities used. In this plot, the total oxygen production of the culture is given rather than the oxygen output per liter of suspension, as shown in Fig. 5.

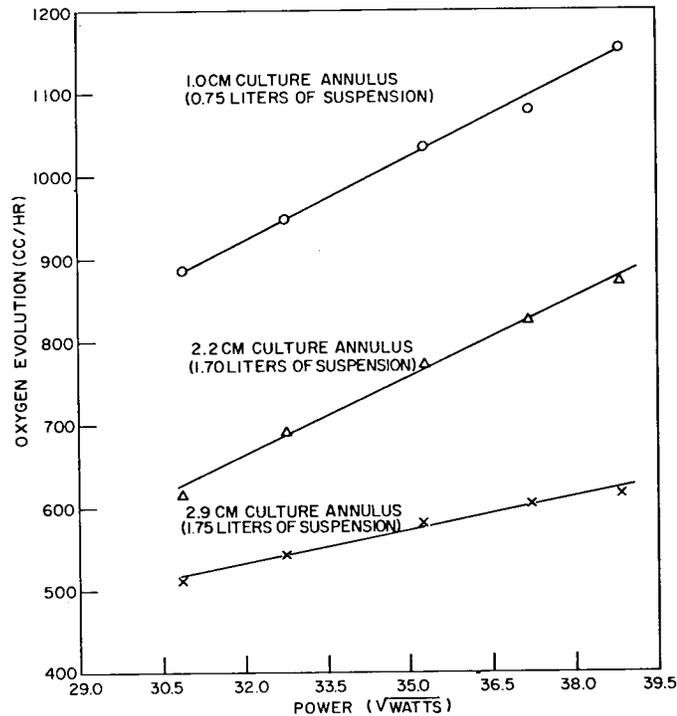


Fig. 6 - Oxygen production as a function of power supplied

It is obvious from Fig. 6 that the rate of oxygen evolution was proportional to the square root of power. This relationship follows from concepts already discussed. It is seen in Fig. 5 that a linear relationship exists between oxygen evolution,  $v_o$ , and the logarithm of the incident light intensity,  $\log I_o$ . This is expressed mathematically as

$$v_o = k_1 \log I_o + b_1 \quad (1)$$

where  $k_1$  is the slope and  $b_1$  is the intercept on the  $v_o$  axis.

Similarly, a linear relationship was found to exist between  $\log I_o$  and lamp voltage,  $E$ , as follows:

$$E = k_2 \log I_o + b_2 \quad (2)$$

where  $k_2$  and  $b_2$  are the slope and intercept, respectively, of the second linear equation.

Solving Eqs. (1) and (2) for  $\log I_o$  and equating, we get

$$v_o = k_3 E + b_3 \quad (3)$$

In accord with Eq. (3), straight lines were obtained when the rate of oxygen evolution was plotted against lamp voltage for all three culture thicknesses.

Since voltage is proportional to the square root of power, Eq. (3) takes the form

$$v_o = k_4 W^{1/2} + b_3$$

This equation describes the data plotted in Fig. 6. The intercepts of the lines in Fig. 6 were found to have minus values. This was expected, since some light and therefore power is necessary to compensate for the oxygen consumed in the endogenous respiration of the cells. By extrapolation of the lines in Fig. 5, the intensity of the light required to compensate for cell respiration could be estimated. However, it is felt that further experiments should be carried out at light intensities lower than those previously used before this extrapolation is justified.

The results shown in Fig. 6 emphasize the advantage of having short light paths in an algal culture unit. The unit was capable of producing more oxygen when the smallest (1.0-cm) culture annulus was used despite the fact that this annulus contained less than half the culture volume of the other two annuli. Moreover, the incident light intensity was higher, for a given voltage, in the 2.9-cm culture annulus, since the annulus was closer to the light source. Thus, under the experimental conditions employed, culture thickness was found to be more important from the viewpoint of oxygen productivity than either culture volume or light intensity for the three culture thicknesses considered.

Not only was more oxygen produced when the 1.0-cm culture annulus was used, but it was produced more efficiently on the basis of power utilization. In Fig. 7, the oxygen output per watt (efficiency) for the three culture thicknesses is plotted against power, and it is seen that the efficiency with which oxygen is produced decreases with power input. A straight line is drawn through the points as a first approximation. (Actually a true linear relationship cannot exist between the two variables, since oxygen evolution is linearly related to the square root of power, as shown in Fig. 6.)

The decrease in the efficiency of oxygen production with power input is not surprising, since more light undoubtedly is wasted, i.e., not absorbed by the cells, as the light intensity is raised. It would be expected that more light would be lost at shorter light paths, and this is borne out by the greater slope for the 1.0-cm culture annulus. However, the slope of the line for the 2.9-cm annulus is greater than that for the 2.2-cm annulus. This apparent anomaly may result from the fact that the 2.9-cm annulus was closer to the light source than the other two annuli, so that the culture was exposed to higher light intensities.

The efficiency of the unit, the total oxygen output, and the oxygen output per unit volume of suspension are all dependent, of course, on the position of the culture annulus

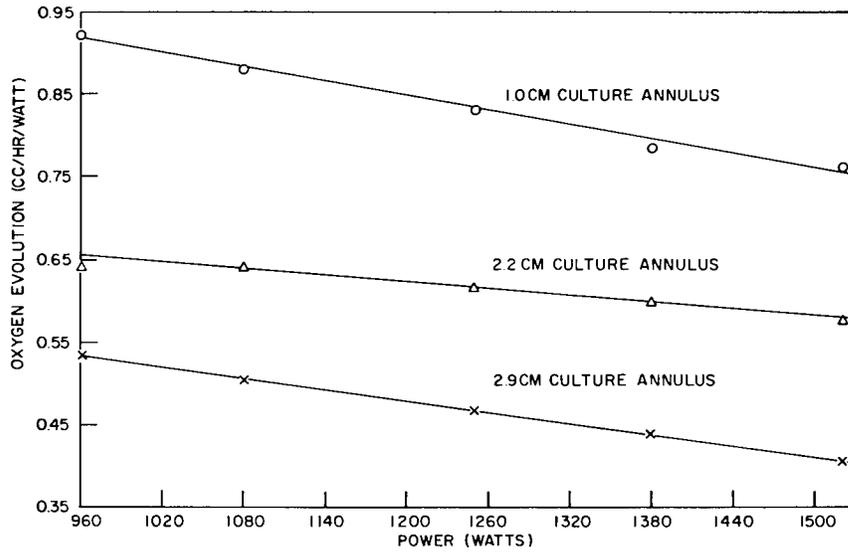


Fig. 7 - Efficiency of oxygen production in terms of power supplied

in the unit, because both culture volume and incident light intensity change with the location of the annulus. As a given annular space, say one centimeter, is moved closer to the center of the unit, the higher light intensity would increase the oxygen productivity per unit volume of suspension, but this is accomplished at the expense of culture volume. The result may be that the oxygen output of the unit would be lowered as the culture annulus is moved closer to the center. It is premature to predict from the available data the magnitude of the effect of changing the position of the culture annulus on oxygen production. For example, Fig. 6 suggests that the extent of the change of oxygen production with power input depends on the location of the culture annulus in the unit. As stated earlier, the 1.0- and 2.2-cm annuli were the same distance from the center of the unit, and the slopes of these two lines in Fig. 6 are seen to be very similar. On the other hand, the 2.9-cm annulus was closer to the center of the unit, and, possibly as a result, oxygen production was not affected as much by changes in the power input, as evidenced by the smaller slope. It is hoped that further experiments using other culture annuli will allow more definite conclusions to be made on the culture thickness and the distance from the light source necessary to provide optimum oxygen production by the unit.

## GENERAL DISCUSSION

### Volume and Power Requirements

It is clear that the most efficient design of an algal gas exchanger would be one in which the light sources are close together, because this promotes greater oxygen production and also greater efficiency in the conversion of electrical energy to useful chemical energy. There may be a limit, still to be determined, beyond which this close packing of light sources is not favorable, but the results to date show the importance of this effect.

Table 3 provides a comparison between the volume and power requirements of two systems having different light paths, the first corresponding to the six-lamp unit and the second to a unit of a uniform 1-cm light path. In these calculations it is assumed that the lamps are encased in 50-mm cooling jackets and are spaced to give the same light paths as in the small gas exchangers just described; e.g., a 10-mm light path would result from the cooling jackets being 20 mm apart. For the purposes of the calculation

Table 3  
Comparison of Volume and Power Requirements for Gas Exchangers  
Having Different Light Paths (Production Capacity for 100 Men)

Light Path	Oxygen Production (cc at STP/hr/ liter susp.)	Volume of Susp. Required (liters)	Total Volume (liters)	Power Required (kw)
12 mm to 37 mm (6-lamp design)	670	3860	6330	5320
10 mm	1430	1810	3620	3225

no volume provision will be made for auxiliary stirring apparatus, but it will be assumed that the productivity of each unit will be the same as if the turbulence achieved were equal to that obtained in the experimental units. Also the volume of the blower equipment will be disregarded, since it would be the same for any unit.

Obviously there is much to be gained by placing the light sources close together, because the volume and power requirements for the system having the short light path are much less than for the design in the six-lamp unit. From the standpoint of total volume of the system, the algae unit is competitive with the present CO<sub>2</sub> absorption and O<sub>2</sub> production systems. However, the power requirement of more than 3200 kw is enormously greater than the 75 kw expended by the Treadwell electrolytic generator now in use in the Polaris submarines.

There is reason to believe that the power requirement may be significantly decreased in the future with the availability of more efficient light sources. One such source, still in the experimental stage, provides about six times the light quanta per watt as the Quartz-line lamps used here. By decreasing the light path to less than 10 mm the oxygen productivity should be increased significantly over the current amount; therefore a combination of two such improvements could result in at least a tenfold improvement in efficiency. An algal unit thus requiring 300 kw would compare favorably with the present systems, because it would serve to scrub out some of the "exotic" vapors from the atmosphere (2) which require separate treatments now.

#### Settling and Adhesion of Cells

The limit to the close spacing of light sources may be determined by the tendency of the cells to adhere to the walls of the container. There is no adhesion problem in the six-lamp unit used in these studies because of the extreme turbulence provided by the 1/3-hp motor, but this luxurious use of power and volume could not be tolerated in a ship-board model. In the one-lamp unit, however, there has been a tendency of the cells to adhere to the walls of the vessel. This effect is so pronounced that oxygen production decreases significantly after about two days because the cells stick to the surface of the cooling jacket around the light source and thereby decrease the light intensity.

Whether the adhesion problem can be alleviated by the use of surface treatments on the glass remains to be seen. Settling of the cells on any flat surfaces must be considered also. It is doubtful, for instance, that light sources could be used in a horizontal position because of the additional settling surface they would provide. Here again, sufficient turbulence could solve the problem, and it is presumed that engineers trained in the art could provide some solutions not anticipated here.

### Reproducibility

Discussions of power requirements and the problem of sticking cells are necessarily unfavorable to the adoption of the algal system, because they suggest problems still to be solved. A surprising advantage of the system is its reproducible behavior. Studies with the six-lamp unit, in which conditions of culture can be readily duplicated, have assured the reproducibility of the results, and there is every reason to believe that a shipboard unit designed to provide more oxygen than required would be satisfactory. Some margin should be provided, since it is inevitable that the cooling jackets around the light sources would become dirty from the use of sea water and would attenuate the light somewhat, or that light sources would occasionally burn out. But there is no reason to anticipate a possibly dramatic decrease in oxygen productivity.

In a recent report, Matthern (10) describes a gas exchanger operated for 139 days in which no significant change in growth developed. However, a batch process was involved in which approximately 80 percent of the suspension was harvested each day and replaced with regenerated medium. A continuous dilution technique would be envisioned for shipboard use and would assure even more uniform results.

### CONCLUSIONS

Many variables affect the oxygen production of algae, but the most important is light intensity. In the studies conducted here, intensities as high as 34,000 foot-candles have been used to good advantage, and there is reason to believe that even higher light intensities could be used.

Gas mixtures containing 1.5 to 3.5 percent  $\text{CO}_2$  have been used in this study. Within this range of concentrations the oxygen production of the six-lamp unit varies with the  $\text{CO}_2$  supply rate (i.e., the  $\text{CO}_2$  concentration in the input gas times the flow rate). However, when 100-percent  $\text{CO}_2$  is used as the input gas, the oxygen production is severely inhibited.

The principal disadvantage of the algal system as a means of purifying submarine atmospheres is the high energy requirement of the presently available light source. This would vary according to the design of the system, primarily with the spacing of the light sources, but at present the energy required is 30 kw per man if the cooling jackets around the light sources are 20 mm apart. This high power requirement means that the system is not feasible for use on submarines at this time or in the near future. By placing the lamps even closer together, the oxygen production per watt is increased, but a practical difficulty arises from the tendency of the algal cells to adhere to glass surfaces unless sufficient agitation is provided. Any impeller used to provide turbulence becomes less effective the closer together the cooling jackets are placed. Despite the uncertainty of the optimum spacing of the lamps and the corresponding volume of algal suspension necessary to provide for the oxygen demands of the crew, the total volume of the system would be competitive with the volume of equipment now used to provide the same functions on nuclear submarines. However, there is reason to anticipate significant reductions in the electrical-energy requirement, because lamps still in the experimental stage have an efficiency six times greater than those used here.

Reliability is one of the surprising attributes of the algal system; if the important factors, i.e., light intensity, rate of dilution with fresh medium, and rate of  $\text{CO}_2$  input, are controlled properly the algal cells will provide a constant oxygen production. Changes in light intensity cause an immediate change in oxygen production, but changes in the dilution rate or in the composition of the culture medium have more subtle effects which may not be observable for several days.

## FUTURE PLANS

The Polaris-supported feasibility study for submarine application has now been completed. However, it is planned to extend in a longer-range program some of the studies reported here. For example, the upper limit of light intensity which can be used profitably should be determined, as well as the effect of decreasing the light path below 10 mm.

Factors which affect the adhesion of algal cells to glass surfaces involve another area of study. This problem is an important one if the system is to be operated continuously for long periods. Cells cultured under widely divergent conditions will be analyzed for chlorophyll, nitrogen, trace metals, etc., in an effort to correlate their constitution with their physical properties. An obvious remedy for the sticking problem, that of treating the glass surfaces with Teflon or similar materials, will also be evaluated.

Because of the limited solubility of  $\text{CO}_2$  in water, the effect of pressure on the mass culture of algae will be studied. Presumably at elevated pressures the culture should be saturated with  $\text{CO}_2$  at a lower flow rate of a given gas than at atmospheric pressure, but the point should be investigated. Less predictable may be the results of experiments in which high magnetic field strengths and sound waves of varying frequencies are imposed on the algal cells.

Another study already underway will determine the adaptation of algal cells to changes in culture conditions.

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## Chapter 3

### Monoethanolamine Stability Studies

H. Ravner and C. H. Blachly

#### INTRODUCTION

Monoethanolamine (MEA), the regenerative absorbent in CO<sub>2</sub> scrubbers, is an important component of the chemical system devised to ensure a habitable atmosphere aboard nuclear-powered submarines. However, this amine has the fault of being toxic in relatively small quantities; its full effect on personnel and equipment is yet to be established. A second deficiency is that its stability is not considered adequate under operating conditions normally encountered in the scrubbers. The latter limitation may be more fully stated as follows: (a) a major oxidative degradation product is ammonia, which cannot be tolerated in a ship's atmosphere; (b) its useful life as an absorbent is relatively short, posing a logistics problem when a ship is on extended patrol; and (c) it darkens rapidly in use, making analytical determinations of its service life difficult and uncertain with color indicators.

A program to eliminate or alleviate most of these and related scrubber problems has been carried on at the Mare Island Navy Shipyard. A major contribution of this work with respect to improving the stability of MEA was the recommendation that a chelating agent, the monosodium salt of N, N-diethanol glycine, sold under the trade name of Versene Fe-3 Specific (VFS), be incorporated into all amine solutions (1,2). Since iron was considered a major catalytic contaminant of the amine, it was also recommended that a low-iron-content material be specified for use. Both recommendations are now incorporated in the specification covering the requirements for scrubber-grade MEA (3).

The research program on MEA stability being conducted at NRL is designed to elucidate the factors affecting the oxidative degradation of the amine, such as the catalytic influence of metals, the nature and significance of the oxidation products, and the effect and efficiency of additives which retard this breakdown. To obtain a reproducible reference material of adequate purity, all MEA used in this work was of analytical grade which had been vacuum-redistilled using a high-efficiency column. All dynamic oxidation experiments were conducted under reflux conditions with approximately 4 N solutions in glass cells, using air containing 1 percent CO<sub>2</sub> by volume unless otherwise specified. Oxidation temperatures were generally 131°F (55°C), judged to be a reasonable compromise for the range of temperatures to which MEA is exposed under oxidizing conditions in CO<sub>2</sub> scrubbers; air flow was 1 cc/ml MEA/min.

#### NRL PROGRESS TO DATE

##### MEA Oxidation Products

Under the laboratory oxidation conditions described, substantially all of the basic material found in the effluent air is ammonia, little or no MEA being carried over as an aerosol. Figure 8 illustrates ammonia evolution during a typical oxidation run.

Unexpectedly, a product giving a peroxide reaction has been found in very low concentration in oxidized MEA solutions, but not in such solutions containing VFS or other

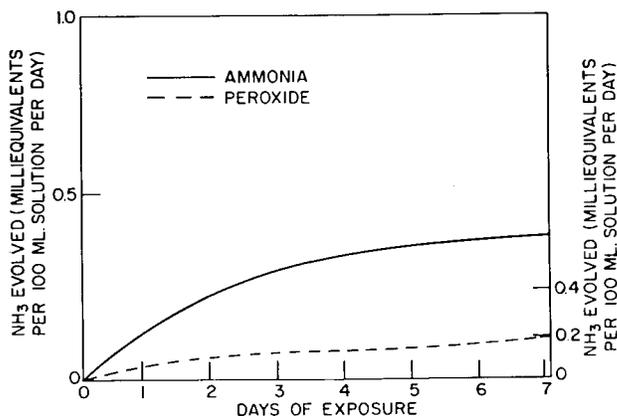


Fig. 8 - Ammonia and peroxide generation during oxidation of 4N MEA solutions

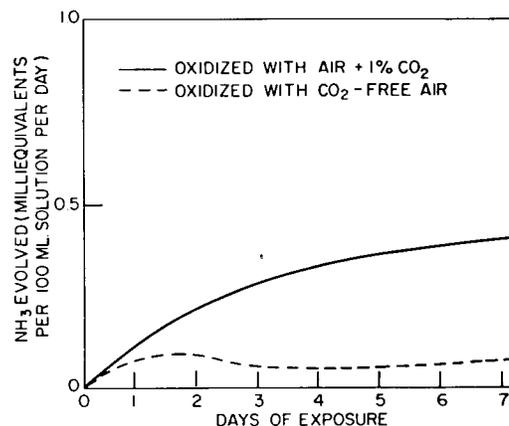


Fig. 9 - Relative stability of carbonated and uncarbonated 4N MEA solutions

effective stabilizers. This peroxide (or peroxides) is generated together with ammonia, but is not found when ammonia is absent. It is generally accepted that a variety of organic compounds oxidize autocatalytically via a peroxide mechanism; many such compounds are successfully stabilized by antioxidants which destroy peroxides or retard peroxide formation, thus interrupting the autocatalytic oxidation chain. The possible significance of MEA-derived peroxides is that they may play a similar role in the oxidation of the amine. Other aspects of the study of MEA-derived peroxides will be considered below. A typical graph of peroxide formation vs oxidation time is included in Fig. 8.

In addition to ammonia and peroxides, nonbasic nitrogen-containing compounds are formed when MEA solutions are oxidized. These compounds accumulate in the scrubber solutions, but serve no useful purpose, since they are not capable of combining with  $\text{CO}_2$ ; they may, in fact, be detrimental to the service life of the solution, because they may further decompose to form noxious products. In the course of a previous study (4) on the use of refractive index as a means of determining MEA normality, it was demonstrated that these nonbasic nitrogen compounds markedly increase in concentration with time. A useful collateral dividend from this study was a convenient and rapid method for the determination of the concentration of these compounds, making available an independent estimate of the degree of degradation of the amine solutions.

#### Effect of $\text{CO}_2$ and Temperature on MEA Stability

As shown in Fig. 9, the carbonated form of MEA appears to be considerably less stable to aeration-oxidation than the uncarbonated compound. It is probable that, other conditions being equal, the decrease in stability is a function of the degree of carbonation. It is not unexpected, of course, that stability of the MEA is also related to temperature. It is surprising to note, however, that whereas at  $174^\circ\text{F}$  MEA exposed to oxygen gas containing one percent  $\text{CO}_2$  evolves a considerable quantity of ammonia in 24 hours, no ammonia is detected at  $75^\circ\text{F}$  in the course of a week (Fig. 10). These data confirm operational experience that, to obtain maximum useful life, scrubber solutions should be maintained at as low an operating temperature as is feasible.

#### Effect of Metals and Metal Salts on MEA Stability

The oxidation rate of many organic compounds is materially increased in the presence of certain metals or their salts; the degree of catalytic potency depends on the particular

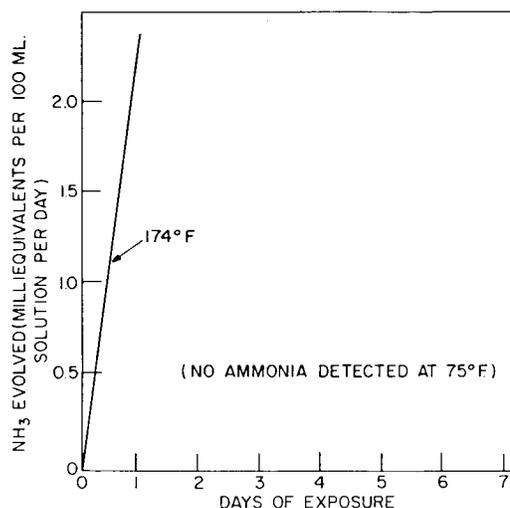


Fig. 10 - Effect of temperature on stability of 4N MEA exposed to oxygen containing 1 percent CO<sub>2</sub>

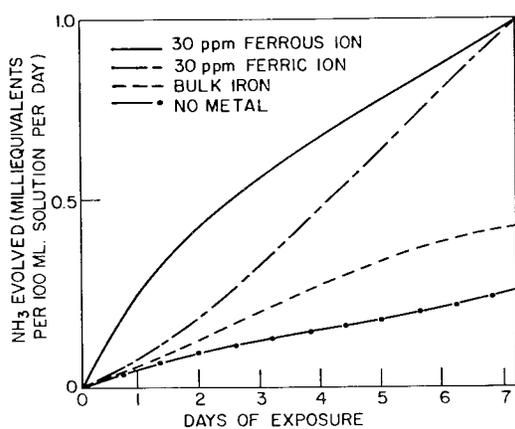


Fig. 11 - Effect of iron on 4N MEA oxidation stability

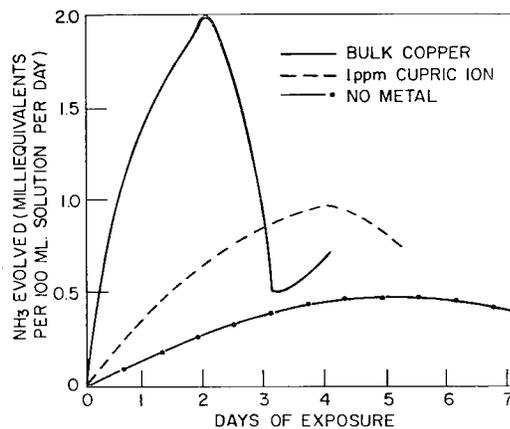


Fig. 12 - Effect of copper on 4N MEA oxidation stability

metal present. Because iron is a common contaminant of MEA, it was of interest to assess its effect on the stability of the MEA solutions. The data in Fig. 11 show that, as measured by NH<sub>3</sub> evolution, iron in bulk form imparts only slight additional instability to the amine, whereas both the ferric and ferrous salts in concentrations of 30 ppm have a more perceptible adverse effect. Although to date copper has not been regarded as a significant contaminant in MEA scrubber solutions, its pro-oxidant activity for many organic systems is so pronounced that its effect on the amine stability was investigated (Fig. 12). Copper, both as the bulk metal or as the cupric salt, drastically accelerates oxidative degradation of the amine.

The adverse effect of copper on the amine was sufficiently serious that it became of interest to analyze year-old retained scrubber samples from SEAWOLF and SKIPJACK for their copper contents. Unexpectedly, these contents were in the range where their

Table 4  
Analysis of NAUTILUS Samples

Sample	Iron Content (ppm)	Copper Content (ppm)
Evaporator Water	none	5.0
LIMEA	7.0	2.5
Scrubber 1 (400 hr operation)	19.0	8.5
Scrubber 2 (800 hr operation)	35.0	13.5

adverse effect on MEA stability would be appreciable. To secure additional data on the iron and copper contents of MEA solutions from operational scrubbers, arrangements were made with Squadron 10 to obtain water, LIMEA (Low-Iron MEA), and MEA scrubber samples under specified conditions. The analysis (Table 4) of NAUTILUS samples obtained under this arrangement reveals that the scrubber make-up water (so-called evaporator or potable water) contained no iron; the base stock LIMEA (containing VFS), however, contained 7 ppm iron, in excess of the specification limit of 3 ppm. The iron content of the two scrubber solutions increased approximately linearly with operating time, up to 35 ppm for scrubber 2 after 800 hours of operation. The iron in the scrubber samples presumably had its origin in make-up additions of LIMEA, and from attack on the materials of scrubber construction. The copper analyses were revealing: the LIMEA contained 2.5 ppm of copper, the evaporator water 5.0 ppm, and the scrubber solutions up to 14 ppm after 800 hours of operation. Since the scrubber does not contain copper as a material of construction, the presence of this element in the amine solutions must result from makeup additions of both LIMEA and evaporator water. Since evaporator water is piped through copper tubes, its copper content is not surprising. Another possible source of copper in the scrubber solutions is fine copper dust particles from shipboard machinery, which may have entered the scrubber via the air intake. It should be noted that the copper concentrations found in the two NAUTILUS scrubber solutions, like those from SEAWOLF and SKIPJACK, are in the range where, in laboratory experiments, they exert an appreciable adverse effect on MEA stability.

#### Effect of Chelating Agents on MEA Stability

Stabilizers for MEA solutions can function by different mechanisms: (a) they may act as conventional antioxidants which interrupt an autocatalytic chain reaction; (b) they may be metal deactivators which, although they themselves are not antioxidants, nevertheless prevent additional instability being imparted to the amine by catalytically active metals; or (c) they may be both antioxidants and metal deactivators. Figure 13 reveals that VFS has the characteristics of a conventional antioxidant for MEA, since it stabilizes the amine when no metal catalysts are present. It is not too surprising that VFS is also effective in the presence of bulk iron because, as has been demonstrated, the metal has only slight catalytic activity. Ferrous salts are, however, more strongly catalytic, but since VFS does not chelate with them in alkaline carbonated solutions, no metal deactivation occurs. Consequently VFS does not effectively inhibit the degradation of MEA when iron salts are present (Fig. 13).

The tetrasodium salt of ethylenediamine tetracetic acid (EDTA), like VFS, is an excellent antioxidant for MEA in the absence of metals (Fig. 14). In the same figure it is seen that EDTA retains its effectiveness with 20 ppm of cupric ion present, whereas under the same conditions, VFS to a large degree loses its effectiveness. This difference in activity may be ascribed to the fact that EDTA is a far more satisfactory chelating agent for copper under the test oxidation conditions than is VFS. Thus, EDTA exemplifies,

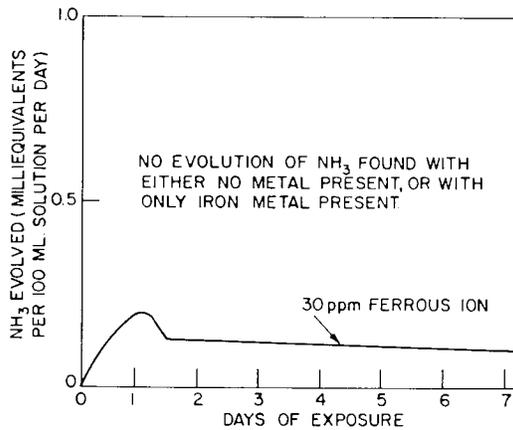


Fig. 13 - Effect of 1.5 percent VFS on 4N MEA oxidation stability in the presence of iron

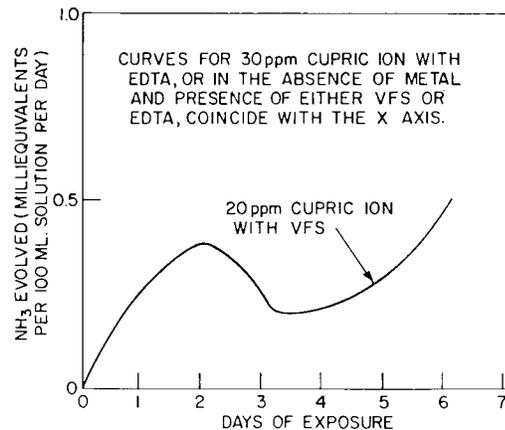


Fig. 14 - Effect of 1.5 percent VFS and 1.5 percent EDTA on 4N MEA oxidation stability in the presence of copper

at least under laboratory conditions, a dual-purpose stabilizer for MEA, effective as both an antioxidant and a metal deactivator. Its effectiveness when other catalytic metals are present has not as yet been determined.

Other chelating agents which have been briefly examined for their antioxidant activity in MEA solutions are disalicylalpropylenediamine (DSPD) and mercaptobenzothiazol (MBT). DSPD offers no antioxidant protection to MEA, either in the presence or absence of copper; MBT, however, appears to be a more effective antioxidant under both conditions.

#### Reaction of Chelating Agents with Peroxides

Many antioxidants function in a variety of organic systems by reacting with peroxides, thus interrupting autocatalytic oxidation chains. Preliminary experimental data indicate that chelating agents such as VFS react with peroxides. The data, although not conclusive, indicate that MEA may oxidize autocatalytically via a peroxide mechanism, or that the chelating agents function as antioxidants by reacting with, and destroying, chain-propagating peroxides.

#### CONCLUSIONS

The data from this study indicate that the useful life of CO<sub>2</sub> scrubber solutions is dependent not only on the time they have been in service, but also on the concentration of metal contaminants they may have acquired during such service. VFS, the presently used stabilizer for MEA, appears to be an effective antioxidant, but this effectiveness is perceptibly diminished when catalytic metals such as copper are present in parts-per-million concentration. Additives which combine antioxidant activity with the ability to deactivate catalytic metals offer the possibility of imparting additional stability to scrubber solutions. The mode of degradation of MEA under service conditions has not been definitively established, but it may involve a peroxide-catalyzed mechanism.

#### FUTURE WORK

The study of the effect of trace-metal contaminants in promoting MEA oxidation will be continued; samples from operational scrubbers and from metal bench-test cells will

be analyzed to determine both the metals generally present and their concentrations. This work may contribute to a reassessment of the specification requirements for MEA, since, for example, the base stock LIMEA sample from NAUTILUS contained sufficient copper to impair the stability of the amine in laboratory tests. Similarly, the merits of preventing the introduction of catalytic metals into MEA from such sources as evaporator makeup water will be evaluated, together with the feasibility of employing specific additives for specific contaminants, e.g., EDTA when copper is present. A report is being prepared establishing the need for using only battery-type water in the scrubber.

The study of the significance of peroxide formation during MEA oxidation, and the antioxidant role played by peroxide-destroying additives, will also be continued. This aspect of the project has thus far been hampered by the fact that the peroxides are formed in such minute concentrations as to make their isolation and characterization difficult.

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## Chapter 4

# Comparison of Carbon Dioxide Removal Systems

R. R. Miller

### INTRODUCTION

The importance of the removal of carbon dioxide from submarine atmospheres has caused it to receive a considerable amount of study and experimentation. Several effective methods for this removal have resulted, but the very number of such methods creates a problem in choosing an optimum system for shipboard use. Further factors not immediately apparent are also involved in such a choice, including the training of servicing personnel, the effect of the resulting atmosphere on the crew, the dependability of the equipment, and the costs of manpower and electrical power.

The factors influencing the selection of a single shipboard system are such that equally comprehensive knowledge of each is not likely to be available. With the probability that not all systems will be measured in the same units, a rather arbitrary decision must be made in the choice of the candidate systems. A unit such as the monoethanolamine (MEA) scrubber, which has performed creditably on all the U.S. nuclear submarines, is at a big advantage with respect to any proposed changes in the system. Changes, however, are inevitable as soon as obviously superior methods become available.

In a previous report, a comparison was made of oxygen sources and carbon dioxide absorbents (1). The present chapter brings up to date the key features of the carbon dioxide removal systems, including those of particular importance in choosing an optimum system.

### THE MEA SCRUBBER

The monoethanolamine (MEA) scrubber, with the varied operation from ship to ship, is as yet relatively unknown with respect to average service and average effectiveness. The MEA solutions last from a few hundred hours to five or six months without change. The attention, service, and parts required to keep the unit in operation vary considerably from one unit to another and from one ship to another, but in every case they are greater than desirable. The power requirement varies from about 10 to 18 kw, which is not at all excessive for the work accomplished. The scrubber unit is relatively compact, having measurements of approximately  $4 \times 4 \times 6$  ft, with a volume of about 100 cu ft. The total weight is close to 4,000 pounds. The down time on the operation of the scrubber has been a serious fault, but one that could be eliminated through design and improvement in the quality of parts.

The efficiency of the unit is lower than is reasonable. An increase in efficiency would be of considerable convenience and value to the fleet. There are a number of indications that the scrubber as used is limited entirely by the efficiency of the stripper unit. Data indicate that  $\text{CO}_2$ -rich amine to the stripper contains about 46 volumes of  $\text{CO}_2$  per volume of liquid (saturated for 4 N MEA), and the lean ratio is dropped only to about 37 volumes of gas to volume of liquid. At the rates of liquid discharge from the stripper (1 to 1-1/2 gal/min), the concentration of  $\text{CO}_2$  in MEA in the absorber is lowered little from the saturation value. The  $\text{CO}_2$  absorption, thus, is being accomplished in a MEA solution already highly carbonated. In an Operations Manual (2), it was stated that  $\text{CO}_2$  could be

reduced from 1.5 to 0.2 percent by the scrubber with an air flow of 250 cfm. This would be 24 lb/hr of CO<sub>2</sub> removed. These figures were in all probability from data taken when the scrubber concentration of carbonate in the MEA was not near a saturation value. If a rate of absorption is calculated from the laboratory results of Gadomski (3), the absorption of CO<sub>2</sub> on a scrubber having 250-cfm air flow with 1 percent CO<sub>2</sub>, through 12 cu ft of packed column and 40 percent carbonated MEA solution, the unit should absorb 18 pounds of CO<sub>2</sub> per hour (about all of the CO<sub>2</sub> contained in the air used at 250 cfm). The air flow could be increased, which would normally increase the amount removed, but the big increase could be obtained only by reducing the carbonate content of the MEA through reducing its concentration in the lean MEA solution from the stripper. A study of the efficiency of the stripper should result in a design that would show appreciable improvement in the overall efficiency of the scrubber unit. A preliminary study of this phase is under way at NRL.

The operation of the scrubber unit is not expensive, aside from repairs and parts, since the service life of the amine is a few hundred hours per charge. The service life of the amine may be extended, as shown in Chapter 3. The present cost would run less than a cent an hour, and the power requirements are on the average about 12 kw. If scrubber units of this type are to be continually used, some redesign and use of another amine, such as Alkazid M (4,5), should be considered.

#### THE SULFATE CYCLE

In the sulfate cycle, water is electrolyzed into hydrogen and oxygen, and in the process, the alkali and sulfate ions are separated. Through reaction with the water in the cell compartments, the ions form alkali hydroxide and sulfuric acid. The alkali hydroxide formed would be used to remove CO<sub>2</sub> from the submarine atmosphere. In operation the oxygen required would be the controlling factor, since the alkali produced is more than twice that needed to absorb the respiratory CO<sub>2</sub> produced from the generated oxygen. Thus, the absorption would take place in a caustic solution less than 50 percent carbonated. References 3 and 6 give a  $K_{Ga}$  value (lb moles of CO<sub>2</sub> absorbed/hour/cubic foot of packing/atmosphere of pressure of CO<sub>2</sub>) of 2.3 for 2 N NaOH. In a scrubber unit, as presently operated, absorption of CO<sub>2</sub> would amount to about 12 pounds per hour. Reference 3 showed that an increase in liquid flow in the scrubber increased the  $K_{Ga}$  values. Three times the liquid rate used in the present scrubber would give a value for NaOH of 2.8, or 14-1/2 pounds of CO<sub>2</sub> absorbed per hour.

The volume of a unit suitable for 100 cu ft of oxygen per hour has not been calculated, but due to the multiple-cell arrangement and suitable ducting to collect the gases separately, the unit would certainly be larger than the present scrubber. This unit would require the absorber and the CO<sub>2</sub> collecting and disposal equipment now use, along with the electrolytic cells and the unit for the recombination of the acid and alkali carbonate solutions. However, the unit would furnish all the oxygen required. The operational costs would be essentially the maintenance and the power required. The sulfate is not expensive and could be used continuously. The power required would be high, as the power requirement of any electrolytic process will be. A unit for 100 cu ft of oxygen per hour would require the flow of approximately 13,700 dc amperes between the cell electrodes. If the voltage runs as high as the laboratory cells (about five volts), the power requirement could be as high as 75 kw. By whatever amount the voltage required per cell could be reduced, there would be a corresponding decrease in power required. Neglecting ionizable compounds which could collect in the sulfate liquid, the electrolytic gases should be pure.

### THE IONICS EXCHANGE ABSORBER UNIT

The Bureau of Ships has contracted with Ionics, Inc., for construction of a pilot plant unit suitable for sustaining ten men, employing ion-exchange cells. The unit is based on absorption of CO<sub>2</sub> on an ion-exchange resin, where the resin is continually activated by electrolysis. In this process, water is electrolyzed and the oxygen is available for breathing. The hydrogen and carbon dioxide are collected and disposed of overboard. The volume estimated for the complete unit is nearly double the present scrubber. The unit would require blowers for air, a CO<sub>2</sub> compressor, water pumps similar to those now in use, and a hydrogen compressor. For 100 men the power requirement was estimated at 75 to 80 kw. If the development work demonstrates suitable absorption efficiency, this unit would have many desirable features. Toxic materials or noxious vapors would not be evolved, a heated stripper for CO<sub>2</sub> would not be required, and the unit would have fewer moving parts and seals. The evaluation study would determine K<sub>Ga</sub> values for the CO<sub>2</sub> absorption, and a comparison could be made of this type of unit with the sulfate cycle. A recent report (7) on a unit to furnish oxygen for 120 men has shown an estimated power requirement of 108 to 113 kw with a volume of 177 cu ft and a weight near 11,000 pounds.

### MOLECULAR SIEVES

A system based on adsorption by sieve has not yet been engineered to the extent that a precise volume can be stated for a 100-man unit. However, it would probably be in the neighborhood of 100 cu ft. It would remove CO<sub>2</sub>, water, hydrocarbons, and other absorbable vapors but would not furnish oxygen. The sizes given in Ref. 8 were based on the removal of 14.7 pounds of CO<sub>2</sub> per hour. The power requirement would be similar to the MEA scrubber, i.e., from 10 to 14 kw. The unit would require careful operation to prohibit water from entering the CO<sub>2</sub> absorption bed, but it could be operated on a fixed cycle, completely on instrument control. Thus, it would require little or no attention, and the dependability would rest in the quality of the instrumentation. There would be no fumes or vapors in the vicinity, and the air would be clean, dry, and of excellent quality. The quantity of molecular sieve required in a unit (three beds for CO<sub>2</sub> and three beds for water) has been estimated to be between 2,400 and 3,000 pounds. As a rough estimate, the cost of the molecular sieves would probably be \$1.00 per pound. A well-engineered system of this type might give unsurpassed performance for the removal of air impurities from the atmosphere of submarines. In both Great Britain and France prototype molecular-sieve systems are under development, utilizing low-temperature removal of the water before absorption by the sieves (9).

### ALKALI METAL COMPOUNDS FOR SUBMARINE AIR PURIFICATION

Alkali peroxides and superoxides have been mentioned often for submarine use. The use of sodium peroxide was evaluated in the early 1940's (10), and 4,000 generators were manufactured to furnish oxygen gas at 7 lb gauge pressure, with a few to furnish gas at 100 lb pressure. They were built to operate in an automatic fashion on the principle of the Kipp generator for the length of time that a charge lasted. Data on the production of oxygen from various oxides evaluated in these generators are given in Table 5.

For sodium peroxide, 45 lb were placed in the generator, and 100 cu ft of oxygen was produced, along with a sodium hydroxide solution in which CO<sub>2</sub> could be absorbed. For the use of 100 men, this would last one hour and furnish about 27 gallons of alkali solution. (In order to reduce the charges per day to one quarter the number, and also to give a more reasonable volume of alkali solution for scrubber use, a unit using four times the charge listed above might be more reasonable.)

Table 5  
Production of Oxygen from Oxides

Test No.	Material	Weight		Water Temperature		$\Delta t$ (°F)	Total Oxygen Evolved STP		Oxygen/lb of Material (cu ft)
		lb	kg	Initial (°F)	Final (°F)		cu ft	liters	
1	Solozone	44	20.0	-	-	-	88.5	2510	2.01
2	KO <sub>2</sub>	27	12.3	55	95	40	91.8	2600	3.39
3	Heated Mixed Oxide	23	10.4	55	104	49	68.3	1930	2.97
4	MSA Mixed Oxide	19.8	9.0	55	95	40	59.0	1670	2.98
5	Solozone	44	20.0	60	183	123	93.9	2660	2.13
6	Solozone	44	20.0	109	211	102	96.4	2730	2.19
7	KO <sub>2</sub>	29.3	13.3	115	135	20	93.6	2650	3.21

A typical unit could be constructed similar to that shown on Fig. 15. When the unit is charged, a tube between the inner and outer chambers opens, and water would flow into the peroxide chamber, reacting until a preset pressure was developed. The pressure-control valve on the pipe connecting the two chambers would then close, and further action of the peroxide would force the water from the peroxide chamber, stopping the reaction. As gas is drawn from the unit, the pressure would fall, the valve would reopen, and the

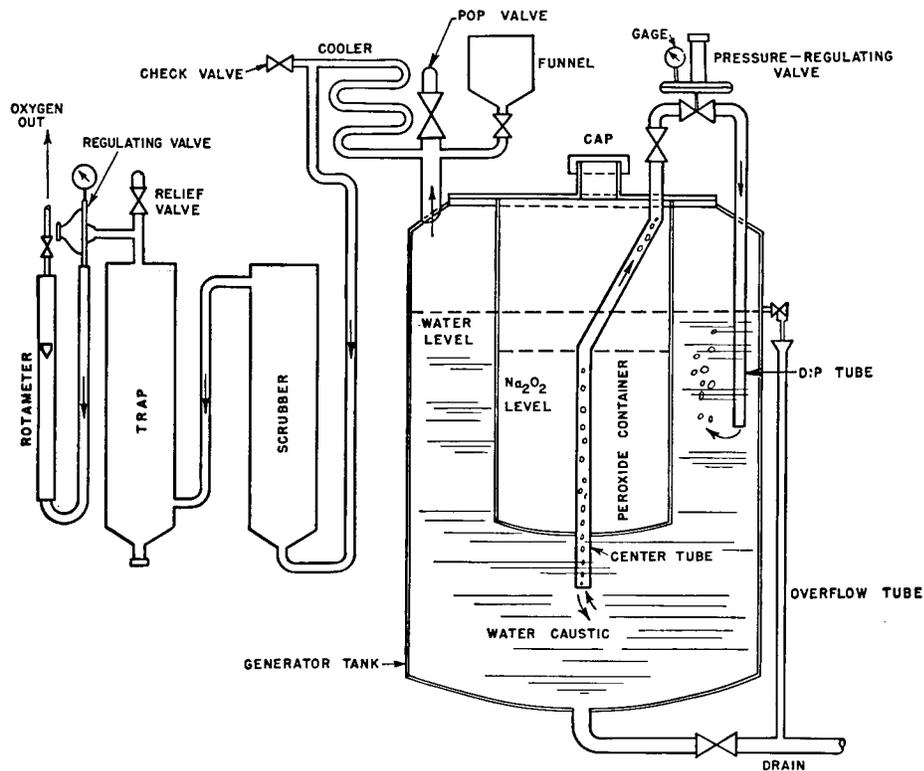


Fig. 15 - Oxygen generator

cycle would repeat itself. When reaction of a single charge was complete, the alkali solution would be transferred to an MEA-scrubber-type absorber for the removal of carbon dioxide from the submarine air. When the second charge was completed, the carbonate in the scrubber could be run overboard and the new alkali transferred to the scrubber, the cycles being repeated in a continuous manner.

Approximately 10 lb of CO<sub>2</sub> would be produced from the 100 cu ft of oxygen consumed in the breathing cycle. The normality of the hydroxide produced and the amount of CO<sub>2</sub> that could be absorbed to form carbonate are shown in Table 6. Two other available oxides have been included with the sodium peroxide. In the case of KO<sub>2</sub>, the hydroxide produced would absorb (by the formation of carbonate) about five pounds of CO<sub>2</sub>. Thus, this oxide could not be used alone to furnish the oxygen and CO<sub>2</sub> absorbent. A mixture of sodium peroxide and potassium superoxide (KO<sub>2</sub>) could be adjusted to furnish the required capacity for CO<sub>2</sub> absorption, since the sodium compound has excess capacity to the oxygen furnished. An excess of CO<sub>2</sub> capacity has been calculated for the mixed oxide to avoid the slow rate of absorption in nearly saturated carbonate solution. Bicarbonate formation has not been considered because of the slow rate of absorption in the carbonate solutions.

The present cost of superoxide makes the use for oxygen production a comparatively expensive item. Chlorate-candle oxygen is comparable in price to that from sodium peroxide; both are high compared to the cost of pressurized gaseous oxygen. Comparable costs of the systems discussed are shown in Table 7.

Table 6  
Oxide Reactants in One Hour of Generator Operation

Oxide	Wt Oxide Charge (lb)	Oxygen (cu ft)	Normality of Hydroxide	CO <sub>2</sub> Absorbed (lb/hr)	Density of Oxide (g/cc)	Cost per lb (dollars)	Oxide per cu ft (lb)
Na <sub>2</sub> O <sub>2</sub>	45	100	5.01	15.2	1.51	0.20	95.0
KO <sub>2</sub>	28	100	1.69	5.13	0.93	1.00	58.4
Na <sub>2</sub> O <sub>2</sub> 45% K <sub>2</sub> O <sub>4</sub> 55%	36	100	3.04	13.5	1.22	0.70	77.0

Table 7  
Comparison of Carbon Dioxide Absorption Systems

System	Volume (cu ft)	Wt (lb)	O <sub>2</sub> Absorption	Pro-duced	Cost to Charge System (dollars)	Cost/hr on Basis of Charge (dollars)	Power (kw hr/hr)	Cost per cu ft O <sub>2</sub>
MEA Scrubber	100	4000	yes	no	20	0.0	10-18	-
Sulfate Cycle	175	-	yes	yes	12	0.0	75	\$0.00 and 750 watt hr
Ionics Unit	177	11000	yes	yes	?	0.0	100+	\$0.00 and 1000 watt hr
Molecular Sieve	100+	6000	yes	no	3000	0.0	10-14	-
Alkali Oxides	100	2000	yes	yes	9 to 28	9 to 28	4-8	9 to 23¢ and 60 watt hr

## CONCLUSIONS

Neglecting the algal cycle, which is discussed in another chapter, a number of methods of removing CO<sub>2</sub> have shown capacity to remove the CO<sub>2</sub> from submarine atmospheres. The MEA carbon dioxide scrubbers, as operated, require considerable improvement to serve their purpose in case of national emergency, when problems in supplying parts can become really acute. Excessive wear on some parts, possibly due to the operation of those parts beyond their design capacity, is the chief contribution to the lack of extended dependability of the units.

The immediate prospects for better CO<sub>2</sub> removal systems in nuclear submarines are based on: (a) continued improvements in the MEA scrubber, (b) the Ionics resin-membrane system for oxygen generation as well as CO<sub>2</sub> removal, and (c) the sulfate cycle.

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## Chapter 5

### The Mark IV Atmosphere Analyzer

F. S. Thomas

#### INTRODUCTION

The Mark III and the new Mark IV Atmosphere Analyzers are the service equipment in nuclear submarines for determination of the concentration of the principal components of the submarine atmosphere. The development and modification of the Mark III and earlier atmosphere analyzers have been chronicled previously (1-3). The development and the initial production of the Mark IV analyzer (Fig. 16) was described in the previous report (3). With the termination of production of the Mark III analyzer the emphasis on the analyzer research has been concentrated on the problems with the Mark IV, and little improvement in the Mark III has been attempted since the investigations previously reported.

The Mark IV analyzer is basically an updated redesign of the Mark III analyzer, taking advantage of advances in the science of instrumentation and removing areas of known difficulty in the previous analyzer. The Mark IV still has the limited analysis objectives of the previous analyzers.

The Mark IV analyzer contains four positive-filter, monobeam, infrared analysis channels, each designed for determination of a particular component in the submarine atmosphere. There is one channel each for carbon dioxide, Freon-12, and carbon monoxide. The fourth infrared channel, originally included as a spare, is also set up for carbon monoxide unless otherwise needed. In the newer submarines, which have both Freon-12 and Freon-11 equipment, there is need for separate determination of these Freons, and analyzers for these ships have the fourth infrared channel sensitized for Freon-11. There is also included a simple thermal-conductivity channel for hydrogen and an oxygen channel of the paramagnetic, deflection, visual-readout type. All Mark IV units contain provision for inclusion of a long-optical-path, ultraviolet photometer, and six units contain this channel. This ultraviolet channel is nondiscriminatory and sensitive to a number of toxic materials, particularly to mercury, and less so to ozone and a wide variety of aromatic and substituted hydrocarbons. The sampling system contained in the Mark IV operates at essentially ship ambient pressure.

To the end of 1962, more than two-thirds of the total production of Mark IV analyzers had been completed. No appreciable submarine operating experience had been accumulated.

After the first few Mark IV analyzers had been built and passed acceptance tests at the manufacturer's plant in early 1962, there were no further deliveries for a considerable time due to the inability of the manufacturer to build the radiation-detector subassemblies, especially those for the Freon-12 channel, which would pass the required acceptance-test procedure. Since these acceptance tests are necessarily of limited duration, the question was raised as to the operating characteristics which could be expected in continuing operation beyond the period of the acceptance tests.

#### NRL OPERATION OF MARK IV, SERIAL NO. 4

One of the early production units was diverted to NRL for continued operation beyond that of the acceptance tests which it had passed at the manufacturer's plant. This unit was

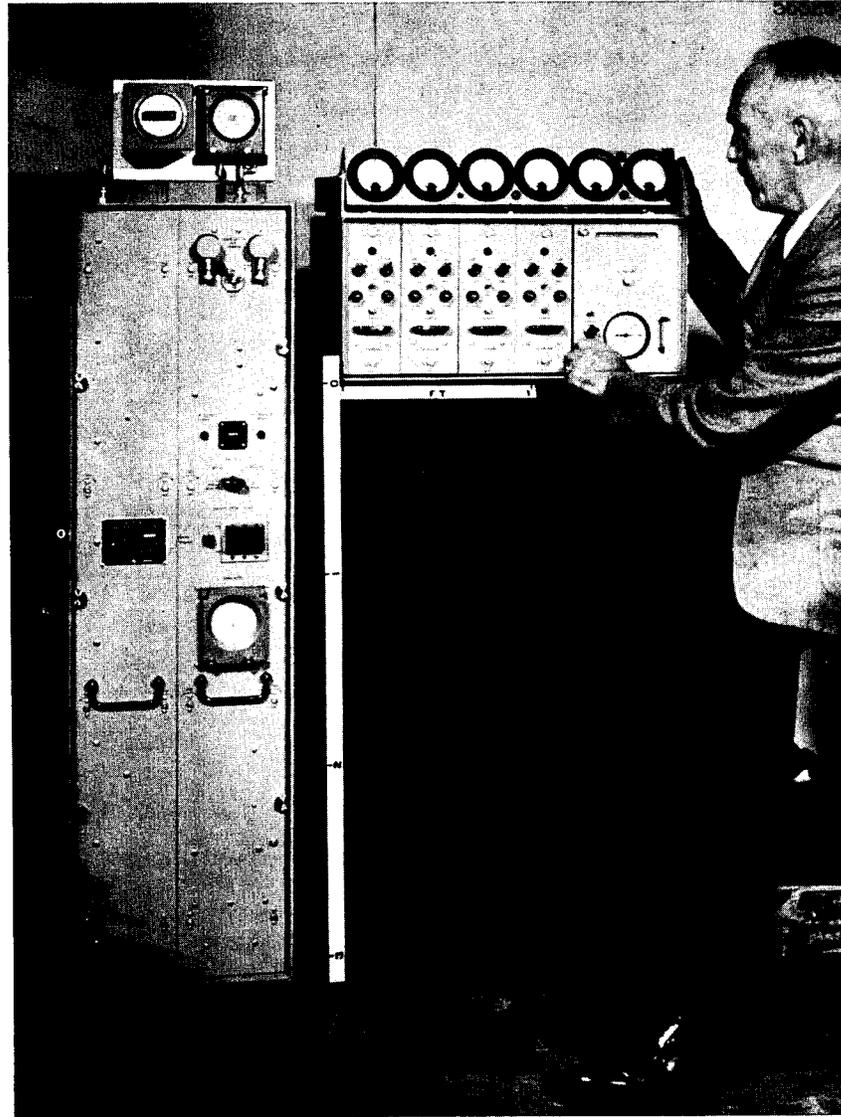


Fig. 16 - The Mark IV atmosphere analyzer

placed in operation in accordance with the information contained in the accompanying technical manual. The results of operation of this unit for about two months showed that in most respects the mechanical operation of the unit appeared excellent, with only a few worthwhile changes suggesting themselves during that time. These suggested changes have now been made, including backfit to previously produced units. In this same period of operation, however, there was an excessive incidence of radiation-source failures and especially of gradual changes of the infrared channel operation to the point where they no longer met the specification requirements. This was due principally to changes in the radiation receiver, which produced crossover sensitivity to water vapor. These results, although significant, were from trials on a single unit and hence provided an insufficient sample to apply with any degree of assurance to the entire group of Mark IV analyzers built and to be built.

## MARE ISLAND EVALUATION

At NRL's suggestion, the Bureau of Ships, in order to provide a larger sampling, arranged for six units to be diverted to the Mare Island Naval Shipyard for operation in the instrument shop in a simple test routine for about 1000 hours each, after which they would be forwarded to the original destinations. This test routine was designed to determine zero and span stabilities, crossover sensitivities, and the general characteristics of the mechanical operation. This additional information on possible sources of trouble in analyzer operation was intended mainly to permit the manufacturer to investigate suitable remedial measures, as necessary, prior to service use.

Operation of the first five units in this longer test gave much better performance in the critical gas-analysis area than would have been expected from the early operation of unit 4. In fact, further operation of unit 4 with more recent radiation detectors and sources also gave much better results in this area. Three-fourths of the infrared channels in the Mare Island test gave stability and crossover performance equal to or better than acceptance-test specification requirements. One-half of all the infrared channels gave results much better than required by the specification. The channels in which performance was less than satisfactory were those for carbon monoxide and Freon-12; here there was a gradual increase in crossover sensitivity to water vapor occurring in the radiation detectors. All five of the carbon dioxide and four of the five Freon-11 channels gave excellent operation throughout the test period. All of the radiation sources in this test gave satisfactory operation, except for the burnout of one Freon source.

The hydrogen and oxygen channels gave excellent operation for the test period. The data taken on these, although inadequate in some respects, indicated that the calibration on some of the oxygen units might be giving readings higher than the sampled gas (a maximum of about 7 percent of the reading). This has been verified in the later Mare Island test results. Also, for the hydrogen channel there appeared to be a need for revision of the table of values for "Response to Other Gases" as given in the technical manual for the instrument. Correction of these should be readily accomplished.

Again, mechanical performance was good except for the appearance in some units of a pump problem, especially as to bearing life and inadequate pumping ability in the evacuation mode.

In the latter part of 1962, an NRL research advisory committee reported (4), after study of the Mark IV principles and equipment and the results obtained in the NRL and first Mare Island test operation, that there was no apparent fundamental reason why the Mark IV should not be an excellent replacement for the Mark III, if and when mechanically and electrically stable radiation detectors were being consistently produced.

Toward the end of 1962, a second group of analyzers had been delivered to Mare Island for testing similar to that described above. Limited inspection of early data from the tests on these analyzers indicates that little, if any, improvement has been attained in the production of radiation detectors which do not show the gradual increase in crossover sensitivity. In these tests there appears to be an increased rate of source failures for no obvious reason. Determination of other characteristics, such as zero and span drift rates, requires further study of the data taken.

The results of preliminary laboratory investigation and two shipboard trials of a prototype ultraviolet channel by laboratory personnel have verified its possible shipboard utility as an alarm type of analyzer. Further laboratory investigation and possibly shipboard trials appear necessary before a sufficient basis would exist for recommendation of the inclusion of the ultraviolet channel in all of the Mark IV units.

## CONCLUSIONS

It would appear from the results of the operation of the several units, particularly in the later NRL and the first Mare Island test period, that the Mark IV analyzers potentially can carry out satisfactorily the limited submarine-atmosphere analysis objectives intended for the units. The overall results of these test runs showed further that there remained several areas requiring development and modification. Probably the most important and difficult of these is the refinement of manufacturing techniques and test procedures, which is essentially a problem of quality control, in order to produce consistently radiation detectors of sufficient drift and crossover stability for long-term operation.

## FUTURE PLANS

Since the potential success of the Mark IV analyzer has been shown increased effort should be directed toward removal of the basic causes of the present inability to produce consistently radiation sources and detectors of reasonably long useful life. The Mare Island test should be extended as long as possible to verify improvements by the manufacturer. If the needed improvement cannot be attained within the present design of these components, redesign without changing the basic operating principles should be investigated. Alternative remedial measures worthy of investigation might include the use of gas optical filtering to remove crossover sensitivities and the use of mechanical instead of electronic modulation of the radiation to permit design of a more rugged radiation source.

Modification of analyzer test and calibration procedures, usable aboard ship, are needed which take into account the results of the Mark IV test program, especially as to the determination of crossover sensitivities and the reduction of their effect on the shipboard analysis results obtained.

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## Chapter 6

### Gas Chromatography as a Submarine Atmosphere Monitor

M. E. Umstead

#### INTRODUCTION

The feasibility of using gas chromatography to monitor the predominant gases and a few of the trace gases in the atmospheres of nuclear submarines is being explored. Chromatography could offer some real advantages over the present type atmosphere analyzer. All the gases would be measured by the same analytical method and, if the need should arise, other gases could be measured with only minor modification of the original instrument. The gas chromatograph should be relatively free from interference by other components of the air and is capable of high reliability with little maintenance. The chemical and petroleum industries now use many completely automatic chromatographs to monitor the composition of various process streams. There have been reports of instruments being in use for a year or two without the failure of any component part. The chief reason why atmosphere analysis aboard nuclear submarines is not a rather straightforward application of gas chromatography is the necessity of measuring a few gases in the parts-per-million range.

Table 8 lists the gases to be analyzed and the concentration ranges which should produce full-scale deflections on the chromatograph (1). It also lists the desired precision of measurement for each gas. Freon-11 is now being used aboard some of the newer ships and must be added to the list. The studies reported here do not include this Freon. A full-scale response for 400 ppm with a precision of  $\pm 5$  ppm is a reasonable sensitivity requirement for this substance. It was not anticipated that the requirements of Table 8 for the trace gases would be readily met with existing commercial equipment. However, these values are representative of the concentrations actually found aboard ships and present a goal toward which an atmosphere-analyzer chromatograph can be designed.

Table 8  
Gases and Concentration Ranges to be Analyzed

Gas	Concentration Range (full scale)	Desired Precision
Nitrogen	0-100%	$\pm 1.0\%$
Oxygen	0-25%	$\pm 0.2\%$
Hydrogen	0-5%	$\pm 0.2\%$
Carbon Dioxide	0-5%	$\pm 0.1\%$
Freon-12	0-200 ppm	$\pm 5$ ppm
Carbon Monoxide	0-100 ppm	$\pm 3$ ppm
Methane	0-200 ppm	$\pm 5$ ppm

Two gas chromatographs were purchased to analyze for these gases in submarine air (1). These units were not intended to be final seagoing versions, but rather prototype instruments built from manufacturers' stock parts to demonstrate whether or not gas chromatography was feasible for this application and capable of higher reliability than the present analyzer. One of the units was a standard automatic industrial chromatograph, the other a semiautomatic instrument designed specifically for these gases. Both chromatographs employed thermal-conductivity detectors.

## PRESENT STATE OF DEVELOPMENT

### Industrial Chromatograph

The industrial chromatograph obtained was a standard commercial instrument of the type commonly used in industry. It was completely automatic in operation and incorporated a bar graph type of data presentation in which only the peak heights of the components of interest are recorded. By manual operation, a complete chromatogram in the usual form also may be obtained. The column system was designed by the manufacturer for the separation of the gases.

An evaluation at NRL revealed some serious shortcomings of the instrument. The columns used were not suitable for the separation of Freon-12 and gave poor resolution for some of the other components. The detector lacked adequate sensitivity for the detection of those gases in the parts-per-million range. An excessive amount of base-line drift was found also. It subsequently was modified by the manufacturer at his plant to attempt to correct these deficiencies.

The modifications did not significantly improve the sensitivity of the instrument. With the present thermal-conductivity detector and column configuration, the maximum sensitivity that could be obtained for carbon monoxide was a full-scale deflection for about 800 ppm. This is not satisfactory for monitoring shipboard carbon monoxide.

It has been concluded that the likelihood of increasing the sensitivity of this unit to the desired level is too small to merit further work. It is currently planned to discontinue the attempt to monitor carbon monoxide and methane with this instrument and to redesign the column system for the measurement of the other components only. A thorough study of the capability of this chromatograph for monitoring these remaining gases will be carried out, with particular emphasis on evaluating the automatic features of the instrument.

### Semiautomatic Chromatograph

The other chromatograph was a specially built instrument designed specifically for this application. Its detection system consisted of two thermal-conductivity cells with high-sensitivity thermistors. It was semiautomatic in operation; sample injection and column switching were done automatically, peak attenuation manually. Data presentation was based on the usual chromatogram displayed on two separate strip-chart recorders.

Except for poor sensitivity to carbon monoxide and methane, the instrument gave generally good performance. More than adequate sensitivity was available for the detection of the other components. Its response to carbon monoxide was too low to be considered useful for the routine shipboard monitoring of this gas. Although Freon-12 also must be measured in the parts-per-million range, its detection does not present as much of a problem as does carbon monoxide and methane. Freon-12 is one of the first components to be eluted from the column in which it is separated. Thus it emerges as an extremely sharp peak, a condition highly favorable to high detection sensitivity. Methane and carbon monoxide are the last of the components to be eluted from the molecular-sieve column.

Hence they produce rather broad peaks leading to reduced detection sensitivity. It has been concluded that the presently available thermal-conductivity detection systems are not capable of providing the sensitivity needed for monitoring carbon monoxide.

Except for carbon monoxide and methane, the instrument showed excellent repeatability for samples of Mark III calibration gas and compressed submarine air run intermittently over a three-month period. The precision requirements of Table 8 were readily met and for most gases surpassed. The high level of precision was obtained by manually measuring peak heights. If an automatic data-presentation system such as a bar graph or meter were used, the resolution between some of the components would have to be improved. In some cases, a trace-gas peak following a larger one due to a gas present in high concentration is elevated from the base line by a residual tail from the larger peak. An automatic readout system could not discriminate between the residual tail and the true height of the peak.

#### Karmen Detector

Because of the difficulty of obtaining sufficient sensitivity from thermal conductivity to monitor carbon monoxide, the possibility of using one of the ultrasensitive ionization detectors was explored. Unfortunately, most of the common types of ionization detectors do not respond to fixed gases of the type to be monitored. Dr. Karmen at NIH recently introduced a new type of detector based on the electrical-breakdown properties of helium (2). The manufacturer of the semiautomatic chromatograph found this detector to be extremely sensitive to fixed gases and recommended its use to measure carbon monoxide in an atmosphere-analyzer chromatograph. A contract for the modification of the semi-automatic chromatograph was made, and one of the thermal-conductivity detectors was replaced by one of the Karmen type.

The Karmen detector is based on the principle that a stable, low-current, electrical discharge can be initiated in an inert gas such as helium by an electric field. As long as pure helium flows through the detector, the voltage of the discharge remains constant. The addition of a small quantity of a foreign gas changes the potential of the discharge, and the voltage change serves as a measure of the concentration of this gas in the detector.

The detector consists of a metal block containing a cylindrical hole  $3/16$  in. in diameter and about one inch in length. This serves as the cathode of the discharge and is at ground potential. The anode is a rod  $1/16$  in. in diameter mounted axially in the hole of the cathode by a good insulator. Ports are provided so that carrier gas can flow in one end and out the other. The anode is connected to a high-voltage power supply through a high-value resistor that limits the current to about one microampere. Changes in the potential of the anode are measured by an appropriate electronic device.

Studies at NRL have confirmed that the Karmen detector is indeed highly sensitive to the fixed gases. Full-scale response has been obtained for less than 100 ppm of carbon monoxide in spite of the long retention time, over 20 minutes, produced by the present column system. This sensitivity can be even further increased by a factor of 20 to 40 times without base-line noise becoming objectionable.

Although the use of this detector is highly desirable from the standpoint of sensitivity, it has some serious disadvantages. It is not linear over a wide range. With increasing concentration of a foreign gas in the detector, the breakdown potential first decreases until it reaches a minimum and then increases with a different slope. A component in low concentration thus produces a simple negative peak, whereas one in moderate or high concentrations produces a W-shaped curve. The minimum in the breakdown voltage-concentration curve makes difficult the measurement of both the high and low components of a sample in a single run. In order to use this detector in an atmosphere monitor, it must be

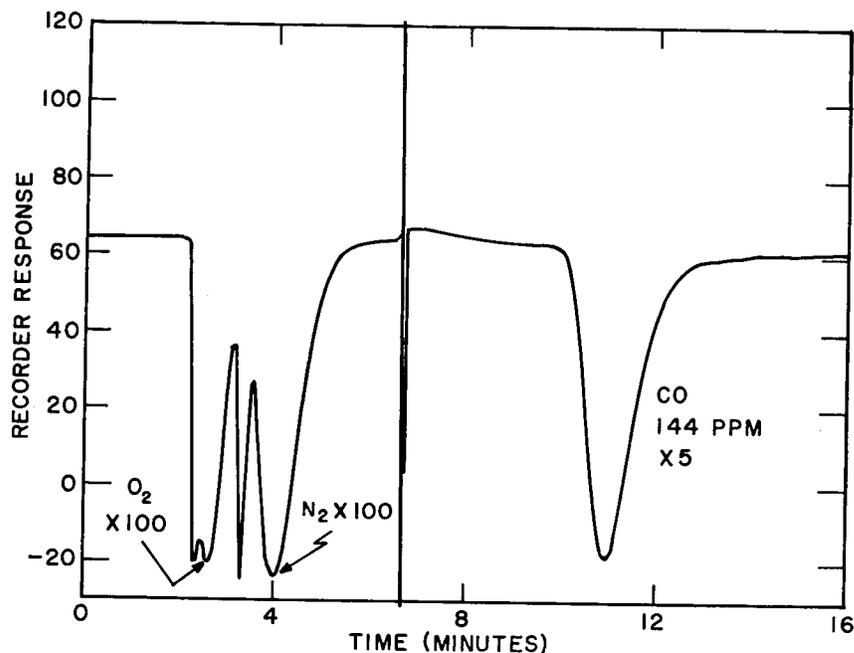


Fig. 17 - Separation of a mixture of CO in air by a molecular-sieve column and detected by a Karmen detector; sample size 0.2 ml

established that a sample size can be chosen so that the concentration of each component of interest falls on a linear portion of the curve, or that separate samples of different sizes must be injected to measure components in high and low concentration ranges.

Figure 17 illustrates the response of the Karmen detector to a mixture of 144 ppm of carbon monoxide in air. The reversal of the oxygen and nitrogen peaks can be seen. Greater sensitivity to carbon monoxide may readily be obtained by increasing the sample size or decreasing the attenuation.

The response of the Karmen detector is sensitive to the purity of the helium used. During the initial trials at NRL, the high sensitivity obtained by the manufacturer could not be reproduced. It was found that this was due to contamination of the helium with about 500 ppm of air, enough to decrease the sensitivity by more than a thousand times. The contaminated tank of helium used appears to be an isolated case; subsequent cylinders of Grade A helium obtained from Navy stock have performed satisfactorily. Impurities in helium in the low parts-per-million range do change the response of the detector but do not lower it enough to be troublesome. Response changes due to varying amounts of impurities in different helium cylinders can be compensated for readily by a simple recalibration step.

Tests of the Karmen detector to date have shown an excessive amount of base-line drift, enough to make automation difficult. The cause of the drift is not apparent. With only helium flowing through the detector, the instrument appears to remain quite stable for days. Periodic sample introduction seems to increase the drift rate greatly. The response of the chromatograph to the same sample introduced at different times has not been constant. It is now believed that this may have a direct correlation with the drift.

The high sensitivity attainable with the Karmen detector justifies further investigation of this system. Its nonlinearity of response restricts its usefulness somewhat and

will probably limit its use to the trace gases only. It is hoped that the drift and varying-response problems can be solved and that this detector can be incorporated into a useful atmosphere-analyzer chromatograph.

#### CONCLUSIONS AND FUTURE PLANS

Studies with two gas chromatographs designed for atmosphere analysis and equipped with thermal-conductivity detectors have indicated that all the gases of Table 8 except carbon monoxide can be measured with high precision if the chromatogram is recorded in the usual fashion and of peak heights are measured manually. It has been concluded that presently available thermal-conductivity detectors are not capable of delivering the desired sensitivity for carbon monoxide and methane. Methane is not determined by the present atmosphere analyzer. It now appears that the need for monitoring methane does not justify the added complications to a chromatograph that should be required for its detection. Methane is eluted directly after nitrogen and in low concentrations is obscured by the tail of the nitrogen peak. It is currently planned to discontinue the attempt to monitor carbon monoxide and methane with the industrial chromatograph and to redesign the column system for the measurement of the other components only. A thorough study of the capability of this chromatograph for monitoring these remaining gases will be carried out, with particular emphasis on evaluating the automatic features of the instrument.

The Karmen detector is extremely sensitive to the fixed gases and shows promise for the determination of carbon monoxide. Further work on this detector is necessary to eliminate drift and varying response problems. The problem of incomplete separation of carbon monoxide from the tail of the nitrogen peak is still at hand and becomes more serious with the use of the Karmen detector. Some studies of potentially more efficient columns are contemplated.

Because of the very limited linear range of the output of the Karmen detector, it is now felt that the most practical approach to an atmosphere-analyzer chromatograph might be the use of the Karmen detector for carbon monoxide detection only and thermal conductivity for the other components. The use of the Karmen detector for carbon monoxide detection only and some suitable valving should enable a better separation to be made of carbon monoxide from nitrogen and prevent other components from entering the detector that may have an adverse effect on it. In this way it is hoped that the stability and reliability of the detector might be improved.

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## Chapter 7

# Organic Contaminants, Sampling and Analysis

J. E. Johnson

### INTRODUCTION

Organic compounds are an important class of trace contaminants which are present in submarine atmospheres. It is important to identify the compounds present and estimate the concentrations in the atmosphere so that toxicologists may consider their significance in terms of the continuous exposure of 60 days or longer often met in operations today. In some cases the decomposition of such compounds in the catalytic burner must be considered in terms of toxic or corrosive products which may be emitted.

The study of organic contaminants in submarine atmospheres has progressed along several fronts. The routine sampling system (1) based on collection of vapors on activated carbon and subsequent desorption at a Navy laboratory has been continued successfully by a number of submarines, especially the SSB(N) type. Also, valuable data have been gained from samples of main-filter carbon which have been submitted by several nuclear submarines.

In addition to the carbon-sampling program, the detailed analysis of samples obtained from the submarines by several means has been pursued. This approach has included more detailed study of the oils obtained by desorption from carbon. For example, identification and quantitative estimation of a number of aromatic hydrocarbons has been accomplished. Compressed-air samples taken on board several operating submarines have been analyzed at NRL. Special sampling techniques have been developed for analysis of aldehydes in submarine atmospheres.

### CARBON-SAMPLING PROGRAM

In the current operation of this program, the activated carbon, which is contained in flat, pancake-type cartridges, is exposed in a sampler-blower apparatus by shipboard personnel. During 1962, most of the exposed canisters were shipped to the Materials Laboratory, now the U.S.N. Applied Science Laboratory, at the New York Naval Shipyard for desorption to establish an estimate of the concentration of organic contaminants, primarily hydrocarbons, present in the ships' atmospheres. In addition to the distribution of these data (2) to the operating submarines and other interested groups, sealed samples of desorbed oil were sent to NRL for further study. The Bureau of Ships has recently transferred the desorption-analysis work from the Applied Science Laboratory to the U.S.N. Marine Engineering Experiment Laboratory, Annapolis, Md.

A summary of the analyses made on samples taken during 1962 by operating submarines and analyzed at USNASL is given in Table 9. Samples were obtained from ten different submarines, representing more than 20 different patrols or cruises. These data show generally that the SSB(N) submarines particularly had achieved fairly good control of the hydrocarbon contamination. Occasional samples taken from main filter carbon have confirmed these analytical carbon data.

Table 9  
Summary of Total Hydrocarbon Concentrations  
Found by Carbon Sampling Method

Average Exposure Dates	Concentration (mg/m <sup>3</sup> )	Ship
2-62	0-3	GEORGE WASHINGTON
2-62	2-10	ABRAHAM LINCOLN
1-62	0-22	THEODORE ROOSEVELT
3-62	40-72	ETHAN ALLEN
3-62	19-30	ROBERT E LEE
5-62	0-13	ROBERT E LEE
4-62	0-40	PATRICK HENRY
5-62	0-3	SCAMP
7-62	0-2	GEORGE WASHINGTON
7-62	0-2	ETHAN ALLEN
8-62	0-94	ROBERT E LEE
8-62	0	THEODORE ROOSEVELT
7-62	0	PATRICK HENRY
8-62	15-80	NAUTILUS
10-62	0	PATRICK HENRY
6-62	1-20	ABRAHAM LINCOLN
9-62	0-12	ABRAHAM LINCOLN
10-62	1-22	SHARK
10-62	0-54	GEORGE WASHINGTON
10-62	0	ETHAN ALLEN

Table 10  
Hydrocarbon Content of Atmosphere of  
USS ROBERT E LEE Based on Carbon Sampling

Number of Hours Submerged	Hydrocarbon Content (mg/m <sup>3</sup> )
1	0
40	0
120	Started painting
373	19
495	55
1023	94
1119	53

The results in Table 9 based on samples of carbon from ROBERT E LEE on the patrol in which the concentration of hydrocarbons ranged from 0 to 94 mg/m<sup>3</sup> are explained by the fact that a heavy application of an oil-based paint occurred during this patrol. The data from the carbon samples analyzed are given in Table 10. No painting was done during the first five days (120 hours) of this submergence, and this is reflected by the data. During the rest of the patrol 63 gallons of paint were used, an average of about one gallon per day. The total amount of solvent released into the atmosphere (about 3.3 lb per gallon of paint) represents a gross rate of contamination. In spite of the removal by combustion in the CO/H<sub>2</sub> burner and adsorption by the carbon filter beds,

the carbon-desorption data show that a total hydrocarbon concentration of at least 94 mg/m<sup>3</sup> was reached in the atmosphere. Subsequent analysis at NRL showed that the aromatic hydrocarbon content of the desorbed oil was 23.1 percent, corresponding to 21.7 mg/m<sup>3</sup> of aromatic hydrocarbons in the atmosphere. The fact that buildup of the hydrocarbon concentration was gradual is doubtless attributable in large part to the removal by adsorption on the main-filter carbon. Of course, during this entire period the CO/H<sub>2</sub> burners were destroying large amounts of hydrocarbon vapors. Unfortunately, samples of the main-filter carbon were not received at NRL for analysis and verification. However, it was calculated that if there had been no filter carbon used, and if the burner was the only removal agent, the equilibrium concentration during almost the entire patrol would have been at least 150 mg/m<sup>3</sup> of hydrocarbon vapors.

#### HYDROCARBON ANALYSIS

Special interest in the potential toxicity of the aromatic hydrocarbons makes more detailed analyses for this group of importance. In Table 11 are listed additional analyses of "hydrocarbon oils" which had been recovered from carbon samples. With the exception of a sample from PATRICK HENRY, all the samples in this group were very close to the average figure of 27.7 percent aromatics. Whereas there is presently no good explanation for the nonconformity of the PATRICK HENRY sample, it is worth noting that this sample is one taken from a main filter carbon bed after 1100 hours exposure. There seems to be a tendency for aromatic-hydrocarbon content of the carbon to increase as exposure time becomes very long.

Table 11  
Analysis\* of Submarine "Oils" by Hydrocarbon Types

Sample	Ship	Content (Volume percent)		
		Aromatics	Middle † Fraction	Saturates
C-214	ABRAHAM LINCOLN	29.6	7.3	63.1
C-201	GEORGE WASHINGTON	28.2	6.3	65.6
C-221	SNOOK	25.2	7.9	66.8
N-662	ROBERT E LEE	23.1	3.4	73.6
N-689	NAUTILUS	23.7	5.9	70.4
N-554	PATRICK HENRY	37.0	6.5	56.5
Average		27.7	6.2	66.0

\*Determined by the FIA Method (ASTM 1319-58).

†Usually referred to by petroleum chemists as olefins.

It is also of interest that the average of 27.7-percent aromatics, although distinctly lower than earlier reports of 35 to 50 percent (3), is still considerably higher than has been found in several paint thinners which have been analyzed by the FIA method (4). The "saturates" fractions in Table 11 have been checked several times by infrared analysis and have been shown to contain less than 0.5 percent aromatics (the limit of the infrared

method under the conditions used). This fraction is very complex and is known to contain isoparaffins, n-paraffins, and naphthenes. The "middle fraction" is normally thought of by users of the FIA analytical method as "olefins," or nonaromatic unsaturated hydrocarbons. More detailed studies of several of these fractions indicates that it is a very complex mixture which is only partly olefinic in nature.

Table 12  
Analyses for Volatile Aromatic Hydrocarbons

Hydrocarbon	Content, Percent of Total Sample			
	N-554 PATRICK HENRY		N-662 ROBERT E LEE	
	MATLAB*	NRL †	MATLAB*	NRL †
Benzene	3.5	0.3	4.1	0.4
Toluene	5.4	2.7	6.8	3.7
m/p-Xylene	15.2	6.3	13.0	12.5
o-Xylene	16.1	2.4	6.6	3.4
Subtotal	40.2	11.7	30.5	20.0
Total Aromatics by FIA Method (NRL)	-	37.0	-	23.1

\*Method based on an indirect chromatographic analyses (Ref. 2, Report 30) (now USNASL)

†Method based on FIA separation (Ref. 4) followed by direct chromatographic analysis

In the more recent reports (Ref. 2, Reports 30-47) by USNASL of hydrocarbon content based on carbon-desorption analysis, some of the samples were reported to contain stated percentages of several individual aromatic hydrocarbons based on an analytical technique described in Ref. 2, Report 30. This is a gas chromatographic method in which the aromatic hydrocarbons, benzene, toluene, m,p-xylene, and o-xylene are determined by difference following extraction with concentrated sulfuric acid. Two of these same oil samples were analyzed in detail at NRL by a direct chromatographic method based on FIA fractionation. These data are given in Table 12, together with the USNASL data. The greatest difference found is an approximate ten-fold magnification of the benzene values by the USNASL indirect method. It is significant also that the concentration of several of the other hydrocarbons were found to be much higher by the indirect method. In both samples the aromatic content represented by these five compounds as determined by the indirect method was in fact definitely higher than the total aromatics found by the FIA method. Consequently, it must be concluded that the data reported in Ref. 2 on aromatic hydrocarbons are significantly in error.

Detailed analyses have shown that the aromatic fractions of these oils are indeed represented by a great many compounds. To illustrate this fact, quantitative analyses of the aromatic fractions of these two oils in terms of individual hydrocarbons are given in Table 13. In these cases the total aromatics represented by 13 individual compounds from

Table 13  
Composition of Aromatic Fractions of Submarine  
Oils Desorbed from Activated Carbon

Hydrocarbons	Concentration (Percent of Aromatic Fraction)	
	N-554 PATRICK HENRY	N-662 ROBERT E LEE
Benzene	1.5	1.6
Toluene	11.8	9.9
Ethylbenzene	8.7	10.0
m/p-Xylene	27.1	33.5
o-Xylene	10.2	9.3
i-Propylbenzene	1.3	3.2
n-Propylbenzene	1.5	1.9
m/p-Ethyltoluene	4.3	6.0
o-Ethyltoluene	-	-
1,3,5-Trimethylbenzene	3.3	5.1
1,2,4-Trimethylbenzene	6.5	7.2
Subtotal (Percent of aromatic fraction)	76.2	87.7

benzene to 1,2,4-trimethylbenzene are 76.2 percent and 87.7 percent of the total aromatics fraction. The portion represented by the compounds toluene through o-xylene is proportionately much higher than would be expected in straight petroleum distillates of this boiling range, such as a diesel fuel or paint thinner. Studies of catalytic combustion of individual hydrocarbons over Hopcalite suggest that some enrichment of aromatic hydrocarbons may result from their somewhat greater resistance to combustion. Additional analyses leading to the identification and estimation of individual aromatic hydrocarbons are being pursued.

#### TOTAL HYDROCARBON CONTENT BY DIRECT ANALYSIS

In preparation for studies of the hydrocarbon content of submarine atmospheres in situ, development of a total hydrocarbon method based on a flame ionization detector has been underway. The goal is to achieve a method which can give the total hydrocarbon content in a few minutes on shipboard. The flame ionization detector has a very high sensitivity, which is desirable for this application. Unfortunately, the presence of relatively large concentrations of methane and Freon precludes the possibility of a continuous measurement, because the flame ionization detector responds to these two compounds also. It is often the case that either one of these compounds, always present in the atmospheres of nuclear submarines, may more than equal in concentration the total concentration of all other hydrocarbons. Consequently, in order to get a good estimate of the latter, some provision must be made to eliminate the interference of methane and the Freons.

The approach currently under development is based on a gas chromatographic method known as the "backflush" technique. An interesting point in this development is that it

results in an elegant determination of methane and Freon-12 while at the same time removing them from interfering in the total hydrocarbon analysis.

The approximate description of the method at the present state of development is as follows: A sample of submarine air (about 5 cc) is put into the system either by syringe injection or by means of a sampling loop. The sample is swept into a chromatographic column, and the column is flushed with a 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. The area represented by this peak is measured and the total hydrocarbon content is calculated, based on calibrations with air samples of known hydrocarbon content.

In this regard, several samples have been obtained from operating submarines by means of an oil-less compressor used to fill stainless steel bottles up to 180 psi of submarine air. These bottles of air are returned to NRL to be used in developing the back-flush method. It will be necessary to determine the actual hydrocarbon content in the submarine's atmosphere to compare with that found in the bottle samples. But these samples permit testing the procedure against all the complexities of authentic submarine atmospheres.

#### NONHYDROCARBON ORGANIC CONTAMINANTS

Eye-irritation difficulties have been reported by several nuclear submarines (5). Because of these reports, some attention has been given to sampling and analysis techniques which are specific to the detection and determination of aldehydes. Certain aldehydes such as acrolein, formaldehyde, and crotonaldehyde are reported to be irritating to the eyes at concentrations in air of as little as one part per million or less (6).

An analytical method for total aldehydes was developed from a method studied at the Bureau of Standards (7). The detection of aldehydes by this procedure is basically dependent on the catalysis by the aldehyde group of the oxidation of p-phenylenediamine by hydrogen peroxide. The method as developed at NRL was demonstrated to be sensitive to as little as 0.01 ppm of total aldehyde. It was determined that the response was very nearly equal for all aldehydes studied, including acrolein, formaldehyde, acetaldehyde, and crotonaldehyde.

Specific methods for the estimation of formaldehyde and acrolein, based on colorimetric principles, have been adapted from procedures studied at the Air Pollution Laboratories of the Department of Health, Education, and Welfare in Cincinnati, Ohio.

A special sampling scheme based on the use of bubblers containing sodium bisulfite has been developed which allows samples taken on shipboard to be sent to NRL for analysis. These samples have been successfully analyzed by colorimetric and gas chromatographic methods.

Traces of aldehydes such as acetaldehyde and formaldehyde have been found in a few instances (5). However, acrolein, which is a powerful eye irritant, has not been found.

#### CONCLUSIONS

Much useful information has already been obtained by both direct and indirect methods on the organic-vapor contaminants present in submarine atmospheres. In spite of its acknowledged deficiencies, the carbon-sampling program has shown that it is possible to follow hydrocarbon concentration changes in the ship as a function of contamination by paint. From the oils obtained from the analytical and main filter carbons it is also possible

to determine the amounts of aromatics and aliphatics and to identify most of the aromatics present. However, the present carbon-sampling scheme does not allow for the ship's company to obtain an analysis of organic pollutants in situ, hence development of a direct method for hydrocarbon analysis is desirable. Preliminary studies based on a gas chromatographic "back-flush" technique indicate that development of this procedure for analysis of total hydrocarbons on shipboard may be feasible.

#### FUTURE WORK

Several instances of severe local corrosion in nuclear submarines have been reported during the past year. Some work with the aqueous phase obtained during steam desorption of activated carbon indicates that useful information may be obtained by this means concerning the acidic components of the atmosphere. It is planned to pursue this effort further.

Further detailed analysis of the desorbed oils is planned. Attention is being directed toward high-molecular-weight hydrocarbons as well as organic compounds other than hydrocarbons.

The development of analytical methods for the determination of total hydrocarbons on shipboard is being pursued. This will include further refinement of the back-flush chromatographic method.

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## Chapter 8

### Chemical Constituents of Nuclear-Submarine Atmospheres

H. W. Carhart and V. R. Piatt

#### BACKGROUND

As is obvious from the earlier chapters, and reports of this series, the problem of analyzing nuclear-submarine atmospheres in the presence of a large number of interfering contaminants is both critical and extremely difficult. The long and progressive experience of NRL in investigating the newer analytical techniques and applying them directly to the "best closed space on earth" has exemplified the need for superlative equipment and techniques to get a truthful picture of the potentially toxic chemical hazards in man-occupied closed spaces. A summary of quantitative data has appeared in two earlier reports (1,2), and a more recent list, though on a qualitative basis only, appeared in the previous progress reports of this series (3,4). With the passage of time and in face of continued (but inadequate) references to this earlier data by scientists in the submarine and other closed-space programs, it has become desirable to bring the data up to date.

#### PRESENT STATUS

Because the original lists (1,2) of identified atmospheric components have since been augmented largely by hydrocarbons, it is convenient to separate the lists into hydrocarbons and nonhydrocarbons. Thus Tables 14 and 15 comprise those atmospheric components which have been identified quantitatively in nuclear-submarine atmospheres, with the hydrocarbons in Table 15 only. It is noted that most of the atmosphere-concentration changes since the earlier lists have been toward lower values, indicating in general that the nuclear submarines are now much cleaner. It is particularly gratifying to see the large decrease in hydrocarbon concentrations. However, a notable exception is the Freon-12 concentration, which often hovers between 300 and 400 ppm in some submarines, yet which is less than 50 ppm in many of the submarines. The improved atmospheric picture is probably indicative of one or more of the following conditions: (a) the increased electrostatic precipitator capacity decreased the amount of aerosols passing through the burner, (b) improved ship control of painting just before or during submergence or of other sources releasing organic matter into the atmosphere, and (c) improvements in operation and maintenance of the CO<sub>2</sub> scrubber and CO burner.

The meaning of the relative concentrations of aromatic and aliphatic concentrations has been described adequately in Chapter 7. It should be pointed out that the accent in analytical objectives has been on hydrocarbons; thus less attention has been paid to the oxygenated and otherwise modified hydrocarbons, many of which are more easily burned in the CO burner.

The earlier list of compounds identified only qualitatively in submarine atmospheres has been decreased by those compounds subsequently determined on a quantitative basis, but has been considerably increased by the addition of numerous hydrocarbons, again resulting in a splitting of the list, as seen in Tables 16 and 17. Most of the hydrocarbons

Table 14  
Compounds, Other Than Hydrocarbons, Quantitatively Identified  
in Nuclear-Submarine Atmospheres

Material	Chemical Formula	Highest Concentration Normally Found	Reference	Maximum Acceptable Concentration in ppm (ACGIH)*	90-Day Exposure Limits in ppm*(5)
Ammonia	NH <sub>3</sub>	2 ppm	6	100	25
Arsine	AsH <sub>3</sub>	0.015 ppm †	7	0.05	0.01
Carbon Dioxide	CO <sub>2</sub>	0.8 - 1.1%	8	5,000	10,000
Carbon Monoxide	CO	30 ppm †	6	100	25
Chlorine	Cl <sub>2</sub>	1 ppm	9	1	0.5
Freon-12	CCl <sub>2</sub> F <sub>2</sub>	50 ‡	8	1,000	500
Hydrogen Fluoride	HF	0.3 ppm	10	3	0.1
Hydrogen	H <sub>2</sub>	0.35%	8	-	3% §
Methyl Alcohol	CH <sub>3</sub> OH	6 ppm	10	200	3
Methyl Chloroform	CH <sub>3</sub> CCl <sub>3</sub>	6 ppm	11	500	-
Monoethanolamine	HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	<1 ppm	10	0.5 (tentative)	1
Nitrogen	N <sub>2</sub>	80%	Numerous	-	-
Nitrogen Dioxide	NO <sub>2</sub>	0.1 ppm	10	5	0.5
Nitrous Oxide	N <sub>2</sub> O	27 ppm	10	-	-
Oxygen	O <sub>2</sub>	20%	Numerous	-	17% min
Ozone	O <sub>3</sub>	0.05 ppm	10	0.1	0.05
Stibine	SbH <sub>3</sub>	0.01 ppm	7	0.1	0.05
Vinylidene Chloride	CH <sub>2</sub> CCl <sub>2</sub>	2 ppm	11	-	-
Water Vapor	H <sub>2</sub> O	60% RH	Numerous	-	-

\*Limit either not applicable or not established by American Conference of Governmental Industrial Hygienists for materials listed with a dash in this column.

†By Drager arsine unit; other indications no higher than 0.005 ppm.

‡Values in excess of 25 ppm may include high N<sub>2</sub>O concentration as measured on the Mk III Analyzer.

§Values up to 400 ppm on some ships apparently due to correctible leaks.

§Based on explosive limit.

Table 15  
Hydrocarbons Quantitatively Identified in Trace Amounts  
in Nuclear-Submarine Atmospheres

Material	Chemical Formula	Highest Concentration Normally Found (ppm)	Reference	Maximum Acceptable Concentration in ppm (ACGIH)*	90-Day Exposure Limits(5)*
Acetylene	$C_2H_2$	0.5	10	-	2.5% †
Benzene	$C_6H_6$	0.01	Chapter 7	25	-
Ethylbenzene	$C_6H_5C_2H_5$	0.21	Chapter 7	200	-
m,p-Ethyltoluene	$CH_3C_6H_4C_2H_5$	0.34	Chapter 7	-	-
Hydrocarbons, total (excl. Methane) ‡	$C_xH_y$	25 †	Chapter 7	-	10 ppm (12)
Mesitylene	$1,3,5-(CH_3)_3C_6H_3$	0.29	Chapter 7	-	-
Methane	$CH_4$	118	13	-	5.3% †
iso-Propylbenzene	$C_6H_5CH(CH_3)_2$	0.04	Chapter 7	-	-
n-Propylbenzene	$C_6H_5(CH_2)_2CH_3$	0.07	Chapter 7	-	-
Pseudocumene	$1,2,4-(CH_3)_3C_6H_3$	0.57	Chapter 7	-	-
Toluene	$C_6H_5CH_3$	0.25	Chapter 7	200	20 ppm
m,p-Xylene	$(CH_3)_2C_6H_4$	0.95	Chapter 7	200	3 ppm
o-Xylene	$1,2-(CH_3)_2C_6H_4$	0.32	Chapter 7	200	1 ppm

\*Limit either not applicable or not established for materials listed with a dash in this column.

†Based on explosive limit.

‡Total of all hydrocarbons, excluding methane but including aromatic and aliphatic and irrespective of individual identification or measurement.

§Most values currently reported as less than 5 ppm.

Table 16  
Compounds, Other Than Hydrocarbons, Qualitatively Identified in Trace  
Amounts in Nuclear-Submarine Atmospheres

Material	Chemical Formula	Reference	Maximum Acceptable Concentrations in ppm (ACGIH)*
Acetaldehyde	$CH_3CHO$	14	200
Acetic Acid	$CH_3COOH$	14	10
Acetone	$CH_3COCH_3$	14	1,000
Ethyl Acetate	$CH_3COOC_2H_5$	15	400
Ethyl Alcohol	$C_2H_5OH$	14	1,000
Formaldehyde	$HCHO$	16	5
Freon-114	$CF_2ClCF_2Cl$	17	1,000
Isopropyl Alcohol	$CH_3CHOHCH_3$	15	400
Methyl Ethyl Ketone	$CH_3COCH_2CH_3$	15	200
Methyl Isobutyl Ketone	$CH_3COCH_2CH(CH_3)_2$	14	100
Sulfur Dioxide	$SO_2$	17	5

\*MAC either not applicable or not established for materials listed with a dash in this column.

Table 17  
Hydrocarbons Qualitatively Identified in Nuclear-Submarine Atmospheres

Material	Chemical Formula	Reference	Maximum Acceptable Concentrations in ppm (ACGIH)*
iso-Butane	$(\text{CH}_3)_2\text{CHCH}_3$	15	-
n-Butane	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	15	-
iso-Butene	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	15	-
1-Butene	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	15	-
2-Butene (trans)	$\text{CH}_3\text{CH}=\text{CHCH}_3$	15	-
2-Butene (cis)	$\text{CH}_3\text{CH}=\text{CHCH}_3$	15	-
n-Butylbenzene	$\text{C}_6\text{H}_5(\text{CH}_2)_3\text{CH}_3$	15	-
sec-Butylbenzene	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$	15	-
tert-Butylbenzene	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_3$	15	-
n-Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	18	-
1-3-Dimethyl-5-ethylbenzene	$1,3-(\text{CH}_3)_2-5-\text{C}_2\text{H}_5\text{C}_6\text{H}_3$	17	-
n-Dodecane	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	15	-
Ethane	$\text{C}_2\text{H}_6$	15	-
Ethylcyclohexane	$\text{C}_2\text{H}_5\text{C}_6\text{H}_{11}$	18	-
Ethylene	$\text{C}_2\text{H}_4$	17	-
o-Ethyltoluene	$1-\text{CH}_3-2-\text{C}_2\text{H}_5\text{C}_6\text{H}_3$	15; also Ch. 7	-
n-Heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	18	500
n-Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	18	500
Isoprene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	15	-
Methylcyclohexane	$\text{CH}_3\text{C}_6\text{H}_{11}$	18	500
n-Nonane	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	18	-
n-Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	18	500
iso-Pentane	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	15	-
n-Pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	18	1,000
Propylene	$\text{CH}_2=\text{CHCH}_3$	15	-
n-Undecane	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3$	18	-

\*MAC either not applicable or not established for materials listed with a dash in this column.

in Table 17 were included in the list prepared in the last annual progress report (4). It is noted that several of the compounds from the latter list have now been included in Table 15 in trace quantities after laborious analysis of chromatographic charts, which could well be extended to still other compounds if a need arose.

As the result of this continuing analytical effort, a further breakdown has appeared desirable of those compounds previously reported (1,2) to exist as gases in practically all cigarette smoke. Thus it is of interest to note that eight compounds were identified earlier in both cigarette smoke and nuclear-submarine atmospheres (Table 18); seven additional compounds appearing in cigarette smoke have subsequently been identified in nuclear-submarine atmospheres (Table 19); nine compounds appearing in cigarette smoke have not yet been found in a nuclear submarine (Table 20). There appears to be no question but that the latter compounds do exist, at least momentarily, in the nuclear submarine as long as smoking is permitted.

Table 18  
Gases and Vapors Previously (1,2) Reported Both in Cigarette  
Smoke and in Nuclear Submarine Atmospheres

Material	Chemical Formula	Maximum Acceptable Concentration in ppm (ACGIH) *
Acetylene	$C_2H_2$	-
Benzene	$C_6H_6$	25
Carbon Dioxide	$CO_2$	5,000
Carbon Monoxide	$CO$	100
Ethylene	$C_2H_4$	-
Formaldehyde	$HCHO$	5
Methane	$CH_4$	-
Methyl Alcohol	$CH_3OH$	200

\*MAC either not applicable or not established for materials listed with a dash in this column.

Table 19  
Gases and Vapors Previously (1,2) Reported in  
Cigarette Smoke and Subsequently Identified in Nuclear  
Submarine Atmospheres

Material	Chemical Formula	Maximum Acceptable Concentration in ppm (ACGIH) *
Acetaldehyde	$CH_3CHO$	200
Acetone	$CH_3COCH_3$	1,000
iso-Butylene	$(CH_3)_2C=CH_2$	-
Ethane	$C_2H_6$	-
Isoprene	$CH_2=C(CH_3)CH=CH_2$	-
Propylene	$CH_2=CHCH_3$	-
Methyl Ethyl Ketone	$CH_3COCH_2CH_3$	250

\*MAC either not applicable or not established for materials listed with a dash in this column.

Table 20  
Gases and Vapors Previously (1,2) Reported in Cigarette Smoke  
But Not Yet Found in Nuclear Submarine Atmospheres

Material	Chemical Formula	Maximum Acceptable Concentration in ppm (ACGIH)*
Butadiene	$\text{CH}_2=\text{CHCH}=\text{CH}$	1,000
Diacetyl	$\text{CH}_3\text{COCOCH}_3$	-
Furan	$\text{C}_4\text{H}_4\text{O}$	10 (19)
Hydrogen Cyanide	$\text{HCN}$	10
2-Methyl Furan	$\text{C}_4\text{H}_3\text{OCH}_3$	-
Methyl Chloride	$\text{CH}_3\text{Cl}$	100
Furfuraldehyde	$\text{C}_4\text{H}_3\text{OCHO}$	-
Propionaldehyde	$\text{C}_2\text{H}_5\text{CHO}$	-
Diethyl Ketone	$\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$	-

\*MAC either not applicable or not established for materials listed with a dash in this column.

It should also be pointed out that these tables do not cover the particulate matter in smoke, but this has already been included in the first report of this series (2). The relative toxicological significance of particulate matter versus gases is beyond the scope of this report, although it is obvious that both types of components affect greatly the performance of both man and equipment in the submarine.

In analyzing atmospheric samples taken from nuclear submarines, we have seen chromatographic peaks far exceeding 200 in number, with many of these obviously being multiple peaks. No real effort has been made to identify other than the most prominent peaks. This example demonstrates that there are at least 200 discrete compounds existing in submarine atmospheres, albeit in low concentrations.

## CONCLUSIONS

With such large numbers of atmospheric contaminants assailing the eyes and noses in the nuclear submarines, it is surprising that the crews are not more affected than they are. Moreover, many of the known eye and nose irritants are effective in much lower concentrations than have been measured, and some of the other contaminants affect the equipment unseen by the human eye until it is too late. It is therefore advisable to continue the exploration and analysis of submarine atmospheres until these sensory and equipment effects can be related to their ultimate causes. The toxicological effects of these trace contaminants are largely still unknown; they are difficult to reconnoiter until after more quantitative determinations have been made.

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## Chapter 9 Hopcalite-Catalyzed Combustion

J. G. Christian

### INTRODUCTION

Previous laboratory studies have shown that Hopcalite is effective for catalyzing the combustion of organic compounds of several structural types as well as aerosols of several oils (1,2,3).

Although hexane and the higher aliphatic hydrocarbons are completely oxidized over Hopcalite at 300°C, methane is oxidized but slightly at this temperature and only 30 percent even at 400°C. It was thus of interest to investigate the behavior of several aliphatic hydrocarbons of intermediate chain length, e.g., ethane and propane.

Several organic nitrogen compounds of selected structural types as well as ammonia were chosen for study because of the known or suspected presence of such compounds aboard nuclear submarines. In addition, nitrogen compounds were under suspicion as possible sources of nitrous oxide. Nitrous oxide possesses infrared absorption characteristics which cause interference with the shipboard carbon monoxide infrared channel in the Mark III Atmosphere Analyzer. It was therefore necessary to learn whether nitrogen compounds known or suspected to be aboard could lead to amounts of nitrous oxide sufficiently high to produce spurious carbon monoxide readings.

Freon-11 (trichlorofluoromethane) was studied further, since it is being used aboard some nuclear submarines. Improved chromatographic equipment and procedures permitted the quantitative description of this compound's behavior upon passage through the burner.

### APPARATUS AND PROCEDURE

The laboratory-scale catalytic reactor which was built to duplicate the shipboard CO/H<sub>2</sub> burners as to catalyst, space velocity, and temperature has been described previously (1). (The term "space velocity" denotes the volume of furnace feed passing through a unit volume of catalyst per unit time and is expressed in reciprocal time units.)

The desired concentrations of the gaseous substances studied were produced by controlling their flow from a pressurized cylinder with a fine needle valve through a rotameter, or soap-bubble flowmeter, followed by mixing with the main air stream. Gas chromatography was used to compare the inlet with the outlet concentration of the hydrocarbons, nitrous oxide, the liquid nitrogenous compounds, and Freon-11. Known concentrations of the liquid compounds studied were prepared by diverting a portion of the CO<sub>2</sub> free air stream through a weighed bubbler containing the compound of interest and recombining it with the main air stream. In addition, the influent and effluent concentrations of ammonia were determined by collecting a measured volume of the stream of interest in 0.05 N H<sub>2</sub>SO<sub>4</sub> and analyzing for ammonia by the Folin-Farmer modification of the Nessler procedure (4). Nitrogen dioxide (NO<sub>2</sub>) was determined by the method of Jacobs and Hochheiser (5). Infrared spectroscopy, with known mixtures of pure nitrous oxide in air as standards, was used to identify and measure the concentration of this gas in the furnace

effluent air and thus confirm gas chromatographic results. The Perkin-Elmer model 154-A gas chromatograph did not provide sufficient sensitivity to nitrous oxide, so concentration was effected by collecting a two to four liter sample of the furnace effluent on a silica gel trap at dry-ice temperature and flushing into the analytical column at boiling-water temperature by means of a four-way valve. As in previous work, the carbon dioxide in the furnace effluent air was measured dynamically by use of a Liston-Becker model 15-A nondispersive infrared analyzer calibrated with tank breathing air of known CO<sub>2</sub> content.

The furnace effluent was examined for phosgene during work with Freon-11 by means of a detector tube filled with silica gel impregnated with paradimethylaminobenzaldehyde and phenylalphanaphthylamine, which couple to form an emerald-green color in the presence of phosgene.

All studies were made at a constant space velocity, 21,000 hr<sup>-1</sup>.

## RESULTS

### Lower-Molecular-Weight Hydrocarbons

Using the percent of the theoretical carbon dioxide obtained as the criterion, the combustion of ethane and propane is shown (Table 21) to be incomplete at 315°C (600°F), the temperature presently prescribed for shipboard operation. Results obtained earlier for methane are given for comparison. By way of contrast, Table 22 shows that the higher hydrocarbons, hexane and above, are readily oxidized at this temperature.

Table 21  
Combustion of the Lower Alkanes Over Hopcalite

Compound	Temperature (°C)	Theoretical CO <sub>2</sub> Found (percent)
Methane	400	30
	300	2
Ethane	315	12
	260	6
Propane	315	25
	260	11

Table 22  
Combustion of the Higher Hydrocarbons Over Hopcalite

Compound	Theoretical CO <sub>2</sub> Found (percent)		
	350°C	300°C	200°C
Benzene	92	87	74
1,2,4-Trimethylbenzene	100	98	55
tert-Butylbenzene	96	96	86
n-Hexane	97	97	77
n-Decane	96	98	89
2,2-Dimethylbutane	98	84	40
Octene-1	94	89	83
Cyclohexane	91	-	-

Table 23  
Hopcalite-Catalyzed Oxidation of Nitrogen Compounds at 315°C

Compound	Inlet Concentration (ppm)	N <sub>2</sub> O Formed (% Theoretical)
Ammonia	140	70
Monoethanolamine	19	20
Morpholine	35	16
Pyridine	40	17

Note: Raising the furnace temperature diminished the yield of N<sub>2</sub>O from monoethanolamine and ammonia

### Nitrogen Compounds

All of the nitrogen compounds studied formed remarkably high yields of nitrous oxide (N<sub>2</sub>O), as shown in Table 23. The formation of nitrous oxide by the catalytic oxidation of ammonia has been reported previously and even suggested as a method for the commercial production of nitrous oxide for use as a refrigerant (6). Kobe and Hosman obtained a 71-percent yield of nitrous oxide by the catalytic oxidation of ammonia over a manganese-bismuth oxide catalyst. They obtained their maximum yield at 200°C and a space velocity of 300 to 360 hr<sup>-1</sup> (6). A search of the literature did not reveal a previous report of the formation of nitrous oxide from organic nitrogen compounds.

Morpholine and pyridine were studied at 315°C only. In the case of ammonia and monoethanolamine, raising the furnace temperature diminished the yield of nitrous oxide. Raising the furnace temperature from 315 to 348°C diminished the yield of nitrous oxide from ammonia from 70 to 49 percent. Kobe and Hosman also reported a drop in the yield of nitrous oxide from ammonia as the catalyst temperature was raised (6). The yield of nitrous oxide from monoethanolamine dropped from 20 percent at 315°C to about half this value at 400°C. Exact data are not available because of the low concentrations of monoethanolamine studied.

Although 70 percent of the influent ammonia was converted to nitrous oxide at 315°C, less than 1.5 percent of the influent ammonia survived passage through the burner as ammonia, and no more than 0.35 percent of the theoretical amount of nitrogen dioxide (NO<sub>2</sub>) was found in the effluent. The balance of the ammonia is presumably converted to nitrogen and water, as reported by Kobe and Hosman (6).

As a test of the stability of nitrous oxide under the oxidizing conditions used, pure nitrous oxide in air was passed into the furnace at 315°C. Gas chromatographic comparison of the nitrous oxide concentration in the furnace inlet and outlet streams showed no destruction of the compound. Thus, it is clear that the stability of nitrous oxide could permit a buildup in its concentration aboard submarines despite the existence of no more than a single part per million of nitrogenous precursor.

### Freon-11

Freon-11 has been studied further since more sensitive gas chromatographic equipment has become available. This compound is degraded much more extensively than is Freon-12 at the same temperature. When the restudy of Freon-11 was begun, the Hopcalite catalyst previously used in Freon work was employed. The apparent extent of destruction was studied at several temperatures, and the results are plotted in Fig. 18. The data points represent essentially instantaneous values obtained as the furnace

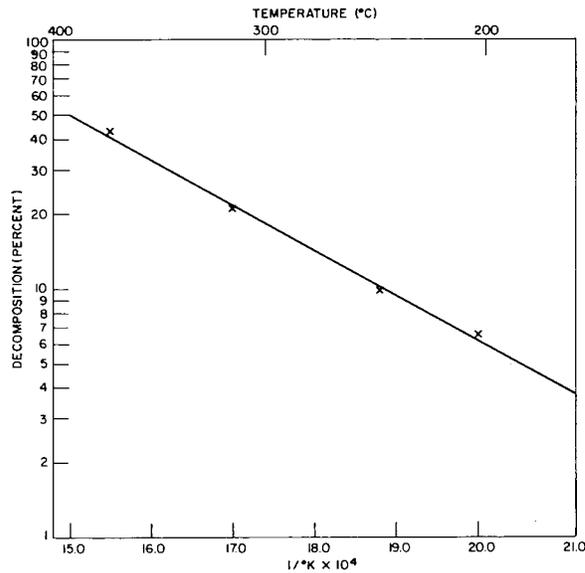


Fig. 18 - Extent of decomposition of Freon-11

temperature was lowered fairly rapidly. Following this study, a fresh charge of catalyst was placed in the furnace, and the furnace was operated for 6-1/4 hours at 315°C. During this time the extent of destruction of the Freon-11 fell from 50 to 32 percent. The furnace effluent smelled strongly of halogen and tested strongly acid to universal indicator paper within five minutes after the start of the run, and continued to do so for the duration of the run. When samples of the furnace effluent were drawn through phosgene detector tubes, no phosgene was detected. The sensitivity of these tubes is such that had 0.1  $\mu\text{g}/\text{liter}$  (0.03 ppm) of phosgene been present, it would have been detected.

## CONCLUSIONS

It has been shown that the lower-molecular-weight hydrocarbons, especially methane, are not completely oxidized under the conditions studied, including those that simulate operating conditions in submarines. This is in contrast to the higher hydrocarbons, whose combustion is substantially complete. It has also been shown that under simulated submarine conditions, ammonia and organic nitrogen compounds yield nitrous oxide on oxidation catalyzed by Hopcalite, and that the nitrous oxide itself is resistant to further reaction. This explains why a gradual buildup in concentration of nitrous oxide can occur on long dives. In contrast to Freon-12, which is highly resistant to decomposition in the burner, Freon-11 decomposes extensively to yield acid vapors that could be troublesome because of their corrosive nature.

## FUTURE PLANS

The studies on Hopcalite-catalyzed oxidation of organic materials have been completed as far as they relate to the submarine-atmosphere problem. No future work on this subject is planned at present.

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## Recommendations

The major recommendations to the Bureau of Ships contained in the previous NRL annual submarine-habitability report have been implemented, but again at a far slower pace than desirable. These three recommendations are therefore repeated, but modified to indicate the objectives attained as well as those not yet met.

1. The Bureau of Ships has initiated a specific program at the Marine Engineering Laboratory (formerly the Engineering Experiment Station) aimed at determining the effect on materials of the degradative surfaces and atmospheres in nuclear submarines. This is yet but a minor program and falls short of the needed determination of composition specifications required for materials used in construction or going aboard nuclear submarines.

2. The Bureau of Ships has issued a supplemental Habitability Data Book, September 1962, which should greatly assist shipbuilders in modification of equipment and procedures to minimize atmospheric contamination, but further distribution of information on the experience of different shipbuilders is still necessary to ensure currency and completeness.

3. The Bureau of Ships has monitored the production of the Mark IV Atmosphere Analyzer through long-term testing of each unit at the Mare Island Naval Shipyard and is checking that ships and installations return faulty components to the manufacturer for replacement; there is still need to ensure that the manufacturer institute proper quality control in the initial production of the equipment.

In addition to these recommendations, with final action yet incomplete, the following new recommendations now become necessary:

1. The Bureau of Ships should followup the Ionics, Inc., ion-exchange system for oxygen generation and carbon dioxide absorption as long as the system continues to demonstrate its current promise.

2. The Bureau of Ships should continue to make design improvements in the CO<sub>2</sub> scrubber, including the provision of battery-quality makeup water.

Future interests and action of NRL in the field of submarine atmospheric habitability will continue to be guided by the following considerations:

1. All research and development will continue to be performed with the view of applicability toward an integrated air-purification system.

2. Studies on the causes of MEA degradation should be curtailed as soon as an adequate degradation inhibitor can be obtained and the causes can be ameliorated.

3. Investigations should continue on: (a) refinements on the Mark IV Atmosphere Analyzer, (b) methods of air sampling and analysis, including infrared and mass spectroscopy, as well as gas chromatography, (c) the CO<sub>2</sub>-H<sub>2</sub> reaction which might eliminate the need for pumping these gases overboard, (d) innovations on manufacturer-furnished chlorate candles and improved filters for the candles, and (e) a satisfactory water-thinned paint for application while submerged.

4. NRL will also continue to provide consultative services to the Bureau of Ships and the Special Projects Office as required, as well as to contractors who are referred to NRL by these offices.

5. As a continuing policy, promising research ideas will be pursued as part of NRL's program, even when there appears to be no immediate applicability to submarine needs.