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ANNUAL PROGRESS REPORT

THE PRESENT STATUS OF CHEMICAL RESEARCH IN ATMOSPHERE PURIFICATION AND CONTROL ON NUCLEAR-POWERED SUBMARINES

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July 14, 1961

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FOREWORD

The expanding nuclear-submarine fleet of the U.S. Navy has made the "habitability" of the submarine an increasingly important factor in its ability to accomplish its assigned mission. As the number of personnel who must be trained to operate essentially research-type equipment continues to rise, the need also rises for the equipment to become more reliable, versatile, and maintenance-free.

In April 1960, the U.S. Naval Research Laboratory issued NRL Report 5465, "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines." This report summarized the development of an adequate atmospheric system for submarines and covered in some detail the research at NRL through calendar year 1959.

The present report is essentially a summary of the progress made in submarine-atmosphere control by NRL during calendar year 1960. The reader is referred to the earlier report for the historical accounts and development of the various components. Research and development studies on atmosphere control which are being conducted at other Naval installations, such as the Naval Medical Research Laboratory (New London), Mare Island Naval Shipyard, Navy Toxicology Unit, Naval Medical Research Institute, Naval Engineering Experimental Station, and the Materials Laboratory, or by Naval contractors, are not discussed in any detail in this report.

The Bureau of Ships Fleet Assist Project is continuing to provide unique opportunities to conduct essential research and experimentation in the only truly "closed-space" laboratories in the world – the nuclear submarines. The SARGO in the fall of 1959, the SKATE in the fall of 1959 and spring of 1960, the TRITON in the summer of 1960, the HALIBUT and SEAWOLF in the fall of 1960, and the SKIPJACK in the past winter carried both BuShips and NRL scientific personnel on a series of important cruises. In addition, other submarines have contributed through sample collections by ship personnel. Typical cruises attested to the convenience and safety of chlorate candles, the efficiency of the MEA detector tubes, the advantages of water-thinned paints, the economies of adding Versene to MEA for CO_2 adsorption despite incomplete scientific justifications, the versatility of the NRL leak detector, the overall reliability of the NRL Mark III Atmosphere Analyzer notwithstanding difficulties with some of the channels, the cleanliness of the atmosphere during no-smoking periods, etc.

The total research and development effort by the Chemistry Division, NRL, during 1960 remained substantially the same as in 1959, with about 20 man-years of direct effort at a cost of approximately half a million dollars. Financial support came mainly from the Bureau of Ships, supplemented by the Office of Naval Research and the Special Projects office.

PROBLEM STATUS

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

FOREWORD

AUTHORIZATION

NRL Problems C08-05, C08-18, C08-27, C08-30
Project SF 013-08-03, Tasks 4092, 4093, 4094, 4095

NRL Problems C08-32 and C08-33
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ANNUAL PROGRESS REPORT

THE PRESENT STATUS OF CHEMICAL RESEARCH IN ATMOSPHERE PURIFICATION AND CONTROL ON NUCLEAR-POWERED SUBMARINES

SUMMARY OF PROGRESS

INTRODUCTION

The advent of controlled nuclear power makes possible the true submarine–one that can submerge indefinitely and live and fight under the surface of the ocean. That we are approaching the goal of indefinite submergence is well attested by the SEAWOLF's record-breaking 60-day dive in 1958, and by the still more recent 66-day dives of the GEORGE WASHINGTON and PATRICK HENRY while on their first operational cruises "on station." Nobody can say with sureness when the first 90-day cruise will occur. It will surely be accompanied by the continuous generation of oxygen in a plant capable of providing the submarine's entire source of oxygen. It may also be accompanied by the first major psychological problems associated with such long separation of the crew from home and family.

The preceding annual report (1) outlined chronologically the development of submarine air-replenishment equipment in the United States from the days when only a few hours' submergence was necessary and possible to the time of the record submergence of the SEAWOLF. The status of research studies at NRL was also presented. This is the first supplementary annual progress report.

OXYGEN SOURCES

Of widespread interest at the present time, particularly to those associated with the Polaris submarines, is the Treadwell high-pressure oxygen generator (Figs. 1 and 2). It was this generator which contributed heavily to the ability of the GEORGE WASHINGTON and PATRICK HENRY to set their recent endurance records. The generators, at that time rated at 75 cubic feet of oxygen per hour (less than ample to carry the submarine's entire load), were able to stay in successful operation long enough to supplement the cylinder oxygen of the ships and to set the records. Additional generators of this type with larger capacity (120 cu ft per hour) are currently planned for the other Polaris submarines.

In view of certain disadvantages of this Treadwell generator, among which are weight and cost, an effort is being made to investigate other oxygen generators. A "bipolar cell," similar to the above monopolar cell but constructed so that each electrode alternately serves as anode and cathode, is under development by the Bureau of Ships for installation on several of the forthcoming nuclear submarines. Such a cell would be much simpler and should result in volume and cost savings. The "split-cell" type of generator (Chapter 16, Ref. 1) has even simpler construction, and operation and would require less power. The latter cell will be installed on two of the new nuclear submarines.

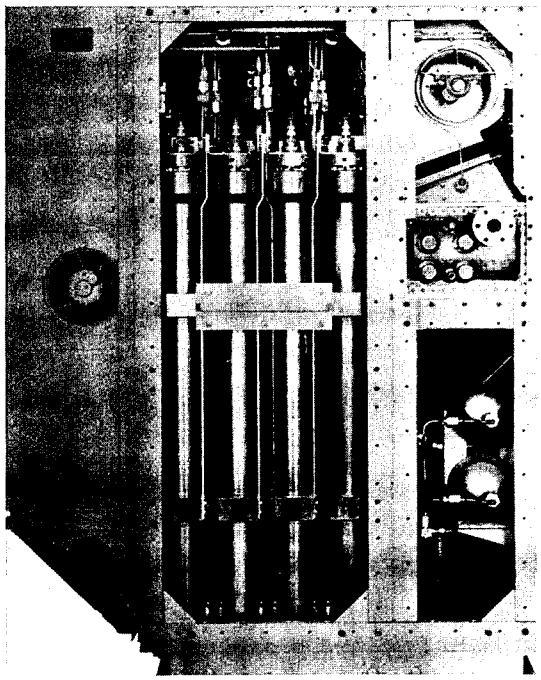

Fig. 1 - The Treadwell cell, cells and cooling system

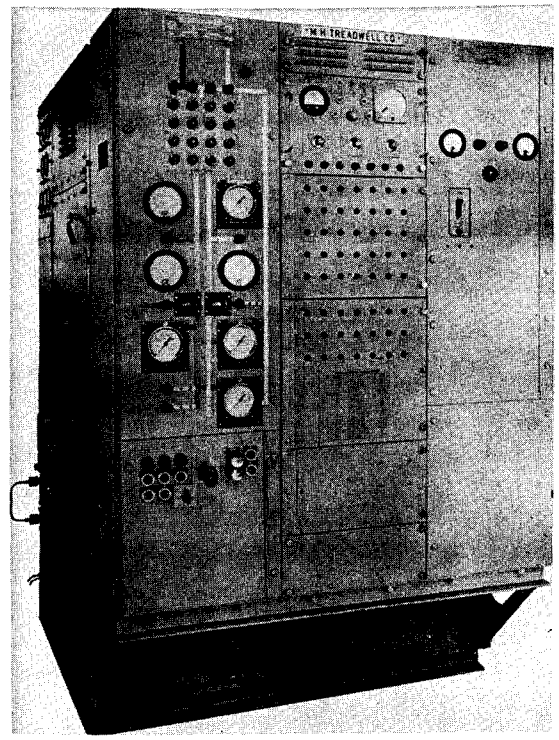

Fig. 2 - Control and rectifier face

Another promising candidate for the oxygen source is the sulfate-cycle system. 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 and the sodium sulfate subsequently being regenerated (Chapters 17 and 18 of Ref. 1, and Chapter 1 of this report). The NRL pilot model of the system is working satisfactorily in limited runs; a continuous 30-day run is expected by the end of 1961. One of the most difficult problems anticipated with the longer runs is a suitable diaphragm for controlling the flow rate of electrolyte, which in turn governs the concentration of the sodium hydroxide in the cathode compartment and the sulfuric acid in the anode compartment. While this problem is being studied (Chapter 1), other ways of solving the problem are worth considering. Ionics, Inc., having become aware of this problem in such cells during a study contract on an Office of Naval Research project, has proposed the use of a cation ion-exchange membrane that would permit a much simplified construction. Most cation ion-exchange membranes to date have been rather fragile and without the strength and structure required in such a cell. However, Ionics, Inc. has been able to develop a much stronger membrane which the company proposes to use in a sulfate-cycle cell. As a result, NRL has secured from Ionics four prototype cells which have demonstrated the capability of the membranes to operate for several months without difficulty. It has been possible to prepare three normal caustic with a current efficiency of 90 percent operating at about 4.2 volts per cell at 95 °C. These cells operate at 29 amps, which is equivalent to 100 amps per square foot of membrane area. The concentration of the sulfuric acid and the caustic can be increased or decreased simply by changing the feed rates of sodium sulfate to the cathode and anode compartments.

Another promising system for oxygen production and carbon dioxide absorption is the photosynthetic cycle of green algae (Chapter 19 of Ref. 1, Chapter 2 of this report). Increasing knowledge of Chlorella pyrenoidosa and improved equipment for handling the suspensions are narrowing the avenues of approach in what is essentially a feasibility study for application to submarines.

A very good oxygen source for emergencies and for extending short submergences is the chlorate oxygen candle (Chapter 15 of Ref. 1 and Chapter 3 of this report), which is essentially a mixture of sodium chlorate and finely divided iron powder. Much progress has been made in the manufacture of a candle which gives greater oxygen yield per unit volume. Similar progress has been made in determining its storage and operating characteristics.

To place the oxygen-producing techniques and carbon dioxide-absorbing materials on a comparative basis, Chapter 4 has been prepared on the weight economics of a large number of candidate materials and techniques. This study shows that the choice of technique and material is dependent on the time of submergence. Several new compounds are introduced that might be very effective if available in sufficient quantity and purity.

Another possible source of oxygen is the dissolved oxygen in sea water. NRL was requested to evaluate this "gill technique" because of a proposal to use ultrasonics to extract the oxygen. A preliminary survey of the literature indicated that there was a considerable variation in oxygen content of the sea water in different areas, including some areas where there was practically none. The ultrasonic technique was studied and found to be no better than other conventional methods for removing dissolved gases. A by-product has been the development of a technique for stripping the dissolved gases with an inert gas and utilizing a gas chromatograph to complete the analysis (Chapter 5).

CARBON DIOXIDE REMOVAL

Several of the attractive carbon dioxide absorption systems have been mentioned above. The regenerative system employing monoethanolamine (MEA) is currently used on all nuclear submarines (Chapter 11 of Ref. 1, Chapter 6 of this report). MEA is a highly efficient carbon dioxide absorbent. However, MEA has an appreciable vapor pressure, is not completely oxidation-resistant, and is considered highly toxic. Hence, modifications and alternative systems must be investigated. The most efficient immediate solution would be to decrease the degradation rate of MEA without increasing the toxicity problem. Because of the work of the Mare Island Naval Shipyard on Versene and other proposed chelating inhibiting agents, NRL is investigating the true reasons for MEA degradation and will subsequently examine a selection of additives to prevent such degradation (2).

Some progress has also been made on the use of Alkazid M as a CO_2 absorbent (Chapter 12 of Ref. 1, Chapter 7 of this report). Alkazid M is an aqueous solution of the potassium salt of the amino acid, N-methylalanine. The German manufacturer is ready to make it available for U.S. distribution, and later manufacture, if given enough incentive for possible sales. Since Alkazid M is superior to MEA in having less toxicity and greater degradation resistance, it is the leading candidate for MEA replacement, should this become necessary.

An improved canister manifold system for CO_2 absorption has been developed (3). It is reliable, simple, and easily used. The latest version of the manifold is shown in Fig. 3. Pelletted lithium hydroxide, LiOH, which has been demonstrated to be a good carbon dioxide absorbent (Chapter 10 of Ref. 1), is used in the canisters.

Fig. 3 - Lithium hydroxide manifold

ATMOSPHERE SAMPLING AND ANALYSIS

Additional research on the analysis of submarine atmospheres using gas chromatography has yielded information (Ref. 4, and Chapter 8 of this report) about compounds not previously identified. None of these compounds are highly toxic, particularly in the trace quantities found, and the toxicity worry continues to be about compounds previously identified.

Progress has been made on the Atmosphere Analyzer, Mark III, for identifying the major components of the atmosphere (Chapter 9). This model must serve as the workhorse analyzer until the Mark IV is in production. However, with a view toward simplification and improvement of routine atmosphere analysis even beyond that expected from the Mark IV, preliminary studies have begun to determine the feasibility of gas chromatography for this purpose. The increasing reliability and simplicity of commercial chromatographs make this an attractive avenue of approach.

An earlier study on hydrocarbon contaminants (Chapter 4 of Ref. 1) led to the conclusion that painting was the major source of contamination. On the SEAWOLF's 60-day dive, the record for low hydrocarbon was set by abstaining from painting for a month prior to the dive as well as during most of the dive. Subsequent studies on carbon adsorption (Chapter 10) have improved both the adsorption and desorption techniques, and confirmed the finding about paints spectacularly when the SARGO set a new low-hydrocarbon record after having been painted almost exclusively with water-thinned paints during overhaul. The routine recovery of hydrocarbons from carbon canisters by steam desorption is now done at the New York Naval Shipyard Materials Laboratory; comparative data from the Materials Laboratory and NRL agree favorably. The ratio of aromatics to aliphatics found in the hydrocarbons in nuclear submarines has been found to be considerably higher than previously reported.

Due to the continued uncertainty about the amounts of arsine and stibine evolved from the lead-acid batteries on nuclear submarines, special methods have been developed for their analysis (Chapter 11). Although an inadequate number of samples has been taken, the preliminary indication is that the amounts of arsine and stibine present in the atmosphere are much less than the respective permissible concentrations.

Since the possibility of ozone generation exists in certain high-voltage equipment, such as electrostatic precipitators, a special technique has been developed for its analysis (Chapter 12). With a permissible concentration of only 0.05 ppm, it is imperative that a reliable method of analysis be available. While no dangerous concentrations of ozone have been measured on the nuclear submarines, the presence of ozone as identified by smell has been reported several times.

A study on the analysis of contaminants in aviator's breathing oxygen has appeared so pertinent to the oxygen-source problem on nuclear submarines that it has been included in this report (Chapter 13). The similarity is not only that personnel still need stored oxygen both in airplanes and submarines, but also in that liquid oxygen is used as the source of oxygen in both instances. In the airplane, odor rather than toxicity is the prime complaint; in the submarine, both odor and toxicity must be considered.

The analytical technique for MEA and ammonia described previously (Chapter 6 of Ref. 1) has been refined and the storage stability of the detector tubes improved (Chapter 14 of this report). Commercial production of the tubes is now being negotiated, and the air-sampling pump is available from the American Instrument Company.

The NRL Freon leak detector previously described (Chapter 3 of Ref. 1) has been improved (Chapter 15 of this report) with the production of six prototype models (Model E-5753). Several trials aboard nuclear submarines have been successful, but a more complete evaluation is still needed before recommendations are made for Fleet procurement. In the meantime, another miniaturized version of the leak detector has been developed by the Equipment Research Branch of NRL (5) which incorporates several electronic innovations and promises to provide a lighter and more versatile instrument. Both versions are superior to competitive industrial models, since they are not limited to Freon or halides, but can detect any gas which has a thermal conductivity significantly different from that of air. A decision on production for Fleet use is expected by the end of 1961.

ELIMINATION OF CONTAMINANTS

The best single eliminator of organic contaminants continues to be the CO/H_2 burner (Chapter 7 of Ref. 1, Chapter 16 of this report). Several studies have been made and are continuing on the cause of corrosion in the heat exchanger of the burner. Methods have been developed which use absorbent marble chips for the elimination of some of the fluorides which might be causing part of the trouble. The Desomatic Company has now produced, under a BuShips contract, a single 500-cfm burner which is essentially a larger Mark II burner but still capable of being passed through the 25-in. hatch opening.

The best method of contaminant elimination is to prevent their formation. Thus, the earlier work on water-thinned paints (Chapter 9 of Ref. 1) has led to the development of specifications for efficient paints (Chapter 17 of this report) which have already proved effective. They undoubtedly contributed materially to the low hydrocarbon concentration on the TRITON. Pilot quantities of the paint have been formulated at NRL for experimental use on other nuclear submarines. It is hoped that commercial production in accordance with the specifications will soon be adequate for all needs.

The study of the influence of aerosols on submarine atmospheres (Chapter 20 of Ref. 1, Chapter 18 of this report) has been continued. These studies have served to confirm the earlier findings as regards source and concentration of the aerosols. The backfit of electrostatic precipitators has been completed on both the NAUTILUS and SEAWOLF, with early indication of success in reducing the aerosol concentration to the predicted (and desirable) level. The formation of aerosols of triaryl phosphate lubricants (Cellulubes) has been shown to be possible with potentially toxic results. However, the increased electrostatic precipitator capacity plus the ability of the Desomatic burner (Chapter 19 of this

report) to oxidize such aerosols both tend to keep the toxicity problem at a minimum under normal conditions. It is understood that triaryl phosphate materials are being eliminated from use in the Polaris submarines.

The thermal degradation of the triaryl phosphate materials has been emphasized in a separate study (Chapter 20). This study indicates that during exposure to air at elevated temperatures, oxidation, hydrolysis, and pyrolysis of the esters occur to yield acidic, tarry residues and volatile mixtures of phenols and water. The study is being continued to determine the effect of long-term exposure of the esters to air at lower temperatures.

The earlier study of molecular sieves for removal of carbon dioxide (Chapter 13 of Ref. 1) has been extended to the use of type 13X molecular sieve for the removal of organic contaminants (6). Such a system was found to furnish a high degree of air purification at fast flow rates and low influent concentrations, and for concentrations in a parts-per-million range (although greater than 5 ppm), the system has high equilibrium capacities for most organic vapors. The chief disadvantage is that a high temperature is required for regeneration of the sieve when water is present.

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PART I
OXYGEN SOURCES

CHAPTER 1

THE SULFATE-CYCLE SYSTEM

The 1960 report contained chapters (Refs. 1 and 2) which discussed preliminary work on the two major components of the sulfate-cycle system–the electrolytic cell and the CO_2 absorption apparatus. The results were so promising that, early in 1960, it was decided to merge both efforts and the accompanying manpower and build a laboratory-scale pilot plant which would be able to operate as a complete unit for as much as 30 days or longer. Such a plant is now in operation and is discussed in section 3 of this chapter.

The electrolytic cell previously described in detail (1) was utilized in additional runs and then was rebuilt for use in the pilot plant. The extra runs provided data for calculation of voltages and for theoretical treatment of the lead alloy anode. The runs also confirmed anode diaphragm difficulties when glass cloth, which had been tried under the electrolytic grade of chrysotile asbestos paper, disintegrated at an early stage. Although the sulfate-cycle system seems increasingly more promising, the problem of obtaining satisfactory anode diaphragm materials has not yet been solved, and a special study of such materials is contained in section 1 of the chapter. Section 2 covers progress in the CO_2 absorption and desorption studies subsequent to the 1960 report.

For convenience in reviewing the sulfate-cycle system, Fig. 4 is repeated from the 1960 report (1). An 18-percent aqueous solution by weight of sodium sulfate is fed into the electrolytic cell. Oxygen and sulfuric acid are formed at the anode and hydrogen and

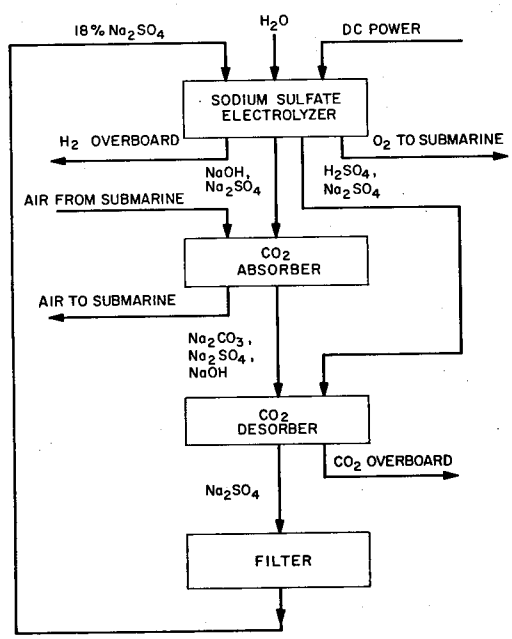

Fig. 4 - Flow sheet of sulfate cycle

sodium hydroxide at the cathode. The oxygen is released to the ship's atmosphere, and the hydrogen is pumped overboard. The sodium hydroxide is passed into the absorber, where it absorbs carbon dioxide from the ship's atmosphere. The latter solution is then pumped to the desorber, where it reacts with the sulfuric acid from the electrolyzer, liberating the CO_2, which is pumped overboard. The resulting sodium sulfate solution formed in the desorber is then recycled to the electrolyzer. Unelectrolyzed sodium sulfate is also present in the streams of acid and caustic leaving the electrolyzer, and in the CO_2-rich stream from the absorber. Some of the previous studies and those in this report pertain to the effect of the sodium sulfate in the CO_2 absorption process.

SECTION 1. DIAPHRAGM MATERIALS

J. A. Young

One problem associated with the electrolytic cell for the sulfate-cycle system is the requirement for acid- and alkali-proof diaphragms. A study of the diaphragm problem was initiated in 1959, with the object of developing materials which would be practical for the proposed shipboard use of the cell. These studies have included (a) the screening of commercially available textiles and papers which were considered capable of withstanding the chemical environment of the cell, (b) the design and construction of equipment for the realistic evaluation of the properties of candidate diaphragms, and (c) the evaluation of diaphragms prepared from experimental hand sheets containing various fibers, resins, and mixtures.

The physical and chemical properties required of the diaphragms can be deduced from a brief review of the cell and its operation. The cell consists of three parts: the anode, the cathode, and the central, or supply, chamber. The anode and cathode diaphragms provide the compartmentation, since they separate the perforated electrodes (about 25-percent open area) from the supply chamber. The electrolyte used is an aqueous solution containing 18-percent sodium sulfate by weight. The solution fills the central chamber and is held to a constant pressure which may be varied up to 20 in. of H_2O. The solution flows from the central chamber through the diaphragms and perforated electrodes and drains off the outer free surface of the electrodes. There it is collected from the bottoms of the anode and cathode chambers. Electrolysis produces oxygen and sulfuric acid at the anode and hydrogen and sodium hydroxide at the cathode. The gases are collected through vents in the top of the anode and cathode compartments. Under normal operating conditions, the anolyte and catholyte contain, in addition to sodium sulfate, a concentration of about 5-percent H_2SO_4 and 5-percent NaOH, respectively. Operating temperature is held to 50 °C by electrolyzing at a current density of 100 amp/ft^2. The diaphragms thus serve a dual role, since they are used to control the flow of solution and also act as a barrier to prevent back diffusion into the central chamber of gases liberated at the electrodes.

From the above description of the cell and its operation, the physical and chemical properties required of the diaphragms include (a) dry strength sufficient to enable storage, handling, and insertion into the cell, (b) wet strength sufficient to insure service life measured in months, (c) ability to provide and maintain the desired solution flow rate, (d) resistance to 18-percent sodium sulfate solution, (e) resistance to 5-percent H_2SO_4 for the anode diaphragm and 5-percent NaOH for the cathode diaphragm, and (f) resistance to the oxidizing or reducing atmospheres at the electrodes.

It was recognized at the outset that major emphasis should be given to the development of a practical anode diaphragm, since the use of commercially available, electrolytic grade, asbestos paper was expected to serve for the cathode diaphragm. However, in all the studies to date, cathode diaphragms have been included in the hope that the same material could be utilized for both diaphragms. In any event, the service life expectancy of both diaphragms will be determined from the studies now being made.

In order to study the performance of diaphragms, it has been necessary to fabricate equipment especially designed for this purpose. The initial study of materials considered for use as diaphragms included only the determination of liquid flow rate as a function of pressure and time. The apparatus developed for this purpose is illustrated in Fig. 5. The original device was constructed of brass, but the latest model was fabricated from stainless steel. The apparatus has three parts: a chuck with an integral collecting funnel for holding the sample, a standpipe which contains the supply liquid, and a lock ring which secures the chuck and standpipe. A sample of 2-1/4 in. O.D. is required. The exposed area is 2 in. in diameter (3.14 in.^{2}). The sample is supported on a plate perforated to the same free area as the electrodes in the cell. The height of liquid above the sample, and hence the pressure, is variable up to the height of the standpipe, which is 18 inches. The liquid level in the tube is held constant by use of a demand feeder.

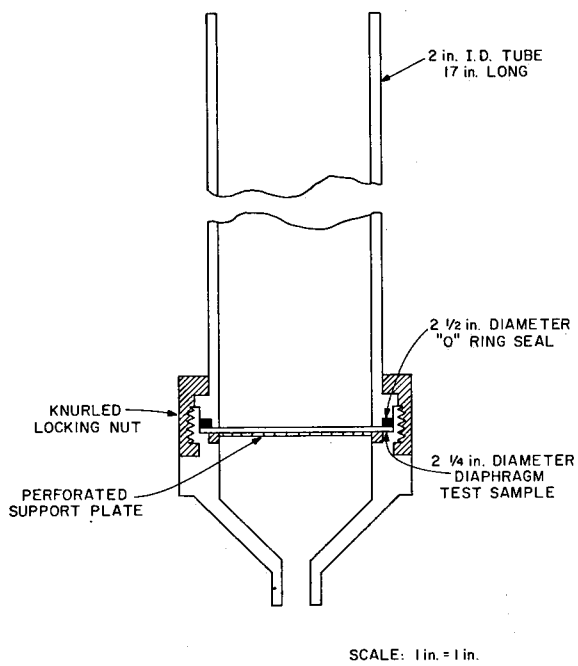

Fig. 5 - Percolation apparatus, scale 1 in. = 1 in.

The simple flow apparatus described above was sufficient to provide quantitative and reproducible flow-rate data of value for the screening of materials. However, it was recognized that more realistic performance data were needed to guide the developmental studies of diaphragms and that such information could be achieved only by reproducing the operating conditions and environment of the cell.

Three miniature cells patterned after the cell previously described were designed and constructed. The design of the small cell is illustrated in Fig. 6. These miniature cells are constructed of 1/2-in. Lucite to simplify fabrication and to allow inspection during operation. The cell is nominally 4 x 4 in. in overall dimensions. The internal dimensions of each chamber are 3 x 3 x 3/4 in., and each is supplied with a top and bottom inlet tube. The electrodes used for these cells are fabricated from 1/8-in. pure lead for the anode and 1/16-in. stainless steel (304) for the cathode. Each electrode is nominally 4 x 4 in. The electrodes are perforated in a staggered pattern by 189 holes 1/8 in. in diameter which are contained within the exposed area of 3 x 3 in. The cell thus requires an anode and cathode diaphragm with an exposed area of 3 x 3 in. The diaphragms are cut

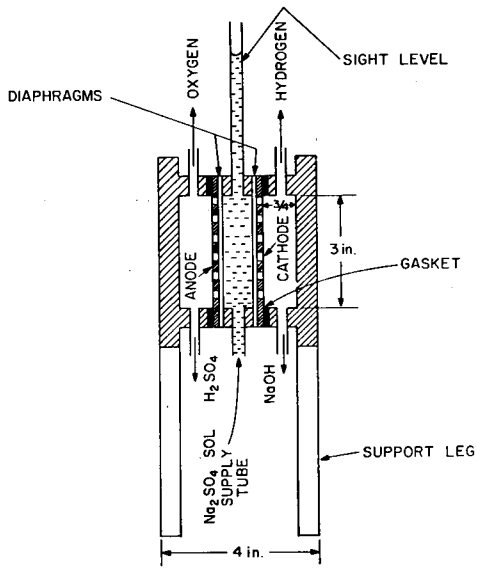

Fig. 6 - Miniature sulfate cell

to 3-1/2 x 3-1/2 in. to allow 1/4 in. for sealing in the peripheral gasket. The whole assembly is held together by pressure supplied by the symmetrically located bolts. The miniature cells are about one-tenth the size of the full-scale cell. This size was selected to allow diaphragms to be cut from standard 6-in.-diameter hand sheets.

The sodium sulfate solution is supplied to the central compartment by means of the bottom tube. The pressure of the solution is maintained constant by use of a constant-head device (3). The anolyte and catholyte are collected from the bottom outlets of the anode and cathode chambers. An S-shaped tube is attached to each of these outlets to provide a liquid-filled trap to prevent the escape of gas except through the top outlet. The pressure in the central compartment is indicated by use of a glass tube attached to the top outlet from the chamber. The temperature is monitored by means of a metal thermometer inserted into the solution contained in the central chamber.

The initial studies involved a screening of commercially available materials which were considered capable of withstanding chemical degradation in service. Textiles and papers containing or composed entirely of Teflon, Dacron, Orlon, polyethylene, and polypropylene were examined as to their ability to provide the liquid permeation rate desired. In this work, liquid flow as a function of differential pressure and time was determined by using the apparatus previously described. Distilled water and 18-percent sodium sulfate solution were used as test liquids. The desired flow rate through the 2-in.-diameter sample was 1 milliliter per 8-in. head per minute. The maximum thickness of diaphragm was set at 0.060 in., although a thickness of about 0.040 in. was preferred, to reduce the electrical resistance of the cell. None of the commercially available materials tested, which included different weaves, thicknesses and compositions, was found to satisfy these requirements. Fiber swelling of Dacron and Orlon, as evidenced by the diminution of flow at constant pressure as a function of time, precluded the use of these materials. The desired flow rate could not be obtained with Teflon fabrics, mixed Teflon and Dacron fabrics, porous polyethylene papers, polypropylene scrim, or laboratory-prepared paper of Teflon fiber mixed with other fibers.

Since none of the commercially available materials examined were suitable for use as anode diaphragms, the development of new materials was initiated. In this development, three approaches have been made.

The initial approach was the use of fine-fiber glass paper treated with Teflon and silicone emulsions. It was expected that these inert substances would partially plug the pores of the paper and thus provide the desired percolation rate. Glass paper providing an initial flow of 200 ml/min under the test conditions was treated with these emulsions, and sheets having the desired flow rate were obtained. The emulsion-treated sheets were found, however, to be only surface-treated, because the paper, acting as a filter, prevented the penetration of the emulsion particles. Microscopic as well as wetting studies of the internal layers showed them to be essentially free of the additions. In addition, these studies showed that the low flow rate was obtained by blocking all but a small area of the paper. The tensile strength of the treated sheets was five times that of the original glass paper, due to the bonding by the additives. Nevertheless, diaphragms composed of three such sheets easily and quickly ruptured (within 48 hours) when evaluated in the miniature cell. It was evident that once the central, untreated layers of the paper became thoroughly wet with solution, the thin, surface-treated layer did not have sufficient strength to prevent failure.

These data indicate that surface treatment alone is not sufficient and that the burst strength of the diaphragm may be more indicative of serviceability than tensile strength. Attempts were made to provide a uniform distribution of the additives by treating glass fibers in the beater prior to formation into a sheet. Although hand sheets were prepared in this manner, the sheets did not have sufficient strength to insure that the method could be scaled up for use of a miniature Fourdrinier paper machine. The tensile strength of the wet sheet is too low for it to be carried across the pressing and drying sections of the paper machine. It was therefore concluded that the use of emulsion-treated glass fiber paper for use as a diaphragm was not promising and would not be considered further.

The second approach has been the development of mixed sheets of hydrophobic and hydrophylic fibers. The desired flow rate would be achieved by adjustment of the proportion of these fibers in the sheet. The normal beating of the fibers before sheet formation would insure uniformity of the paper. Fine fiber polypropylene, prepared by use of NRL's fiber machine, was selected as the hydrophobic fiber of choice. A commercially-available polyester fiber, Acrilan, was selected for the hydrophylic fiber, because its ability to fibrillate under extensive beating provided added strength to the final sheet. Studies showed that eight hours of beating in the paper beater and a heat treatment of the final sheet for 30 minutes at 150°C provide a sheet with adequate strength for use as a diaphragm. Diaphragms consisting of three sheets of this paper, each 0.020 in. thick and containing 65-percent polypropylene and 35-percent Acrilan by weight, were found to provide the desired flow rate. Three sheets were used per diaphragm to reduce the effects of pinholes or non-uniformity of the paper.

Although diaphragms with adequate strength and the desired flow rate have been prepared using these composite sheets, one factor is believed to limit their practicability. Since this type depends on the wetting properties of the solution to limit flow, the difficulty arises of insuring the absence of wetting agents in the original solution or of a change in surface tension from contaminants. The first case was observed when one diaphragm under test in the miniature cell lost control with a change in the supply solution. Subsequent investigation revealed that a wetting agent was present in the fresh stock solution, since the surface tension of this solution was found to be only 42 dynes/cm. Although methods are available for detection and monitoring the surface tension of the sodium sulfate solution, the practicability of a diaphragm based on the wetting properties of the fibers is seriously questioned.

The latest approach, which is being intensively studied, is the treatment of glass and asbestos with a commerically available, ketone-soluble, fluorine resin. The resin used is Viton, which is a copolymer of hexafluoropropylene and vinylidene fluoride. A solution of this polymer in 95-percent methyl ethyl ketone and 5-percent methyl isobutyl ketone (MIBK), is used to treat the papers. Microscopic studies showed that the use of 5-percent

MIBK improved the film formation by increasing the drying time by a twofold factor. The sheets to be treated are immersed for one minute in the solution, then removed at a constand rate by use of a motorized pulley. The rate of removal was adjusted to prevent excessive runoff. Longer treatment time in the bath does not give additional weight gain. However, redipping in the same solution or one of higher or lower concentration does increase the total weight gain. It is thus possible to use a few solutions and by multiple treatment to obtain a gain in weight over a wide range. The solutions used contain 5, 35, 50, and 70 grams of Viton per 1000 ml of mixed solvent. For the same conditions, the weight gain has been found to be reproducible to within 1 percent. Glass-fiber paper of the same type as that used in the emulsion treatment was used in this work. For this paper, the desired flow rate in the cell was obtained when the paper comprising the diaphragm contained 48 percent of Viton by weight. The evaluation of diaphragms prepared from this paper is incomplete. However, it has been shown that the Viton is uniformly distributed throughout the sheet and that a large increase in both dry and wet tensile strength and Mullen burst strength is obtained from this treatment.

Corollary studies of Viton-treated asbestos paper are also in progress. Since the untreated asbestos provides the flow rate desired, the intent is to add sufficient Viton to give added strength without reducing the flow properties significantly. It has been found that the addition of 2.7-percent Viton by weight to asbestos paper increases the wet tensile strength fivefold. It reduces the sodium sulfate solution flow rate from 1.1 ml/min to 0.8 ml/min. This diminution in flow rate is not considered to limit the use of asbestos paper so treated, since it is expected to provide longer service life, while slightly higher liquid pressure can be used to achieve the desired flow rate. Only preliminary evaluation of these Viton-treated glass and asbestos papers has been accomplished to date. Further studies are required for definitive conclusions.

SECTION 2. CO_2 ABSORPTION AND DESORPTION

S. T. Gadomski

In the sulfate-cycle system, an aqueous sodium hydroxide and sodium sulfate solution is used for the absorption of CO_2. In previous work (2), absorption tests were made with caustic sulfate solutions in a 6-in.-diameter column packed with 1/2-in. Intalox saddles. Additional tests have been made in the same column with Monoethanolamine (MEA), the absorbent in the shipboard CO_2 scrubbers, to compare the absorption performance of MEA with a somewhat typical caustic sulfate solution. Results are shown in Table 1. For all these tests, the height of the packed bed was 3 ft, the percentage of CO_2 in the influent air was 1 percent, and the absorber temperatures were 76 °F.

Under these conditions MEA is about twice as efficient as caustic sulfate in the removal of CO_2. However, with an increase in liquid rate at the same air rate, the relative efficiency of caustic sulfate as an absorber is improved.

If the data of Table 1 were used to obtain some conception of the size of a caustic sulfate absorber required in the sulfate cycle by relating to the size and performance of Mare Island (MEA) scrubbers, the sulfate scrubber would be placed at a greater disadvantage than necessary. While the two liquids were compared under similar conditions, these flow conditions are not representative of the Mare Island scrubber.

With the cross-sectional area of the Mare Island scrubber taken as 3 sq ft, an air rate of 250 cfm at STP and a liquid rate of 20 cpm yield air and liquid flow rates of about 400 and 3400 lb/hr/ft^2. Under these conditions the removal rate of CO_2 is about 13.5 pounds per hour with 1-percent CO_2 in the influent air. Table 2 provides data for a laboratory test

Table 1
Concurrent Absorption of CO_2 by Aqueous Alkaline Solutions

Factor	4.7 Normal MEA			1.1 Normal NaOH 16 wt % Na_2SO_4		
Air Rate (lb/hr/ft^2)	554	550	528	527	526	518
Liquid Rate (lb/hr/ft^2)	6,650	8,400	10,000	6,700	8,400	11,900
Degree of Carbonation (percent)	40	40	40	47	47	47
Effluent CO_2 (percent)	0.36	0.34	0.31	0.69	0.67	0.61
CO_2 Removal (lb/hr)	1.01	1.06	1.07	0.46	0.56	0.59

Table 2
Concurrent Absorption of CO_2 by 4.7 Normal MEA in the Laboratory Column

Factor	Run No. 1	Run No. 2	Run No. 3
Air Rate (lb/hr/ft^2)	419	413	401
Liquid Rate (lb/hr/ft^2)	5,500	6,650	10,000
Degree of Carbonation (percent)	40	40	40
Effluent CO_2 (percent)	0.25	0.23	0.20
CO_2 Removal (lb/hr)	0.91	0.92	0.93
Absorber Temperature (°F)	75	75	75

which approximates these conditions. A comparison of Tables 1 and 2 shows that, at approximately the same liquid rate, a decrease in the air-mass rate from 554 to 419 lb/hr/ft^2 reduces the removal rate of CO_2 by MEA about 10 percent.

Caustic solutions, without sulfate, have been tested in concurrent flow with liquid and air flow rates as high as 32,600 and 1640 lb/hr/ft^2, respectively (4). At present the maximum rates in the studies of caustic sulfate solutions at NRL have been 11,900 and 518 lb/hr/ft^2. It is possible that higher rates, particularly in air flow, will improve the absorption performance of caustic sulfate. By contrast, MEA is efficient at relatively low flow rates of air and liquid. To gain additional removal capacity with MEA by utilizing the higher flow rates possible in concurrent flow is a step which would probably lead to additional problems of MEA degradation and air contamination. Since caustic sulfate is nonvolatile, these higher flow rates should be permissible in the sulfate cycle. Therefore, at the cost of additional power, the sulfate-cycle absorber may not be as large as visualized from an examination of Table 1.

The removal of CO_2 from the carbonated caustic solution of the sulfate cycle is accomplished by neutralization with electrolytic sulfuric acid. A stirred reactor with pH control appears to be a practical apparatus for combining the two fluids. In order to determine the difficulty, if any, of CO_2 evolution from such a neutralized product, batch and continuous methods of operation were studied.

In the batch tests, a measured volume of carbonated caustic of known concentration was reacted with a given amount of acid. Agitation was provided by a magnetic stirrer, and the evolved CO_2 was measured in terms of quantity and time of evolution. The heat of reaction resulted in an average liquid temperature of 90 °F. The data obtained are given in Table 3. The last time given represents completion of CO_2 evolution.

Table 3
Batch Tests

Run No.*	Time After Addition of Acid (seconds)	Volume of CO_2 Evolved in Milliliters (STP)	Ratio of CO_2 Evolved to Total CO_2 Content of Carbonated Caustic
I	14.4	422	0.77
	63.0	484	0.88
	94.8	493	0.90
II	16.4	510	0.94
	66.2	527	0.97
	99.0	530	0.98
III	9.7	320	0.29
	16.7	546	0.50
	64.4	765	0.70
	182.3	827	0.75
	252.9	833	0.76

* I. Solution neutralized to pH of 4.25, about 18 percent by weight of Na_2SO_4.

II. With some excess of acid, solution pH of 3.10.

III. With some deficiency of acid, solution pH of 6.05.

In the first run the caustic was almost completely neutralized–stoichiometric pH should be about 3.93. The Bunsen coefficient for CO_2 in an 18 percent by weight solution of sodium sulfate is 0.250 at 90 °F. Since the total volume of product was 200 ml, at least 50 ml of CO_2 would be retained by the liquid as dissolved gas.

The second run, with an excess of acid, resulted in the quickest and most complete removal of CO_2.

In the third run most of the CO_2 remained in the bicarbonate form (HCO_3^-) and was not liberated. The rate of evolution was also much slower than in the preceding runs.

These batch tests reveal that CO_2 is readily evolved if the carbonated caustic is neutralized efficiently. Exact neutralization at temperatures higher than 90 °F to decrease the solubility of CO_2 in the sodium sulfate should be most practical.

The batch tests were not as precise as some of the data might indicate. The volume of CO_2 evolved at a given time could have been in error by ±5 percent. A further uncertainty was introduced by the acid-adding step, since it was difficult to add the acid in exactly the same time period for each test.

The relatively large stirrer in comparison with a small volume of solution generated a violent mixing action which probably would not be duplicated in any continuous method of operation. In continuous neutralizations, the flow of reactants was small in comparison

to the volume of the reactor. While this resulted in satisfactory removal of CO_2, such a situation is not too helpful in estimating equipment size in larger installations. Additional tests would be required to resolve this problem. It was observed, however, that CO_2 formation does not seem to cause any foaming difficulties.

SECTION 3. SULFATE-CYCLE PILOT PLANT

S. T. Gadomski and A. L. Pitman

The laboratory-size sulfate-cycle pilot plant has been designed, assembled, and is now undergoing short-run trials (of less than 24 hours). It is a complete unit which generates oxygen, removes atmospheric carbon dioxide, and regenerates sodium sulfate to complete the cycle.

This plant will not be required in the laboratory to maintain a sealed atmosphere, since the working area cannot be isolated. This leads to a simplification, since auxiliary items such as compressors for CO_2 and H_2 removal need not be included. The CO_2 which leaves the plant will be dispersed by an air-conditioning system, while O_2 and H_2 will be vented outdoors. Operation of the absorber will be adjusted so that the ratio of CO_2 released by the neutralizer to O_2 produced by the electrolyzer will yield the respiratory quotient.

Initially, O_2 will be generated by the plant at the rate of 0.7 cu ft per hour. This output is disproportionately small, compared with the overall space occupied by the plant. A more compact arrangement could have been planned, but this would not be desirable in the laboratory. The large physical size of the plant has, in fact, resulted in convenience and ease in fabrication, installation, and maintenance of both plant and analytical equipment.

Another apparent inconsistency is the lack of scale between plant components. The absorber and neutralizer, for instance, are both several times larger than required when compared to electrolyzer output. This situation is also the result of practical considerations. The electrolyzer was already available from earlier sulfate-cycle studies. The neutralizer, which has to accommodate numerous lines, a rotating-shaft seal, and electrodes for pH control, resisted excessive miniaturization. Absorber dimensions were fixed primarily by the packing size. Despite this disparity in equipment size, the required tasks of O_2 generation and CO_2 removal can be scaled in relation to each other.

Since contaminants in the working fluids would make the operation of the plant more difficult to evaluate, materials of construction have been selected for corrosion resistance. Plastics which generally would not be suitable for submarine duty have been extensively used because of their chemical resistance, machinability, and availability. As a bonus, utilization of a plastic such as Lucite permits useful visual observations of liquid distribution in the absorber packing and CO_2 formation in the neutralizer. Some of the materials in the plant may be used in a full-size unit. Most noteworthy are the following materials. Polypropylene Pall rings are used as packing in the absorber. These are 5/8 in. in nominal size, and their weight is less than 5 pounds per cubic foot. The ceramic Intalox Saddles used previously, although more efficient in absorption than the Pall rings, are not suitable for continuous operation in a caustic medium. Carpenter 20 steel is used in the shaft and propeller of the neutralizer. This component, which operates at higher than ambient temperatures, may have to withstand severe corrosive conditions.

The method of operating the plant is best explained with the aid of a flow diagram (Fig. 7). An aqueous solution of alkali sulfate is pumped from the regenerated feed tank to a constant-head tank. The rate of addition of this solution to the electrolyzer can be

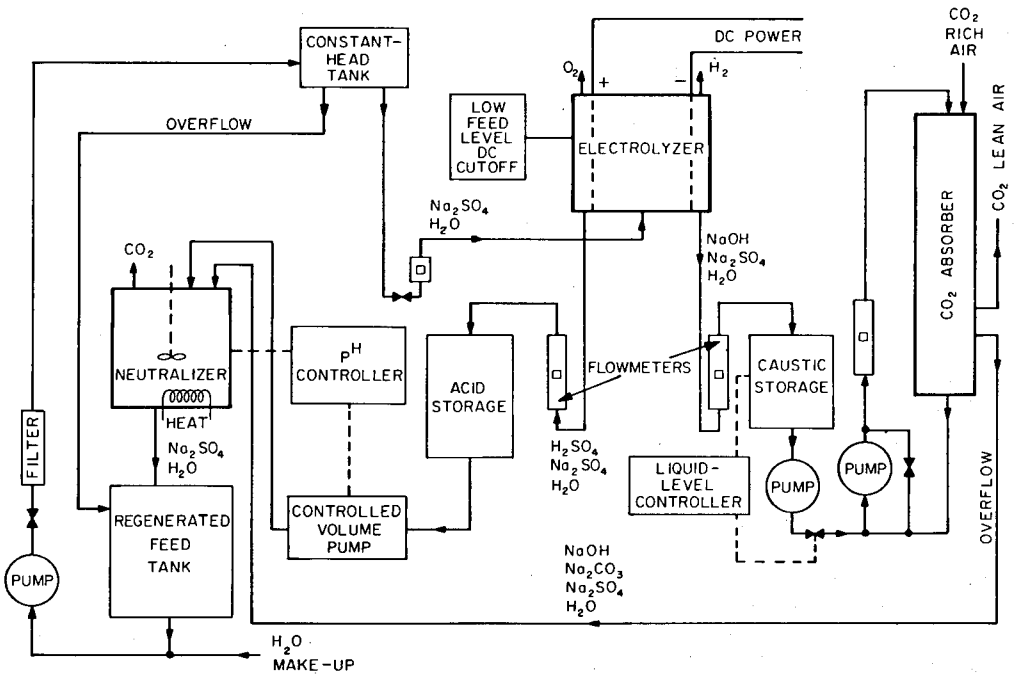

Fig. 7 - Laboratory sodium sulfate cycle plant

maintained constant. As a result of the electrolytic decomposition of water in the presence of an alkali sulfate, aqueous solutions of sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) are produced. Each of these solutions, containing some alkali sulfate, is collected separately in storage tanks.

In transferring the caustic from its storage tank to the absorber, it is desirable to regulate the pumping rate so that it matches the caustic output of the electrolyzer. This is accomplished by means of a liquid-level controller. A pressure-sensitive diaphragm in the caustic tank detects a change in liquid level from a predetermined height. A signal is then sent to a controller which operates a pneumatic control valve on the discharge side of a centrifugal pump.

In the absorber the caustic and the air enriched with CO_2 are passed concurrently downward over a packed bed (4). To maintain efficient contact between the air and caustic, the liquid is recirculated by a recycle pump. As additional caustic is sent to the absorber, which operates at a fixed liquid level, partially carbonated caustic overflows to the neutralizer.

Electrodes for pH control which are mounted in the neutralizer sense the alkaline condition and transmit an electronic signal to a pH recorder-controller. This controller sends a pneumatic signal to a positioner which regulates the stroke length, and therefore the pumping rate, of a diaphragm pump. The acid solution is now pumped to the neutralizer as required by the rate of caustic flow and the set point of the pH controller. This results in the neutralization of acid and caustic, liberation of CO_2, and regeneration of alkali sulfate.

Distilled water must be added to replace losses which occur as a result of electrolytic decomposition and evaporation in the absorber and neutralizer. If this water is added at a constant rate to the suction side of the pump, it should be quickly and thoroughly mixed

into the alkali sulfate solution. A specific-gravity measurement at the constant-head tank will then indicate the necessary correction in water addition.

The laboratory sulfate-cycle pilot plant, despite its small size, lack of scale in equipment size, and wide use of strictly laboratory materials and methods, will do its required task, which is to operate as a cycle while maintaining a balance between O_2 and CO_2. To evaluate the plant's performance, it will be necessary to operate the cycle continuously over an extended period of time. The first goal will be a continuous 30-day operation with an aqueous solution of sodium sulfate, 18 percent by weight, as the feed to the electrolyzer. The information gained by this project should be of great value in the design of larger plants.

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CHAPTER 2

ALGAE IN A PHOTOSYNTHETIC GAS EXCHANGER

P. J. Hannan

The initial report of this series (1) contained a chapter by J. M. Leonard in which the objectives and some of the preliminary findings of the algae project were given. The purpose of this chapter is to summarize the findings of the past year and also to make an appraisal of the problem based on personal observations and discussions with others working in the field.

PHYCOLOGICAL STUDIES

The organisms selected by Ritchie (2) as a result of screening studies were compared with the Sorokin strain (3) of Chlorella pyrenoidosa. It was found that the growth rate of the latter was greater than those isolated by Ritchie, so all of the experiments reported in this chapter have been conducted with the Sorokin strain. It is planned to continue with this organism unless some factor becomes apparent that shows it would not be suitable. Such factors as long-term stability, foaming properties, odor, and the like must be weighed finally, but its high growth rate and its high temperature optimum (39 °C) make it very attractive.

EXCHANGER TRIALS

The first gas exchanger used was described in last year's report. This unit provided practical experience in the problems associated with mass culture of algae, but its deficiencies indicated the need for a unit with greater flexibility. Figure 8 is a diagram of the second gas exchanger, which was designed as an adaptable laboratory model. The algal suspension was contained in glass tubes placed in a flat coil in each of five metal trays. Each tray contained approximately 100 ft of glass tubing (3/8 in. I.D.) with a volume of around 2 liters, making a total of 10 liters of suspension illuminated at all times. The bottom of each tray was transparent Lucite, providing illumination to the tubes from below as well as above. The purposes of this design were to provide easy means of:

1. Varying light sources (fluorescent or incandescent lights can be used).

2. Varying the thickness of suspension being illuminated (by changing the diameter of the tubing).

As shown in Fig. 8, the algal suspension was pumped from the reservoir A through the illuminated glass tubing into the gas separator B, from which it drained back into the reservoir for recycling. At point C the CO_2-air mixture was introduced. Bubbles of the gas were in intimate contact with the suspension until released at the gas separator, from which they were led through a Beckman oxygen analyzer, Model F-3 and a Liston-Becker CO_2 analyzer, Model 11.

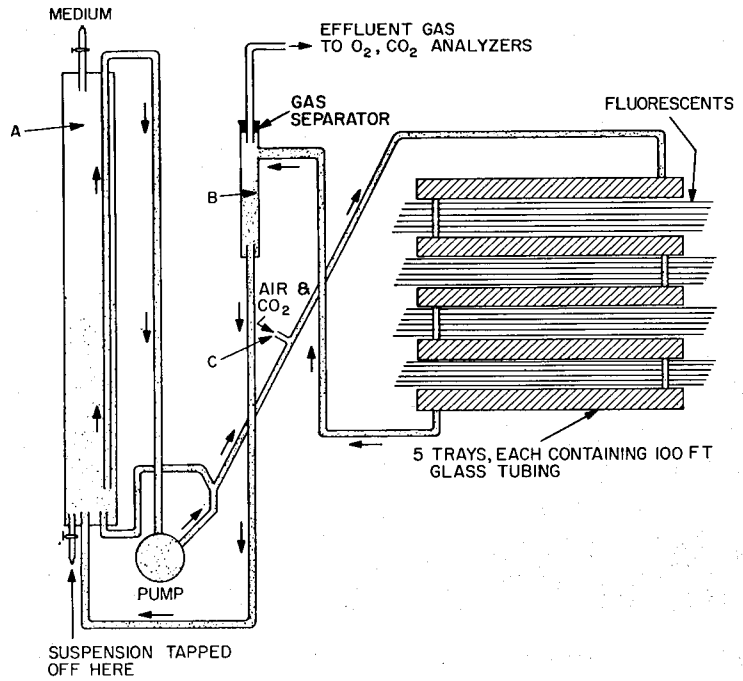

Fig. 8 - Schematic diagram of pilot plant

The purpose of the reservoir was to stabilize the system against momentary changes in pumping speed or gas flow. The CO_2-air mixture was passed through at approximately 450 cc per minute, providing a contact time of 10 minutes with the suspension. Starting with a 5-percent CO_2 content, the gas was CO_2-free by the time it had gone through the system, providing 1500 cc oxygen per hour. The algal suspension was maintained at an average density of 6 to 7 cu mm of cells per ml of suspension.

The unit was operated continuously for 24 days, with generally satisfactory results. Fresh medium was supplied on a batch basis. The chief initial disadvantage of the unit was the rather slow circulation rate through the tubing, which allowed the cells to stick to the walls of the glass tubes and the rubber connectors, making it impossible to determine the number of cells present. However, after several weeks' operation the cells were washed free of the walls of the tubing, perhaps because of the release of surface-active agents by the cells or an increased rate of flow.

This pilot plant is now being used in a slightly different manner. High-intensity incandescent lights are being used in place of fluorescent lamps, and only two trays containing glass tubing are in use. The rate of flow of the suspension is much greater, and there is less tendency for the cells to stick to the walls. The reservoir has been eliminated, and the suspension is led directly from the gas-release chamber back into the lighted area. A photoelectric device has been inserted into the line between the gas separator and the tubing, and the density of the suspension is recorded automatically.

SMALL-CULTURE EXPERIMENTS

The unit shown in Fig. 9 was used to study the effects of changes in the culture medium. The test tubes used were 25 x 300 mm; 40 ml of suspension (0.3 cu mm packed cells/ml) was placed in each tube, and every 24 hours thereafter half of the suspension

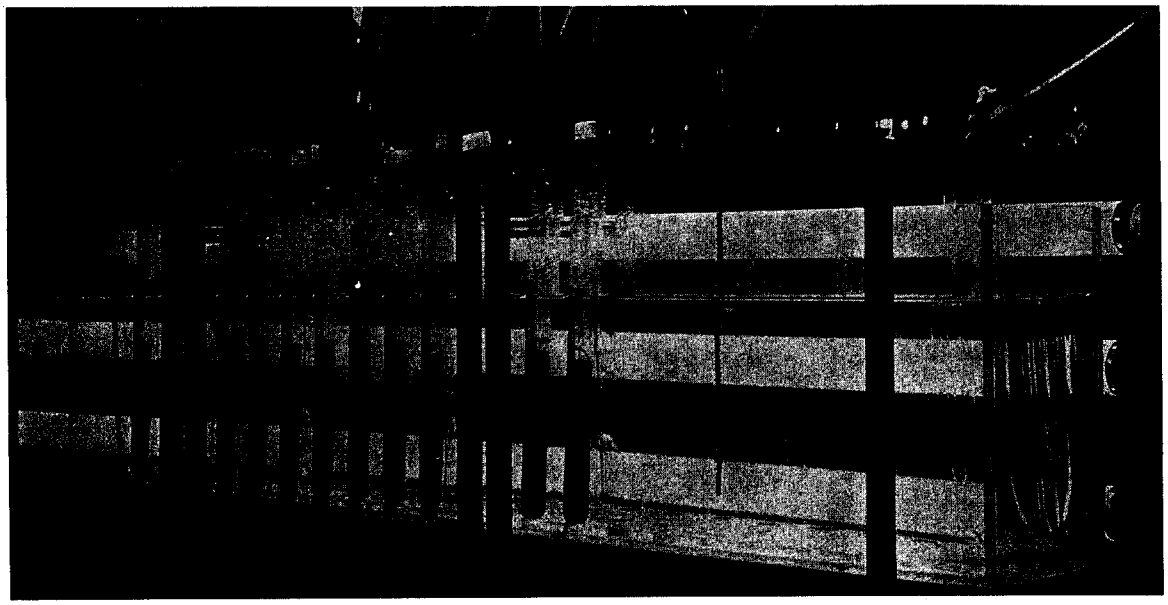

Fig. 9 - Apparatus for studying the growth rate of algae

was removed and replaced by fresh medium. Colorimeter readings were taken just prior to the replenishment of the medium each day for three days. In order to keep the colorimeter readings in the region in which Beers' Law applied, 1 ml of suspension was diluted to a total of 10 ml.

Typical Growth Promoters

The literature contains several references to plant growth regulators which have had a beneficial effect on algae. Perhaps the most remarkable was an increase of 261 percent in the growth rate of Chlorella by the addition of 33 ppm phenylacetic acid, as reported by Brannon and Bartsch (4). However, we have noted that phenylacetic acid and the other compounds listed in Table 4 had an inhibitory effect on the Sorokin strain of Chlorella, a fact which has been confirmed by others (5). Naphthaleneacetic acid was the most toxic, giving 89-percent inhibition during the first day's growth at a concentration of 100 ppm, while the least toxic was phenylacetic acid. The algae showed a tolerance, in time, to the effects of indole-3-acetic acid, indole-3-butyric acid, and also phenylacetic acid.

Esters of Phosphoric Acid

High-energy phosphates play an important part in the growth processes of any living organism, and it was postulated that one of the limiting factors in the growth rate of algae might be the accessibility of phosphorus compounds to the cytoplasm of the cell. It was hoped that by providing the culture medium with organically bound phosphates, the transport of these phosphorus compounds across the cell membrane might be quicker than that of inorganic phosphorus and thus result in an increased growth rate. The carbohydrate phosphates listed in Table 5 were incorporated in the medium at concentrations of 100, 200, and 400 ppm phosphorus in addition to the regular inorganic phosphorus content of 570 ppm. Table 5 also shows the effect of substituting organic phosphate entirely for inorganic (at the 570-ppm level) and that of increasing the inorganic to 970 ppm. It is obvious that the four compounds tested have a beneficial effect on the growth

Table 4
Effect of Typical Growth-Promoting Compounds

Compound	ppm	Percent Growth Compared With Control Sample		
		1 Day	2 Days	3 Days
Phenylacetic acid	2.5	85	92	94
	5	90	108	103
	10	100	103	105
	25	100	118	
	50	100	100	
	100	93	110	
Naphthoxyacetic acid	2.5	86	110	103
	5	85	100	80
	10	75	81	87
	25	77	62	58
	50	53	46	42
	100	31	23	23
Naphthaleneacetic acid	2.5	92	97	100
	5	90	74	108
	10	67	74	85
	25	64	56	56
	50	42	23	23
	100	11	0	0
Indole-3-acetic acid	2.5	68	84	95
	5	77	88	100
	10	91	100	87
	25	68	72	
	50	57	62	
	100	25	?	
Indole-3-butyric acid	2.5	92	97	100
	5	90	74	108
	10	67	74	85
	25	81	86	
	50	54	83	
	100	30	50	
2,4-Dichlorophenoxy-acetic acid	2.5	90	85	91
	5	90	89	87
	10	89	82	88
	25	79	67	51
	50	69	56	50
	100	48	35	41

NOTES - 1. Concentrations of 2.5, 5, and 10 ppm tested simultaneously at one time, 25, 50, and 100 ppm tested at another.

2. Third-day readings were omitted in some cases.

Table 5a
Effect of Organic Phosphates on Growth

Compound	Phosphorus (ppm)		Percent Growth Compared With Control Sample		
	Carbohydrate Phosphate	KH_2PO_4	1 Day	2 Days	3 Days
Glucose-1-phosphate	400	570	128	93	106
	200	570	121	93	101
	100	570	113	110	113
Fructose-1, 6-diphosphate	400	570	138	123	114
	200	570	124	131	122
	100	570	114	127	118
Sodium glycerophosphate	400	570	104	119	108
	200	570	108	118	110
	100	570	110	121	119
Calcium glycerophosphate (not soluble at higher conc.)	100	570	117	126	133
	50	570	111	114	126
	25	570	110	115	124

Table 5b
Comparison of Total Organic Phosphorus With Total Inorganic Phosphorus

Compound	Phosphorus (ppm)		Percent Growth Compared With Control Sample		
	Carbohydrate Phosphate	KH_2PO_4	1 Day	2 Days	3 Days
Fructose-1, 6-diphosphate	570	0	118	109	109
Fructose-1, 6-diphosphate	970	0	126	95	91
Potassium di-hydrogen phos. (KH_2PO_4)	0	970	95	84	77

rate. The first three seem to have a more pronounced effect in the early stages, while the calcium glycerophosphate progressively stimulates the growth. However, this experiment was performed only once, and the results should be considered in this light. The total substitution of organic phosphate, at the 570-ppm level, provides satisfactory growth, but 970 ppm phosphorus, either as total inorganic or total organic, has its limitations.

These carbohydrate phosphate esters are stronger acids than phosphoric acid, and they do not exist in an un-ionized form until the pH is lowered to less than 1.0. Therefore, their utilization by the algae must be accomplished by some means other than permeation of the cell and subsequent hydrolysis. However, the hydrolytic products of calcium glycerophosphate, for example, provide a growth stimulus, as shown in Table 6.

Table 6
Effect of Hydrolytic Products of Calcium Glycerophosphate on Growth Rate (at a level of 100 ppm organic P)

Hydrolytic Product	Quantity of Product (ppm)	Percent Growth Compared With Control Sample		
		1 Day	2 Days	3 Days
Ca^{++} (as $CaCl_2$)	129 as Ca (compared with 8 ppm in control medium)	130	125	121
Glycerine	294	126	139	133
P (as in KH_2PO_4)	100 as P (above the normal level of 570 ppm, total P being 670)	111	112	93
Ca^{++}	129			
Glycerine	294	119	122	108
P	100			

Each of the products of hydrolysis, singly and in stoichiometric combination, produced beneficial results of the same magnitude as the calcium glycerophosphate itself. Probably the glycerol type would be the most effective in promoting growth, but it would probably not have an effect on the oxygen production by the organism, which is the primary goal of this work.

There is something to be said for the use of the carbohydrate-phosphate esters in promoting fast growth. A detailed account of the succession of observations made during this study is not necessary here, but it is worth noting that the controls at times showed unexplainable declines in growth rate after a few days culturing. In each case the medium which contained some organic phosphorus did not show this decline.

INCANDESCENT LIGHTS

The efficiency of fluorescent lights in terms of light energy per unit of power input is greater than incandescent lights. But in terms of energy per unit volume of the light source, the incandescents can be more efficient by a factor of 3000 (6). Since the volume of an algal unit in a submarine is a more critical factor than its electrical efficiency,

incandescent lights are to be preferred in the present state of our knowledge. A comparison of incandescent and fluorescent Power Groove lights (General Electric) is shown in Table 7.

Table 7
Comparison of Power Groove Fluorescent Lights
and 1500-Watt Incandescent Lights

Lights	G.E. Model	Watts	Length (in.)	Diameter (in.)	Lumens
Fluorescent	F 48 PG 17/CW	48	45	2-1/16	6,900
Incandescent	1500 T3Q/CW	1500	10	3/8	33,000

An algal unit in a submarine will probably consist of a large tank in which incandescent lights are submerged in the suspension. Assuming this design, the parameters demanding immediate investigation are:

1. The optimum light intensity for a given suspension density, and the proper distance between lights

2. The optimum suspension density for the production of oxygen.

Other factors must be determined, but the point being investigated now is the optimum spacing of the lights.

The heat generated by 1500-watt lights must be dissipated efficiently if the light is to be immersed in an algal suspension without unduly increasing the temperature. In Fig. 10 is shown a glass jacket designed to accomplish the necessary cooling. The inner diameter is 1-1/2 in., and it contains the light which is held in a brass framework. The cooling is accomplished by forcing air through the inner chamber and water through the cooling jacket.

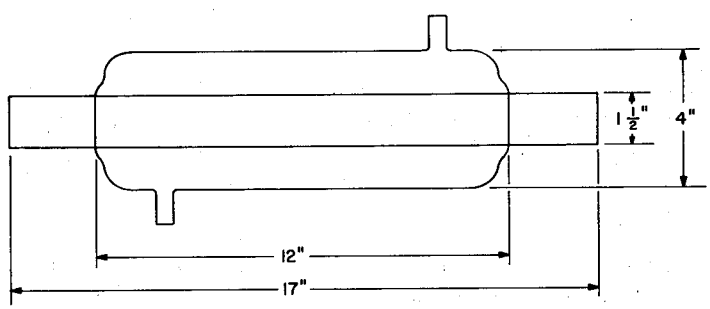

Fig. 10 - Glass jacket for cooling algal suspension

Figure 11 is a sketch of a unit in which one jacketed high-intensity light was used to illuminate suspensions contained in tubes of different diameters. Two different suspension densities, 0.3 mm^3/ml and 1.2 mm^3/ml, were exposed to light intensities ranging from 2000 to 4700 foot-candles. Colorimeter readings (1 ml suspension diluted to 10 ml total) were taken hourly for six hours. The difference in readings between the third and fourth

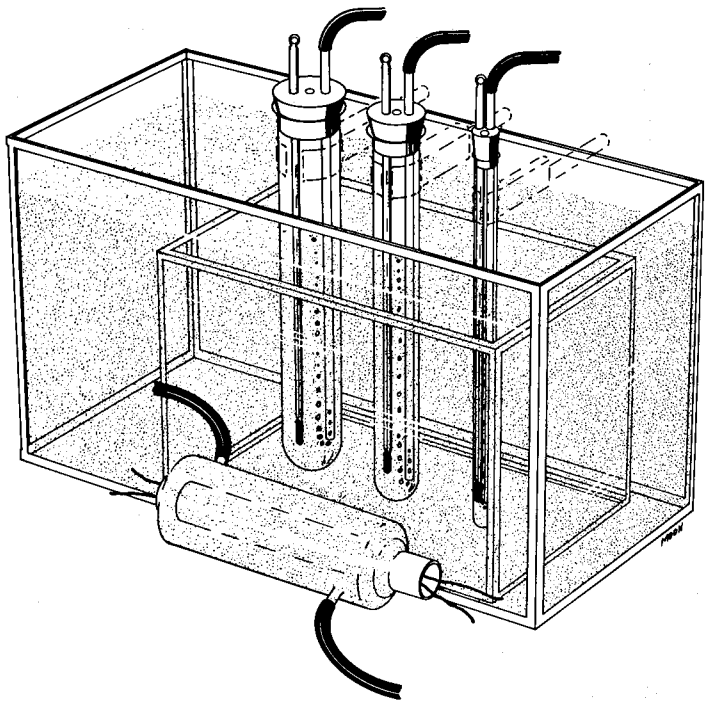

Fig. 11 - Illumination of algal suspensions contained in 1-, 2-, and 3-in.-diameter tubes

hours was used to calculate the doubling time of the suspension during the logarithmic growth phase. The diameters of the test tubes used were 1 in., 2 in., and 3 in., and the interrelated effects of suspension density, illumination, and tube diameter are summarized in Table 8. For the sake of clarity the same results are plotted in Fig. 12.

Table 8
Doubling Times for Suspensions of Different Densities

Light Intensity (foot-candles)	Initial Suspension Density (mm^3/ml)	Diameter Tube (inches)	Doubling Time (minutes)
2,000	0.3	1	171
2,000	0.3	2	211
2,000	0.3	3	194
3,200	0.3	1	187
3,200	0.3	2	203
3,200	0.3	3	223
4,700	0.3	1	208
4,700	0.3	2	191
4,700	0.3	3	208
2,000	1.2	1	333
2,000	1.2	2	486
2,000	1.2	3	618
3,200	1.2	1	311
3,200	1.2	2	390
3,200	1.2	3	583
4,700	1.2	1	258
4,700	1.2	2	346
4,700	1.2	3	377

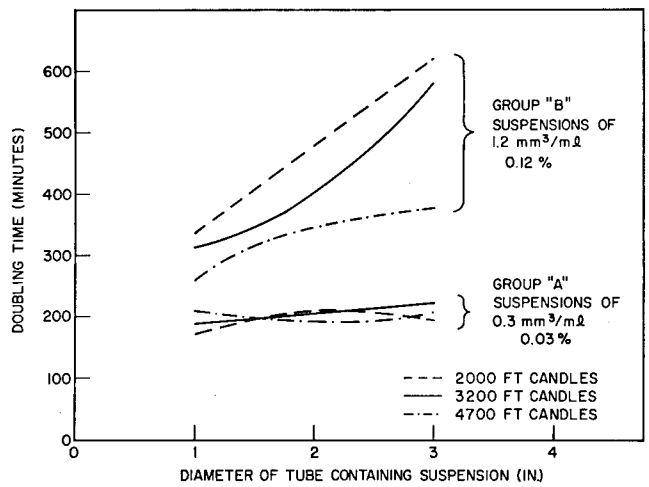

Fig. 12 - Doubling time as a function of tube diameter, suspension density, and light density

It may be seen readily that the thinner suspensions (group A in Fig. 12) are sufficiently transparent that the 2000-foot-candle intensity penetrates through the 3-in. section as well as the 1 in. and the growth rates are similar. In a suspension four times as dense, the 2000-foot-candle intensity is not as productive as the 4700 foot candles. The effect is barely noticeable in the group A (0.03 percent) cultures, but it is appreciable in the group B suspensions (0.12 percent). Since only three points are plotted for each curve, there is uncertainty about their true shape.

Experiments in progress now consist of placing culture tubes of varying diameters, and containing different suspension densities, between two incandescent lights. By plotting the growth rates obtained against the light intensities used, it is hoped that optimum conditions may be determined. The results obtained to date are not complete enough to include in this report.

FUTURE PLANS

A new unit is being constructed to produce algae at a rapid rate and in large quantities. It is a Lucite container in which three jacketed lights are placed so that the maximum light path through the algal suspension is 2 inches. Such an apparatus is needed to provide the large amounts of fresh algae involved in the studies with dense suspensions. It will also provide useful data on oxygen production and carbon dioxide removal at varying flow rates of the input gas.

The experiments involving dense algal suspensions (perhaps in the 2 to 8 percent wet-volume range, corresponding to 20 to 80 mm^3/ml) will provide the data necessary for the design of an algal farm suitable for submarine use. A small model containing eight or ten lights will then be made and its performance studied.

Some automation is required to operate a sizeable pilot plant, and preliminary study along this line has been done. A photoelectric unit has been developed to determine the density of the suspension and record it automatically. This same device will also be used to activate solenoid valves, permitting the simultaneous introduction of fresh medium and removal of an equal quantity of suspension. Thermistors connected to suitable relays will be used to turn off the lights if the temperature rises above 39 °C.

A subject requiring investigation is the proper diameter for the cooling jackets surrounding the lights. This diameter, which determines the closest distance the cells may approach the light source, has a bearing on the maximum light intensity to which any cell may be exposed. There is some disagreement among competent investigators concerning the proper diameter for this jacket, and some experimentation is required to provide a definitive answer.

Another subject to be investigated is the production of gases other than oxygen by the algae. A brief trial with a Perkin-Elmer hydrocarbon detection apparatus indicated that some hydrocarbons are produced under certain conditions. This effect, if indeed it is real, certainly would have a bearing on the feasibility of the use of algae. In this regard, bacteria-free cultures should be used; otherwise the contributions of both types of microorganisms to the gas phase would be mixed. The problem of maintaining sterile conditions in a large vessel under the influence of thousands of cubic feet of input gas is a formidable one. The thought at present is to sterilize the entire system initially with a propylene oxide-CO_2 mixture, to sterilize the medium, and then to remove microorganisms from the gas stream by passage through micropore filters.

Some problems to be resolved in the design of an efficient algal gas exchanger have been pointed out (7). In certain instances straightforward but time-consuming solutions are foreseen, but others might be difficult and require more man-hours than can be provided under the existing organization.

On the basis of present knowledge one can be rather sure that 75 liters of suspension will provide sufficient oxygen for one man. This figure has been obtained by at least two investigators and has been approached in the work conducted at NRL. In none of these studies was the apparatus designed with the thought that it represented optimum efficiency. The algae used has a fast growth rate, but much remains to be learned of its performance under intensive culturing conditions, and the knowledge necessary to attain peak performance is being gained slowly. Assuming that 75 liters of suspension per man is a firm figure, the volume for a crew of 100 men would be approximately 7500 liters. For the sake of comparison, the ordinary CO_2 scrubber aboard a submarine is approximately 3 ft 9 in. x 3 ft 9 in. x 6 ft 8 in., a calculated volume of 2800 liters. (Two such scrubbers are on each nuclear submarine, but normally only one is operated at a time.) Since the algae would perform the dual function of CO_2 removal and O_2 production, the disparity in the two figures is not intolerable. However, the additional volume of light sources, dehumidifiers, etc., attendant to the algal process must also be considered.

A number of promising developments have occurred, some of them in very recent weeks. One of these is the performance of a porcelain candle bacteriological filter as a gas sparger. Very large quantities of gas may be passed through this filter with only a slight back pressure; the two major benefits of this type of sparger are the fine bubble dispersion, which provides very rapid CO_2 saturation of the medium, and the minimum displacement of liquid. For example, it is possible to force 50 liters of gas per minute through a volume of only 25 liters suspension, and the level of the liquid is raised less than 5 percent. The displacement of liquid by input gas had been regarded previously as a major problem, but present indications are that this bacteriological filter will perform admirably.

A recent discovery (8) might have a bearing on the oxygen productivity of algae. It was found that the addition of 0.1 percent polyvinyl alcohol to the culture medium provides an increase of 300 percent in the chlorophyll content of Chlorella cells. While the work was not concerned with oxygen production, there is reason to think that it must also be increased. This strange chemical effect prompts the thought that much work should be done in improving the culture medium. The current emphasis, in this and other laboratories, has necessarily been placed on the design of new equipment, but there is little doubt that the culture medium can be improved as a result of more research.

It appears that several hitherto ignored factors must be investigated. For instance, there is reason to suspect that the physical dimensions of gas bubbles around a light source may have an effect on the growth rate of the algal cells. Perhaps the diffraction of light by bubbles causes alternately a lens action, which increases the light intensity on the cells, and a diffraction which results in comparative darkness.

The hope of several investigators is to increase the productivity of the algae so that 20 liters would be sufficient to sustain a man's oxygen needs. Whether this will be realized in the near future is impossible to say, but there is some hope that such a figure might be reached.

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CHAPTER 3

CHLORATE CANDLES

J. K. Musick and P. R. Gustafson

INTRODUCTION

The chlorate candles now in use are made by mixing the ingredients with 3 percent by weight of water and pressing. Salt dissolved in the water acts as a binder for the pressing operation, and the water is removed afterwards by drying. The composition by weight of the finished candle is 88 percent sodium chlorate, 4 percent iron powder, 4 percent barium dioxide, and 4 percent steel fiber. The candles are about 6-3/8 in. in diameter, 11-1/4 in. long, weigh about 26-1/2 pounds, and deliver about 120 cu ft of oxygen. The candles differ from those previously used by the use of steel wool instead of asbestos as the fibrous ingredient.

CANDLES

During the interval of about one year since the last report, the new candles were tested on a cruise of the SKATE. The chlorine problem appeared to be solved, since 70 candles were burned without releasing a detectable amount of chlorine. Also, Draeger tube tests made at NRL indicated less than 1 ppm of chlorine evolved from the new candle. However, carbon monoxide is still evolved to a limited extent.

One somewhat undesirable characteristic of the new candle is that it burns at a variable rate. During some spurts of activity, the rate of oxygen production suddenly increases to almost three times its average value. The cause of this variable burning rate is not known, although it would seem reasonable to suspect that the candle mixture is not entirely homogeneous.

On the basis of information which indicated that an efficient chlorate candle had been developed in France, two such candles were procured and tested at NRL. The candles were packed and shipped in containers which were also candles designed to be used on their furnaces. The NRL tests did not show the French to have any significant advantage over the Mine Safety Appliances Corp. (MSA) candles, partly because each French candle container, by serving as the furnace, penalized the comparison on a weight-and-volume basis. The French candle had a square cross section and consisted of four pressed blocks stacked one atop another. The whole candle was packed in soda lime with a glass blanket filter above the soda lime. An electric igniter was fitted into the top of the candle, and the canister had a safety rupture disc on the bottom. The candle weighed about 16 pounds and was rated at 2 cubic meters (about 70 cu ft) of oxygen. Calculated on the basis of weight loss, one of these candles produced about 51 cu ft of oxygen. However, in this test, the bottom block, or about one-fourth of the candle, failed to burn. The gas produced by this candle was tested for chlorine and carbon monoxide with Draeger and Kittagawa tubes. At the start of burning, a very low but unknown amount of chlorine and a fairly large amount of carbon monoxide were indicated. After starting, a small amount of chlorine and 0-20 ppm of carbon monoxide were indicated. However, when one of these candles was burned without its surrounding layer of soda lime, carbon monoxide concentrations as high as 2000 ppm and chlorine concentrations of 200 ppm in the effluent gas were measured.

FURNACE AND FILTER

During the SKATE cruise, faulty operation of the smoke filter resulted in the use of fewer candles than had been provided for the test. As a result of this and other experiences, the report on the cruise recommended that:

1. The chlorine filter on the candle furnace be eliminated
2. The frame of the candle furnace be shortened by eliminating the tip-down feature
3. The furnace side arm be removed and the smoke filter be placed on top of the furnace
4. A water scrubber be used for a smoke filter if possible, since the present filters clog rapidly and are inconvenient.

NRL subsequently was asked to investigate the feasibility of developing a water scrubber to replace the smoke filter. At NRL, several types of smoke filters, including a water scrubber, an electric precipitator, and a glass-blanket filter were considered.

One possible advantage of a glass-blanket filter element is that it might be packed in the same container with the candle at the factory. If a system such as this could be proved feasible, it would eliminate the need for supplying filters separately, and at the same time would make a fresh filter element available for installation in the filter each time a fresh candle was placed in the furnace. For this reason, one of the glass-blanket discs, commonly packed with the candles, was fitted in a specially designed holder and tested with a number of the asbestos-type candles. It successfully filtered the smoke from three of these candles and clogged sufficiently to raise the burning pressure to 15 psi shortly after the fourth candle was ignited. On the basic of these tests, a flat cylindrical filter to contain two of the glass-blanket filter discs was built. It was designed to filter the gas from one furnace charge of two candles and to have the filter discs replaced each time the furnace was recharged. This filter was tested on a cruise of TRITON in August and September 1960. The Mine Safety Appliances Company made their own design of the same type of filter, built a new furnace, and provided a supply of the glass-blanket discs, all of which were tested on the same cruise.

The new furnace was designed along the lines suggested in the SKATE report. The chlorine filter was eliminated, and the smoke filter was placed on top of the furnace to permit reducing its widths. The tip-down feature was eliminated to permit making the furnace lower. The performance of the glass-blanket filter on the TRITON cruise (fall of 1960) was unsatisfactory. Here it clogged sufficiently to lift the furnace lid and permit the smoke to escape before the second candle had completely burned, although the laboratory tests had indicated it would handle six candles. The difference in performance is apparently due to the different candles used. Asbestos-type candles were used in the laboratory tests and steel-wool candles aboard TRITON. As mentioned before, the steel-wool candle burns at a variable rate, which at times is very high. Furthermore, an examination of the smoke residue collected on the filter indicates that the composition of the smoke from the two candles is different. The residue from the steel-wool candle is dark brown in color, having the appearance of caked mud. Its composition with respect to barium, iron, and sodium chloride is near that of the candle. That from the asbestos candle is lighter in color and appears to be more porous. In any event, if the glass-blanket filter is used, more filtering area is required for the steel-wool candle. A new filter is being designed.

STORAGE SAFETY

Several tests were made to determine the ignitability and burning characteristics of chlorate candles under storage conditions. In these tests, the asbestos candles were used, and they were not removed from their metal canisters. They were burned generally in groups of three, stacked either vertically or horizontally, and either with or without such organic matter as wood, carboard, and battleship linoleum. The candles were ignited by heating for two to eight minutes, with a small gas-oxygen torch, an area on the canister over the candle igniter. Holding a red heat on this spot for a few minutes would ignite a candle. When a candle was ignited without burning a hole in the canister, internal pressure would slowly bulge the canister ends and then rip the circular seam joining the end to the cylindrical body. The sudden release of pressure would displace the canister a few inches. If no organic matter were present, the candle would then burn normally to completion, scorching the paint on contacting canisters but not igniting other candles. If organic matter were present in sufficient quantity, then all metal canisters and all candles would ignite and develop into a considerable conflagration. Even if no organic material were present, it was possible to ignite the metal canisters in the area next to the igniter. When this happened, it appeared that the torch burned the hole in the canister. However, oxygen from the candle may have helped the torch ignite the metal and certainly was instrumental in sustaining the fire. Water is effective in extinguishing the fires. However, it was observed that application of a stream of water to burning candles sometimes resulted in a low-order, explosion-like reaction which displaced the candles a foot or two. It was surmised that this reaction may have been due to the sudden generation of steam. Color movies were taken of the burning tests.

HOT-PRESSED CANDLES

Instead of adding water to the candle mixture and pressing, it is possible to cast chlorate candles and obtain the advantages of higher density, better handling characteristics, and elimination of the drying procedure. However, the casting process is difficult to employ in production, because the insoluble ingredients tend to settle from the molten mixture before it solidifies. Also, the melting point of the candle mixture is near the decomposition temperature of the sodium chlorate.

A possible new fabrication method that may combine some advantages of both the wet-pressed candle and the cast candle is that of pressing or extruding a heated candle mixture. Hot-pressing or hot-extrusion of candles may be feasible and may eliminate the need for using water, because physical changes in the solid state (softening, sintering, increased mobility of the molecules, etc.), occur before the melting point is reached (1). In view of these facts, a study was made to determine the effect certain variables have on the physical properties of candles prepared by the hot-pressing method. The variables studied were type of fiber (binder), size of fiber, particle-size distribution in the candle mix, pressing pressure, and pressing temperature. For the purpose of these studies, six types of candles were used. All six types had the same weight composition (88 percent sodium chlorate, 4 percent iron powder, 4 percent barium dioxide, and 4 percent fiber) and, except for particle-size distribution, differed only in the type of fiber binder and method of pressing. These different types of candles are described in Table 9.

Figure 13 shows the effect of pressing pressure on candle density for the MSA mixture pressed at room temperature and for the 2S mixture pressed at various temperatures. The other candle mixtures listed in Table 9 show the same relationship between pressing pressure, pressing temperature, and candle density as does the 2S mixture. The figure shows that the theoretical crystal density (2.70) is reached at about 12,000 psi and 225 °C. However, at 200 °C this density is not obtained even at 40,000 psi. The candle specimens used to obtain the data of Fig. 13 had a height-to-diameter ratio of about 0.5. Specimens of the

Table 9
Types of Candles Studied

Mixture No.	Fiber Type and Size	Particle Size, d_w (microns)*	Method of Pressing
1S	Steel wool, grade OO (Brillo) avg. length 4 mm, avg. diam 0.02 mm	225	Hot Pressed
2S	Steel wool, grade 2 (American Steel Wool Mfg. Co.) avg. length 6 mm, avg. diam 0.06 mm	210	Hot Pressed
MSA	Same as 2S	Same as 2S	3% water added just prior to pressing at room temperature; cake dried at 115°C for 48 hr. This corresponds to present candle.
3S	Steel wool, grade OO-Sf (super-fine) American Steel Wool Mfg. Co., avg. length 0.7 mm, avg. diam 0.02	240	Hot Pressed
6G	Glass fiber, furnished by Mine Safety Appliance Co., avg. length 0.7 mm, avg. diam 0.02 mm	225	Hot Pressed
7G	Same as 6G	400	Hot Pressed

*The weight mean diameter, d_w, is the diameter of a particle whose weight multiplied by the number of particles in the sample equals the weight of the sample (2).

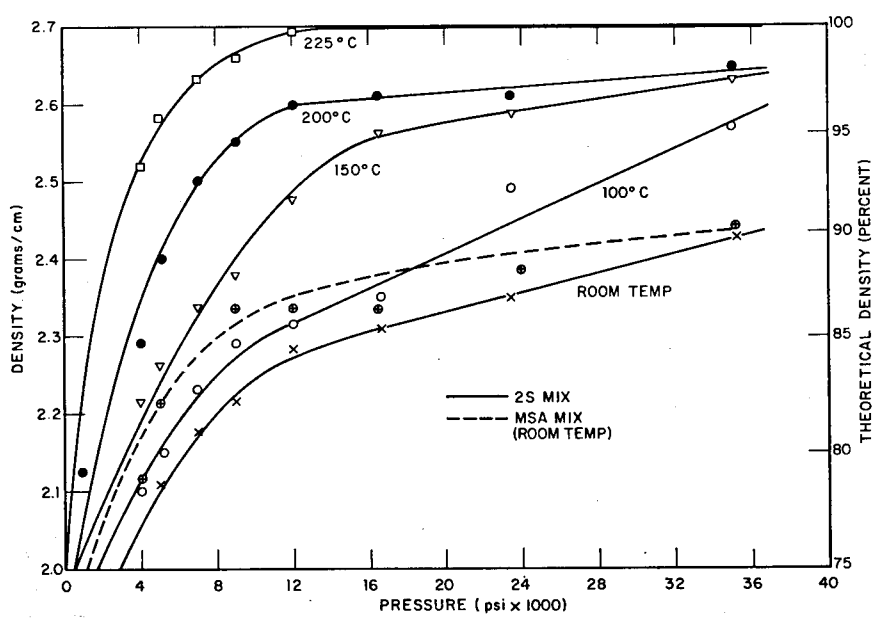

Fig. 13 - Effect of pressing pressure and temperature on density of 2S and MSA candle mixes

same material similarly pressed, but of a different size and height/diameter ratio (1.0), were found to have a density about 0.1 g/cc less than the corresponding specimens of 0.5 height/diameter ratio.

Figure 14 shows the compressive strengths measured for the various candle mixtures pressed to different densities. These data show that a bonding fiber such as fiber glass or steel wool is necessary for holding the cake together. For example, a ten-gram cake containing no fiber and pressed to a density of 2.4 g/cc is crushed completely by 1000 psi, while the cakes containing fiber and pressed to the same density can withstand pressures of the order of 7000 psi. A comparison of the rupture pressures of 1S and 3S mixtures in Fig. 14 indicates that the strength of the cake is affected by fiber length, which should not be too small if strength of the cake is important. Also, a comparison of the rupture pressures of mixture 1S with that of 2S and MSA indicates that the length-to-diameter ratio of the fibers should not be too small.

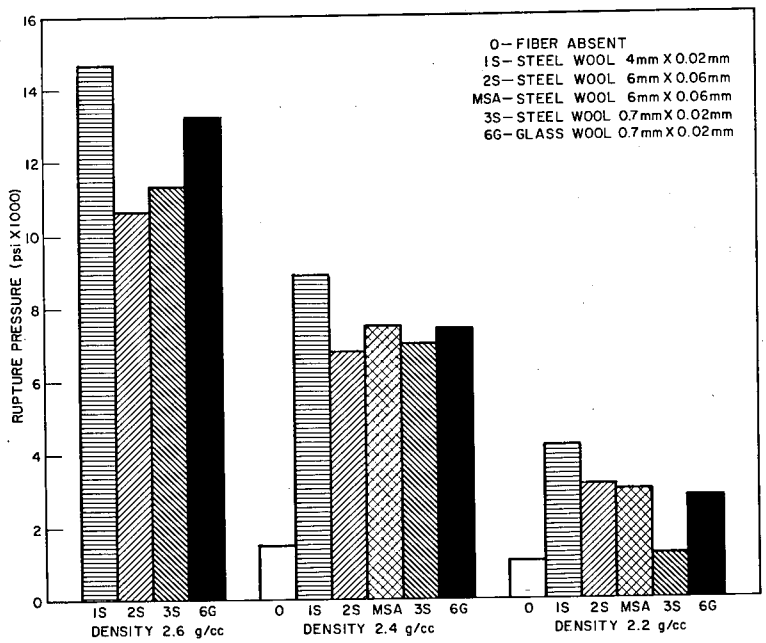

Fig. 14 - Effect of fiber and density on strength of chlorate candles

The particle-size distribution in the candle ingredients has a significant effect on candle strength. This is illustrated in Fig. 15, in which the rupture pressures of 6G and 7G mixtures are compared at different densities. The 6G and 7G mixtures differ only in particle size of the ingredients other than the binder. Figure 15 also shows that the strength of 7G samples (larger particles) is only about 1/3 that of 6G samples at densities of about 2.5. It was found that decreasing particle sizes to values significantly lower than those of the 6G mixture (50 percent <325 mesh as compared with 17 percent <325 mesh for the 6G mixture) did not appreciably increase the candle strength.

CAUSE OF HALOGEN FORMATION DURING COMBUSTION

Spectrochemical analysis of agricultural-grade sodium chlorate did not reveal, even in trace amounts (0.001 percent or less), such cations as Zn, Al, Cu, B, etc., which are

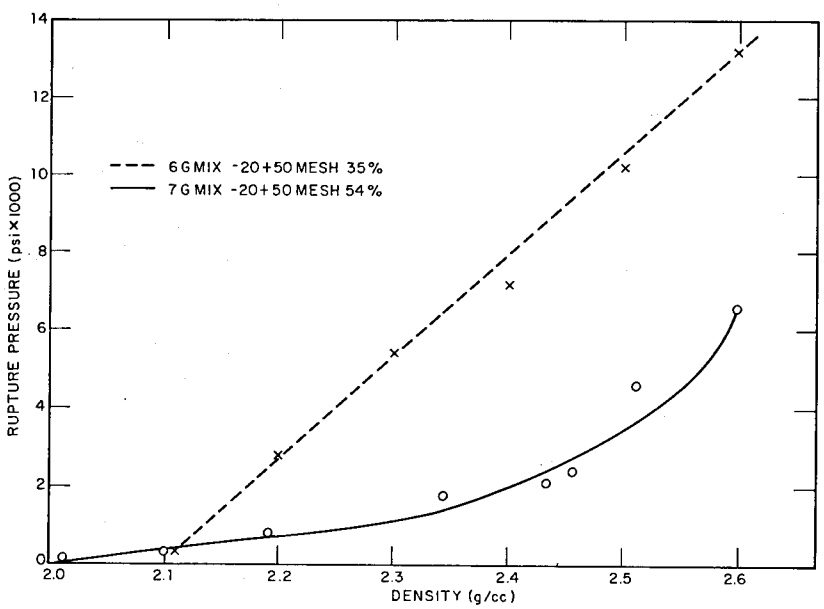

Fig. 15 - Effect of particle size on strength of chlorate candles—candle 10 grams, diam 2.36 cm, height about 1 cm

possible chlorine-producing cations (3). Furthermore, an iodometric analytical procedure sensitive to 0.001 percent did not detect the presence of sodium hypochlorite or sodium chlorite.

Since agricultural-grade $NaClO_3$ used in candle manufacture did not have a contaminant level capable of halogen production, except a remote possibility of $NaBrO_3$, the halogen must arise from the decomposition of sodium chlorate through a side reaction during burning or through a detrimental action of a main ingredient. In either case, the most probable halogen-producing intermediates will be sodium hypochlorite (4,5) and sodium chlorite (6).

In order to determine the extent to which these intermediate compounds are formed, the tests summarized in Table 10 were made. In these tests, samples of the mixtures were placed in a porcelain crucible and ignited with a torch. The reaction was allowed to proceed for 30 seconds (during which time the reaction temperature was measured with a thermocouple), and then was stopped by plunging the crucible into an ice bath or by an air stream. The samples were than mixed and analyzed for chlorite and hypochlorite by iodometric and arsenite methods. The chlorine content thus determined was used to estimate the quantity of chlorine that would have evolved if the entire sample had reacted instead of the approximately 20 percent which did react. This quantity is stated in Table 10 in terms of concentration (ppm Cl_2) in the total oxygen in the sample. Table 10 shows that NaCl, or combinations of iron, NaCl, and NaCl-H_2O, are not responsible for intermediate compound formation. However, factors such as the physical state of the candle (4A unpressed and 5A pressed), the water content (1D, 2D), and the amount and kind of metal (6A to 9A and 1B) appear to be of significance.

The data in Table 11 were obtained in the same way as were those of Table 10, except that a nickel-platinum crucible was used. Here "internal ignition" means that the material, while covered with a fused compound, was ignited at the bottom by heating the crucible. Table 11 shows that only water that is prevented from rapid evaporation from the candle interior during combustion is capable of producing NaClO, $NaClO_2$, or both. Samples 1F

Table 10
Effect of Candle Ingredients on Chlorine* Evolution

Sample No. and Mixture	Mixture Modifications	Reaction Temperature (°C)	NaClO (wt-%)	NaClO (wt-%)	Conc. Chlorine (ppm)
4A	Unpressed	790	0	0	0
5A	Pressed	780	0	0.018	80
6A	Mixture A with 3% iron added, unpressed	760	0	0.018	80
7A	Mixture A with 3% Al added, unpressed	780	0.011	0.006	85
8A	Mixture A with 8% iron added, unpressed	780	0	0.020	85
9A†	Mixture A with 16% iron added, unpressed	780	0	0.018	80
1B	Cast	810	0	0.014	60
1C	Dry, unpressed	830	0	0	0
2C	Mixture C with 2% H_2O added, unpressed	810	0	0	0
3C	Mixture C with 14% iron added, unpressed	810	0	0	0
4C	Mixture C with 14% iron and 2% H_2O added	840	0	0	0
1D	Dry, unpressed	820	0	0.005	20
2D	Mixture D with 0.3% H_2O added, unpressed	820	0.015	0	80

Mixture A: 88% $NaClO_3$, 4% iron, 4% glass wool, 4% BaO.

Mixture B: 78% $NaClO_3$, 12% iron, 6% glass wool, 4% BaO_2.

Mixture C: NaCl with oxygen flowing through the molten mass.

Mixture D: Reagent $NaClO_3$.

*This chlorine evolved may have been in the form of one or more of several volatile toxic compounds – Cl_2, Cl_2O, ClO_2, HOCl, etc., but it has been calculated as Cl_2 in this report.

†Reaction could not be stopped by cooling.

Table 11
Effect of Entrapped Water on Chlorine Evolution

Sample No. and Mixture	Mixture Modifications	NaClO (wt-% X 10^{-3})	$NaClO_2$ (wt-% X 10^{-3})	Conc. Chlorine (ppm)
1E	Trace H_2O, open	0	0	0
2E	0.7% H_2O, open	0	0	0
3E	1% H_2O, open	0	0	0
4E	2% H_2O, open	3.5	0	20
5E	0.1% H_2O, 20% Fe, open	0	1	5
6E	0.1% H_2O, sealed*	0	9	40
1F	0.3% H_2O, open	15.0	0	80
2F	0.3% H_2O, 33% NaCl, open	15.0	0	80
3F	4% H_2O, open	11.0	2.5	70
4F	2% H_2O, sealed* Ignition on top	1.5	16	80
5F	2% H_2O, sealed* Internal ignition	0	36	160
6F	2% H_2O, sealed† Internal ignition	22.0	47	325
7F	0.1% H_2O, sealed† Internal ignition	7.5	0	40
8F	2% H_2O, 33% NaCl, Sealed* Ignition on Top	9	2.5	50

Mixture E: 88% $NaClO_3$, 4% Fe, 4% glass fiber, 4% BaO.

Mixture F: Reagent $NaClO_3$, BaO or BaO_2 not present.

*External surface (top) sealed with fused $NaClO_3$, M.P. 250°C.

†External surface (top) sealed with fused NaCl, M. P. 800°C.

Samples E and F powdered – combustion 30 seconds, crucible cooled in ice bath.

through 4F all yield about the same amount of chlorine irrespective of the water content. In these tests ignition occurred on the top surface of the candle mixture and water was able to evaporate quickly. In 5F and 6F the top surface was coated with a layer of fused $NaClO_3$ or NaCl, and the candle mixture was ignited at the bottom of the crucible. Since all surfaces were sealed, rapid water evaporation was restricted and the chlorine rose to 160 and 325 ppm. On the basis of melting point, one would expect a sample with fused NaCl to be sealed better and therefore evolve a larger amount of chlorine; Table 11 shows this concept to be valid. When the water content was lowered to a trace amount, as in sample 7F, but with the effective seal maintained, the chlorine dropped to 40 ppm.

Table 12 shows the role of catalysts in $NaClO_3$ decomposition. Catalyzed decompositions of $NaClO_3$ did not form sodium perchlorate. In uncatalyzed decomposition, sodium perchlorate is formed in large amounts (6). The role that catalysts play appears to be the acceptance of one or more oxygen atoms from the sodium chlorate molecule, forming a NaClO or $NaClO_2$ intermediate:

$$\text{Reaction (a):}\quad NaClO_3 + \text{Catalyst} \rightarrow \text{Catalyst (O)} + NaClO_2$$

$$\text{Catalyst (O)} + NaClO_2 \rightarrow NaCl + \text{Catalyst} + 3/2\ O_2$$

$$\text{Overall reaction:}\quad 2NaClO_3 \rightarrow 2NaCl + 3O_2$$

$$\text{Reaction (b):}\quad NaClO_3 + \text{Catalyst} \rightarrow \text{Catalyst (O)}_2 + NaClO$$

$$NaClO + \text{Catalyst (O)}_2 \rightarrow \text{Catalyst} + O_2 + NaCl + \text{(O)}$$

$$\text{or Catalyst} + 3/2\ O_2 + NaCl$$

$$\text{Overall reaction:}\quad 2NaClO_3 \rightarrow 2NaCl + 3O_2$$

The existence of these intermediates has verification in Tables 10 and 11 and also in Refs. 4 and 5 for the sodium hypochlorite intermediate, and Ref. 6 for $NaClO_2$. In uncatalyzed decomposition, another $NaClO_3$ molecule (having a kinetic energy level below the decomposition point) could become the oxygen acceptor (reaction a). In so doing, sodium perchlorate would be formed. The overall reaction:

$$2NaClO_3 \rightarrow NaClO_4 + NaCl + O_2$$

Table 12
Catalytic Decomposition of $NaClO_3$ by a Metallic Surface*

Temperature (°C)	Principal Reaction	Approximate Initial Reaction Rate
325	$2NaClO_3 \rightarrow 2NaCl + 3\ O_2$	0.1%/minute
350	$2NaClO_3 \rightarrow 2NaCl + 3\ O_2$	1%/minute
400	$2NaClO_3 \rightarrow 2NaCl + 3\ O_2$	98%/minute
Up to 420	$2NaClO_3 \rightarrow 2NaClO_4 + NaCl + \frac{1}{2}\ O_2$	Uncatalyzed Decomposition (6)

*Nickel-Platinum crucible, NRL data.

If water is present, reaction mechanism b may be favored (4,5):

$$NaClO_3 \xrightarrow{H_2O} NaClO + O_2$$

If this occurs at a lower temperature, then instantaneous breakdown of NaClO would not occur (this fact is shown by the buildup of NaClO and $NaClO_2$, Table 11), and formation of the HOCl intermediate would be possible (5).

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CHAPTER 4

WEIGHT ECONOMICS OF CARBON DIOXIDE AND OXYGEN EQUIPMENT FOR CLOSED SPACES

R. R. Miller

INTRODUCTION

There are a number of systems which may be used to remove carbon dioxide and replenish oxygen in closed spaces for breathing purposes. Carbon dioxide may be physically adsorbed on solids, chemisorbed in liquids or on solids, reacted in replacement reactions with oxygen, or destroyed by electrolysis or photosynthesis. Oxygen can be transported pure as a liquid or gas, produced from oxides, or recovered from the electrolysis of water or the destruction of carbonate. Some of the systems which could be used to furnish a reaction for either one or both of the gases will be considered in this chapter. The type of system selected will depend to a great extent on the total operating time required, and the optimum system for short periods of use will differ from one planned either for intermediate or long periods of time, although the rates of operation may be identical. The maximum length of time one such system will be serviceable before another system becomes optimum may depend on construction details, but the general principles of operation will point to the reasons why one system becomes inadequate and another becomes desirable. The fact that a system must be regenerative is obvious when one considers the months of use now envisioned for some projects, but the time elapsed before a regenerative system becomes optimum is not so easily established. The relative weights of carbon dioxide and oxygen systems will be reviewed here and compared on a basis of separate and combined operation.

Calculations of the material needed for a period of time have been made on the basis of a unit to absorb the carbon dioxide exhaled by two men. The rate of work has been assumed to be equal to that of a man standing (i.e., standing on earth at sea level; a weightless condition should reduce the oxygen consumption), where oxygen consumption is 0.7 cu ft per hour and carbon dioxide production is 0.56 cu ft per hour, both measured at 0°C and 760 millimeters of mercury pressure (1). For two men this would be 1.4 cu ft of oxygen and 1.12 cu ft of carbon dioxide per hour. These quantities are 0.125 pound of oxygen and 0.137 pound of carbon dioxide per hour. The choice of equipment in this discussion is arbitrary to some extent, but it is not unrealistic when one considers bench or shipboard evaluations in the fields under discussion.

CARBON DIOXIDE ABSORPTION

Lithium hydroxide (LiOH) can be used to chemisorb carbon dioxide from air onto the porous particle of the anhydrous hydroxide. It has been shown (2) that in a number of experiments an average of 31.5 pounds of lithium hydroxide in five canisters, ventilated with air containing from 0.75 to 1.5 percent of carbon dioxide, absorb 27 pounds of carbon dioxide. This amounts to an absorption efficiency of 92.1 percent of the theoretical, and the value is a reasonable efficiency to expect in a breathing cycle.

Lithium hydroxide was used in cylindrical canisters, 6-1/2 in. in diameter and 12 in. in length, which held an average of 6.3 pounds of the lithium hydroxide and had an air flow of approximately 12 cu ft per minute. A canister half as long, with half the air flow, would accommodate 6 cu ft of air per minute, and at 1-percent carbon dioxide would ventilate 3.6 cu ft of carbon dioxide per hour through the canister. The larger canisters have removed an average of 60 percent of the passing carbon dioxide; on this basis, the smaller canister would absorb more than 2 cu ft per hour. This is in excess of the 1.12 cu ft required for two men as stated above. The total weight of the smaller canister would be 4.1 pounds (assuming 1 pound of empty canister), and it should last for 20 hours. The ease of calculation would be increased if based on a one-day cycle. For operation this length of time a canister would have to weigh 4.72 pounds. A suitable blower and filter should not weigh more than 5 pounds. The change of filters would add insignificantly to the weight. Thus, by starting with 9.7 pounds and adding a 4.7-pound canister at 24-hour intervals, there should be an adequate and continuous removal of carbon dioxide. A plot of the weight of material needed against the number of days is given in Fig. 16, neglecting the weight of the electrical power source. For comparison, similar plots are graphed for other carbon dioxide absorption and oxygen generation systems.

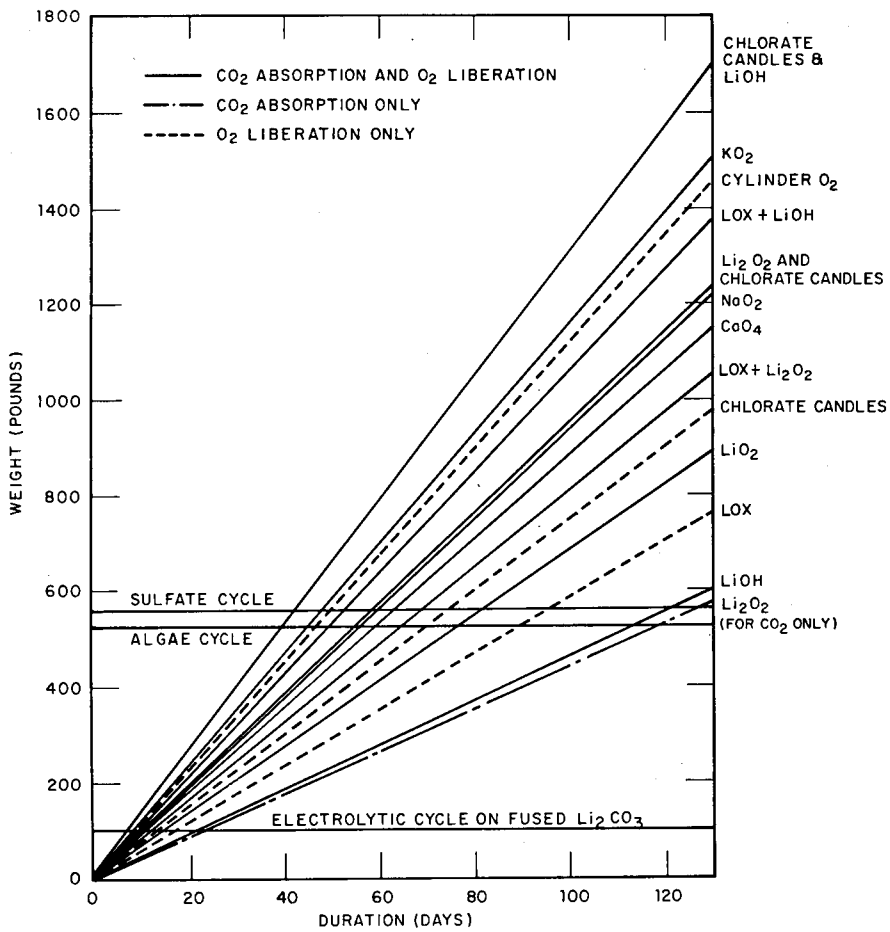

Fig. 16 - Total weights of air-purification systems vs time of use for two men

OXYGEN PRODUCTION

If oxygen sources are considered on the same weight basis, three methods–oxygen candles, cylinder gas, and liquid oxygen–can be compared.

Chlorate candles (3,4) in practical size as presently packaged give 120 cu ft of oxygen (STP) from 26-1/2 pounds of candle; hence, there is produced 10.6 pounds or 40-percent oxygen by weight. The volume of the container is 355 cu in., and the apparent density (g/cc) of the available oxygen is 0.823. These candles were not designed in order to save weight, and so it can be assumed that an overall density of available oxygen in any properly designed unit could be at a minimum of 0.80, provided that we also assume that the unit would be self-contained (i.e., the igniter and filter sealed in the candle burned in the packaging container). A plot of the weight needed to furnish oxygen at the rate of 0.125 pound per hour is also shown in Fig. 16.

Oxygen cylinders have not been designed specifically to save weight. Recent work on this aspect of the problem (5) has suggested the possibility of obtaining a weight of 1.5 pounds per cylinder holding 1.06 pounds of oxygen, but the problem of how to fabricate this type of cylinder has not been solved. However, a practical unit studied in the same reference had 4.1 pounds of cylinder for 1.1 pounds of O_2 at 7500 psia. This cylinder could be made lighter with better metal drawing operations. Assuming there is a suitable valve and pressure-reduction unit weighing not more than 5 pounds, and calculating on a total system weight of 27.4 pounds, 6.0 pounds of oxygen would be delivered; this weight would increase by 22.4 pounds for every two days (at a rate of 0.125 pound of oxygen per hour). The calculated weights plotted against time are also shown in Fig. 16.

The use of liquid oxygen with containers (6) which were one-half the loaded weight of liquid oxygen has given acceptable flow rates under specification testing. The most acceptable units depended on ambient-atmosphere heat for vaporization of the oxygen. When such units were not available, electrically heated units were developed with an efficiency approximately the same as that of the above units. The weight required for a given interval of time was taken as twice the weight of oxygen required for the same interval. These data are also included in Fig. 16.

SYSTEMS FOR BOTH CARBON DIOXIDE AND OXYGEN

With potassium superoxide (KO_2) to furnish oxygen and absorb carbon dioxide, the efficiency of the carbon dioxide absorption can be attained with somewhat of an excess of oxygen. This may require some adjustment in the time intervals. The chemical equation for the absorption may be expressed

$$2KO_2 + CO_2 \rightarrow K_2CO_3 + 1.5O_2.$$

The volume ratio of oxygen to carbon dioxide is 1.5, while the amount of oxygen consumed by two men is 1.4 cu ft as compared with 1.12 cu ft of carbon dioxide generated, or a ratio of 1.25. Calculating on the basis of 100 percent of the theoretical carbon dioxide absorption, 44 pounds are absorbed on 142 pounds of potassium superoxide, or 3.23 pounds of superoxide are required per pound of carbon dioxide absorbed. Then, 0.137 pound of carbon dioxide per hour would require 0.44 pound of superoxide per hour. A 24-hour period would require 10.6 pounds, and with a canister, probably one pound in weight, an 11.6-pound canister would last 24 hours. A blower unit of five pounds is assumed to be adequate (a blower the same size as for the lithium hydroxide canister has been chosen, although submarine containers showed an average of slightly less than 40-percent absorption efficiency on the potassium superoxide exposed to carbon dioxide) (7). On this basis, a 16.6-pound system would require an additional 11.6 pounds once each day. The results are plotted in Fig. 16.

Similar calculations can be made on sodium superoxide by considering the weight of the canister and blower system to be the same as the values used in the previous calculations; the resulting calculated weights against time are plotted in the figure. The chemical equation for the sodium reaction is as follows:

$$2NaO_2 + CO_2 \rightarrow Na_2CO_3 + 1.5O_2.$$

REGENERATIVE SYSTEMS

A rough estimate made on an experimental sulfate-cycle system (8) for oxygen production and carbon dioxide absorption shows that a unit of about 560 pounds is required for two men. The weight to be added to a unit of this type would be the water required to make up the loss by electrolysis. Since this weight might be recovered water, a constant weight against time is shown in Fig. 16.

It is difficult to find data concerning the weight factors involved in the photosynthetic method of liberating oxygen through the use of algae. In an ONR symposium report (9), the volume of 1-percent suspension of algae for one man were given by three different sources as 25, 100, and 230 liters of water. However, in Chapter 2 of the current report, 75 liters is indicated as more probable. In the 75-liter system, increased for a two-man rate, 262-1/2 pounds of 1-percent suspension would be required. The complete system would approach 525 pounds, assuming that the algae suspension would be half the weight of the complete unit. In these preliminary estimates, no added weight has been allowed for the minerals or water required for the unit. Therefore, a plot is given for the algae system in Fig. 16 as a constant-weight unit.

SPECULATIVE SYSTEMS

Other chemicals of possible interest in the control of atmospheres and breathing cycles will be listed below. However, no experimental work has been done with systems using these particular compounds. Lithium peroxide can be made in good purity and, while a satisfactory reaction with carbon dioxide and water vapor has not been demonstrated, its use could be advantageous on a weight basis. From the chemical equation,

$$Li_2O_2 + CO_2 \rightarrow Li_2Co_3 + 0.5O_2,$$

it is evident that for each two molecules of carbon dioxide, one molecule of oxygen would be available, or for the 1.12 cu ft of carbon dioxide produced by the two men, 0.56 cu ft of oxygen would be recovered. This would leave 0.84 cu ft, or 60 percent of the requirement per hour to be furnished by another source. On calculating the Li_2O_2 requirement, 0.143 pound would be used per hour, or 3.43 pounds per 24 hours. If this quantity were packed in a canister weighing 1 pound, the total requirement for 24 hours would be 4.43 pounds. On the assumption that a 5-pound blower is used, the weight requirement of the system against time is plotted in Fig. 16. Other values are also included assuming that liquid oxygen or chlorate candles are used to furnish the additional oxygen.

Another very promising superoxide for use in the purification of breathing air is lithium superoxide. While Refs. 10, 11, and 12 have appeared in the literature and have mentioned the preparation of this compound, no pure solid material has been available for examination of the reactions with water vapor and air. The calculated weight of material required is 1.77 pounds per pound of carbon dioxide absorbed, or 5.85 pounds of a superoxide per 24 hours, in order to absorb the carbon dioxide for two men. Assuming that the container weighs 1 pound and the blower system 5 pounds, 11.84 pounds would last 24 hours.

An additional weight of 6.84 pounds would be required each 24 hours. Calculations on this basis are shown in Fig. 16 for the rate requirement plotted against time. The equation for the reaction is:

$$2LiO_2 + CO_2 \rightarrow Li_2CO_3 + 1.5O_2.$$

A similar equation for calcium superoxide is,

$$CaO_4 + CO_2 \rightarrow CaCO_3 + 1.5O_2.$$

Calculations of the weight of this material required against time also have been plotted in Fig. 16.

As pointed out before, the choice of weights for canister and blower systems are quite arbitrary, and redesign for lightness could materially change the total weight of any system. But in each case the redesign would tend to have the same influence in all systems; in other words, the relative positions of the various combinations would probably not change. From the calculations made, the best chemical absorbent system for CO_2 alone would be Li_2O_2, but it would also furnish some oxygen. On the other hand, the available data indicate that liquid oxygen would be the lightest oxygen source. Both of these examples are based essentially on a short time use, but even from the rough data used, these systems could be most efficient for a period of months. The system which for short periods of time would be most satisfactory on a weight basis for both CO_2 absorption and oxygen liberation should be calcium superoxide, since the existence of lithium superoxide is somewhat questionable.

It was mentioned earlier that the superoxides would give off excess oxygen which on extended use would require some adjustment to prohibit the percentage of oxygen in the atmosphere from rising above the desirable level. Recent work (13,14) has shown that it may be entirely possible to adjust the ratio of oxygen liberated to carbon dioxide absorbed on superoxides by controlling the relative humidity of the incoming air. In this case, the resulting carbonate would be a mixture of the alkali carbonate and the alkali bicarbonate. More work is required in this field, however, before satisfactory conditions can be specified for the stoichiometric use of superoxide for both carbon dioxide absorption and oxygen production.

Another development, that of electrolysis of molten lithium carbonate (15), is of considerable interest as a method of revivifying air for breathing purposes, but it has not reached the stage at which any weight efficiencies can be realistic. However, an estimate of two-man needs from the one-man experimental unit indicates that the total weight may be near 100 pounds. This is shown in the figure. This electrolysis appears to furnish a suitable alkali for the absorption of CO_2 and liberation of oxygen both at the anode and cathode of the electrolytic cell. The equation for the electrolysis may be written

$$Li_2CO_3 \rightarrow Li_2^{++} + CO_3^{=}.$$

Then at the cathode, the reaction is,

$$Li_2^{++} + 2e \rightarrow 2Li,$$

and it is suggested that the lithium reacts with lithium carbonate in the following manner:

$$2Li + Li_2CO_3 \rightarrow 2Li_2O + C + O.$$

This furnishes one oxygen molecule per two molecules of CO_2 destroyed. This generates Li_2O, a suitable alkali for the absorption of CO_2 in the liquid melt as demonstrated. At the anode, the results would be explained by the discharge of the CO_2 ion as follows:

$$CO_3^{=} - 2e \rightarrow CO_2 + O.$$

The CO_2 would be reabsorbed by Li_2O in the melt originating at the cathode. This reconstitutes the lithium carbonate without the destruction of CO_2 as such. In this case, the overall reaction would furnish one mole of O_2 for each mole of CO_2 consumed, which corresponds to the preliminary results obtained. This system would require the electrolysis of a small amount of water to bring the ratio of oxygen to CO_2 to the proper value (1.25), but overall it appears an interesting method for use where lightness of system is of importance.

Various combinations of the systems considered are shown in the figure, but it is obvious that for any extended period of time some regenerative system will be necessary. It is also quite obvious that for any flights into space of days or a few weeks, air revivification can best be accomplished by using some chemical absorbent of carbon dioxide and some chemical source of oxygen. When volumes and weights are not so limited, the ease of operation and handling may be the most controlling feature in the choice of a system for the air purification.

That there will be considerable variation in the calculations made on the weights of systems is indicated by an article recently published (16) which gives weights of gaseous oxygen and liquid oxygen, along with an estimate of weight of the photosynthetic gas-exchange system. While the calculations in Ref. 15 are for one man, the relative weights of his system compared to those calculated for this article are as follows: 310 to 410 pounds for gaseous oxygen, 205 to 205 pounds for liquid oxygen, and 140 to 262 pounds for the algae system. The higher weights used in this chapter are offset, to some extent, by the fact that approximately 1-1/2 times the oxygen consumption per man was used. Only a highly engineered unit for the particular purpose will determine the final efficiency for any single system.

Most of the calculations above indicate that there is a possibility of satisfactory use of these methods for revivification of breathing atmospheres. However, the details on some of the better-known systems are not sufficient to justify designing a system in detail, and some of the "speculative systems" need considerable research work before they could be considered at all as satisfactory methods.

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CHAPTER 5

THE ANALYSIS OF SEA WATER FOR ATMOSPHERIC GAS CONTENT

D. D. Williams

The purpose of this chapter is to delineate, briefly, the status of a current oceanographic problem which owes its origin to the submarine habitability program.

Early in 1959, an industrial proposal to ONR suggested the development of an ultrasonic "gill" for the purpose of utilizing sea water as a source of breathing oxygen and as a toxic-gas "sink" aboard nuclear submarines (1). The application of ultrasonics for the extraction and subsequent analysis of dissolved gases was intriguing, and an analytical apparatus utilizing this principle was proposed. A reasonably thorough literature survey showed that the bulk of available oxygen data was confined to rather limited geographical areas and raised a serious doubt as to the sufficiency of the oxygen supply in all portions of the world's oceans (2). This finding indicated a need for an oxygen analyzer which could be installed on operating submarines for the purpose of gathering additional data while transiting the various oceans, particularly the Arctic regions.

In the original concept of such an analytical instrument, it was proposed that an ultrasonic "stripper" be used to separate the dissolved gases from sea water. The feasibility of the ultrasonic technique was implied in the original proposal (1). An equally unique instrument for analysis of the separated gases was also available–the gas chromatograph. This instrument promised to give simultaneous oxygen and nitrogen content data.

The initial laboratory investigation was to determine the "stripping" efficiency of an ultrasonic generator. Using the classical "wet" chemical (Winkler) procedure for oxygen analysis (3) as a guide, a study was made of various stripping methods. Samples of air-saturated, distilled water (100 ml) were subjected to each of several stripping techniques and then analyzed for residual oxygen content. The percentage of original oxygen removed was arbitrarily called the "degassing efficiency," and the relationship of this value to time gave rate data of relative significance.

Figure 17 is a plot of degassing efficiency versus time for the various techniques studied. It is quite evident that the ultrasonic stripper is not efficient, and that it is governed by Henry's law of partial pressures, as are the other techniques. The various rates shown reflect the degree of surface exposure and/or mixing as the controlling factor in degassing efficiency. Ultrasonics is thus shown to be simply a means of remote agitation of second-rate efficiency, requiring a supplemental vacuum (4).

The effectiveness of inert-gas purging was unanticipated. Its application to this problem was intriguing, inasmuch as the proposed analytical instrument utilized a stream of helium as a carrier and reference gas.

A portable gas chromatograph of the thermal-conductivity type was obtained (5), coupled to a multirange Leeds and Northrup recorder, equipped with a sampling valve and calibrated for oxygen and nitrogen using known volumes of air. This equipment proved to be sensitive to as little as 0.001 cc of gas, which is the amount of oxygen that might be found in 1 ml of sea water with low oxygen content. This sensitivity can be increased by a factor of ten if the base-line stability can be improved.

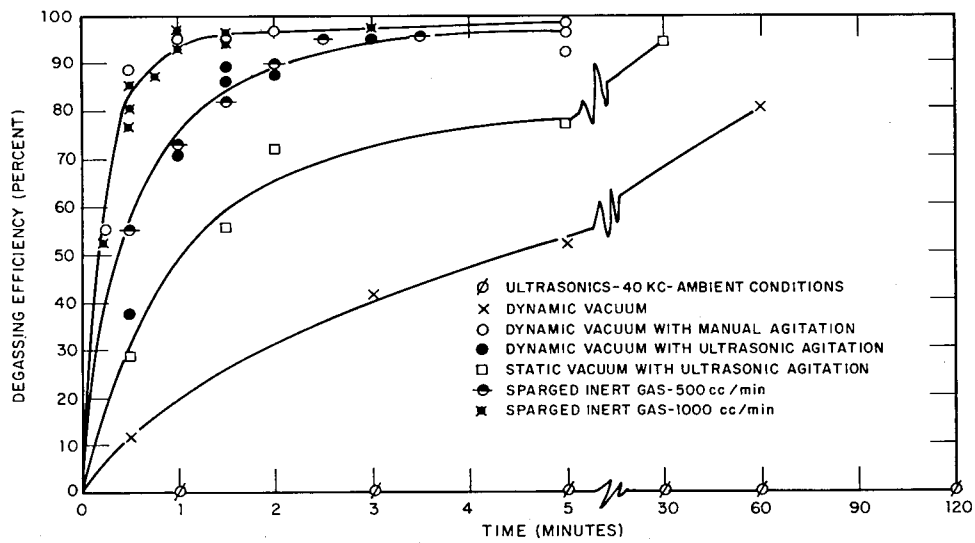

Fig. 17 - Degassing rates (100-ml samples, 25 °C)

A system whereby a sample of liquid water was injected directly into the gas chromatograph was tested and quickly abandoned because of pressure perturbations in the plotted data due to bubble formation in the injection pot. The presence of liquid water in the instrument was undesirable, also, since it would necessitate frequent column replacement.

Various small, packed, two-phase stripping columns were then constructed, tested, and rejected. The principal fault was in the difficulty of maintaining accurately measured flow rates of the feed water and stripping gas (helium). Unattended operation was impossible because of flooding resulting from minor pressure fluctuation in either of the feed streams.

A spinning multiple-disc, gas-liquid exchanger patterned after one designed by the Energy Conversion Branch of Electronics Division at NRL (6) was constructed. This stripper embodies some attractive features for this application. The flow rates of the gas and liquid are not interdependent; this makes variable flow ratios possible. Stripping efficiency remains high for a rather wide range of flow ratios and can be varied, independent of flow rates, by changing the speed of disc rotation. The pilot model of this equipment has been incorporated into a system which utilizes continuous stripping of flowing water with helium and intermittent sampling of the equilibrated oxygen-nitrogen-rich effluent. Efficiences, based on "wet" chemical analysis of before-and-after water samples, are being compiled for ratios of gas and liquid flow of 1/10 through 10/1. Stripping efficiency and analytical response are high for much of this range. Figure 18 shows typical response curves for three consecutive analyses using this technique. A study leading to the establishment of optimum operating parameters awaits the receipt and installation of an output integrating motor for the recorder and an improved version of the disc stripper.

It is anticipated that the final version of this instrument will embody components which will simultaneously measure temperature, pressure, density, and pH, as well as the oxygen, nitrogen, and possibly the CO_2 content of the sampled sea water. Such an instrument should be completed and tested on a submarine during 1961.

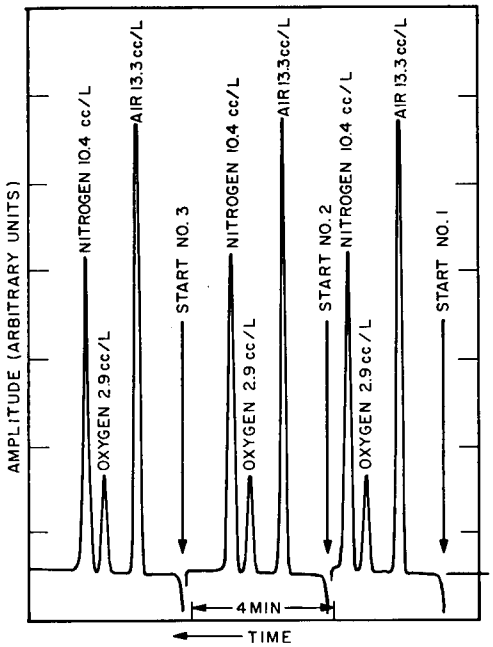

Fig. 18 - Typical response curves (three consecutive runs–tap water at 20°C, stripping ratio 1:1, 5-cc sample. Oxygen content by Winkler method was 2.85 cc/liter.)

A literature survey indicated an unpredictable and, possibly, an insufficient supply of oxygen gas in sea water for submarine use. A concurrent study revealed the ineffectiveness of ultrasonic degassing as a means of stripping gases from water. These findings cast serious doubt on the feasibility of the proposal to construct an ultrasonic "gill" for the provision of a breathing atmosphere for submarines from the sea. The literature survey also indicated a need for more analytical data on the gas content of the world's oceans.

An instrument, using inert-gas stripping and gas chromatographic separation and detection, has been assembled and bench tested. Adequate sensitivity to oxygen and nitrogen has been demonstrated. Shipboard evaluation will be made in the near future.

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PART II
CARBON DIOXIDE REMOVAL

CHAPTER 6

THE USE OF VERSENE TO IMPROVE MEA PERFORMANCE

S. T. Gadomski

A chelating agent, Versene FE-3 Specific (1), has been reported by Mare Island (2) as a useful oxidation stabilizer for monoethanolamine (MEA) in carbon dioxide removal systems. Initiation of the investigation of this monosodium salt of N,N-Dihydroxyethylglycine was based on the premise that trace metallic impurities contribute greatly to oxidation.

Degradation of MEA may be observed in the liquid itself, as well as in the air stream. The solution gradually decreases in normality, with a corresponding darkening in color, while the air stream picks up small but significant amounts of ammonia (NH_3).

USS SKATE, SS(N)578, on her trip of May 31 to June 10, 1960, used a low-iron grade of MEA (Limea) in both of her CO_2 removal plants. One plant, however, was operated with a solution containing 2-1/4 percent by volume of Versene. Results of the tests on the SKATE are given in the following paragraphs and in Tables 13 and 14.

Table 13
CO_2 Removal Plant No. 1, with Versene

Accumulated Operating Hours	Normality of MEA	Iron to MEA (ppm)	MEA + NH_3 in Air (ppm)	NH_3 in Air (ppm)
0	4.27	2.0	–	–
4	–*	–	4.5	3.0
30	–	5.1	13.6	12.4
46	4.06	8.0	11.9	8.5
57	–	–	23.0	15.5
72	4.07	10.4	–	–
74	–	–	13.7	7.5
100	3.63	11.0	21.5	11.3

*Not measured.

Table 14
CO_2 Removal Plant No. 2, without Versene

Accumulated Operating Hours	Normality of MEA	Iron to MEA (ppm)	MEA + NH_3 in Air (ppm)	NH_3 in Air (ppm)
0	3.90	2.5	–	–
20	4.04	3.2	–	–
45	3.46*	3.5	19.4	12.9
54	–†	–	15.2	9.0
69	–	–	15.6	9.8
75	3.87	3.9	–	–

*One gallon of concentrated MEA added at 50 hours.

†Not measured.

Normality and iron-content values are reported as found in the absorber. Reboiler samples taken at the same time were very similar to the absorber samples.

Effluent air streams from both plants were tested for MEA and NH_3 content by detector tubes (3). During sampling, filters placed ahead of the detector tubes collected MEA and NH_3 in the aerosol form. Results shown are the sums of gaseous and aerosol concentrations.

The relatively large concentration of air contaminants, MEA and NH_3, resulted from securing the effluent air-purification systems (sodium bisulfate and water scrubbing) during sampling periods. This was done to eliminate misinterpretation from unequal performance by these two purifying units.

Results of the tests are not very conclusive. The best indication of some stabilization was that the normality of the solution with Versene decreased 5 percent, while without the additive, it was 11 percent in 45 hours. After 100 hours of use, MEA with Versene was lighter in color than MEA without Versene after 24 hours. Iron content of the solutions and MEA-NH_3 concentrations in the air did not seem to have much significance.

Other submarines have operated with Versene for longer periods of time. The USS HALIBUT, probably the first to use the additive, found it extended the life of MEA twofold. Another favorable result was reported by the USS TRITON on her 26-day submergence during the fall of 1960. An average of one gallon of MEA per day per scrubber was required for make-up during the 13 days the ship's MEA was used. During the following 12 days of operation, with low-iron MEA and Versene, no make-up was required. At the end of the run, however, the scrubbers required 1.5 and 2 gallons of MEA make-up.

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CHAPTER 7

ALKAZID M

J. C. Goan

In the previous report (1), Alkazid M was discussed as a possible replacement for monoethanolamine as a regenerative carbon dioxide absorbent. Alkazid M is the potassium salt of the amino acid, N-methylalanine, manufactured in Western Germany by the Badische Anilin und Soda Fabrik, A. G. (BASF). It was found that Alkazid M had obvious advantages over MEA in regard to volatility, oxidation stability, and probable order of toxicity. However, the CO_2 absorption rate of Alkazid M was seen to be definitely inferior, although the difference was not great. It seemed evident that further studies on a larger scale would be necessary to provide a practical comparison between Alkazid M and MEA under conditions more nearly like those existing in the present submarine-type CO_2 scrubber.

During the year following the previous report, two independent studies have reinforced the view that further study of Alkazid M is advisable because of its relative stability and nonvolatility. The first of these was a limited evaluation of Alkazid M carried out in a Mare Island scrubber by the U.S. Naval Engineering Experiment Station (2). Although there was not sufficient time available to allow for an exhaustive comparison, these limited studies showed that under identical conditions a 3.5 N solution of Alkazid M removed about 7.9 lb/hr CO_2, as compared with 10 lb/hr CO_2 for a 5 N solution of MEA. The former, it was noted, provided a significantly lower level of air contamination than MEA.

In January 1960, a representative of NRL visited BASF in Ludingshafen and arranged to have carried out a short study of the oxidation stability of Alkazid M. The results of the study, with much experimental detail, were communicated by letter to NRL. The letter stated that over a three-week period of continuous operation of Alkazid M in removing CO_2 from air no detectable deterioration of the solution could be observed. It has been claimed also by BASF that the CO_2 absorption rate of Alkazid M is superior to that of MEA in stripping flue gases.

In summary, the evidence gathered at NRL and elsewhere seems to indicate that Alkazid M has much to commend it as a CO_2 absorbent, provided that an absorption rate somewhat lower than MEA can be tolerated. Its stability and low volatility are very much in its favor. If the toxicity of MEA becomes a more limiting factor than presently accepted by the Navy, redesign of the CO_2 scrubber for specific use of Alkazid M is recommended, in the expectation that a scrubber "tailored" for Alkazid M should increase its absorptive properties.

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PART III
ATMOSPHERE SAMPLING AND ANALYSIS

CHAPTER 8

GAS CHROMATOGRAPHY IN THE STUDY OF TRACE ORGANIC VAPOR CONTAMINANTS

M. E. Umstead

INTRODUCTION

During the past few years, new developments in chromatographic column technology and the invention of highly sensitive detection systems have greatly increased the suitability of gas chromatography for the investigation of trace organic vapor contaminants in nuclear-submarine atmospheres. The use of a long length of capillary tubing whose inner walls has been coated with a suitable partitioning agent as a chromatographic column has made possible column efficiencies unheard of with conventional packed columns (1). New partitioning agents continually are being reported that are capable of resolving substances or classes of compounds that were previously difficult or impossible to separate. In relation to the problem of analyzing nuclear-submarine air, the most significant step forward in gas chromatography has been the development of ionization detectors capable of sensitivities thousands of times greater than those obtainable from the presently available thermal-conductivity type. Those detectors in which ionization is brought about either by argon atoms excited by a radioactive source (2) or by a hydrogen flame (3,4) appear to be the most satisfactory, each having its own distinct advantages and liabilities.

Most of the organic-vapor contaminants in submarine air have been shown to be hydrocarbons and, at present, the concentration of these hydrocarbons is determined more or less routinely by a program of air sampling with carbon canisters (5,6). Although much valuable information has been obtained in this manner, questions have arisen as to the exact qualitative and quantitative significance of the results. A procedure in which an adsorbent such as carbon is not required would be desirable, both for the measurement of total hydrocarbons and the determination of individual compounds. Sensitive ionization detectors for gas chromatography offer new possibilities for the direct analysis of a small volume of submarine air for trace organic contaminants, and they probably can be adapted in the near future to the routine shipboard monitoring of these substances.

CHROMATOGRAPHIC ANALYSIS OF AIR SAMPLES

Work at NRL with a Pye Argon chromatograph as shown that the maximum sensitivity of the instrument was just below that required to analyze submarine air for trace organic contaminants by the direct injection of an air sample into the chromatograph. When dealing with gas samples, not only the absolute quantity of a trace substance is important, but also its dilution in the gas. The volume of the gas sample cannot be increased indefinitely in order to obtain the absolute minimum amount of trace components necessary for detector response. The sample size must not exceed a few milliliters or the peaks becomes excessively broad and resolution of the components is seriously impaired.

Since a few hundred milliliters of submarine air are required to obtain a sufficient quantity of organic contaminants for satisfactory detector response, a means of concentrating the contaminants before introduction to the chromatograph is required. Advantage was taken of the change of retention volume with temperature to concentrate these contaminants to the required level for chromatographic analysis (7). Retention volume–that is, the volume of carrier gas required to move a substance completely through a chromatographic column–varies exponentially with the reciprocal of temperature. It is possible to pass a large volume of submarine air through a column maintained at a low temperature and completely retain all those contaminants in the column whose retention volumes are less than the volume of the air sample. The subsequent heating of the column and backflushing with the carrier gas releases the contaminants into a much smaller volume of gas than the original sample and thus greatly increases the gaseous concentration of the trace contaminants.

Figure 19 illustrates the apparatus used for chromatographing air contaminants. The contaminants are collected and concentrated by the concentrating column and are separated from each other by the analytical column. The sample stream and the carrier gas flow are manipulated by means of a Perkin-Elmer six-way gas-sampling valve to collect and backflush the sample. The operation of the system is as follows. With the ports of the gas-sampling valve in the positions indicated by the solid lines in Fig. 19, a known volume of submarine air is passed through the cold concentrating column. Residual air is flushed from the system with a secondary argon stream (not indicated in Fig. 19), leaving the organic components of the air trapped in the concentrating column. The valves at both ends of the concentrating column are closed, to seal the column, and the cooling bath is replaced by a hot-water bath. After the column has equilibrated with the bath, the valves are reopened and the rotor of the gas sampling valve turned simultaneously so that the ports are now in the positions indicated by the dotted lines in Fig. 19. The primary argon stream then backflushes the sample into the chromatograph.

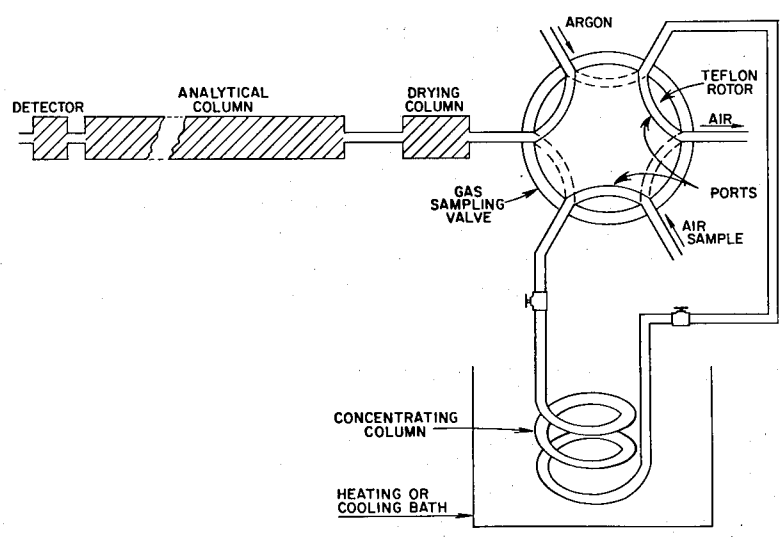

Fig. 19 - Apparatus for concentrating contaminants in air samples

The argon-type ionization detector of the Pye chromatograph necessitates a thorough drying of the sample, since water has a pronounced desensitizing action upon this detector. Both glycerol distributed on a chromatographic solid support and anhydrous KOH have proved fairly satisfactory as drying agents, but the presence of these substances in the system raises questions as to the fate of certain organic compounds other than hydrocarbons. The flame ionization detector is reported to be insensitive to water and may eliminate the need for a drying agent.

The concentrating column currently used consists of a one-foot length of 1/4-in. O.D. copper tubing packed with a silicone oil distributed on Chromosorb (3 parts silicone to 10 parts Chromosorb). Silicone oil was chosen because it remains liquid at the low temperatures used for the sampling step. A dry ice-acetone cold bath to cool the column has proved most satisfactory in the laboratory, but it has some undesirable aspects for submarine use. Argon solidifies at the temperature of liquid nitrogen. For shipboard use, a freezing mixture of $CaCl_2 \cdot 6H_2O$ and ice (-35° to -40°C) appears feasible, but the possibility of adopting a small refrigeration unit is being studied.

An air-sampling technique of this type was tested aboard the USS SKATE during October 1959, but with a less refined concentrating apparatus (7). The concentrating column consisted of a four-foot length of 1/4-in. O.D. copper tubing packed with squalane (3:10) and was maintained at 0°C for sample collection. A boiling-water bath heated the column for the backflush step. Since the six-way gas-sampling valve had not yet been adopted, it was necessary to interrupt the argon flow and open the line to position the heated concentration column. The relatively high sample-collection temperature (0°C) neither provided the desired resolution for the more volatile hydrocarbons detected nor permitted residual air to be purged from the column. This caused an excessively broad air peak that interfered with the detection of hydrocarbons more volatile than hexane.

In spite of these shortcomings, this crude apparatus provided much useful data during its use aboard the USS SKATE. An example of the chromatographs obtained is shown in Fig. 20. A chromatogram of the oil phase desorbed from a carbon canister exposed at the same time is shown in Fig. 21. The analytical column (4 ft x 4 mm I.D.) in both cases contained squalane (5 parts) adsorbed on Chromosorb (100 parts) to which polyethylene glycol 400 (2 parts) had been added to reduce the adsorptive capacity of the Chromosorb for oxygenated compounds.

The retention volumes of the most prominent peaks obtained from the atmosphere of the USS SKATE were compared with those of hydrocarbons that are present in high concentrations in petroleum fractions of the same volatility range. In each case, the retention volume of the selected hydrocarbon matched a major peak from the USS SKATE atmosphere. The atmospheric hydrocarbons identified in this manner are listed in Table 15. Although the retention volumes of these hydrocarbons have been compared through the squalane column only, their coincidence at the various column temperatures strongly supports the assignments.

Chromatograms obtained by direct air sampling showed considerably higher concentrations of hydrocarbons in the octane and lower boiling range than did those from the oil phases desorbed from carbon canisters. An estimate of the hydrocarbon concentration in the USS SKATE atmosphere was made by integration of the areas under some of the chromatographic curves. By the direct air-sampling technique, concentrations ranging from 110 to 186 micrograms per liter (μg/1) were indicated, values consistently higher than those obtained by carbon sampling. The carbon samples were steam desorbed by the Materials Laboratory at the New York Naval Shipyard, who reported values ranging from 39.1 to 81.6 μg/1 (8).

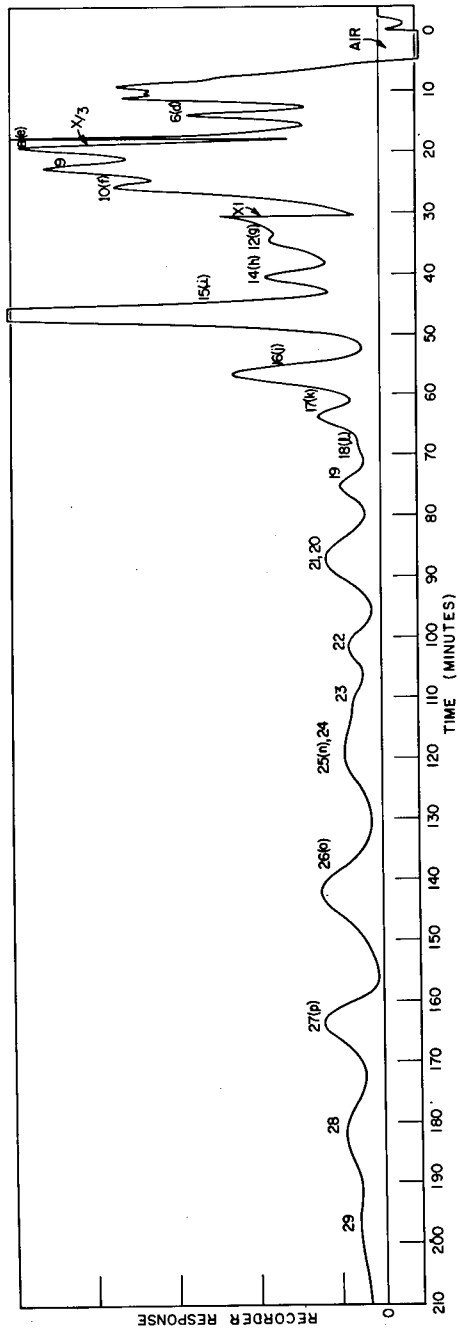

Fig. 20 - Air sample, from Nucleonics Laboratory on USS SKATE, Oct. 1959

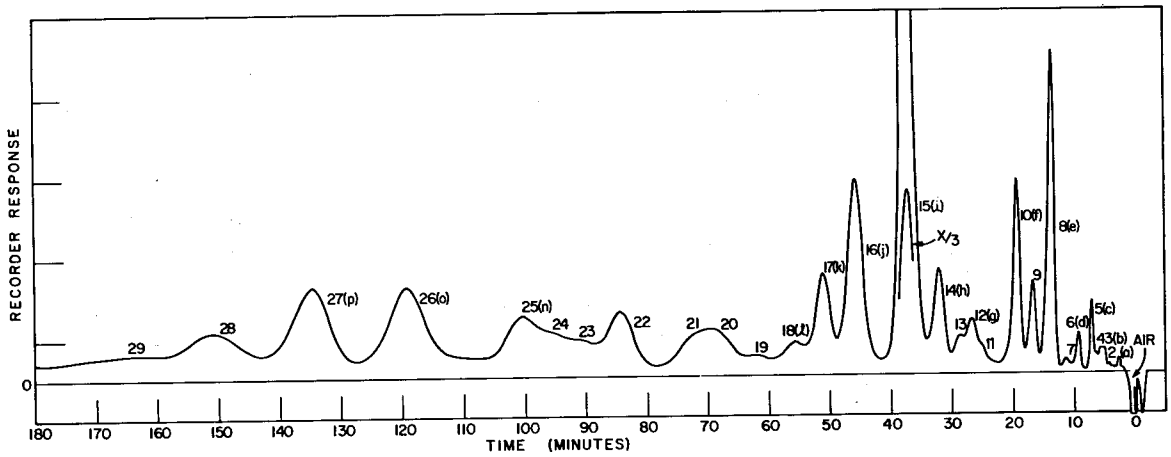

Fig. 21 - Oil desorbed from a carbon sample, USS SKATE, Oct. 1959

Table 15
Tentative Identification of Chromatographic Peaks Obtained from Atmosphere of USS SKATE

Peak*	Hydrocarbon	Relative Retention Volume (n-Heptane-1.00)		
		75°C	50°C	28°C
a	n-Hexane	–†	0.366	0.238
b	Benzene	–	0.704	0.632
c	n-Heptane	1.00	1.00	1.00
d	Methylcyclohexane	1.33	–	–
e	Toluene	1.90	1.89	1.80
f	n-Octane	2.33	2.70	3.05
g	Ethylcyclohexane	3.50	3.76	–
h	Ethylbenzene	4.07	4.51	–
i	m,p-Xylene	4.60	5.25	5.85
j	O-Xylene	5.67	6.44	7.19
k	n-Nonane	5.67	7.21	9.18
l	Isopropylbenzene	6.60	7.86	–
m	n-Propylbenzene	8.33	–	–
n	1,3,5-Trimethylbenzene	11.0	14.2	–
o	1,2,4-Trimethylbenzene	13.1	16.8	–
p	n-Decane	13.1	19.0	–
q	n-Undecane	30.7	–	–

Column: Squalane (5 parts), polyethylene glycol 400 (2 parts) on Chromosorb (100 parts).

*See Figs. 20 and 21.

†Not determined.

During the shipboard study, a brief investigation was made of the effluent air from a few of the Dorex carbon canisters during their sampling period by the same techniques used for submarine air itself. High concentrations of hydrocarbons were found in the effluent. The nature of the chromatograms obtained indicated that the loss of hydrocarbons from the canisters was due both to leakage of air through the carbon bed and to the elution of volatile hydrocarbons.

An example of the better resolution obtained with the improved concentrating apparatus is provided in Fig. 22. The sample was air from the USS SWORDFISH, collected in a cylinder under pressure on Oct. 30, 1959, when the ship had been submerged about seven days. Surprisingly high concentrations of n-pentane and toluene were found in the air, which in general contained higher concentrations of hydrocarbons of C_7 and lower molecular weights and less of the heavier ones than were found in the USS SKATE atmosphere. The chromatogram displayed in Fig. 22 was obtained with a Jarrell-Ash Capillary Chromatograph in which the capillary column had been replaced by a 10-ft, 3/16-in. O.D. packed column containing squalane (5 parts), polyethylene glycol 400 (2 parts) on Chromosorb (100 parts) operated at 58°C. The Jarrell-Ash instrument provides a smaller, more compact unit than the Pye instrument for shipboard use.

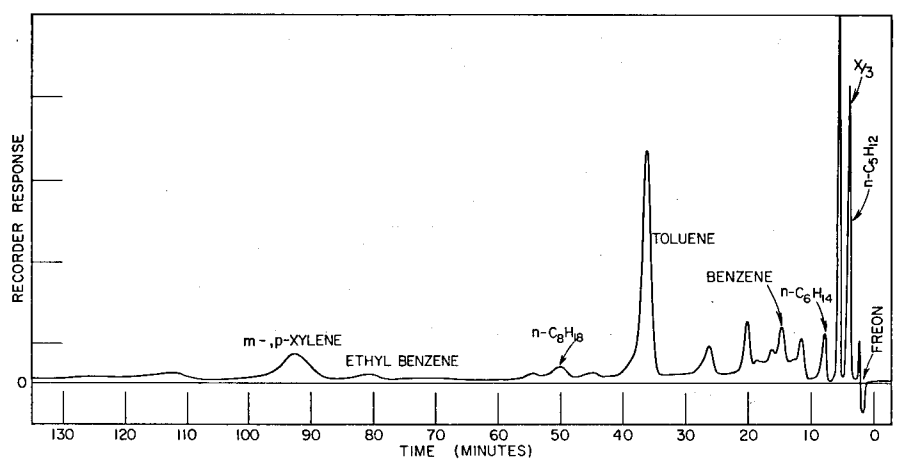

Fig. 22 - Air sample, engine room, on USS SWORDFISH, Oct. 1959

POSSIBLE SOURCES OF ATMOSPHERIC HYDROCARBONS

Shortly after the investigation of atmospheric hydrocarbons in nuclear submarines was undertaken at NRL, it was recognized that painting shortly prior to and during submergence periods and the indiscriminate use of mineral spirits made great contributions to the large quantities of hydrocarbons found in the air (5). Measures were taken by the Fleet to alleviate the situation by stopping painting for a certain period before long dives and restricting the use of mineral spirits.

The USS SKATE had not been painted for three weeks prior to the shipboard study of organic air contaminants during October 1959 but, nevertheless, high concentrations of hydrocarbons were still found in the atmosphere. Because fresh paint had not been applied

for such a long time, and because of the nature of the hydrocarbons found in the air, particularly the high content of aromatics and volatile hydrocarbons, it seemed evident that a reinvestigation of possible hydrocarbon sources was now in order. Such an investigation is in progress, but it is far from complete, and no firm conclusions can yet be drawn.

Paints

Samples of paints of the colors used aboard the USS SKATE were obtained from the paint shop of the Electric Boat Company. The inside of a flask was coated with a paint and the solvent stripped off under vacuum and condensed in a liquid-nitrogen trap. The solvents collected were chromatographed under conditions similar to those used aboard the USS SKATE, and the composition of each was compared with the hydrocarbons found in the atmosphere of the ship.

The most striking feature of the paints thus far investigated was the presence of large quantities of α- and β-pinene, the major constituents of turpentine, and of a mixture of xylenes as the principal components of the paint solvent. Such a composition is characteristic of paint formulations that were superseded a few years ago by newer formulas calling for mineral spirits as the diluent. A chromatogram of the solvent from a "Beach Sand" paint is shown in Fig. 23 and that from "Equipment Grey" in Fig. 24. Peaks characteristic of paint thinner are superimposed over the turpentine and xylene peaks from the "Equipment Grey" condensate, indicating that the paint probably had been thinned with a mineral-spirits thinner. Figure 25 is a chromatogram of hydrocarbon vapors in the air over a sample of "Equipment Grey" paint and should be typical of the components released from a freshly painted surface.

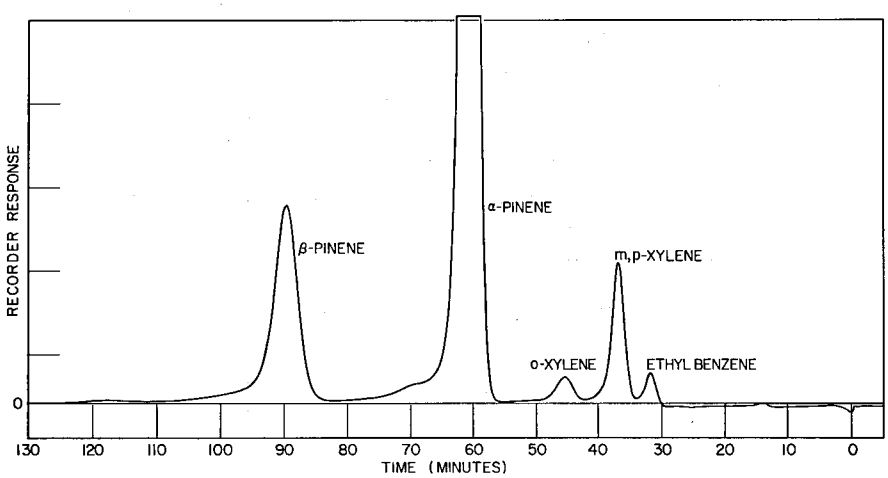

Fig. 23 - Vacuum condensate, "Beach Sand" paint from Electric Boat Company

No turpentine was detected in the atmosphere of the USS SKATE, although small amounts could have been masked by other hydrocarbons. It is not known that the paints used aboard the SKATE were even of the same formulations as those studied in the laboratory. Other paints and formulations must be investigated to complete the picture before many conclusions may be drawn.

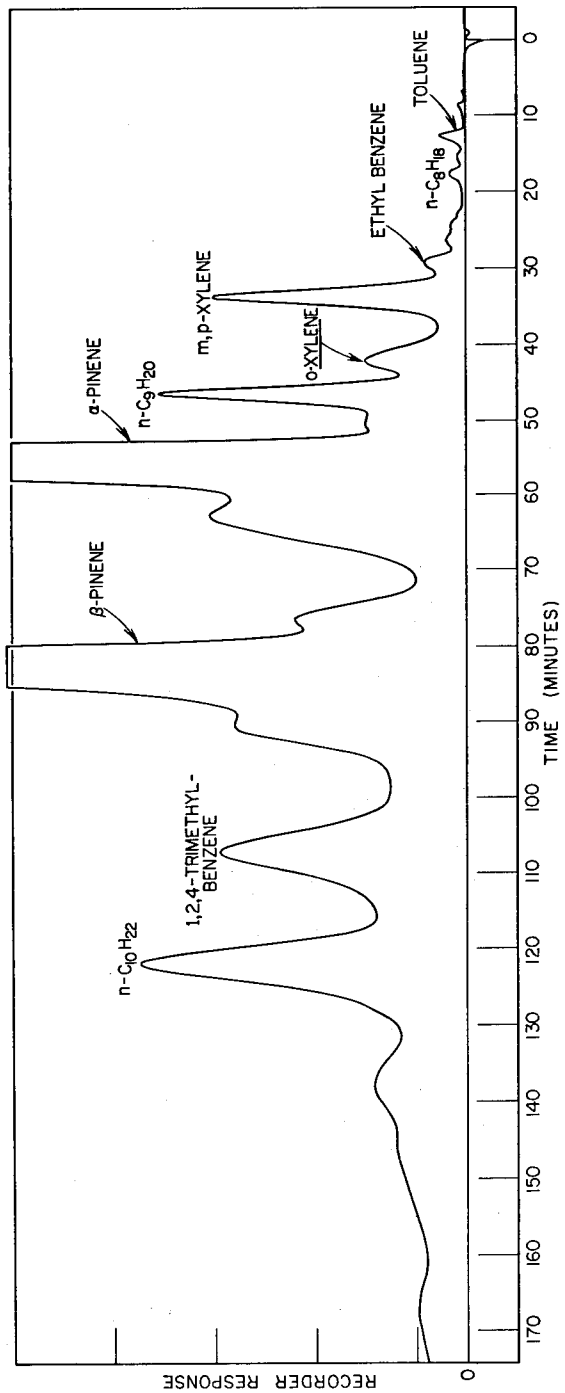

Fig. 24 - Vacuum condensate, "Equipment Gray" paint from Electric Boat Company

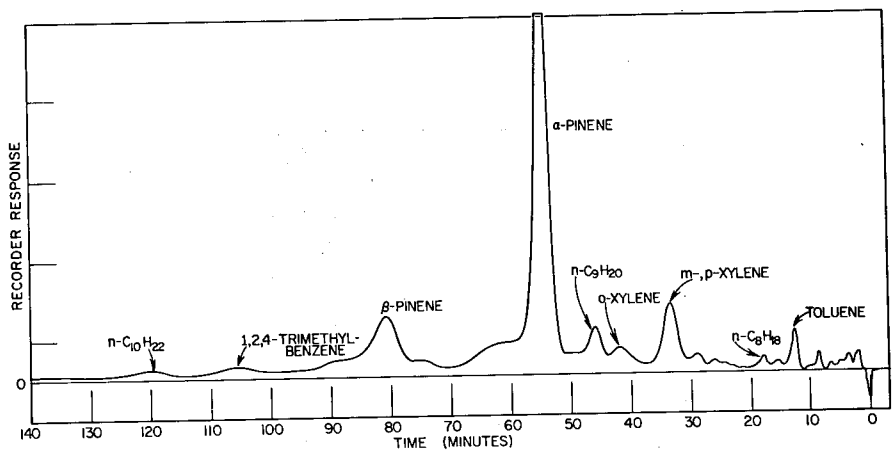

Fig. 25 - Vapors over "Equipment Gray" paint

Paint Thinner

Several samples of paint thinner obtained from various Navy sources have been studied and were found to be quite similar. Figure 26 represents a chromatogram of a sample of paint thinner used aboard submarines by the Electric Boat Company. In general, the hydrocarbon distribution in the thinners leans toward higher molecular weights than that found in the atmospheres of the USS SKATE and the USS SWORDFISH. Also, the aromatic content of the paint thinners studied was much lower than that generally found in submarine air.

Diesel Fuel

Although diesel fuel is composed principally of hydrocarbons much less volatile than those predominating in submarine air, a surprisingly high concentration of volatile hydrocarbons was found in the free vapor space over a sample of liquid fuel. Figure 27 is a chromatogram of the hydrocarbon vapors present in the air over liquid diesel fuel obtained from the tanks of the USS SKATE. Qualitatively, many similarities to submarine air may be seen, both in the hydrocarbon distribution and the relative quantities of individual aromatic hydrocarbons. The initial appearance upon submergence of high hydrocarbon concentrations in a submarine's atmosphere might be explained by the venting of the diesel-fuel tanks.

Lighter Fuel

Samples of several commercial lighter fluids have been obtained, and their composition is being studied. Figure 28 shows the constituents of one brand that was chromatographed with a Jarrell-Ash capillary chromatograph using a 100-ft squalane column at 30°C. The great resolving power of a capillary column may be seen by noting the extreme sharpness of these peaks in contrast to those illustrated in the other figures, all obtained with conventional packed columns. Most of the large peaks appear to be due to normal and cyclic hydrocarbons in the C_5 to C_8 range. Various brands of lighter fluid differed mainly in their distillation range and in the quantity of aromatics present.

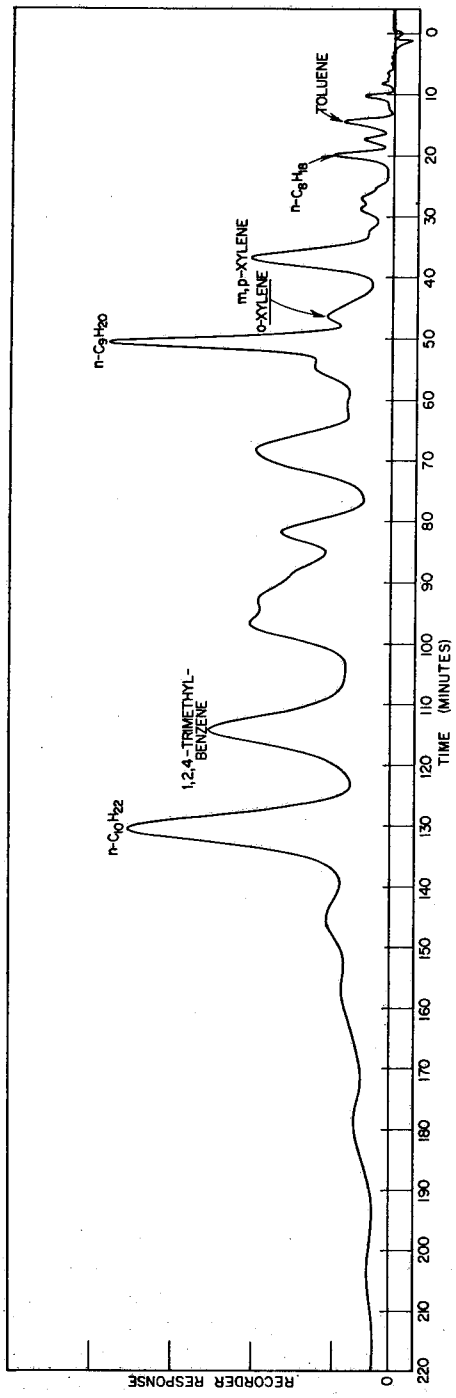

Fig. 26 - Paint thinner from Electric Boat Company

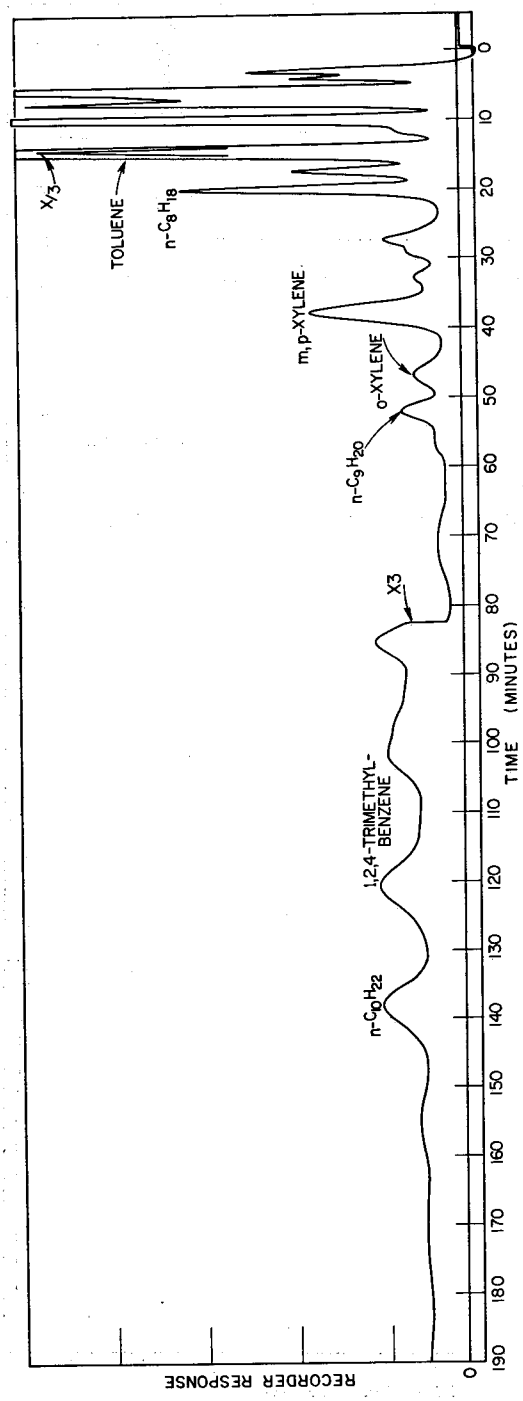

Fig. 27 - Vapors over diesel fuel from USS SKATE

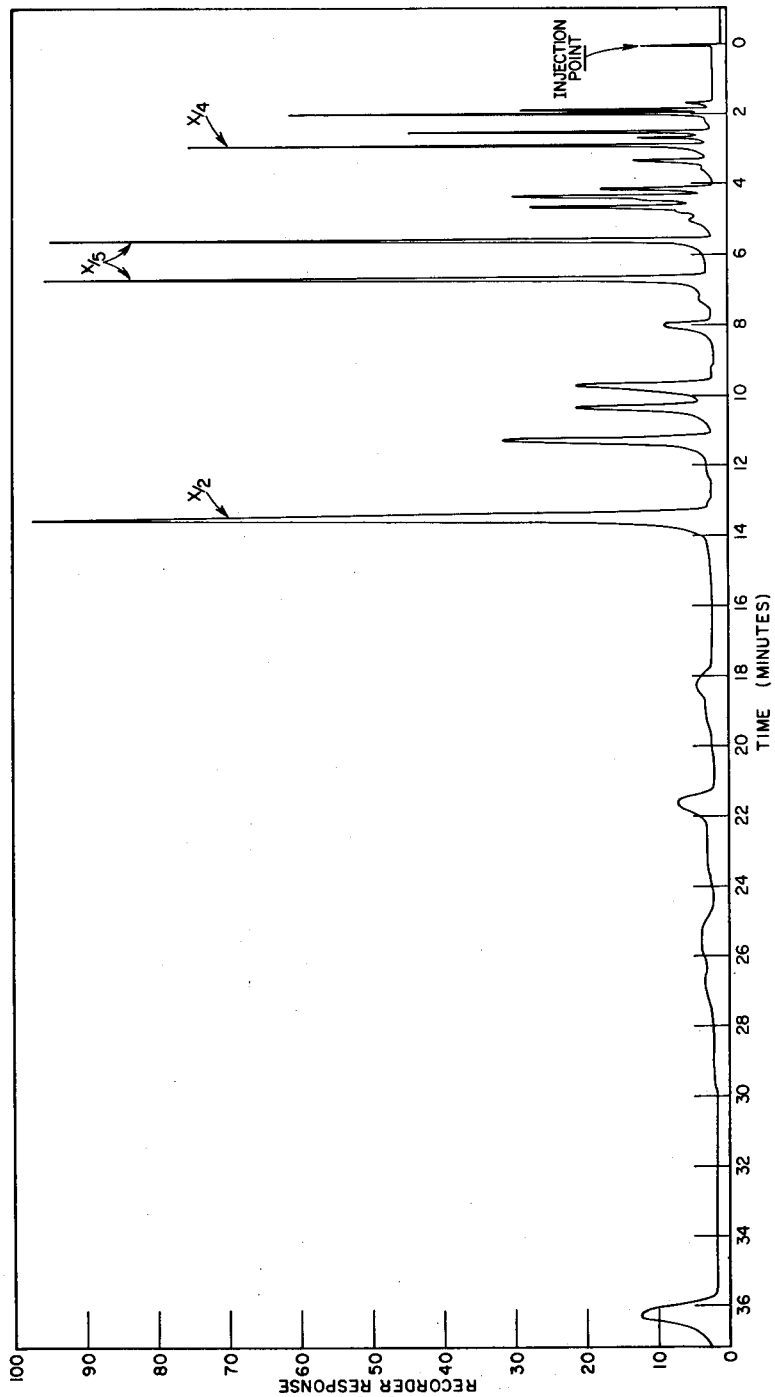

Fig. 28 - Lighter fuel, Jarrell-Ash capillary chromatograph, 100-ft squalane column, 30°C

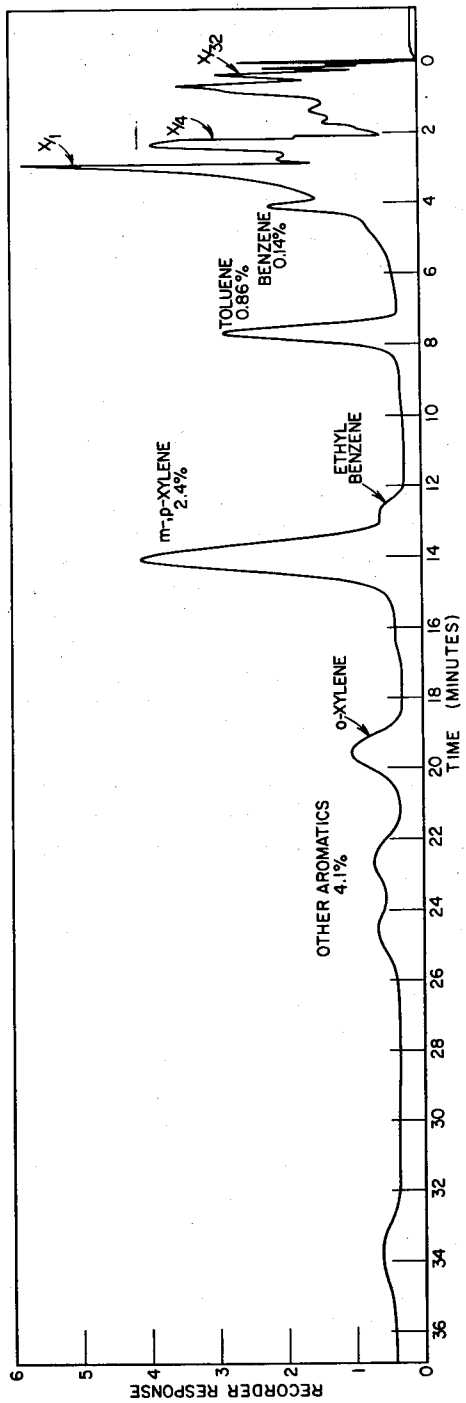

Fig. 29 - Lighter fuel, two-meter B,B'-oxydipropionitrile column, 60°C

A selective chromatographic method for the determination of aromatic hydrocarbons is illustrated by the chromatogram of Fig. 29, obtained with a Perkin-Elmer Model 154 Vapor Fractometer equipped with a two-meter column of β,β'-oxydipropionitrile 2:10 on Chromosorb. The lighter fluid is the same as that shown in Fig. 28. The oxydipropionitrile substrate selectively retains aromatics and passes aliphatic hydrocarbons rapidly. Integration of the area under the aromatic peaks provides a quantitative measure of the aromatic content of the mixture. Aromatics in the fluids investigated ranged from about two percent in one brand to over 20 percent in another. The hydrocarbons found in lighter fuel were in general the same as the lower molecular-weight hydrocarbons present in submarine air. At present, it appears doubtful that the quantity of unburned lighter fuel released aboard a submarine could contribute appreciably to the hydrocarbon content of the atmosphere if the fluid is used only in lighters and not for other purposes. If in the future the hydrocarbon content of submarine air is significantly reduced, the contribution from lighter fuel may become important.

FUTURE PLANS

Recent developments in gas chromatography, including high-sensitivity detectors, efficient columns, and selective substrates, have made the chromatograph an attractive tool for studying the composition of submarine air. It already has proved feasible to analyze for trace organic vapor contaminants by means of an argon-type ionization detector in conjunction with a chromatographic technique for concentrating these contaminants. Studies of this type have been carried out both aboard the USS SKATE and on pressurized air samples returned from the submarine to NRL. Further studies on detectors are being carried out in the hope of eliminating the need for a concentrating step and of providing a seagoing piece of equipment for the routine monitoring of trace contaminants. Further work is needed on selective partitioning agents to separate various classes of compounds such as oxygenates and aromatic hydrocarbons.

The nature of the hydrocarbons found in submarine air by chromatography of direct air samples indicates that hydrocarbon sources other than paint and paint thinner make important contributions to air contamination. An investigation of substances used aboard nuclear submarines is being carried out and at present includes various paint formulations, paint thinner, diesel fuel, and lighter fluids. Further work is needed on all these materials to establish the relative importance of their contributions to atmospheric contamination. The list will be expanded as other substances become suspect.

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CHAPTER 9

THE MARK III AND MARK IV ATMOSPHERE ANALYZERS

F. S. Thomas

The steps leading to the production of the Mark III Atmosphere Analyzer have previously been described (1). Experience with these units in submarines has been highly variable; generally the sources of trouble and the reasons for differences among ships are not apparent. As the sources of the several troubles have become known, Beckman Instruments, Inc., under contract from the Bureau of Ships, has introduced modifications for backfit to the service units to minimize or remove the difficulties. These have included such items as the replacement of polyethylene tubing inside the 100-psi portion of the system, addition of switches to permit operation of the infrared-source motors only when readings are desired, and modification of the pressure-sampling pump to reduce noise, keep oil out of the sampling system, and to improve its pumping performance.

A Mark III analyzer was operated at NRL for several thousand hours for experimental purposes, but without attempting to duplicate shipboard conditions. No major difficulties appeared within the various assemblies during this period of laboratory use. After only a short period of operation of the pump, there was evidence of some movement of oil into the sample system and of intermittent malfunction of the pump valves, indicated by failure to attain the required flow and pressure. Operation of the sampling pump was not required for the purposes for which the analyzer was being used in the laboratory, so after finding these difficulties the pump was secured for the remainder of the time. These pump troubles have now apparently been corrected by the Beckman backfit modifications.

During most of the analyzer operation in the laboratory, the regular sampling system was bypassed so that proof samples of the commercially procured calibration gas could be bled into the analytical elements under controlled conditions. This resulted in a comparison of the gases which showed that all of the available samples, about 2/3 of those prepared under one procurement contract, were comparable with the manufacturer's indicated analysis, except three, which varied in Freon content and one which varied slightly in equivalent hydrogen content. Comparison of these to a high-pressure calibration gas mixture previously prepared at NRL indicated reasonable agreement. Comparison of these to low-pressure, basic standard gas mixtures has not yet been carried out.

The experience gained with the Mark III, and the progress in instrumentation since the basic design criteria for Mark II and III were laid down, made it desirable that this model be redesigned completely before the procurement of further analyzer units. The Mark IV, which is being developed by Beckman Instruments, Inc., under a contract from BuShips, is essentially in the prototype stage. The infrared portions of this instrument (for Freon-12, CO, and CO_2) use basically the same positive-filter analytical method used in the previous analyzers, but application of the method is drastically modified to operate on the monobeam principle (2). This development should yield an analyzer with more stability and less crossover sensitivity between the gas to which the analytical element is sensitized and the various other gases present in the submarine atmosphere. Design changes permit operation of the unit at ambient pressure, which eliminates the need for a compressor and pressure regulator and the maintenance of a tight system for the high pressure. Provision is made in this unit for an experimental, long-path ultraviolet gas

analyzer which should be highly sensitive to a number of toxic materials, particularly mercury, ozone, and benzene. This ultraviolet channel is nonspecific, and identification of the atmosphere contaminant which produces an instrument indication will require the chemical treatment of the input sample by specific absorbents. The oxygen channel has been simplified by the use of a simple, visually indicating, paramagnetic oxygen unit instead of the similar electrostatic balance unit which was originally employed, so that an electrical signal could be obtained for recording purposes. The hydrogen channel of the Mark III may be eliminated, but if used it will remain essentially unchanged.

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CHAPTER 10

CONCENTRATIONS OF HYDROCARBON VAPORS IN SUBMARINE ATMOSPHERES BY CARBON SAMPLING

W. D. Smith and J. E. Johnson

INTRODUCTION

For the study of atmospheric pollutants in nuclear submarines, the first samples collected by adsorption with activated carbon were taken during the habitability cruise of the USS NAUTILUS in the spring of 1956 (1,2). These samples were taken from the main air filters, which were an integral part of the ship's air-purification system. This method of obtaining samples had several inherent disadvantages and was later replaced by a more flexible method employing a modified commercial sampling unit (Dorex canisters). Such units were made available for atmosphere sampling on the USS NAUTILUS, USS SEAWOLF, and USS SKATE between the spring of 1957 and the spring of 1958. All early samples were processed by vacuum desorption and by steam desorption (1).

Infrared analysis of the recovered hydrocarbons showed the presence of aromatic as well as aliphatic hydrocarbons. Mass-spectrometer data indicated four main types of hydrocarbons to be present: aliphatic paraffins, cycloparaffins, olefins, and aromatics. It was apparent from the early data that the atmospheres of these submarines were thoroughly contaminated with many different hydrocarbons. The analyses also showed that considerable quantities of hydrocarbons were present–i.e., from 50 mg/m^3 to 171 mg/m^3.

The qualitative compositions of the contaminants in the atmospheres of the different submarines were very similar, suggesting a common source of contaminations. The similarity in composition to mineral spirits and paint thinner indicated that the painting of inboard surfaces might be the major source of pollution. Much of the subsequent sampling of the atmosphere of the nuclear submarine with activated carbon was aimed at the determination of the total hydrocarbon contamination levels, with a hope of relating these to sources of contamination such as the painting of inboard surfaces.

SCOPE AND STATUS OF PRESENT PROGRAM

In March 1959, a program for carbon sampling and analysis of the atmospheres of nuclear submarines on a regular basis was recommended by NRL to the Bureau of Ships (3). The program was soon implemented by the Bureau with the New York Naval Shipyard Materials Laboratory conducting the sampling and analysis and NRL monitoring occasional samples. In keeping with the objectives of this program, a bank of three steam-desorption systems was assembled at NRL. This equipment permitted an independent study of the desorption of hydrocarbons and provided a means for further study of samples of special interest, including the assessment of the effect of remedial measures by comparative studies of samples obtained from different submarines. In order to meet another objective of this program, it has been necessary to evaluate the existing sampling techniques under field and laboratory conditions. These experiments gave rise to a new design in sampling equipment which is currently undergoing further development.

THE ROUTINE SAMPLING OF SUBMARINE ATMOSPHERES WITH ACTIVATED CARBON

The first carbon samples obtained under the new program were samples obtained during the submersion of the USS SKIPJACK in September 1959 (4). These carbon samples were steam desorbed at NRL and at the Materials Laboratory. The combined data are retabulated in Table 16. The total hydrocarbon concentration values found at NRL are in good agreement with those obtained at the Materials Laboratory, the averages being 47 and 52 mg/m^3 respectively.

Table 16
Desorption of Carbon Samples USS SKIPJACK (Sept. 1959)

NRL Sampler No.	Effective Submersion Time (hr)	Sampling Time (hr)	Concentration (mg/m^3)		Remarks
			Mat. Lab	NRL	
*C-58	–†	12	105	89	Painting 25 days prior to submersion, fan room
C-59	3	7.5	33	30	Fan room
C-62	22	48	50	45	Fan room
C-63	62	12	34	32	Lower-level aft mach. sp. CO-H_2 burner exhaust
C-64	74	12	31	32	CO-H_2 burner exhaust
C-61	85	12	82	75	Op. compt., 3rd level
C-60	98	12	40	–‡	Torpedo room
C-57	110	12	54	45	Aft. mach. space
C-58	122	12	90	71	Eng. room, upper level
Average	–	–	52	47	

*Not included in the calculation of the average.

†Unknown.

‡Not run by NRL.

The compositions of the hydrocarbons recovered from the carbon samples collected on the USS SKIPJACK, USS SARGO, USS SKATE, USS SWORDFISH, and USS TRITON during the last year were all essentially the same. Figures 30 and 31 show respectively the vapor chromatograms of samples from the SKATE (Oct. 1959) and the SKIPJACK (Oct. 1959). The average total hydrocarbon concentrations were 58 mg/m^3 and 52 mg/m^3 respectively.

FLUCTUATIONS IN TOTAL HYDROCARBON CONTAMINATION

Previous work has shown a correlation between the painting of inboard surfaces and the total concentration of hydrocarbons in the atmosphere of nuclear submarines (1,5). All sampling in these studies had been done on submarines which had had recent histories of oil-base painting prior to the sampling of the atmosphere. Table 17 summarizes additional data on hydrocarbon concentrations found on several submarines. It will be noted that there are considerable variations in values found on a given ship for a particular cruise, among different ships, and on a given ship on different cruises.

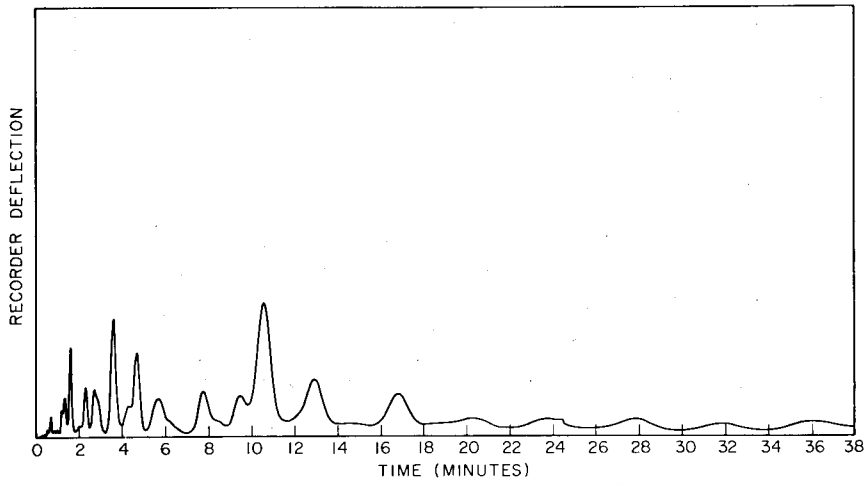

Fig. 30 - Oil desorbed from a carbon sample, USS SKATE, Oct. 1959, 1/4 sensitivity

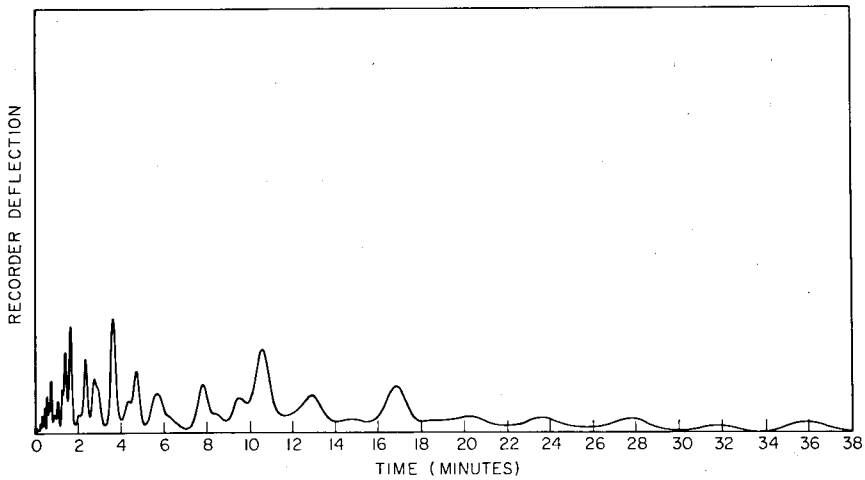

Fig. 31 - Oil desorbed from a carbon sample, USS SKIPJACK, Oct. 1959, 1/4 sensitivity

Table 17
Summary of Total Hydrocarbon Concentrations Found

Exposure Dates	Concentrations (mg/m^3)		Ship
	Range	Average	
*Fall – 58	24 – 85	55*	USS SKATE
9/1/59 – 9/6/59	33 – 90	52	USS SKIPJACK
9/21/59 – 9/28/59	6 - 20	12	USS SARGO
10/19/59 – 10/31/59	39 – 82	58	USS SKATE
3/25/60 – 3/31/60	19 – 47	32	USS SKATE
4/11/60 – 4/22/60	1 – 12	5	USS TRITON
Overall Average	–	32	–

*Not included in the calculation of overall average.

An opportunity to collect samples from the atmosphere of a nuclear submarine that had not experienced oil-base painting for many months came during the October 1959 submersion of the USS SARGO, which was known to have had little or no oil-base painting for a considerable period prior to the cruise. Six carbon canisters were exposed during this submersion. The total hydrocarbon concentrations found are shown in Table 18. The average concentration for the first five samples taken was 12 mg/m^3. The last sample, C-88, which shows a hydrocarbon concentration of 184 mg/m^3, was taken after a period of painting inside the ship. The low average value of 12 mg/m^3 reflects the reduction of total hydrocarbon contamination by the control of inboard painting, while the surge in concentration shown in the last sample illustrates the marked effect produced when painting was resumed.

Table 18
Total Concentration of Hydrocarbon USS SARGO (Oct. 1959)

NRL Sample No.	Effective Submersion Time (hr)	Sampling Time (hr)	Concentration (mg/m^3)	Remarks
C-83	8	12	6	Attack center
C-84	20	12	6	Attack center
C-85	44	12	16	Attack center
C-86	109	12	20	Attack center
C-87	157	12	10	Attack center painting
*C-88	185	12	184	Attack center painting
(Average)	–	–	12	–

*Not included in the calculation of the average.

Gas chromatograms for sample C-83 (before painting) and sample C-88 (after painting) from the USS SARGO, October 1959, are shown in Figs. 32 and 33 respectively. It is apparent that the overall composition of the recovered samples is essentially the same. There is a higher concentration of the more volatile components, which appear earlier in the chromatogram, in sample C-88 (Fig. 33). These samples show the same similarity in composition as the previous samples from other ships. A detailed study was not made on these samples. Such a study has been made of the samples from the USS SKATE, October 1959 (6). This study showed that the hydrocarbons identified were those that are commonly found in high concentrations in petroleum fractions of comparable volatility.

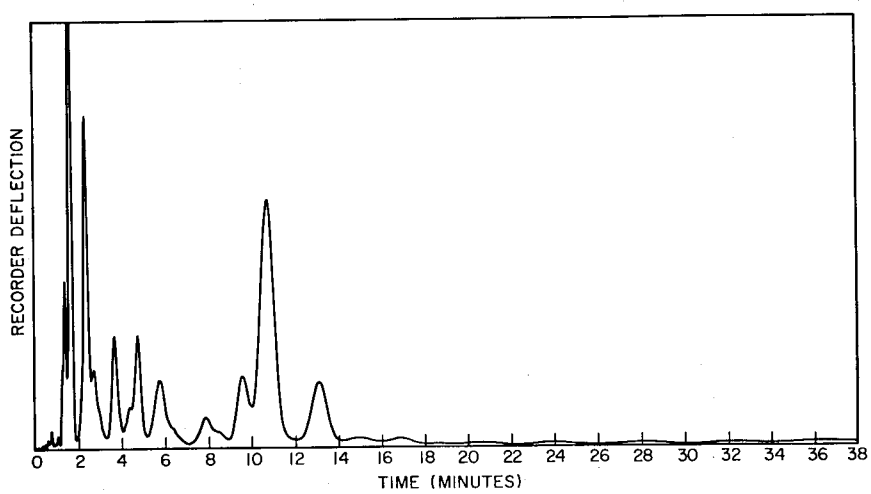

Fig. 32 - Oil desorbed from a carbon sample, USS SARGO, Oct. 1959 (before painting), full sensitivity

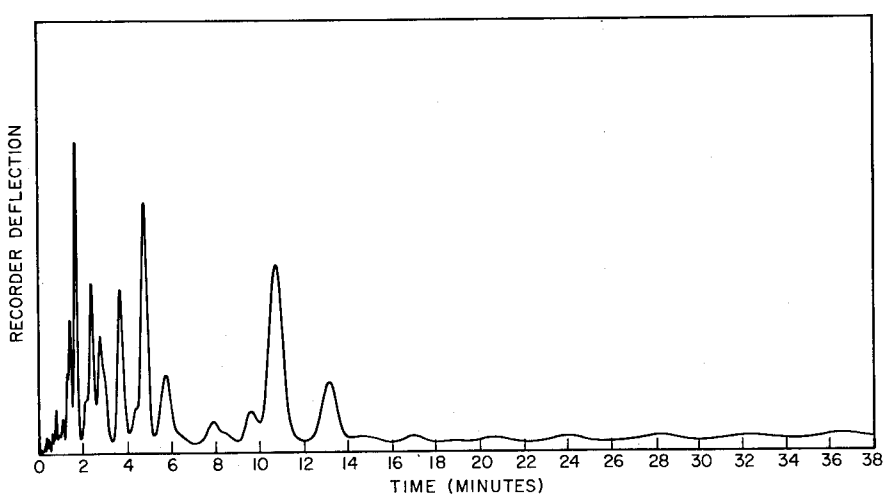

Fig. 33 - Oil desorbed from a carbon sample, USS SARGO, Oct. 1959 (after painting), full sensitivity

THE AROMATICITY OF HYDROCARBON CONTAMINANTS OF NUCLEAR SUBMARINES

Aromatic hydrocarbons were detected by infrared and mass spectrometric methods of analysis in early samples taken from nuclear submarines. Quantitative measurements were not made due to the complexity of these mixtures, specific limitations of the instruments, and uncertainties of the sampling procedure which might be introduced by the selective adsorption and/or desorption of the different hydrocarbon types.

In order to resolve this latter question, a study was begun on the sampling of mixed hydrocarbons with activated carbon from a controlled atmosphere. Studies have been conducted in a large chamber contaminated with a synthetic mixture of eight components, with approximately equal volumes of aromatic and aliphatic hydrocarbons. The average molecular weight of the mixture was 108, and the concentration was maintained constant at 91 mg/m^3.

The atmosphere in the chamber was sampled with a modified commercial unit, and the adsorption and mechanical efficiencies were monitored periodically by drawing out a small stream, burning the hydrocarbons in it completely, and measuring the carbon dioxide produced with a Beckman nondispersive infrared analyzer. The adsorption efficiency was found to be essentially 100 percent up to the breaking time, which occurred after ten hours of cumulative sampling. The mechanical efficiency was found to be low due to leakage at various parts of the unit.

The sampling was terminated when the adsorption efficiency had dropped to approximately 85 percent at the end of 13 hours of cumulative sampling. The adsorbate was recovered by steam desorption and a type analysis was made by the Fluorescent Indicator Adsorption (FIA) technique (7).

The results of the FIA analysis of the recovered hydrocarbons from this study and from hydrocarbons recovered from carbon samples taken from the atmospheres of nuclear submarines are shown in Table 19. The analyses of recovered hydrocarbons in the chamber study gave values of 55 percent ± 2 aromatic and 45 percent ± 2 aliphatic.

Table 19
FIA Analysis of Hydrocarbon Mixtures

Sample No.	Aliphatic (% ±2)	*Aromatic (% ±2)	Remarks
MS 270	46	54	USS SKATE - Oct. 1958
MS 250	59	41	USS SKATE - Oct. 1958
MS 215	64	36	USS NAUTILUS - Aug. 1958
MS 200	90	10	Paint thinner
MS 258	83	17	Paint thinner
C-52X	53	47	USS TRITON - Sept. 1959
C-53X	52	48	USS TRITON - Sept. 1959
C-54X	50	50	USS TRITON - Sept. 1959
C-153X	45	55	Recovered from control chamber
C-153	46	54	Synthetic mixture in control chamber

*Percentage by difference.

The synthetic mixture used as the contaminant in this study was less complex than the mixtures that have been recovered from the atmospheres of nuclear submarines and so does not completely preclude the possibility of selective adsorption and/or desorption during the sampling procedure. It does show that samples can be collected from an artificial atmosphere of eight mixed hydrocarbons containing a high percentage of aromatics without a significant degree of selection during the adsorption or desorption steps. This result gives increased confidence in the use of carbon sampling as a tool in analysis of submarine atmospheres.

THE DESIGN OF A NEW CARBON SAMPLER

A new carbon sampler has been designed and fabricated at NRL at the request of the Bureau of Ships. A prototype model, NRL carbon sampler 1, and the currently employed modified commercial model, are shown in Fig. 34. The modified commercial unit has been described previously (1). The NRL sampler is essentially a small annular canister with a 0.5-in. bed depth, mounted on a small chassis which houses a small "squirrel cage" blower. The canister and blower are modifications of commercial components. The original blower was modified by extending the nozzle and fitting it with an orifice which restricts the flow to 142 liters per minute under operating conditions. Static taps were made on both sides of the orifice and were connected to a differential pressure gauge. All seams were sealed, and the free space around the motor shaft was minimized. The canister is seated against a small rubber gasket and is rigidly held in place by a quick-release plunger, which is fastened to a reinforced retainer post. This design essentially eliminates the mechanical loss that was found to occur in the present sampler. The smaller canister, coupled with the ease of installation and removal of canisters, renders the NRL sampler a more economical and flexible means of sampling on a routine basis.

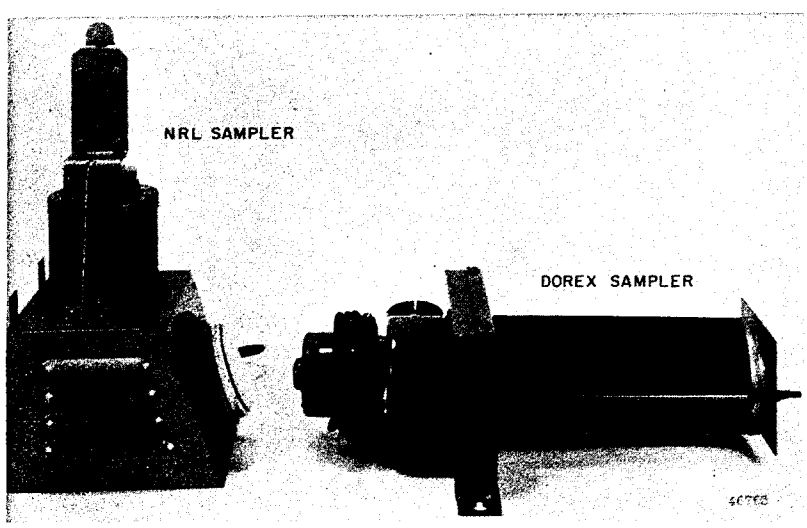

Fig. 34 - Carbon samplers-NRL carbon sampler model 1, and Dorex sampler

Another design, NRL sampler 2, has been fabricated and is being evaluated aboard ship. NRL sampler 2 is very similar in design to NRL sampler 1; the essential difference lies in the design of the canister. In NRL sampler 1 the canister is annular, with a bed depth of 0.5 in., whereas in NRL sampler 2 the canister is flat; i.e., the carbon bed is a

"pancake" 1.5 to 1.7 in. thick. Another feature of the newer design is the incorporation of a plenum space as an integral part of the sampler to assure an even distribution of the flow of air through the carbon. The main advantage of this design is that the canister may be filled easier aboard ship; a second advantage is that the increased bed depth will lessen the probability of elution at longer sampling time at low concentrations of lower boiling contaminants.

EVALUATION OF NRL SAMPLER 1

NRL sampler 1 was given an evaluation in the chamber, as described previously. The adsorption and mechanical efficiencies were measured periodically by analysis of air streams drawn by means of sampling probes inserted into the canister and nozzle. The two readings indicated little or no leakage around the carbon bed. After eleven cumulative hours of sampling, the overall efficiency of the adsorption bed dropped to 98 percent, and there was no mechanical loss.

SUMMARY

1. The routine recovery of hydrocarbons by steam desorption from carbon canisters has been transferred to the Materials Laboratory. Comparative data from the Materials Laboratory and NRL on individual samples agree favorably.

2. The average concentrations of hydrocarbon contaminants found in submarine atmospheres on particular cruises ranged from 5 to 58 mg/m^3 with an overall average of 32 mg/m^3. Considerable variations were found on a given ship for a particular cruise, among different ships, and on a given ship on different cruises. On one cruise of the USS SARGO, on which painting occurred during submersion, the concentration of hydrocarbons rose from an average of 12 mg/m^3 before painting to 184 mg/m^3 after painting.

3. Gas chromatograms of samples from several submarines indicate that the overall hydrocarbon compositions of the recovered samples are very similar, both as to individual components and relative amounts of each.

4. The hydrocarbons recovered from carbon sampling of the atmosphere of nuclear submarines show a high degree of aromaticity, i.e., an average of 46 percent.

5. Two new carbon samplers have been designed and fabricated by NRL. These samplers are much more compact and convenient to use and eliminate the mechanical losses encountered in the units currently employed in the sampling of the atmosphere of nuclear submarines.

FUTURE WORK

As lower concentrations of hydrocarbons are encountered in the nuclear-submarine atmosphere, improved sampling techniques will be required. The use of sampling tubes or columns adaptable to "backflushing," containing single or mixed adsorbents, will be explored as one approach to this problem.

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CHAPTER 11

ARSINE AND STIBINE ANALYSIS

E. T. Johnson

Arsine and stibine are highly toxic and hazardous gases. At low concentrations they have no appreciable odor, and the symptoms of poisoning may not appear until several hours or even days after exposure.

Arsenic and antimony are usually present as impurities in the raw materials from which lead-acid storage batteries are made, and under certain operating conditions the cells will evolve the hydrides, arsine, and stibine. This problem has been recognized by the U.S. Navy for a number of years, with the result that arsenic has always been limited to trace quantities in the lead alloys and electrolyte. In the case of antimony, it has been established that stibine is evolved only during the latter part of the charge, even though the antimony content of the grid alloy may be as high as 8 percent. Arsine, on the other hand, is evolved even on stand if arsenic is present in small quantities in the cell.

The first installation of a battery in a nuclear submarine was by necessity a lead-antimony grid alloy battery. The Bureau of Ships limited overcharging except when ventilating outboard and provided a silver-impregnated carbon in the ventilation system which would decompose any arsine or stibine in the atmosphere while submerged. All the later battery installations on nuclear submarines have used the lead-calcium alloy grid to eliminate the stibine problem and at the same time obtain a greatly reduced rate of self-discharge and longer life. It is essential, however, because of the possibility of contamination, that the present nuclear submarines be checked for arsine and stibine.

While a number of methods of analyzing for arsenic and antimony have appeared in the literature (some have been used as standard methods for years), most are not applicable to the very low concentrations of interest here. The method finally employed for stibine uses an iodine-iodide adsorbing solution in a Folin-type bubbler. After sampling, the excess iodine is reduced in 8-percent sulfuric acid with sodium hypophosphite, and the resulting yellow antimonyl iodide ion determined colorimetrically (1). While arsenic compounds do not interfere, hydrogen sulfide and bismuth do, and they must be either accounted for or eliminated. This method, as now employed, will detect quantitatively 4 μg of stibine in 10 ml of the iodine-absorbing solution. The minimum detectable concentration is limited mainly by a practicable sampling time. At the present time, 24 hours is the maximum sampling time which has been used with 10 ml of absorbing solution and 1/2 liter of air sample per minute. This gives a minimum quantitative limit of 0.0011 ppm of stibine, which is approximately 1/100 of the threshold limit value (0.10 ppm) (2).

The method of analysis presently employed for arsine is a modification of the molybdenum blue method (3), in which 0.6-percent mercuric chloride is used as an absorbing solution in a Folin-type bubbler. After sampling, the sample is oxidized with permanganate in an acid solution and complexed with molybdate by reducing with hydrazine sulfate. The intensity of the resulting moly-blue complex is directly proportional to the arsenic and phosphorus content of the sample. If the presence of phosphorus is suspected, the arsenic can be removed by converting to arsine and evolving into a new absorbing solution. This method as presently employed will detect quantitatively 1 μg of arsine in 20 ml of

absorbing solution. The absorbing solution remains effective after several days of sampling at the rate of 1/2 liter per minute. A 24-hour sample collected at this rate gives a minimum quantitative limit of 0.0005 ppm of arsine, which is approximately 1/100 of the threshold limit value (0.05 ppm) (2).

The rate of evolution of stibine from an antimony-containing cell increases rapidly at the beginning of overcharge and soon becomes practically constant, dependent only upon the current rate and the condition of the cell. The evolution before overcharge is usually too small to detect, but some cells on overcharge have produced 1.5 mg/cell/min at 300 amps, 2.4 mg/cell/min at 400 amps, and 3.2 mg/cell/min at 500 amps. A typical lead-calcium cell has shown the evolution of arsine and stibine listed in Table 20.

Table 20
Amounts of Arsine and Stibine Evolved in Typical Cell

New Cell	Stibine (μg/hr)	Arsine (μg/hr)
Charged stand	Less than 0.2	Less than 0.05
Discharging at 1000 amps	Less than 1.5	Less than 0.36
Charge	Less than 1.1	1.20
Overcharge at 150 amps	7.5	6.00
Overcharge at 300 amps	22.6	5.30
Charged stand	Less than 0.5	Less than 0.17
CELL AFTER SEVERAL CYCLES		
Overcharge at 100 amps	11.5	Less than 1.30
Overcharge at 100 amps	13.0	Less than 1.30

During the past year methods have been modified and adapted to permit sampling and determination of arsine and stibine from several representative submarines in order to ascertain the absence of these toxic gases. An opportunity was taken during a battery ventilation test on the SEADRAGON to collect samples from the battery exhaust duct and in a main air supply outlet while the battery was on overcharge (4). Table 21 summarizes the results of this test.

Table 21
Samples From Battery-Ventilation Test on the USS SEADRAGON

Time, Rate, Conditions, Sampling Point	Stibine (ppm)	Arsine (ppm)
7-1/2 hr at 500 cc/min (6-1/4 hr overcharge) bat. exh.	<0.007	<0.003
8-1/4 hr at 500 cc/min (6-1/4 hr overcharge) main air	<0.006	<0.003
5 hr at 500 cc/min (5 hr overcharge) main air	<0.010	
5 hr at 500 cc/min (5 hr overcharge) bat. exh.	<0.010	<0.001
Drager arsine unit – several places on ship		<0.015
MSA arsine unit – Electrical Equipment Room		<0.005

Samples were also collected during the August-September 1960 TRITON cruise (5). Table 22 summarizes the analysis of these samples.

Table 22
Samples From USS TRITON

Sample	Number of Samples	Battery	Mean of Indicated Value (ppm)	Range of Probable Value (ppm)
AsH_3	7	Stand and Discharge	0.00012	0.00002 to 0.00028
AsH_3	1	Charge	0.00027	0.00013 to 0.00056
SbH_3	1	Charge	0.00076	0.00040 to 0.00119

While samples so far collected give no indications of appreciable contamination, additional sampling is planned to determine if arsine and stibine are equally as low in the air of other nuclear submarines. Since collection of samples is difficult and uncertain at present, a more suitable method of sampling is being sought.

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CHAPTER 12

ANALYSIS FOR OZONE

J. L. Bitner

All the nuclear submarines are being fitted with additional electrostatic precipitator (ESP) units in order to reduce the aerosol content of their atmospheres. Previously only one ESP (in the crew's mess circulation system), with a capacity of 1200 cubic feet per minute (cfm) of air, was placed aboard each ship. The additional ESP units will have a total capacity of approximately 10,000 to 20,000 cfm of air depending on the class of ship. A byproduct of ESP operation is ozone (O_3); therefore, the large increase in the number of ESP units aboard has increased the possibility that the ship's atmosphere will be contaminated with O_3.

Ozone must be controlled in closed spaces because of its toxicity to man and its destructiveness to a large number of substances, such as rubber. Studies with small rodents have been made to determine the extent of this toxicity. It was found that concentrations of 5 parts per million O_3 was sufficient to kill 50 percent of the rodents exposed (1). Continuous exposure to smaller concentrations (1 ppm) built up a tolerance to O_3 in rodents (2). Case histories of six arc welders exposed to O_3 substantiate the claim that O_3 is toxic to man (3); symptoms of poisoning occurred at concentrations of 2.5 ppm and above. The presence of O_3 is believed to be responsible in part for the illness and deaths which have been attributed to several of the Los Angeles smogs. The Bureau of Medicine and Surgery has recently established a threshold limit value of 0.05 ppm of O_3 for 90-day continuous exposure.

The most specific devices for detecting O_3 are those employing physical phenomena. Infrared and ultraviolet spectroscopy have both been used in determining atmospheric O_3 (4,5). Unfortunately these methods require long light paths (400 meters or greater) in order to detect O_3 in the concentrations of interest. Colorimetric and fluorometric methods have also been used (5). In many cases these methods fall short of their desired purpose due either to nonspecificity or to lack of sensitivity. Iodine compounds have been used extensively to determine atmospheric oxidants such as O_3. Various modifications of a procedure which involves the oxidation of iodide ion (I^-) to free iodine (I_2)–iodometry-have been widely used (5,6,7,8,9,10). A number of methods have been used to detect or measure the I_2 released by the oxidant. Coulometry (11,12), potentiometry, and amperometry have all been used. These devices are used to detect iodine and/or to measure it quantitatively; for quantitative measurement, a second agent such as sodium thiosulfate ($Na_2S_2O_3$) or sodium arsenite (Na_2HAsO_3) may be required (6).

The analytical procedure selected for determining O_3 employs potassium iodide (KI) and $Na_2S_2O_3$ as the reacting species and the "dead-stop end-point" amperometric method as the end-point indicator. The amperometric method as used requires two platinum electrodes with a constant potential of approximately 0.1 volt across them.

The ozonometer consists of two sections fitted together with a standard-taper, ground-glass joint (Figs. 35 and 36). The upper section (aerator and liquid collection unit) consists of an outer shell with an exhaust air port attached and an inner, aerating tube which is open only at the lower end. The aerating tube has indentations extending toward its vertical

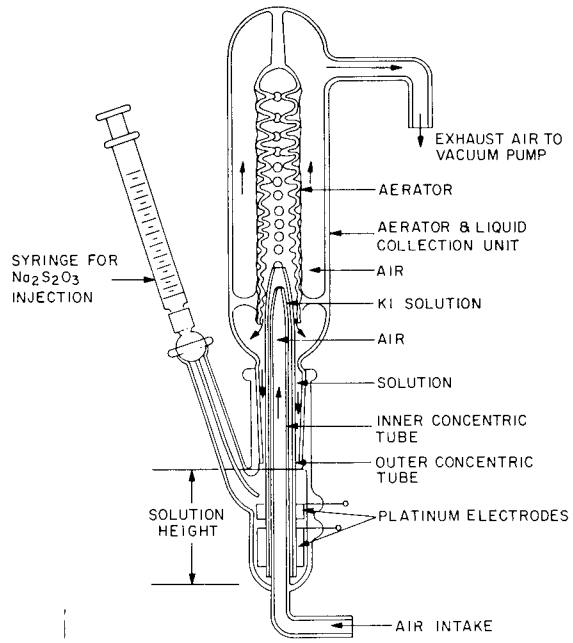

Fig. 35 - Diagram of ozonometer

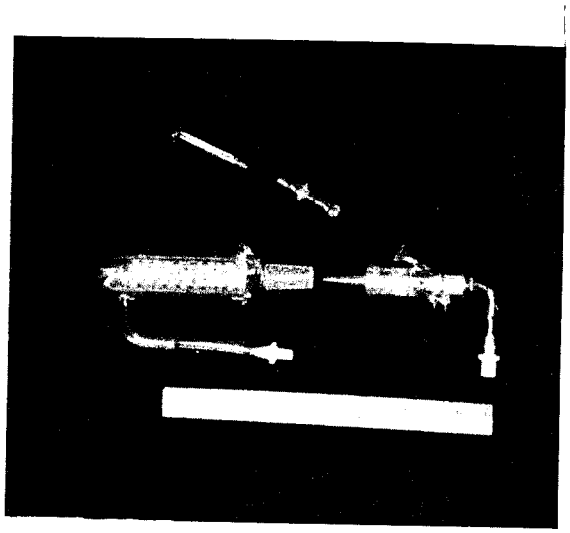

Fig. 36 - Cell and aerator

axis (similar to those of a Vigreaux distillation tube) in order to effect greater contact between the KI solution and the air. The lower section consists of an electrolysis cell with two tubes, both concentric with the vertical axis of the cell, passing through it. The innermost tube passes through the bottom of the cell, whereas the lower end of the outer tube is attached to it. This latter tube has openings near its base which allow the KI solution to pass freely from the cell into the passageway formed by the inner and outer tubes. Both tubes are constricted at their upper end in order to form nozzles. A side arm is attached to the cell as a means of adding the necessary solutions to the cell. The side arm is closed to the atmosphere (except for the short time needed to add liquids) to insure the operation of apparatus. Air flow through the ozonometer is controlled by a calibrated critical orifice situated in the vacuum line between the vacuum source and a silica gel drying column. The drying column is connected directly to the air exhaust port and is used to collect particulate carryover which would otherwise deposit salts in

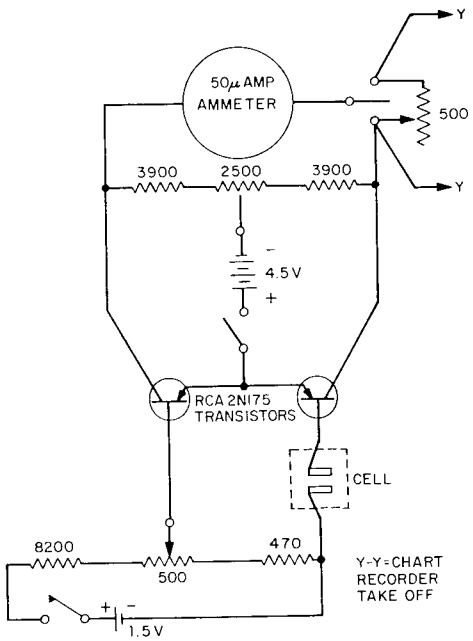

Fig. 37 - Electrical circuit of ozonometer

the critical orfice and in the vacuum source. The electrical circuit employed with this ozonometer is shown in Fig. 37. The two-transistor amplifier increases the distance the needle moves for each increment of current impressed across the ammeter, thus facilitating the detection of current flow. The ammeter is, therefore, used only as a detecting device and does not indicate the true current readings.

To operate the ozonometer, approximately 12 liters per minute (lpm) of atmospheric air is drawn up through the inner concentric tube. This air flow produces an aspirating effect which is sufficient to draw liquid from the cell, through the passageway formed by the inner and outer concentric tubes, and up to the nozzles. The liquid is sprayed onto the walls of the aerating tube; then, under the influence of gravity, it flows back into the cell. The air reverses its direction of flow in passing from the aerating tube to the exhaust port. This reduces the aerosol carryover by the air stream.

Any O_3 in the atmospheric air passing through the ozonometer reacts with the aspirated KI solution at the time of contact. The I_2 formed in the reaction returns to the electrolysis cell in the unreacted KI solution. The I_2 then acts to depolarize the platinum electrodes (polarized due to hydrogen overvoltage), thus allowing a current to flow. This current flow indicates the presence of O_3 to the operator. As soon as the presence of O_3 is indicated, a known amount of standardized (0.002 normal) $Na_2S_2O_3$, in excess of that necessary to react with the I_2, is added to the KI solution in the cell. This causes the current to drop back to its base value due to the reduction of the I_2 by the $Na_2S_2O_3$. The atmospheric O_3 passing through the ozonometer is continuously oxidizing I^- to I_2, which in turn is reduced by the $Na_2S_2O_3$. At the stoichiometric point between $Na_2S_2O_3$ and I_2, the I_2 is no longer reduced; thus, it again depolarizes the electrodes and a current flows through the system. The <u>time</u> required to reach this stoichiometric point is dependent on the concentration of O_3 in the atmosphere as can be seen from the following equation:

(Eq. I) $$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2$$

(Eq. II) $$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

(Eq. III) $$O_3 + 2Na_2S_2O_3 + 2KI + H_2O \rightarrow 2NaI + Na_2S_4O_6 + 2KOH + O_2.$$

To insure that the preceding reactions occur stoichiometrically, they must be carried out in a neutral solution (pH 7-7.05). Any errors due to the initial presence of I_2 are circumvented by taking the time to be that point at which the current magnitude is the same as that at which the $Na_2S_2O_3$ was introduced into the ozonometer.

The concentration of O_3 in ppm can be determined from the experimental data by the following equation:

$$O_3 \text{ (ppm)} = \frac{(12{,}225)\ (N)\ (ml)}{(lpm)\ (T)}$$

where

O_3 (ppm) = parts per million of O_3 in atmosphere

12,225 = volume of equivalent weight of O_3 at the operating temperature and pressure

N = normality of the $Na_2S_2O_3$ used

ml = milliliters of $Na_2S_2O_3$ used

T = time in minutes required to reach stoichiometric point between $Na_2S_2O_3$ and I_2

lpm = flow rate in liters per minute of the atmospheric air through the ozonometer.

A correction factor that allows for the incomplete removal of the O_3 from the air must be included. Using similar solutions (neutral 10-percent KI), the ozonometer's efficiency was 80 percent of that obtained using two bubblers in series (0.1 ppm range). Apparent concentrations of O_3 as low as 5 parts per billion (ppb) have been measured with this apparatus; the ultimate sensitivity of the apparatus has not yet been established.

This ozonometer has been used successfully in the field and is sufficiently portable to be carried by one person (Fig. 38). The ozone-extracting unit, ammeter, solutions, and timer (stopwatch) can all be carried in a 6 x 12 x 14 in. case. The vacuum pump and recorder (optional) are separate units.

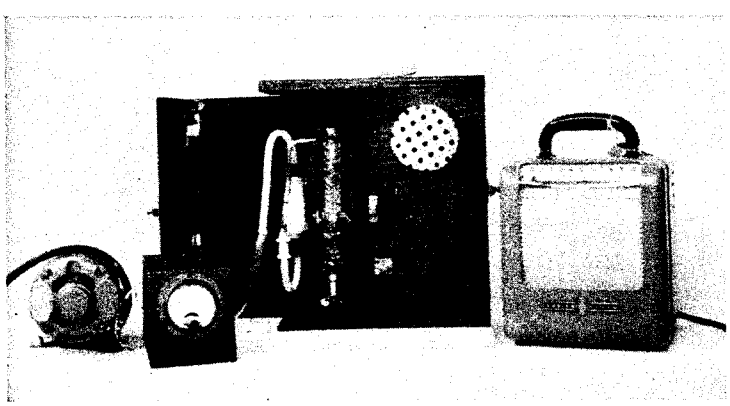

Fig. 38 - Ozonometer

The ozonometer as described requires the presence of an operator; therefore it is of little value for the continuous monitoring of O_3, but it could be used for spot checking. With suitable training, it would be possible for semitechnical personnel to operate the instrument; however, its operation would never attain the convenience of operation of the physical methods.

The major portion of the work done to date has been concentrated on developing a method for quantitatively determining atmosphere O_3 in the parts-per-billion range. The method adopted is not specific for O_3, but it is applicable for the measurement of most oxidants. Much of the equipment that produces O_3 also produces oxides of nitrogen, which also react with KI to form I_2. Several investigators report that their apparatus (using procedures involving KI solutions) has a low sensitivity to nitrogen dioxide in comparison with O_3. Thus nitrogen dioxide did not interfere with their O_3 determinations (12).

A portable meter has been developed for the measurement of ozone in submarine atmospheres. Although the ultimate sensitivity has not been determined, reliable measurements as low as 5 ppb have been made. The unit requires the presence of an operator, but nontechnical personnel, with some training, should be able to operate the instrument. In its present form the meter is not selective for O_3, but it responds to the total amount of oxidants present. Modifications are presently being made to make the instrument more specific for ozone. Ozone concentrations will be measured in operating submarines at the earliest opportunity.

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CHAPTER 13

LIQUID-OXYGEN CONTAMINANTS

R. E. Kagarise

INTRODUCTION

With the advent of more stringent restrictions on the use of paint and cleaning solvents aboard nuclear submarines, a significant decrease in the level of hydrocarbon contamination has been noted (1). As this level is further decreased, a point will eventually be reached at which other sources of contamination will become significant. One such possible source is the liquid oxygen used to charge the bank of gaseous oxygen cylinders. Under normal conditions, this bank is the primary source of oxygen during submergence. The purpose of this article is to discuss the nature and amount of contamination normally present in commercial liquid oxygen and its significance to the nuclear-submarine atmosphere.

It has been known for some time that contaminated liquid oxygen can be a serious problem when used as a source of aviators' breathing oxygen (2). In this case, the aviator is usually breathing pure oxygen and hence is exposed to undiluted contaminants. Moreover, in some aircraft convertor units, fractionation may occur which results in the concentration of contaminants. Under such conditions, oxygen contamination has resulted in obnoxious odors, nausea and vomiting, dizziness and serious disorientation of pilots (2).

Past investigations (2-5) have shown that the main impurities in liquid oxygen consist of carbon dioxide and low-molecular-weight hydrocarbons (C_1-C_4 range), including paraffins, olefins, and alkynes. However, while the observed contaminants could account for, or at least contribute to, the "gasoline-like" odors reported, none are sufficiently toxic at the levels normally encountered to account for the more profound physiological effects, such as asphyxia and nausea. A recent investigation (6) was successful in extending the sensitivity of the analytical method to the fractional part-per-billion range, but the compounds identified were of the same types as those reported by earlier investigators.

SAMPLING AND ANALYTICAL PROCEDURES

The sampling and analysis of the contaminants in liquid oxygen are similar, in many respects, to the study of air pollutants. In one respect, however, the analysis of liquid oxygen is simpler because of the absence of appreciable amounts of water vapor and carbon dioxide. Nevertheless, many of the techniques developed for the study of air pollution are applicable to the liquid-oxygen problem. The relative merits of these various methods have been amply discussed by Magill, et al. (7).

An experimental approach which has been quite successful is described in detail in a recent NRL report (6). Briefly, the sampling method consists of flash evaporating the liquid oxygen and allowing the resulting gas to pass through a bed of activated carbon. The carbon is cooled to dry ice-acetone temperature for improved retentivity of the lower-boiling contaminants. The adsorbed contaminants are desorbed from the carbon by heating under vacuum and are collected in liquid-nitrogen-cooled traps.

The analysis of the desorbed material is achieved by the combined use of infrared spectroscopy and gas chromatography. To achieve maximum sensitivity of the infrared method, a commercial, multireflection gas cell was employed. This cell has an effective path length of 60 cm, but it has a volume of only 22 ml. An additional ten-fold increase in sensitivity could be achieved through the use of scale expansion on the infrared spectrometer.

After obtaining infrared spectra, the desorbate is introduced into a gas chromatograph for further analysis. The chromatograph used in the NRL study (6) employed a thermal-conductivity cell as the detector. Replacement of this unit with a flame ionization detector would presumably result in a sensitivity increase of from 10^3 to 10^4. Such an increase would make this sampling and analytical technique competitive with the human nose, from the point of view of detecting odors. Odor threshold concentrations as low as 3×10^{-7} part per million have been reported (8) for certain particularly odorous materials.

ANALYTICAL RESULTS AND DISCUSSION

The analytical results given in this article are taken, for the most part, from the recent report already cited (6). From a qualitative point of view, they are similar in most respects to the results of Drew, et al. (2). However, since the latter investigators used a mass spectrometer in conjunction with gas chromatography, they were able to detect and measure the rare gases (neon, argon, krypton) and nitrogen.

Some typical analytical results are shown in Table 23. These results assume an adsorption-desorption efficiency of 100 percent and hence are minimum values. As is evident from this table, the major impurity in liquid oxygen is methane. This is not surprising for several reasons. First, the boiling points of -182.96° and -161.5° C for oxygen and methane, respectively, are relatively close. Second, methane is completely miscible in liquid oxygen. Finally, the normal terrestrial atmosphere contains from 1 to 5 ppm of methane, depending upon meteorological conditions and proximity to industrial facilities. Thus, because there is little separation of methane from oxygen during the liquefaction and fractionation process, one would expect a five-fold increase in the concentration of methane in liquid oxygen over the concentration present in air. The fact that none of the samples of liquid oxygen studied have less than 5 ppm of methane is consistent with this explanation. The remaining identified contaminants in liquid oxygen, except for carbon dioxide and carbonyl sulfide, are hydrocarbons which in all probability are produced from the cracking of compressor lubricating oils. Similar compounds are produced in commercial thermal cracking processes.

The unsaturated materials such as the butenes have rather unpleasant odors and probably account for the "gasoline-type" odor which can be noted in nearly all samples of compressed air. Fortunately, the liquefaction and separation process removed most of these compounds from liquid oxygen. In addition, the passage of the liquid oxygen through a bed of silica gel for the primary purpose of removing acetylene effectively removes many of these unsaturated compounds. Thus, most samples of liquid oxygen are essentially free from odors. A cursory study indicated that none of the samples listed in Table 23 possessed a detectable odor.

Carbonyl sulfide or carbon oxysulfide is not particuarly toxic or odorous. However, it reacts with water to form carbon dioxide and hydrogen sulfide. The latter compound is odorous and relatively toxic (maximum allowable concentration in air: 20 ppm, Ref. 9). However, the low level observed in liquid oxygen is roughly one-ten thousandth of the allowable concentration.

Table 23
Summary of Gas Chromatographic Analyses

Compound	Sample			
	1	2	3	4
Methane	66*	10	5	66
Carbon dioxide, ethylene, and ethane	82.6	905.1	103.5	122.5
Propane	12.6	35.6	15.7	276.7
Propylene	0.2	–	0.1	–
Carbonyl sulfide	0.2	–	trace	–
iso-butane	2.6	27.1	5.1	19.9
n-butane	6.3	72.1	11.8	74.9
1-butane and iso-butane	0.9	1.6	0.1	2.4
2-butane (trans)	0.1	0.6	0.1	0.4
2-butane (cis)	0.2	0.5	trace	0.5
iso-pentane	2.3	12.3	1.6	22.4
n-pentane	2.4	6.1	0.9	12.8
Unknown A	–	–	–	1.0
Unknown B	–	–	–	0.7
Unknown C	–	–	–	trace
Unknown D	–	–	–	0.2
Unknown E	–	–	–	trace
Unknown F	–	–	–	1.5
3-methyl pentane	–	–	–	0.6
n-hexane	–	–	–	2.1
Unknown G	–	–	–	trace

*Concentrations of methane are in parts per million; all others are in parts per billion.
Dashes indicate peaks were not found.

As previously stated, none of the liquid oxygen samples listed in Table 23 produced gaseous oxygen which was perceptibly odorous. However, two cylinders containing gaseous oxygen which was known to be odorous were obtained from the U.S. Naval School of Aviation Medicine, Pensacola, Florida. The analyses of these oxygen samples are shown in Table 24, with concentrations being given in parts per million. The presence of significant amounts of nitrous oxide (N_2O) and acetylene is the most obvious difference between these samples and the liquid oxygen samples listed in Table 23. The observed acetylene concentration in both cases is greater than the maximum allowable concentration of 0.05 ppm specified in Military Specification (MIL-0-21749(Aer)) of Dec. 17, 1958, Amendment-1 of Apr. 10, 1959. This specification is for aviators' liquid, breathing oxygen. In addition, the nitrous oxide is approaching the specified maximum concentration of 0.5 ppm, particularly if one takes into account the actual adsorption-desorption

efficiency, which is probably about 50 percent. Since acetylene and nitrous oxide are not particularly odorous, one suspects unidentified contaminants normally removed with these materials as being the odor-producing compounds. The nature of these compounds is speculative at the present time.

Table 24
Analytical Results on Compressed Aviators' Breathing Oxygen

Contaminant	Formula	Concentration (ppm)	
		Cylinder 16	Cylinder 17
Methane	CH_4	16	9
Carbon dioxide	CO_2	3.1	3.4
Nitrous oxide	N_2O	0.30	0.31
Acetylene	C_2H_2	0.20	0.15
Ethylene	C_2H_4	0.05	0.033
Propane	C_3H_8	trace	0.056
iso-butane	C_4H_{10}	0.012	0.012
n-butane	C_4H_{10}	0.038	0.044
iso-pentane	C_5H_{12}	0.025	0.012
n-pentane	C_5H_{12}	0.015	0.036
C-hydrocarbons	C_6H_{14}	Trace of 3 compounds	Trace of 6 compounds

CONCLUSIONS

The normal level of hydrocarbon contamination in commercial liquid oxygen, other than methane, is of the order of 0.5-1 part per million. Of this, the overwhelming proportion (90 percent) is comprised of normal paraffins such as propane, iso- and n-butane, and iso- and n-pentane. The level of methane contamination, on the other hand, is considerably higher and varies from 5 to perhaps 100 parts per million. In view of the fact that methane is not efficiently removed by the Desomatic CO burner, compressed oxygen could be a significant source of the methane present in the atmosphere of nuclear submarines. However, the presently encountered level (40-80 ppm, Ref. 10) is insignificant both from a toxicological and flammability point of view. Of the remaining contaminants that have been identified to date, none appear to be toxic or odorous, particularly at the concentration levels normally observed.

The previous conclusions are applicable to what, for lack of a better term, we shall call normal liquid oxygen, i.e., oxygen which is nonodorous and has a low-level (0.5-1 ppm) of hydrocarbons other than methane. On rare occasions, oxygen is produced which deviates from this norm. Such oxygen is odorous and can produce serious physiological effects when breathed by aviators. Two samples of such oxygen have been characterized by the presence of abnormally high concentrations of acetylene and nitrous oxide. It is suggested that the presence of these compounds resulted from a malfunction of the silica gel adsorption tower in the production equipment. Since neither compound is particularly odorous, it seems logical to conclude that other, as yet unknown, compounds normally removed by the silica gel were responsible for the reported odors.

The obvious question as to whether or not this so-called abnormal oxygen could produce similar undesirable effects when used aboard submarines cannot be answered on the basis of existing information. However, if any particularly unusual atmospheric conditions are encountered in the future, it is recommended that the compressed oxygen be considered as a possible source and that steps be taken to collect a sample of this oxygen for subsequent analysis at NRL.

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CHAPTER 14

DETERMINATION OF MONOETHANOLAMINE AND AMMONIA IN SUBMARINE ATMOSPHERES

D. D. Williams

Additional laboratory work on the method for the determination of monoethanolamine-ammonia (MEA-NH_3) described in Ref. 1 has been confined to the determination of the shelf life of production-model detector tubes and to the continuous-operation life test on a production-model sampling pump.

Original-design tubes, which did not include a protective section of calcium carbonate, exhibit full sensitivity and precision after 21 months storage at 2° to 4° C. However, these tubes failed after one month at ambient conditions. Ambient and refrigerated storage of the improved tubes reveal no failures after nine months. These tests are continuing. Refrigeration of all except current stock is recommended pending final evaluation.

The prototype pump assembly for the air sampler has been in continuous operation for 53 weeks. The only interruption was to service the valve assembly after an inadvertent fouling by silica-gel crystals from a faulty tube. Operational characteristics remain above specifications. A production-model assembly required replacement of the vibrator arm after 17 weeks of continuous operation. Production changes on subsequent models should correct this defect.

Complete MEA-NH_3 detector kits, consisting, essentially, of the items shown in Fig. 39, have been furnished to selected units of the nuclear fleet (2). Data relative to the establishment of tube specifications have been forwarded to BuShips (3). An air-sampling pump, based on NRL design specifications, is in commercial production (4).

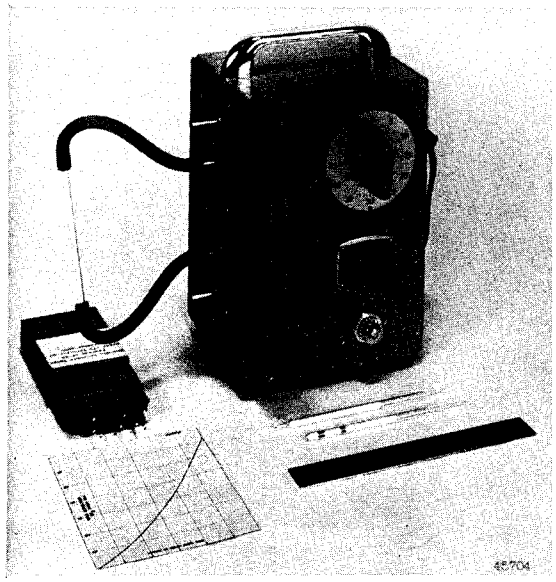

Fig. 39 - MEA-NH_3 detector kit

The successful application of this method and equipment during the Limea-Versene test aboard the USS SKATE (SSN 578) is detailed in Chapter 6 of this report. This test included the determination of MEA-NH_3 aerosols in addition to the gaseous content of scrubber effluent.

A formal report summarizing the development work on this method and equipment is in preparation (5).

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CHAPTER 15

DESCRIPTION OF NRL MODEL E-5753 LEAK DETECTOR

C. C. Minter,* S. F. Anderson,† and R. W. Dolk†

INTRODUCTION

The escape of Freon-12 from refrigeration equipment in submarines and other vessels can contaminate the atmosphere in closed spaces to a hazardous extent if the air is subjected to such high temperatures as are encountered in the CO-H_2 burner on nuclear submarines. It therefore becomes necessary to locate the leak in such equipment as soon as Freon is detected. At present the only commercially available and portable instrument for locating such a Freon leak is the General Electric halogen leak detector, which is extremely sensitive to traces of any halogen compound in the air. However, when Freon leaks into and accumulates in a poorly ventilated space such as a submerged submarine, the early-model GE leak detector loses some of its effectiveness in locating the leak if the concentration of Freon in the background reaches more than a few parts per million (ppm). Since the only apparatus specifically designed for locating halogen leaks appeared less sensitive under certain service conditions, it was decided to investigate the possibility of using for this purpose a thermal-conductivity bridge which would be free from the limitations cited above (1).

The thermal conductivity of Freon 12 at 33° C is 2.45×10^{-5} cal/cm/sec/° C compared with 6.15×10^{-5} for air (2). From measurements at NRL with other gas mixtures, it was estimated that the thermal-conductivity bridge to be used in the leak detector would give an output of approximately 15 millivolts open circuit when a mixture of 1-percent Freon vapor in air was compared with pure air, so that when a mixture of 1 ppm of Freon in air was compared with pure air the bridge should give an output of about 1.5 microvolts. It is not difficult to detect such a small potential difference, and for this purpose the Brown Electronik Null Indicator, model 104W1, is satisfactory.

APPARATUS AND TEST PROCEDURE

Apparatus and procedure for determining the response of the thermal-conductivity bridge to the change in thermal conductivity produced by the addition of very small quantities of Freon 12 to dry nitrogen have been described earlier (3). The results of tests with the thermal conductivity bridge shown in Fig. 40 indicated that the addition of 1 ppm of Freon-12 could be detected when the bridge output was connected to the Brown null indicator with a dc amplifier. A photograph of the early model thermal-conductivity leak detector using the Brown Electronik Null Indicator is given in Ref. 1.

TESTS OF EARLY MODELS

Tests of the early model showed that the time required to draw the sample through 6 ft of plastic tubing 0.105 in. inside diameter is less than 1.5 seconds when the flow rate

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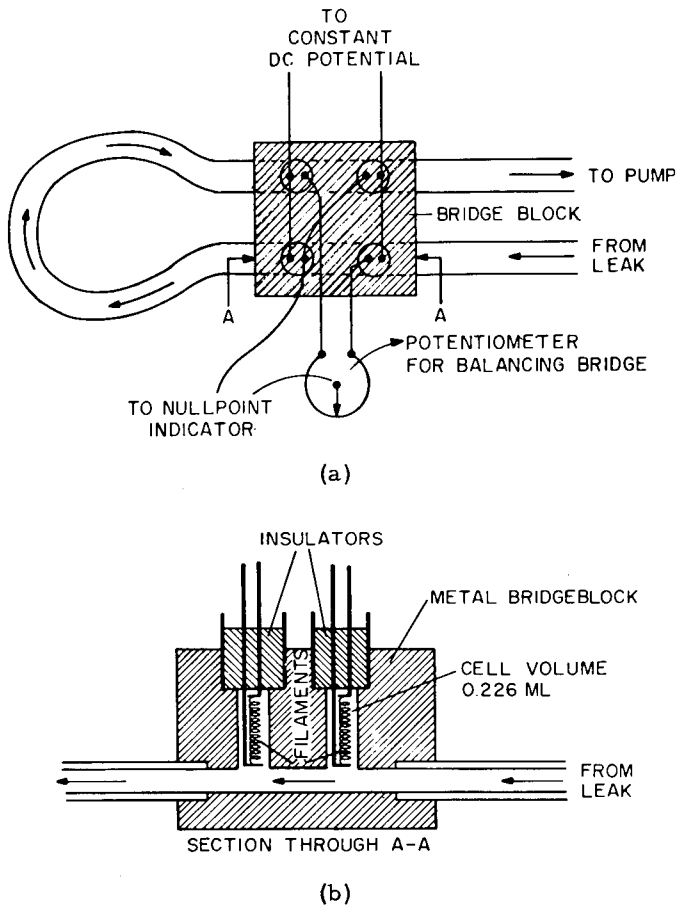

Fig. 40 - Thermal-conductivity bridge in a test version of the leak detector

is 500 cc/min. While this period could be reduced by increasing the flow rate, it was found that the reduction in time is not proportional to the increase in flow rate, because most of the lag time is required for the sample to diffuse into the cells. A total lag time of three to four seconds is regarded as about the best that can be done with the thermal-conductivity bridge, unless the sample actually flows through the cells, which seems to be out of the question at present.

In the early model the deflection of the meter on the Brown null indicator showed when the bridge was unbalanced. Since it is difficult for an operator hunting for leaks to keep his eye on the probe and at the same time to see when the meter was deflecting, it became necessary to place in the probe head some means for indicating when the bridge becomes unbalanced. To accomplish this the meter was removed from the Brown null indicator, and in its place was connected a Weston model 534 galvanometer relay. The contacts of this relay were connected to operate two small incandescent lamps, one red and the other blue, in a Lucite probe head. When both lights are out the bridge is balanced, but when first the red light flashes on and then the blue light, after which both lights are out, an operator knows that the probe had just passed over a Freon leak.

The early models, with a solid-state dc power supply and the Brown null indicator, worked fairly well, but the complete instrument was too large. In addition the development of tube noise would cause the null indicator to oscillate, thereby making it difficult to know

when the bridge was balanced. For these and other reasons it was decided to develop an ac model with a transistorized amplifier. The new model is described below.

DESCRIPTION OF MODEL E-5753

Figures 41, 42, and 43 show photographic views of the complete model E-5753 leak detector, which weighs 21 pounds and is easily portable. The circuit for the leak detector was designed around a commercially available thermal-conductivity bridge, with the flow tubes on one side of the bridgeblock connected in the manner shown in Fig. 40(a). Figure 44 shows a block diagram of the detector, which contains the following basic elements:

1. The thermal conductivity bridge
2. Power supply for bridge
3. Pump for aspirating sample through the bridgeblock
4. Unbalance detector amplifier connected to bridge output
5. Power supply for amplifier
6. Discriminator
7. Indicator lights
8. Line voltage regulator.

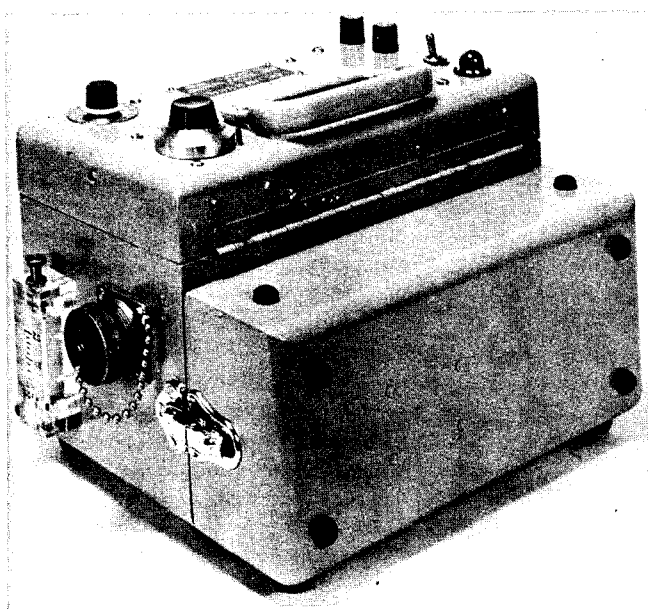

Fig. 41 - The complete model E-5753 leak detector. The detachable part of the case in the foreground contains the external connections shown in Fig. 42.

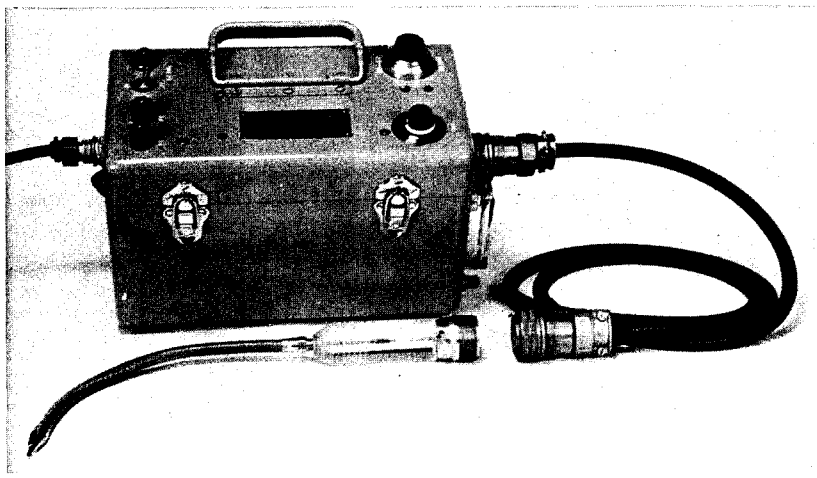

Fig. 42 - View of the leak detector, showing attachment of the probe, Lucite probe head with indicator lights, and connecting tubing

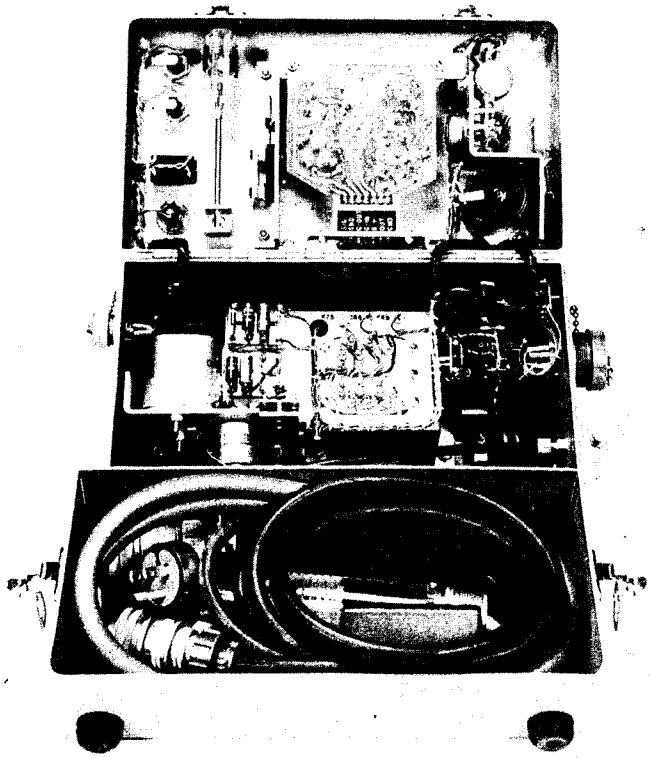

Fig. 43 - Interior view of the leak detector

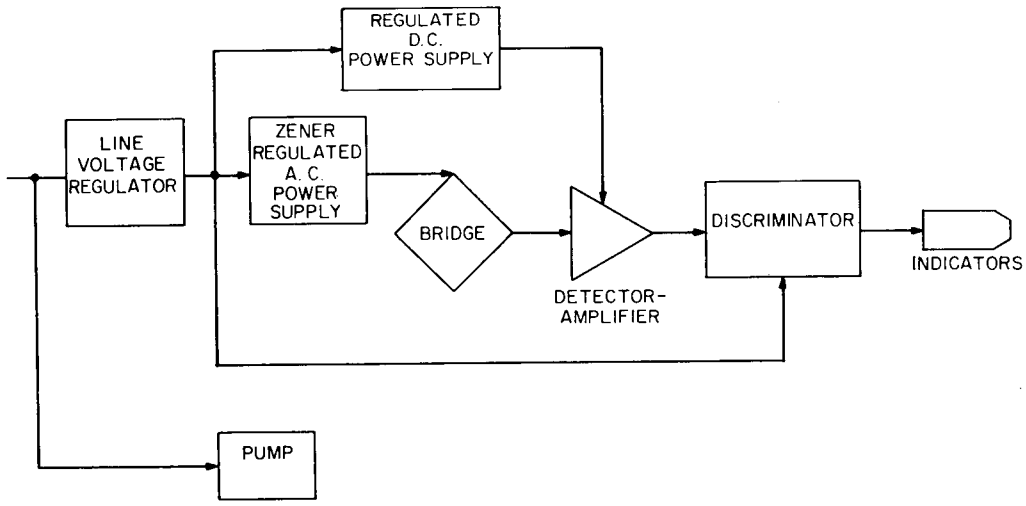

Fig. 44 - Basic block diagram of the model E-5753 leak detector

It was found experimentally that the combined action of the line voltage regulator and a simple Zener diode ac regulator provided satisfactory bridge-current stability. The ac excitation of the bridge also provides an ac bridge unbalance signal which can be amplified in a much more reliable manner than a dc unbalance signal of the same magnitude. A well-regulated ac power input is also necessary for the detector amplifier and for the discriminator. It was found that a small, commercially available line voltage regulator provided a constant source of ac power for all parts of the circuit (Fig. 45).

When both sides of the bridgeblock contain gas of the same thermal conductivity, the bridge can be balanced by means of a ten-turn potentiometer mounted on the cover of the detector case. When the bridge is out of balance in either direction, the bridge output signal goes to the amplifier, which is a five-stage RC-coupled transistorized amplifier. Printed-circuit and plug-in type construction facilitate circuit checking and amplifier replacement. Amplifier sensitivity can be controlled by means of a potentiometer (R10), also mounted on the detector case. Amplifier power is supplied from a bridge rectifier with RC filtering and Zener diode regulation.

The output from the amplifier is transformer-coupled to the discriminator circuit, which controls a split load to the indicators. In this circuit the phase of a reference ac voltage, in this case stepped-down line voltage, is compared with the phase of the amplified signal voltage from the unbalanced bridge. With the bridge unbalanced in one direction, the signal and reference voltages are in phase and the discriminator will fully energize one of the indicator lights. Bridge unbalance in the opposite direction provides a signal voltage which is 180 degrees out of phase with the reference voltage; in this case the discriminator fully energizes the other indicator light, at the same time deenergizing the in-phase indicator light. When the bridge is exactly balanced, both indicator lights glow dimly with equal intensity.

The sensitivity of model E-5753 to traces of Freon 12 was experimentally determined according to the procedure previously outlined (1), and it was found that with the gain of the amplifier set between 60 and 70 percent the indicator gave a clear signal when the concentration of Freon was 4-5 ppm. Sensitivity of this degree is considered satisfactory for service operations.

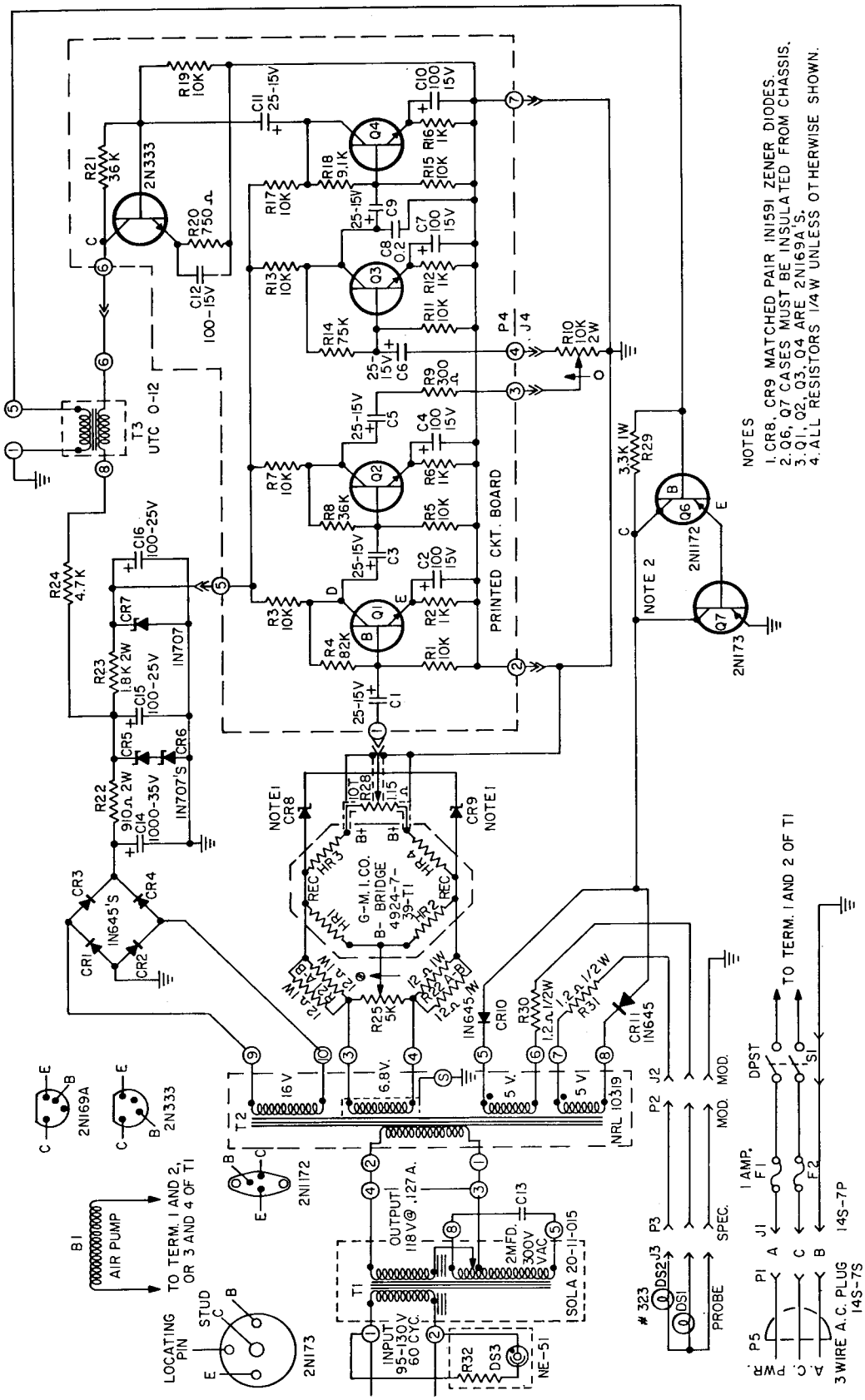

Fig. 45 - Schematic diagram of the model E-5753 leak detector

The first E-5753 instrument made by NRL was subjected to vigorous fleet evaluation, and numerous changes were incorporated in later models, both from the experience gained in making the first model and as a result of the fleet trials. Initial fleet studies have stressed the unit's versatility for measuring leaks in other gases as well as Freon, principally CO_2. An improved, more compact, model recently engineered by the Equipment Research Branch at NRL (4) is currently undergoing laboratory tests and may well supplant the E-5753 before the latter is accepted for the fleet.

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PART IV
ELIMINATION OF CONTAMINANTS

CHAPTER 16

THE CO/H_2 BURNER

F. S. Thomas

The Desomatic burner described previously (1), now the Mark II burner, continues in use aboard the nuclear submarines essentially unchanged. As a result of requests for more burner capacity, Desomatic has produced under a BuShips contract a 500-cfm burner which is essentially the Mark II unit enlarged, but still capable of being passed through the 25-in. hatch opening.

The results of prototype tests on the Mark II burner with materials which would adsorb fluoride inserted into the burner system at several locations have been reported (2). Further information on the relative advantages of the several materials and the physical and chemical tests necessary for selection of suitable calcium carbonate, which was the material recommended for this use, have also been reported (3).

Several instances have been reported in which the burners operating on shipboard have gradually lost air-flow rate to the extent of becoming essentially ineffective. This flow stoppage is due to formation of a layer of material on and in the cold side of the heat-exchanger matrix. Variable success has been attained by the several methods of cleaning which have been tried.

The active portion of this heat exchanger is a stack of about 120 fine-wire, open-mesh, stainless-steel screens. There are 16 of these stacks arranged as sectors of a wheel which upon rotation results in cold air and hot air passing alternately in opposite directions for three-second periods through the individual stacks, with the hot air being cooled by the screens and the cold air heated by the screens.

A heat-exchanger wheel which had become clogged in operation on the USS SKATE was sent to NRL for examination. The assembly and some of the matrix segments were disassembled. The clogging material is present only in the top (cold) side of about the first 25 percent of the screens. The amount of material accumulated in various portions of the wheel was found to be essentially uniform, indicating that it had probably appeared gradually while the wheel was rotating. Several segments were cleaned by washing with water, which removed about half of the material, and then with 2N (6 percent) HCl, which gave an apparently clean matrix. The clogged matrixes were found to have gained about 7 percent and the cleaned matrix to have lost about 7 percent as compared with the weight of a new matrix. In the cleaned matrix, severe attack of the wires to the point of virtual destruction was present in the areas containing the clogging material.

Examination of the clogging material showed that its metallic components were essentially those of 304 stainless steel and catalyst. Other components found were fluoride, chloride, ammonia, and some other nitrogen-containing material. Organic

solvents showed no evidence of the usual, extractable components contained in normal submarine areosol. This material, however, could have been subjected to essentially full burner temperature at times during the period of its use and hence would not be expected to be a typical submarine aerosol accumulation. Assuming the usual concentration of aerosol in the submarine atmosphere and complete collection of it on the matrix from the air passed through the burner, the calculated weight gained would account for only about 1/3 of the weight of clogging material actually found.

The results of the examination of the matrix and of the clogging material indicate that halide corrosion of the screens is taking place during the appearance of the clogging material. The presence of a small amount of halide in the output air from the catalyst bed despite the presence of fluoride-adsorbing material in the catalyst bed has been shown previously (2). Corrosion due to this halide would be expected in the cool part of the heat exchanger, since only there would adsorption of water and halide be sufficient for corrosion.

It appeared desirable to see if the corrosion and clogging would occur in the heat-exchanger material by reasonably duplicating in the laboratory the halide conditions to which the heat exchanger is exposed on the submarine. A small heat exchanger was prepared from screens taken from the hot side of a used matrix. This was exposed alternately, as in the burner, to a cold air stream and a hot air stream. The two air streams were equivalent and contained moisture, Freon 12, and ammonia. The hot stream was passed through a small bed of catalyst heated to burner temperature. After about 200 hours, corrosion of the screen wires and a corrosion product were obtained very similar to that in the shipboard unit. The corrosion was distributed throughout most of the matrix, apparently due to difficulty in making the experimental setup operate reproducibly.

In an approach to separation of the role in this clogging and corrosion of the several componenets in the air input to the shipboard burner, a similar but improved laboratory apparatus was assembled which again employed hot catalyst and the screens taken from the hot portion of a used matrix. This unit was operated for 580 hours on an air stream containing moisture and Freon 12 only. The type 304 stainless steel screen heat exchangers employed in this trial showed a slow and continuous increase in pressure drop and some corrosion. The location, amount, and character of the clogging were not comparable with that obtained in the original shipboard exchanger under study. This test indicated that the effect of Freon alone does not account for the shipboard phenomena, although it is undoubtedly still an important atmosphere constituent in this respect.

As indicated previously, the amount of clogging material present in the shipboard exchanger is at least several times greater than the probable amount of aerosol in the air passed through the exchanger. Despite this the possible effect of aerosol on the production of clogging and corrosion must be determined, since it is well known that a clean stainless steel is more corrosion resistant than the same material when dirty.

From information available in the literature there are several alloys having the necessary physical characteristics for this use which are reported to be much more halide-corrosion resistant. Better-controlled laboratory tests and shipboard tests of these materials should permit determination of whether the halide corrosion alone can produce clogging, the role of aerosol and the various atmosphere components in the clogging, and the selection of a more suitable matrix material if change appears desirable. It is planned to study the various alloy materials which appear promising and to continue tests on corrosion in laboratory-size heat exchangers.

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CHAPTER 17

WATER-THINNED PAINTS FOR SUBMARINE INTERIORS

D. E. Field

INTRODUCTION

The use of organic surface-protecting coatings inside Navy nuclear submarines is essential in protecting the hull and machinery from corrosion. An almost equally important use of paints is to increase the cleanliness and aesthetic appeal of the ship's interior, especially during prolonged undersea voyages. During and prior to these long-submergence cruises, it is mandatory that no painting be done with organic solvent-thinned paints because the toxic solvents from the paints are released into the ship's atmosphere long after application (1). Since extended drying periods are not often feasible before embarking, and since further touch-up painting is desirable during field days while submerged, the most attractive alternative appears to be the specification of paints that contribute no objectionable contaminants to the atmosphere.

At present, the only feasible paint that would not contribute appreciable amounts of organic materials to the atmosphere is that which is water-thinned. The initial NRL effort (2) was to measure and identify the small amounts of volatile components from three basic types of water-thinned latex paints. From the many formulations on the market, only one each of the paints employing styrene-butadiene, polyvinyl acetate, and acrylic ester latices was selected to be analyzed. These were selected carefully after consultation with the manufacturers of each type to obtain as near as possible the paint formulation.

Early in the NRL program, BuShips requested a recommendation for a specific water-thinned paint which might be used in nuclear submarines on an interim basis pending completion of the current research. Based on measurements at NRL and the Navy Toxicology Unit, a proprietary polyvinyl acetate paint was authorized (3) for use on submarine interiors during the period of 30 days prior to departure for sea and after the last dive on patrol. This paint proved unsatisfactory because the extreme flatness of the coating enhanced soiling, whereas soiling was either not apparent or could be readily removed from the semigloss alkyd paint ordinarily used. The NRL effort in this field was then directed toward research to establish specifications for a semigloss latex paint which could be applied to submarine interiors while submerged and also would permit all interested paint manufacturers to compete for this Navy business.

EXPERIMENTAL PROCEDURES

Although proprietary semigloss latex paints with gloss equal to the presently used alkyd paints could not be found, several formulations for such paints have appeared in the literature (4,5,6,7). Paints made from these formulations served as a starting point in seeking a product of adequate gloss, durability, drying rate, and freedom from atmosphere contamination.

Development of Semigloss Latex Paints

In the course of formulating a semigloss latex paint suitable for use on submarine interiors, some 70 formulations were made, tested, and compared with each other and with five commercial latex paints. Only a summary of the important points will be presented in this report.

Attention was focused on polyvinyl acetate (PVAc) and acrylic vehicles, since experience with styrene-butadiene latices for semigloss finishes appeared to be limited. Further, the components and required additive for such formulations are somewhat less toxic. Several formulations of acrylic and PVAc paints appeared to be equal in hardness, scrubbability, cleansability, soil "hold-out," gloss, and weathering. Attention was then focused on the PVAc paint, since its formulation was somewhat less intricate than the acrylic. However, it was noticed that after several months the PVAc paints showed a decrease in gloss that continued with age. Since the acrylic paints had excellent gloss retention, it was decided to concentrate efforts to improve their formulation. The final formula (Table 25) is a result of modification of a commercial formula (7) to increase hiding, gloss, leveling, and to incorporate the best thickener, preservative, antifoamer, and pigment. Although specifications will be written around this formulation, work will be continued intermittently to improve the paint in general and such specific points as leveling and thermal resistance.

The most important part of the new formulation is in the fine pigment grind; it must be above NS 7 to obtain the high gloss. Secondly, the ingredients in the letdown must be added slowly and with good agitation. Stirring is continued until no "fish-eyes" appear in a "brush-out."

Drying Rate of Latex Paint Films and Analysis of the Volatile Components

Evaporation rate of the volatile components from a paint were determined with the equipment shown in Fig. 46 by measuring the change in weight of painted aluminum-foil panels. Ten 2-mil panels measuring 10 by 50 cm were given two coats of paint on both sides. With more than 100 grams of paint on the panels and the ability to weigh accurately to the nearest milligram, weight losses could be measured to 1 part in 100,000.

In order to collect samples of the volatile components and measure weight losses from the instant the paint is applied, an aluminum pan was substituted for the panels. The paint sample was introduced through the hole in the top of the cabinet into the pan after air-flow and humidity adjustments had been made. Humidity of the air stream was regulated by mixing the proper quantities of dry and saturated air. Measurements were made from 0 to 70 percent relative humidity.

Analysis of the exhaust from the cabinet was made by collecting and analyzing condensate in the dry-ice traps shown or by using a copper coil immersed in a dry-ice-acetone bath, and also by bubbling the exhaust through an acidic sodium dichromate solution (8).

A typical example of experimental results follows. Although the drying rate is dependent on paint composition, air flow, relative humidity, temperature, and thickness of the film, in general these paints are very rapid drying. Three changes of air per hour at 5-percent R.H. and 77° F over a 10-mil paint film results in 95 percent of the volatile components from the film being lost in 24 hours. The remaining 5 percent comes off slowly and logarithmically. After 10 weeks the rate was 0.0025 percent per day, and after 19 weeks the rate was 0.0010 percent per day. These final losses were determined to be 100-percent organic material by measuring colorimetrically the oxidation of the chromate solution in the exhaust bubbler. Analysis of the condensate by gas chromatography showed only the presence of ethylene glycol and carbitol in condensate samples after a drying period of one month.

Table 25
NRL Semigloss Acrylic Emulsion Tint Base

Premix	Pounds	Gallons	Percentage by Weight
1. Rutile titanium dioxide, R-100	280.0	8.01	24.70
2. Amberlac 165 (21%)	50.0	5.62	4.41
3. Triton CF-10	2.0	0.23	0.18
4. Tamol 731 (25%)	8.0	0.87	0.71
5. Nopco 1407	2.0	0.26	0.18
6. Carbitol	50.0	5.85	4.41
7. G-11 hexachlorophene	1.0	0.05	0.09

Put above paste over roller mill and grind to 7-8, North Standards, Minimum.

Let Down			
8. Water	80.0	9.60	7.06
9. Rhoplex B-60-A (45%)	360.0	41.60	31.76
10. Rhoplex C-72 (45%)	260.0	29.25	22.94
11. WSR-301 (4%)	20.0	2.48	1.76
12. Polyvinylpyrrolidone (20%)	5.5	0.63	0.48
13. Bubble Breaker 746	5.0	0.14	0.44
14. Pine oil	5.0	0.38	0.44
15. Polyglycol P-1200	5.0	0.48	0.44
	1133.5	106.36	100.00

Adjust to pH 8-9 with 28% ammonium hydroxide.
Tint to BuShips Standard Color with Dispersed Pigment Colors.

Physical Constants			
Weight per gallon	10.66 lbs		
Total solids	51.55%		
Pigment volume content	20%		
Viscosity (approximate)	62 KU		
Gloss (60 deg)	58%		
pH	8		

1 Pigment; 2 Grinding vehicle; 3,4 surfactants; 6 coalescing agent; 7 preservative; 8 thinner; 9,10 vehicles; 11,12 thickeners; 13,14,5 anti-foams; 15 color developer and drying regulator.

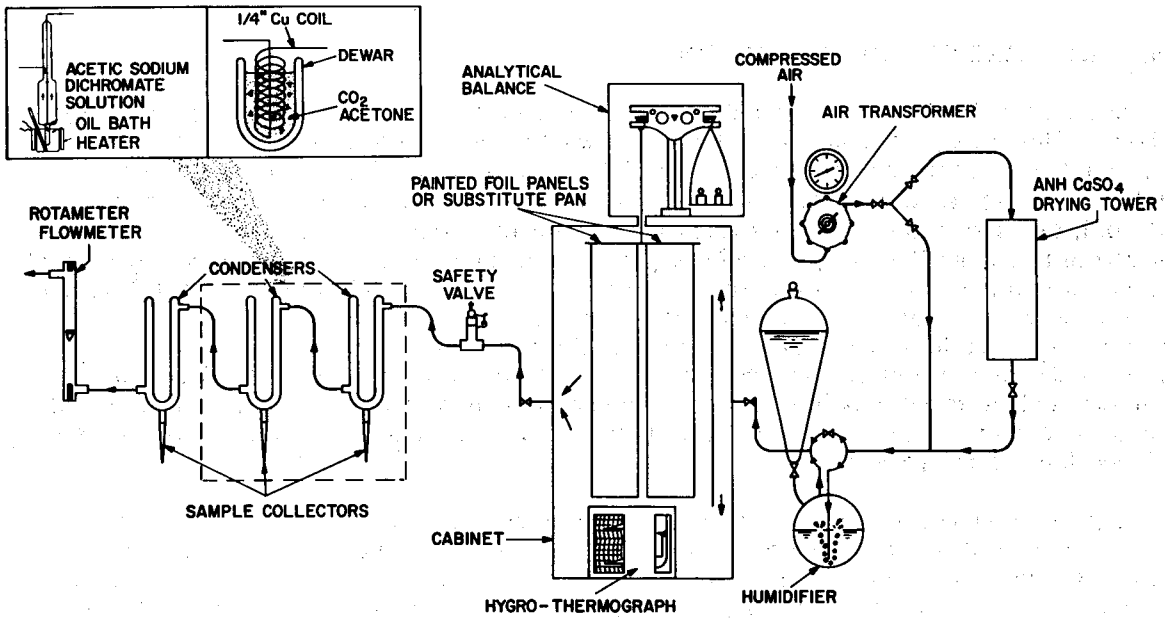

Fig. 46 - Apparatus for measuring evaporation rates from paints

Testing Water-Thinned Paints for Durability

Scrubbability and Cleansability Test – This test was made in accordance with Circular 767 of the Scientific Section, National Paint, Varnish and Lacquer Association, Inc., with a Gardner model 105 Straight Line Washability and Abrasion Machine. The latex paint to be tested was applied over the undercoat (fire-retardant alkyd enamel MIL-P-17970B) on a plate-glass panel with a 10-mil clearance film-caster. After a specified cure time the various soils were applied to the paint film. The panel was scrubbed on the tester with a hog-bristle brush treated with water and grit soap. After 100 oscillations of the brush, the panel was observed for the quantity of soil removal. The same panel was then scrubbed as before, using a 1-percent detergent solution until a break in the film's center indicated failure. After 96 hours of drying the NRL formulation showed excellent soil holdout and removal and further did not fail after 8000 scrubs.

Roof Weathering – Although the NRL formulation was not tested in this group of panels, similar formulations have been exposed at this laboratory for 13 months in racks south at an angle of 45 degrees. These latex paints applied over standard primers have not shown any failures during this period.

Salt Spray Chamber – In this severe test, a number of latex paints were applied over primed steel panels and exposed to salt spray at 100° F, 24 hours a day. Failure would be indicated by surface blistering and the appearance of rust. Failures observed were more indicative of the type primer used than the type latex topcoat. Latex paints in themselves do not appear to be a protective coating against salt spray. Included in this test was an experimental, commercial, water-dispersible zinc chromate primer which apparently withstood corrosion as well as the presently used alkyd, zinc chromate primer (JAN-P-735). The best paint-primer combinations, such as the NRL formulation plus the water-dispersible zinc chromate primer, withstood 550 hours exposure before any perceptible failure.

THE NRL PAINT ON THE USS TRITON

During the 26-day dive of the TRITON from Aug. 22 to Oct. 2, 1960, six gallons of NRL acrylic-latex paint and one gallon of the water-dispersible zinc chromate primer were applied to various areas of the ship. Figure 47 shows paint (pastel green) being applied to the forward passageway. The difference in color from the old paint is due to a deposit of dirty-yellow aerosols (mostly from tobacco smoke) on the bulkheads. It was noticed in this area that the paint lacked proper adhesion and could be removed by scratching with a coin. Emulsion paints are dispersions of resin particles in a 0.1 to 1.0 micron range of diameter; but so are the particles composing an aerosol film. Hence, the resin particles are unable to penetrate the aerosol film to establish adequate contact with the solid substrate on which the aerosol film rests. This filtering effect of the particles of a chalky surface to latex paints for exterior use on homes has been a major problem (9). It is necessary to wash such areas clean before applying latex paint. Figure 48 shows the finished job and the paint's gloss.

Figure 49 shows a painted test area on steam-pipe insulation. This test was used to evaluate the paint on warm and hot equipment, since the paint vehicle is thermoplastic. Surface temperatures on this area ranged from 95° to 300° F. The paint was not firm to a coin scratch above 200° F and was slightly soft but not tacky down to about 170° F. For good durability, it could not be recommended for application on surfaces above 160° F.

In the foreground of Fig. 49 is part of a handrail that was painted white. This was an excellent test area for soil and cleaning resistance, and the paint withstood both tests extremely well.

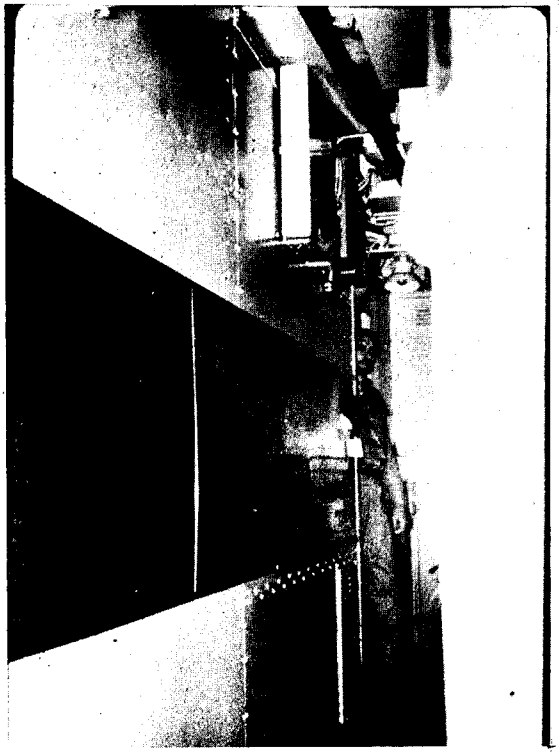

Fig. 47 - Applying latex paint to the forward passageway

Fig. 48 - The finished paint job

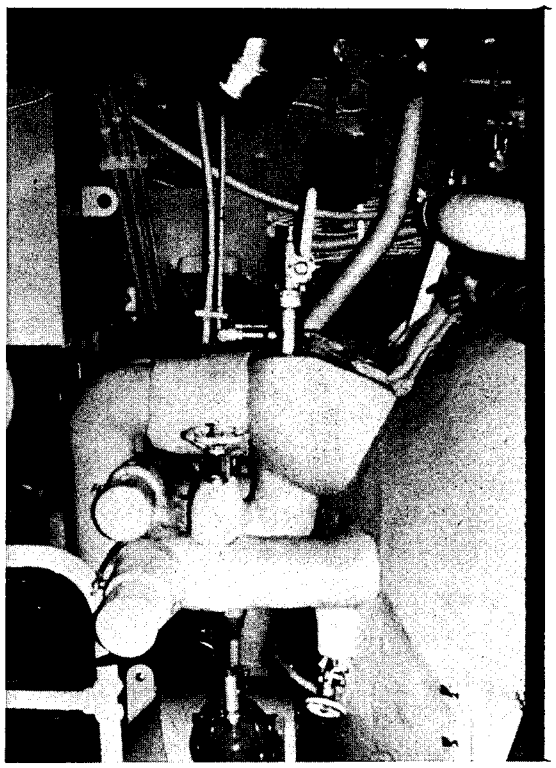

Fig. 49 - Latex paint on steam pipe insulation

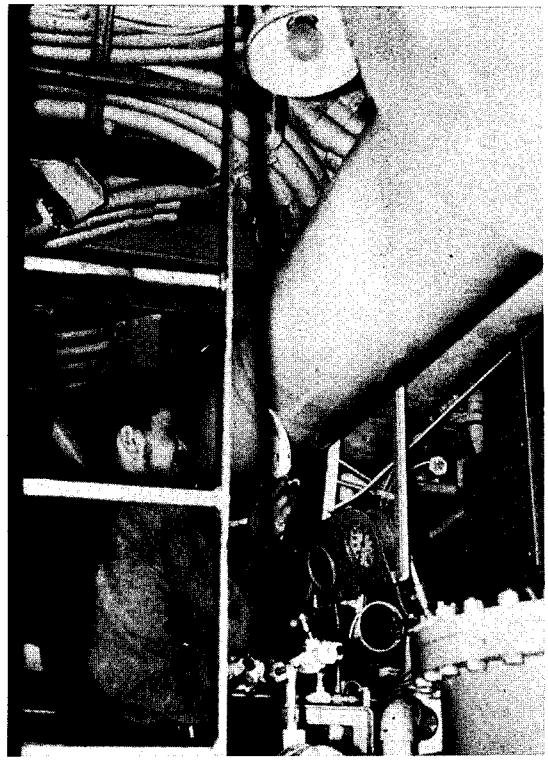

Fig. 50 - Latex paint on moving machinery

To brighten the area, paint was applied to the starboard screw shaft while it was turning (Fig. 50). Since the previous coating was black, two coats were necessary for adequate hiding.

Floor mats under the hatchways to an engine room were painted pastel green. Abrasion resistance was very satisfactory, considering that the paint was applied without any previous special cleaning of the surface. In fact, it was superior to the solvent-type synthetic rubber deck paint when applied under similar conditions. Figure 51 shows only slight wear on one of these mats after about one month of service. (Figures 47 through 51 are pictures taken by William E. McConnaughey, BuShips Code 649B, on the TRITON trip.)

SUMMARY

1. Since proprietary latex paints do not have a gloss equal to the alkyd paints used on submarine interiors, NRL has formulated a paint with an adequate gloss. The paint also does not consitute a health hazard to the crew when applied during sea operations. Of the volatile components, less than 2.5 percent are other than water and are not considered to be very toxic materials.

2. Several gallons of this paint were used during sea operations of the USS TRITON, SSR(N)586, and proved very successful from the standpoints of application, odor, hiding, adhesion, heat resistance, and abrasion resistance. As a top coat over a special commercial water-thinned zinc chromate primer, the paint has good corrosion-resistance properties. This paint was also given a number of durability tests in the laboratory which further proved it to be satisfactory.

Fig. 51 - Latex paint on floor mat

3. Final analysis of air samples taken on the USS TRITON during painting, as well as final analysis of volatiles from the films dried in the forced-air chamber, will be given in a future report.

4. Water-thinned paints are very fast drying. Under ordinary conditions they dry to touch in 20 minutes and may be scrubbed after 24 hours. The small percentage of high-boiling organic constituents in the paint film comes off slowly and logarithmically for months following its application.

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* * *

CHAPTER 18

AEROSOLS IN NUCLEAR SUBMARINES

W. L. Anderson

The effect of noxious gases and vapors in the submarine atmosphere has been studied previously, but until recently no attempt was made to monitor the particulate material (aerosols) suspended in the air. It should be acknowledged that there is little known concerning the physiological effect on man of long-term exposure to aerosols. However, the irritating properties of high concentrations of these materials makes them highly undesirable. It has definitely been established that aerosols have a deleterious effect on delicate instruments and seriously affect the reliability of electronic installations. This, together with the probable ability of certain aerosols to produce carcinoma in man, makes it imperative that the aerosol content in the submarine atmosphere be maintained at an acceptable level.

It has been reported previously (1) that aerosol concentrations in submerged submarines reach a steady state after approximately 100 hours of submergence. The average concentration during this steady-state condition averages 0.4 to 0.5 microgram per liter. This concentration is some five times greater than that found in rural areas away from industrial contamination. It has been established further that about 75 percent of the materials resulted from the cigarette smoking of the crew. It should be emphasized, however, that a major portion of the total aerosol content of the submarine is organic in nature, while only a very small part of the "country air" is of this composition. Thus, although only five times greater in concentration, the submarine aerosol should be considered many times more hazardous for long-time exposures.

The aerosol-sampling program described previously (1) has been continued. Through the cooperation of the medical officers on the operating ships, aerosols were collected on filter papers and then forwarded to NRL for analyses. Samples have been processed from eight different submarines on over sixty separate submergences lasting from several hours to over 1400 hours. Figure 52 shows the typical buildup in aerosol concentration as a function of time of submergence for several cruises of the ships. On every occasion, the overall pattern was the same as that reported previously, and only small differences in steady-state concentrations were observed. No definite correlation between ships and aerosol concentration was discovered. No ship showed either a consistently high or consistently low aerosol concentration. The measured concentration appears to be related to the crew activity and/or the type of patrol operation in which the ship is participating. It should be pointed out that all aerosol measurements to date have been accomplished on ships with the original electrostatic precipitator (ESP) capacity. The first of the ships to receive additional ESP through backfit during overhaul will soon rejoin the operating fleet. It is planned that aerosol measurements will be made on either the SEAWOLF or NAUTILUS at the earliest possible occasion, to ascertain the steady-state concentrations on ships with increased precipitator capacity. If the recommended 10,000 cfm of filtered air can be achieved, it is predicted that the desired steady-state concentration of about 0.1 microgram per liter can be maintained.

From individual bits of data and from interpretation of the chemical analyses of the collected materials, it was estimated that about 75 percent of the aerosol present in the submarine atmosphere originated from cigarette smoking. With the cooperation of the

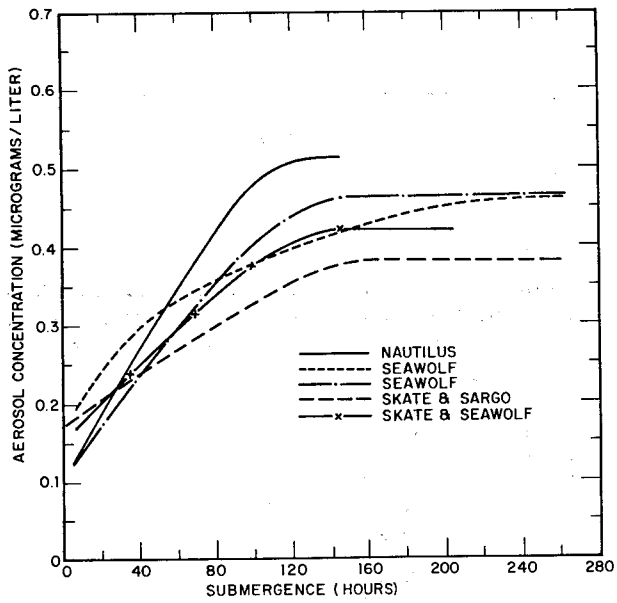

Fig. 52 - Aerosol buildup on typical cruises

entire crews of two of our nuclear submarines, it was possible to verify this estimation. On the round-the-world cruise of the TRITON, a 72-hour no-smoking period was obtained. An aerosol concentration-time plot covering this period is shown in Fig. 53. Unlimited smoking was permitted prior to this period, and the equilibrium concentrations were established at 0.3 to 0.4 microgram per liter. These values are in agreement with those obtained previously at different times and on different ships. After the beginning of the no-smoking period, the concentrations dropped to 0.11 microgram per liter, where it remained fairly constant for the first 36 hours of the test. The remaining 36 hours of the ban showed a slight increase in concentration. (It is believed that the effectiveness of the no-smoking ban may have decreased in the latter portion of the test.) After 72 hours, the smoking lamp was lit and the aerosol concentration increased rapidly to 0.65 microgram per liter. From this maximum value the concentration returned to the 0.3 to 0.4 equilibrium value and remained at this level for the duration of the submergence. It is interesting to note that aerosol concentrations in the absence of smoking are about 1/3 those found during smoking. This means that 65 to 70 percent of the aerosol in the submarine must result from cigarette smoking. This value is in good agreement with the 75-percent figure estimated previously from the chemical analyses.

A somewhat shorter submergence on the SKATE, during which a 24-hour no-smoking period was in effect, produced almost identical results. In this instance the ban was established at the beginning of the submergence, and the original decrease in concentration from the steady-state condition was not observed. The aerosol concentration-time plot covering this period is shown in Fig. 54. Aerosol concentrations during the smoking periods averaged 0.35 microgram per liter, and during nonsmoking 0.12 microgram per liter. The amount of aerosol present attributed to the cigarette smoke is about the same as that found on the TRITON–i.e., 65 to 70 percent.

Patrol activity appears to affect the aerosol-concentration levels in the ship's atmosphere. Of interest is an extensive patrol of the SKATE, during which the ship sustained several lengthy periods of continuous submergence. The aerosol concentration as a function of length of patrol for this trip is shown in Fig. 55. The characteristic buildup to the equilibrium concentration can be observed. Equally apparent is the regular fluctuation of the aerosol content; this has been shown to be related to the variations in personnel activity

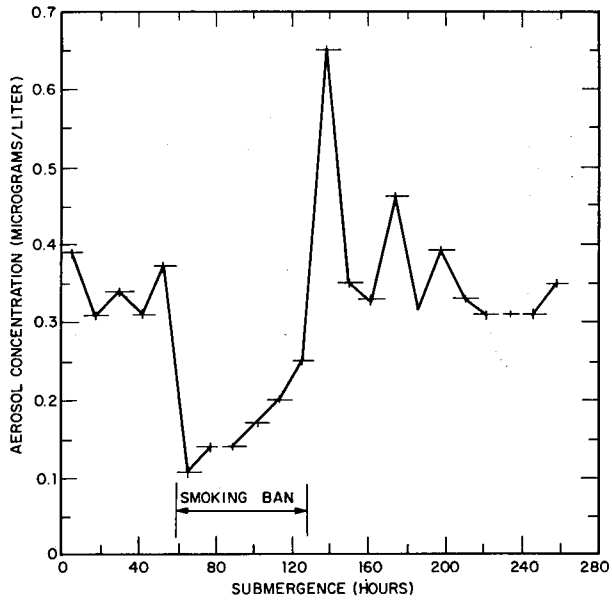

Fig. 53 - Effect of smoking ban on aerosol concentration (USS TRITON)

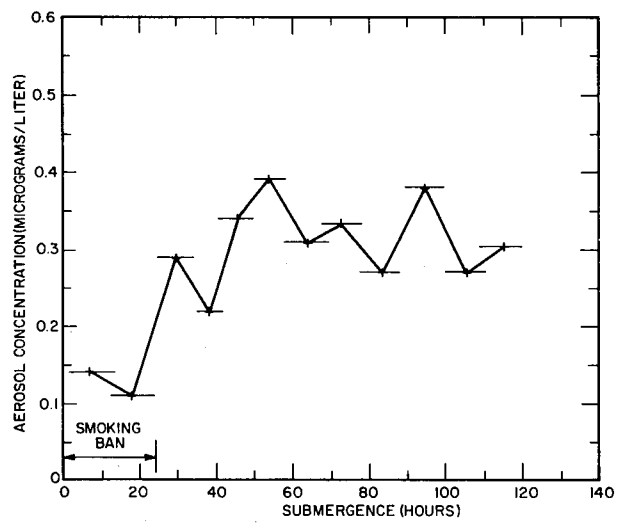

Fig. 54 - Effect of smoking ban on aerosol concentration (USS SKATE)

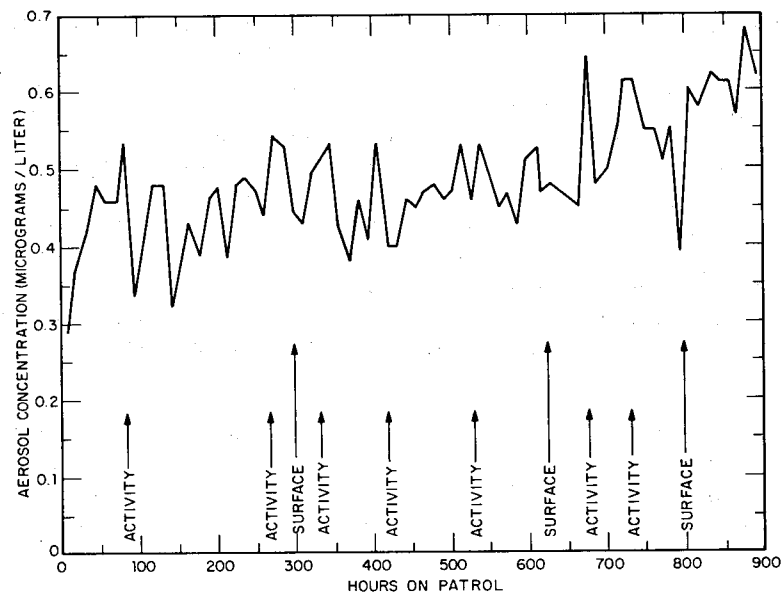

Fig. 55 - Aerosol concentration vs patrol activity (USS SKATE)

during the different periods of the day. Of special interest is the fact that sharp rises in aerosol concentration are directly related to the patrol activity of the ship. When operating under patrol quiet (ventilation half-speed) and patrol ultra-quiet (ventilation off), the aerosol concentration achieved the highest values. However, when the ventilation was resumed, the concentrations returned to the equilibrium levels; this phenomenon was also observed during the respiratory habitability cruise on the SEAWOLF (2).

Of equal interest is the fact that short periods of either surfacing or snorkelling have only a minor effect on the overall aerosol concentrations. It is apparent from Fig. 55 that these operations give only a brief reduction in concentration, and after the operation has been secured, the concentrations quickly return to the equilibrium values present at the start. It is belived that the gradual drift upwards near the end of the patrol was due to a loss in efficiency of the aerosol-removing devices. It is surmised that this situation may be analogous to the earlier occasion (3), when the atmosphere-control equipment experienced reduced efficiency as a result of massive aerosol accumulations.

Upper respiratory infections are often found among the crews of the operating ships. It is typical for a number of infections to appear the first portion of the cruise; however, as immunity to the specific organisms increases, the number of new infections gradually decreases. Contrary to this, certain of the operating nuclear ships have reported a continuance of the infections for the entire cruise. In an attempt to isolate and identify organisms that might be responsible, an aerosol sampling program to include bacteria was initiated. These samples were obtained by NRL personnel as a part of the BuShips Fleet Assist Project. The sampling techniques used previously were modified to include an all-glass impinger capable of removing a high percentage of airborne particles. By careful sterilization of the equipment and charging the impinger with the proper nutrients, any bacteria collected would be maintained in a viable condition. In this manner subsequent growth of the bacteria permitted the identification and determination of the levels of concentration of the various species present in the submarine air. These analyses were performed by the Naval Unit at Fort Detrick, Md.

The bacteria content of the submarine air as a function of time of submergence is given in Table 26. It can be seen that the bacteria content is identical in many respects to the pattern of the total aerosol determined previously. The concentration of bacteria in the air was constant at a relatively low value until submergence. Immediately following submergence the concentration of bacteria increased for a period of about 100 hours, at which point equilibrium was established. During this equilibrium the bacteria content could be directly related to personnel activity in much the same manner as the aerosol. Although many types of bacteria were identified, in no instance was it possible to identify cocci bacteria, normally associated with upper respiratory infections. When the ship was completely ventilated, the bacteria levels returned to the relatively low values determined at the start of the submergence. It is believed that these experiments should be considered preliminary, and further sampling and identification should be conducted at some future date.

The use of Cellulubes as hydraulic and/or lubricating fluids on nuclear submarines has introduced an additional possible contaminant to the submarine atmosphere. Calculations based on the vapor pressures of the basic ingredients show that the material, if present, will exist in the atmosphere as an aerosol.

Techniques were investigated for the detection and quantitative measurement of minute quantities of Cellulube 220 (C-220) suspended in air. Of all the methods studied, the molybdenum blue technique utilized by NMRI (4) has been standardized. This method is not considered adaptable for use on nuclear submarines by untrained personnel. Sampling equipment was furnished to a number of submarines using C-220 as a lubricant in their high-pressure air compressors, and the samples collected were analyzed ashore. From samples collected before the use of C-220 in the submarines, it is estimated that the organic phosphate background is of the order of 0.1 part per billion. This value is well below the permissible limit of 0.06 parts per million (1.0 microgram per liter) for C-220.

Based on the results of the C-220 Fleet sampling program obtained thus far (SKIPJACK, GEORGE WASHINGTON, SEADRAGON, BARBEL, SKATE, TRITON), certain observations can be made. No contamination has been detected in any compartment other than the machinery spaces containing the high-pressure compressors. However, C-220 levels as high as 0.5 to over 1.0 microgram per liter were found in the immediate vicinity of the compressors. Two specific areas of gross contamination were identified as the crankcase breather and the vent on the blowdown tank of the compressors. It was determined that it was relatively easy to contain and/or filter the air from these sources and thus minimize the contamination from these areas. Those ships that have modified their compressor according to recommendation show concentrations of about 0.01 microgram per liter of C-220 in the vicinity of the compressors. The ships that have not as yet been able to accomplish the modification continue to show compressor compartment concentrations as high as 1.0 microgram per liter.

The amount of C-220 carried over to the high-pressure lines and into the air banks was determined on typical compressors operating at the U.S. Navy Engineering Experiment Station. When the lubricators on the compressors were operated as specified by the manufacturers, the carryover to the system averaged about 30 grams of C-220 per hour. This aerosolized material was contained in very large droplets, and over 98 percent of the airborne material was collected in the first few feet of piping and the separator. In no instance was it possible to obtain C-220 from any of the storage flasks. Likewise, in no instance was it possible to detect C-220 in any air bled from the banks of the operating submarines.

Aerosols in nuclear-submarine atmospheres still pose a problem in the efficient operation of navigation, electronic, and other equipment. Because of the organic nature of the aerosol, its deleterious effect on the crew is unassessable. Measurement of the

Table 26
Bacteria Content of Submarine Atmosphere

Sample No.	Date Oct. 1959	Time	Hours of Submergence	Final Count	Predominant Organism	No. of Count Types	Types of Bacteria
1	21	2114	48	None	-	-	-
2	22	0655	58	None	-	-	-
3	22	0700	58	None	-	-	-
4	22	2058	72	None	-	-	-
5	22	2058	72	None	-	-	-
6	23	0648	82	$20x10^6$/ml	Diphtheroid	4	2 Gram ± 1 Gram -
7	23	2120	96	None	-	-	-
8	24	0700	106	$14x10^6$/ml	Gram ±	3	1 Gram ± 1 Gram - Yeast
9	24	1905	120	$3x10^8$/ml	Gram -	2	2 Gram -
10	25	0700	130	$16x10^3$/ml	Diphtheroid	2	2 Diphtheroid
11	25	2115	144	$3x10^8$/ml	Gram -	1	1 Gram -
12	26	0700	154	$81x10^3$/ml	Gram -	2	2 Gram -
13	26	1935	168	$12x10^5$/ml	Gram -	5	4 Gram - 1 Actinomycete
14	27	0645	178	$3x10^8$/ml	Gram -	4	3 Gram - 1 Diphtheroid
15	27	0645	178	$1x10^9$/ml	Gram -	3	2 Gram - 1 Diphtheroid
16	27	2150	192	$13x10^7$/ml	Diphtheroid	3	2 Diphtheroid 1 Gram -
17	27	2150	192	$10x10^7$/ml	Gram -	3	1 Diphtheroid 2 Gram -
18	28	0710	202	$5x10^7$/ml	Diphtheroid	2	1 Diphtheroid 1 Gram - (brown)
19	28	2200	216	$13x10^7$/ml	Gram -	2	1 Gram - 1 Gram - (brown)
20	28	2200	216	$7x10^9$/ml	Gram -	4	3 Gram - 1 Coccus
21	29	0650	226	$5x10^7$/ml	Gram -	2	1 Gram - 1 Gram - (brown)
22	29	2145	240	$3x10^7$/ml	Diphtheroid	2	1 Diphtheroid 1 Gram - (brown)
23	30	0700	250	$2x10^6$/ml	Gram -	3	2 Gram - 1 Diphtheroid
24	30	2200	264	$4x10^7$/ml	Gram -	3	3 Gram -
25	31	0700	274	$5x10^7$/ml	Gram -	5	1 Coccus 3 Gram - 1 Diphtheroid
26	31	0700	274	$6x10^7$/ml	Gram -	6	1 Coccus 4 Gram - 1 Diphtheroid
27	31	2200	Surface	146/ml	Gram -	3	1 Gram - 1 Coccus
28	31	2115	Surface	163/ml	Gram -	3	1 Gram - 1 Diplococci
29	31	2400	Surface	330/ml	Yeast	2	1 Diphtheroid Yeast
30	31	2400	Surface	395/ml	Yeast	3	2 Gram - 1 Diphtheroid

equilibrium concentrations during the past year show that the levels are about the same as those reported previously; conclusive proof has also been obtained to show that 75 percent of the aerosol in the submarine atmosphere results from cigarette smoking. The backfit program for electrostatic precipitators and installation of integrated units in new construction is currently under way. Once this program has progressed beyond the initial stages and control limits have been established for the aerosol concentration, additional measurements will be required before a reassessment of the aerosol problem can be made.

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CHAPTER 19

CATALYTIC COMBUSTION OF AEROSOLS

J. G. Christian and J. E. Johnson

INTRODUCTION

It has been shown in a laboratory study that Hopcalite is a good catalyst for the combustion of hydrocarbons of several structural types as well as for the combustion of a number of oxygenated organic compounds (1). With the exception of methane, all the compounds studied were converted essentially quantitatively to carbon dioxide and water at 300° to 400° C. Methane was oxidized to the extent of only 30 percent even at 400° C.

The presence of liquid substances of comparatively low vapor pressure aboard nuclear submarines provides the possibility that such substances may find their way into the submarine atmosphere in the form of aerosols. For example, such an aerosol could be produced by an accidental leak of lubricating oil at high pressure or onto a hot surface.

Since a portion of the ships' air is passed continuously through the CO/H_2 burner, it is desirable to know whether the Desomatic units would effectively catalyze the oxidation of such aerosols. This question has become of even greater moment with the adoption of aryl phosphate esters for use aboard nuclear submarines. These esters are used as hydraulic fluids and compressor lubricants and have an important advantage over some other substances, since they are remarkably resistant to ignition while effective as lubricants. However, these phosphorus-containing esters are known to produce toxic reactions upon ingestion by man, and it becomes important to learn whether they are detoxified by oxidation upon passage through the combustor.

In addition to the study of aerosols, some work was done to learn the efficiency of the catalyst when oxidation of certain compounds was attempted in the presence of vitiated air. This work was carried out to provide a factual basis for evaluation of opinions voiced aboard some operating nuclear submarines that when oxygen concentration is low the efficiency of the catalyst seems to diminish.

APPARATUS AND PROCEDURE

A laboratory unit was built to duplicate the conditions existing in shipboard Desomatic units insofar as flow rate, residence time, and temperature are concerned (1). The completeness of combustion was determined primarily by measurement of the CO_2 produced by means of a continuously recording infrared analyzer.

Aerosols were produced by means of an aerosol generator patterned after one described previously (2) and shown in Fig. 56. In this generator the aerosol is produced by a shearing action of the air on the fluid contained in can A. The aerosol then passes to can B, where the larger particles are separated out, and thence to the jet impactor C, where particles larger than a certain designated size are removed by impaction on the plate. The size range of particles removed is determined by the air flow, the slit width, and by the distance from the slit to the impactor plate. Since the production of an aerosol

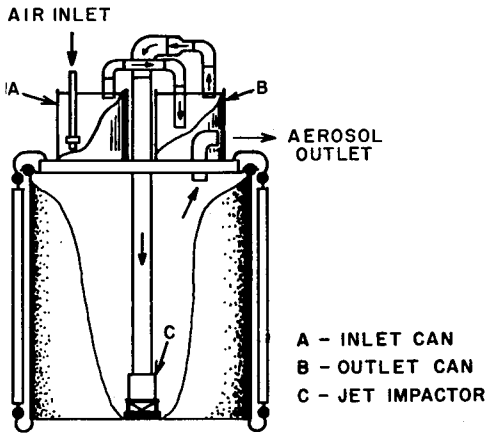

Fig. 56 - Aerosol generator

depends on a shearing action and hence on the viscosity of the fluid, it was necessary to control the temperature of the fluid. To this end, cans A and B were placed in a water bath whose temperature could be controlled to within ±0.2° C.

After exiting from the aerosol generator, the aerosol may be passed directly into the preheater, or a portion of the stream may be diverted for analysis (Fig. 57). The aerosol was analyzed gravimetrically by passing a known volume of the stream through a glass-fiber filter and weighing the material collected. The mass median diameter and number diameter of the aerosol were measured by a light-scattering method described by H. W. Knudson and L. White (3).

When the carbon content of the fluid under study is known either from the empirical formula for pure compounds or by analysis for mixtures such as lubricating oil, the theoretical CO_2 to be expected can be readily calculated.

The low-vapor-pressure fluids studied were dioctyl phthalate (DOP), Navy Symbol 2190 lubricating oil, and a commercial triaryl phosphate fluid (TAP). DOP was studied, since it is a chemical entity and thus of unambiguous composition, permitting ready calculation of the theoretical CO_2. Also, this compound is considered a standard in work

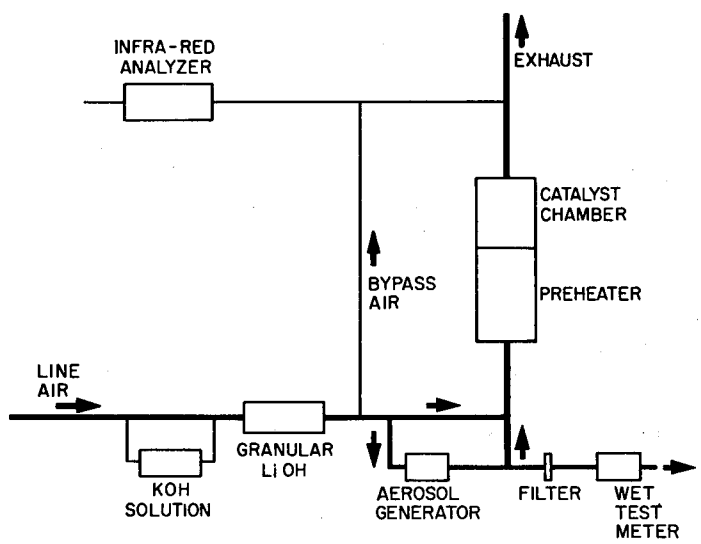

Fig. 57 - Diagram of catalytic combustion apparatus

with aerosols, since it produces good stable aerosols whose characteristics are well known. The 2190 lubricating oil was chosen for study since it is in wide use in the Navy. The TAP, a commercial mixture of cresylic acid phosphate esters, is an example of a class of fluids being used by the Navy as hydraulic fluids and compressor lubricants in nuclear submarines as well as elsewhere. The particular mixture of phosphate esters selected for a given task is determined by the viscosity characteristics desired.

The TAP fluid used in this study was analyzed for carbon and hydrogen content to permit calculation of the theoretical CO_2 to be expected upon complete oxidation. The phosphorus content of the TAP was also determined, since it was desired to learn the fate of this element upon passage of the TAP through the catalytic reactor. Phosphorus analyses were carried out both on the reactor effluent air and aqueous extracts of the catalyst which had been exposed to the TAP aerosol. All phosphorus analyses were carried out using a modification of a method described by Carpenter and his associates (4). The analyses were conducted by photometric measurement of the absorption of the phosphomolybdate blue complex formed from the solution being analyzed using light of 575 mμ in a Lumetron model 402-E photometer.

Low oxygen levels needed in the studies on vitiated air were achieved experimentally by passing tank nitrogen through a flow meter and mixing with the main air stream. Materials whose combustion had been previously studied under normal conditions, i.e., oxygen concentration about 21 percent, were used in these studies. For a further measure of the oxygen level of the gas mixtures used, part of the mixture was diverted through an oxygen analyzer (Pauling meter).

DISCUSSION

Various concentrations of aerosols of 2190 lubricating oil, DOP, and TAP were converted to the theoretical amount of carbon dioxide over Hopcalite catalyst at 300° C, as shown in Table 27. The total flow through the combustor was approximately 1 cfm in all cases. The desired concentrations of TAP aerosol were achieved by regulation of the temperature of the aerosol generator to the appropriate value. The relation between the aerosol generator temperature and the concentration of aerosol produced is given in Table 28. Table 29 shows dimensional properties of the aerosols produced as determined by the light-scattering method previously mentioned (3). These physical properties describe stable aerosols well suited for the work at hand, since they will not tend toward too ready impingement.

Table 27
Combustion of Aerosols Over
Hopcalite at 300°C

Substance Studied	Aerosol Concentration (μg/1)	Extent of Conversion to CO_2
2190 lube oil	100-150	Quantitative
DOP	40-100	Quantitative
TAP	20-60	Quantitative

Table 28
Concentration of TAP Aerosol Produced at Several Temperatures

Generator Temperature (°C)	Aerosol Concentration (μg/1)
30	20
35	25
40	43
45	60

Table 29
Particle Size of Aerosols at 25°C

Diameter (μ)	Dioctyl Phthalate	TAP
Mass median	1.3	1.7
Number	0.82	1.0

As part of a study of the combustion of phosphatic aerosols, one would wish to learn whether phosphorus or its compounds pass through the combustor under the same conditions of operation as normally used on shipboard. Such materials as the various oxides of phosphorus, for instance, would likely have a deleterious effect upon the crew and equipment. On the other hand, should the phosphorus be retained on the catalyst in some form, a possible consequence might be a loss in catalytic activity. In an attempt to resolve this question an extended run was conducted during which TAP aerosols were passed through the combustor at various concentrations until a total run time of 40 hours had been reached. During this extended series the average concentration of TAP was 30 μg/1, and the average air flow rate was 0.9 cfm. A total weight of 1.8 grams of TAP was passed into the catalyst bed which weighed 80 grams.

During part of the 40-hour run a portion of the furnace effluent air was bubbled through water. No phosphorus was detected in this water. At the end of the 40-hour period the Hopcalite catalyst was removed in layers. The bottom layer of the catalyst, i.e., that which first contacted the TAP aerosol, was coated with a thin layer of gray material, the next-to-bottom layer was less gray, and so on until the sixth or top-most layer appeared the same as unused Hopcalite. Portions of each of these six segments of the 5-in. catalyst bed were extracted with hot 10-percent NaOH and their phosphorus content measured by a determination of the absorption at 575 mμ of the phosphomolybdate blue complex formed upon reduction by hydrazine. These analyses are summarized in Table 30.

Photomicrographs of sections of granules of catalyst having the greatest phosphorus content made at about 50 diameters show that the surface coating is quite thin. X-ray diffraction studies have revealed very little of the exact chemical nature of the coating. The indication thus far is that the crystallites present are quite small, of the order of 100 A.

Table 30
Analysis of Catalyst Sections
Exposed to 1.8 grams TAP Aerosol
During 40 Hours Operation

Sample No.	Distance from Bottom of Bed (in.)	Phosphorus (percent)
1	0.0-0.5	0.37
2	0.5-1.0	0.25
3	1.0-2.0	0.20
4	2.0-3.0	0.21
5	3.0-3.8	0.19
6	3.8-5.0	0.08

The total phosphorus lodged on the catalyst was calculated from the phosphorus concentration and weight of each of the several layers. Such a calculation yielded a value of about 170 mg, which is in good agreement with the theoretical amount of 140 mg expected from the total TAP, 1.8 grams, passed into the catalyst. Despite the apparent quantitative retention of phosphatic material on the catalyst, no diminution of the catalytic activity was observed, although as yet no severely critical test has been applied.

At the beginning of the extended series of runs, carbon dioxide was obtained in greater than theoretical amounts. Toward the end of the series the amount of carbon dioxide was nearly at the theoretical value. Since Hopcalite is known to hold a certain amount of adsorbed carbon dioxide at a given temperature, it may be that the lodging of some form of phosphorus results in the displacement of carbon dioxide.

The oxidation of n-decane at 100-120 μg/l and paint thinner at 45-60 μg/l was carried out over Hopcalite at 300° C in vitiated air streams containing as little as 9-percent oxygen. Under these conditions combustion of these substances to CO_2 was complete, showing that the CO/H_2 burner can be expected to operate efficiently under conditions of reduced oxygen concentration.

FUTURE PLANS

Future work will include another extended run, during which a TAP aerosol will be passed into the catalyst for a total of 100 to 150 hours. Periodically during this extended run a critical test of the catalyst's activity will be applied. This test will be a comparison of the activity of the catalyst exposed to TAP aerosol with that of fresh catalyst for the oxidation of a material such as 1,2,4-trimethylbenzene, which is known to be oxidized incompletely over Hopcalite at a temperature of around 200° C. At the end of the extended run the catalyst will be removed from the combustor as before and analyzed for phosphorus content.

It is proposed that the combustion of certain hydrocarbons over Hopcalite be studied in the presence of carbon monoxide. Reports from operating submarines offer the opinion that in the presence of the amounts of CO encountered aboard, the efficiency of the catalyst for the oxidation of hydrocarbons is diminished.

SUMMARY

1. The use of a laboratory catalytic reactor which simulates CO/H_2 burners used on submarines was extended to study the combustion of aerosols.

2. Aerosols of dioctyl phthalate (DOP), Navy Symbol 2190 lubricating oil, and a commercial triaryl phosphate (TAP) were oxidized quantitatively at 300° C.

3. Phosphatic material from the oxidation of TAP is retained quantitatively on the surface of the Hopcalite catalyst with no apparent loss in catalytic activity.

4. Oxidation of hydrocarbons in air-N_2 streams containing as little as 9-percent oxygen proceeds quantitatively.

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CHAPTER 20

THERMAL DEGRADATION OF TRIARYL PHOSPHATES

J. E. Johnson and A. J. Chiantella

INTRODUCTION

Triaryl phosphates (TAP), commercially known as tricresyl phosphates, or phosphate esters, have come into considerable use in the Navy in recent years as hydraulic fluids and compressor lubricants. The important properties of TAP fluids which have made them particularly attractive to the Navy are their very low volatility and their high resistance to ignition and combustion. These features have led recently to several important applications of these fluids aboard nuclear submarines.

Although appealing to engineers because of their functional utility, the announcement of the imminent use of TAP hydraulic fluids aboard nuclear submarines was an immediate cause for concern among those responsible for and interested in the provision of good atmospheric habitability in these submarines. It had been known for some time that TAP compounds may have very serious neurotoxic effects if ingested by man (1). Because of this severe toxicity, the conditions of use and the possible exposure of personnel to these materials came under careful scrutiny.

Under ordinary conditions of use, the toxic hazard from the vapors of TAP is minimal. The vapor pressure of these materials at ambient temperatures is so low that the concentration of the saturated vapor is below the limit set by the Bureau of Medicine and Surgery for long-term continuous exposure. These exposure limits take into account the possiblity that the toxic effects are cumulative.

Although there is little danger from TAP in the form of vapor, the possibility of toxic aerosols had to be considered, since it was conceivable that they could be produced in the atmosphere in concentrations exceeding the limits of safety. Several aspects of this problem are under investigation by other Navy laboratories with regard to the actual toxicity of such aerosols and to the likelihood of their occurrence. In the meantime, it has been shown by studies at NRL* that aerosols of TAP are destroyed by Hopcalite-catalyzed combustion under the conditions of operation of the CO/H_2 burner on shipboard. This fact, as well as the shipboard removal by electrostatic precipitation, will tend to lessen the possiblity of the long-term exposure hazard to such aerosols.

In addition to the vapors and aerosols of TAP, another potential source of volatile materials should be considered in assessing the toxicity and fire hazards in using these fluids. This source is the decomposition of TAP when subjected to the stresses of use. For example, a certain amount of deterioration may result from exposure to higher temperatures during use as a compressor lubricant. It becomes important, therefore, to know the composition of the volatile products which might arise from such deterioration of these esters.

*See Chapter 19.

Consequently, it was decided to study the decomposition of TAP under selected conditions to learn more about the chemical reactions involved. During this study it is important to follow the appearance of decomposition products, both volatile and nonvolatile, because it is through these products that an insight into the pertinent reactions can be obtained.

Some preliminary data have been accumulated in this study on the degradation products of several commercial compressor lubricants which have been suggested for use in nuclear submarines. Based on these observations, a working hypothesis for the mechanism of the degradation of TAP is being evolved.

EXPERIMENTAL PROCEDURE

The TAP fluids were subjected to thermal oxidation in the following apparatus: a 500-ml round-bottomed flask fitted with a tube for bubbling air through the contents of the flask, and a water-cooled condenser to which was joined successively a trap at room temperature and a second trap cooled by a dry ice–acetone bath. In each of these experiments a 250-ml charge of the liquid was heated at 300°, 400°, or 500° F, for the selected time period, either 24 or 72 hours. Air of 8 to 10 percent RH was bubbled at 200 ml/min through the liquid during the heating period. The residues in the flask and the volatiles which were collected in the traps were then subjected to further examination.

EXPERIMENTAL RESULTS

Examination of Volatile Products

In all cases, during the heating period, the odor of phenolic vapors was strongly evident in the air stream even downstream of the dry-ice trap. Usually only a small amount of liquid condensate was collected in the traps, as indicated in Table 31.

Table 31
Thermal Exposure of Phosphate Ester Fluids

Run No.	Sample Fluid	Time (hr)	Temp. (°F)	Residue Appearance*	Distillate	
					Room-Temp. Trap	Dry Ice Trap
1	A	72	300	Light tan	Not taken	-
2	A	27	500	Black, much more viscous	Not taken	-
3	B	24	500	Black, very viscous	4 ml (red-brown)	3 ml†
4	A	24	400	Dark-Brown, slightly more viscous	4 ml (dark-red)	2 ml‡
5	A	24	500	Black, very viscous	5 ml (dark-red)	2 ml‡
6	A	72	300	Dark-tan	None	1 ml‡
7	B	72	300	Black	None	2 ml‡

*Unexposed fluids were lemon-yellow in color.
† Clear and colorless.
‡ Clear and colorless plus trace of red oily second phase.

It was found in all cases that much of the condensate which was collected was water. At 300° F, only a trace of an oily liquid phase was observed with the water which was condensed during a 72-hour run. At higher temperatures a few milliliters of a reddish to reddish-brown water-insoluble or oil phase was collected. In every case a positive test for phenols was obtained by procedures based on the decolorization of dilute potassium premanganate solution or on color changes of a ferric chloride solution.

The oily water-insoluble phase collected during the heating of a TAP fluid at 500° F for 24 hours was examined by gas chromatography using a column of diisodecyl phthalate on Chromosorb at 180° C. A relatively small number of peaks was found (Fig. 58). Some molecular assignments to these peaks were made based on the comparative retention volumes of known compounds. These were phenol (I), o-cresol (II), and a mixture of m- and p-cresols (III).

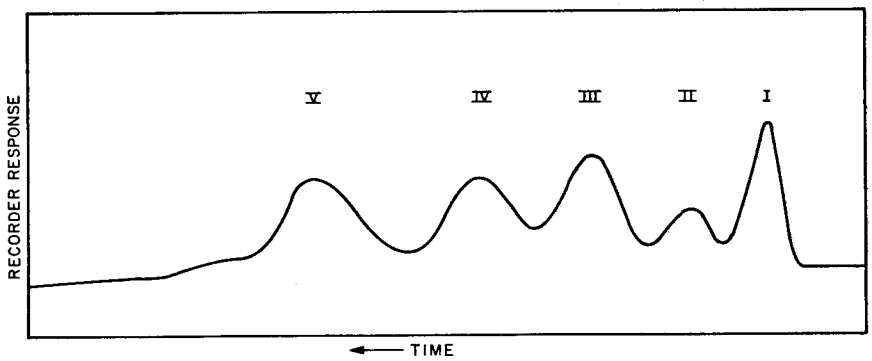

Fig. 58 - Gas chromatograph of oily distillate collected during treatment of a triaryl phosphate at 500°F for 24 hours

The proportion of the oil represented by the five peaks in the chromatogram was estimated to be 85 percent, based on the area under the peaks as measured with a planimeter. This suggests that phenols and alkyl-substituted phenols make up the major portion of the volatile materials from the thermal degradation of TAP in the presence of air.

Examination of Residues

The residues resulting from the thermal degradation of TAP were studied by various means for several reasons. First, it was of interest to determine whether the resistance to ignition and burning of the TAP fluids had been diminished during the chemical and physical degradation of the fluids. Second, the acidity of the residues was determined in view of the interest in the corrosive nature of these fluids after some use. In addition, the foregoing and various other characteristics and properties of the residues are of considerable value in visualizing the chemical reactions associated with the degradation processes involved.

The residues of the heated TAP fluids are described briefly in Table 31. These observations show that profound changes have occurred in the samples, particularly those exposed at 400° and 500° F.

Water extracts of the residues from the heat-treated TAP were prepared by thoroughly mixing 40 g of each residue with 20 ml of distilled water. Positive reactions were obtained for the presence of free phenols in the extracts in all cases; these were particularly strong in the samples exposed at 400° and 500° F. In addition, the water extracts were found to be

quite acidic, with pH values of 2.0 and stronger for extracts of residues which had resulted from 500° F exposures. Samples from the treatment at 300° F for 72 hours had pH values of 2.6 to 2.8.

Quantitative analyses of the aqueous extracts for hydrogen ion and phosphate ion are in good agreement with the proposition that the acidic material is an orthophosphoric acid. The possibility of the presence of monoaryl phosphates cannot be excluded by these data. An example of the titration data obtained from a water extract is given in Fig. 59. This shows a close similarity to the curve of a comparable aqueous solution of orthophosphoric acid.

The acidity of the residues themselves was investigated by means of a technique in which the samples were dissolved in benzene-isopropyl alcohol solvent and titrated with a standard solution of KOH in isopropyl alcohol (2). Titrations such as these in essentially nonaqueous solvents cannot usually be compared directly with aqueous systems in terms of pH, but such titrations yield results which are mutually comparable and from which hydrogen-ion concentrations may be calculated. A typical example of the titration curves obtained from a TAP residue is given in Fig. 60. It is quite evident that two different species of ionizable hydrogen atoms are being observed; one is the relatively easily ionized hydrogen characteristic of a strong acid; the second is characteristic of a weaker acid. The latter is available at a much lower concentration than the first.

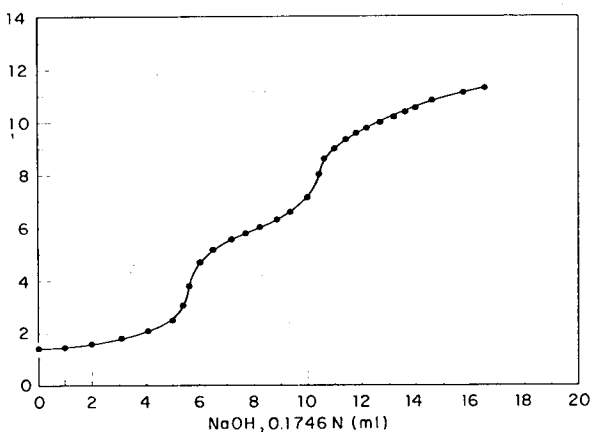

Fig. 59 - Titration curve for 10 ml of water extract of a triaryl phosphate after treatment at 500°F for 24 hours

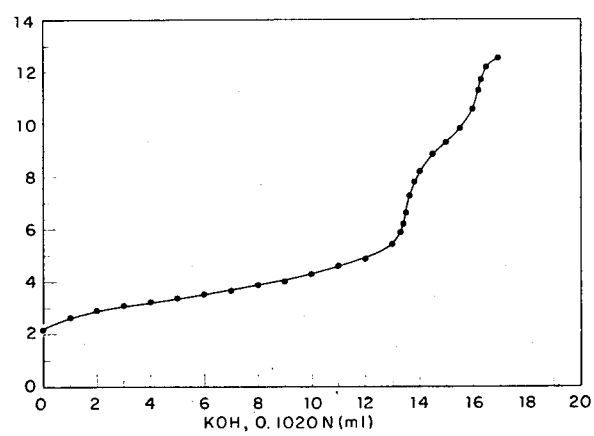

Fig. 60 - Titration curve of a triaryl phosphate after treatment at 500° F for 24 hours

Spontaneous ignition temperatures (SIT) of the residues and untreated fluids were determined by a procedure proposed by the Bureau of Mines (3) as a modification of ASTM procedure D286-30. The untreated fluids had spontaneous ignition temperatures of 1000° F or higher. Heating the fluids in an air stream at 300° F for 72 hours caused no change. Similar treatment at 500° F for 24 hours caused only slight lowering of the ignition temperature. Because of the preponderance of phenols in the volatile decomposition products and their presence in the residues, it was of interest to determine the SIT of such compounds. The SIT of o-cresol and p-cresol was found to be 925° F and 1045° F respectively.

DISCUSSION

The data and observations noted thus far during the study of the degradation of TAP can be woven into a reasonable explanation of the chemistry of the events that occur. The most evident process which takes place is apparently the hydrolysis of the esters. The first step would yield phenols and a diaryl phosphoric acid. Further hydrolysis of the latter would yield monoesters and finally orthophosphoric acid itself. The titrations of the type shown in Fig. 60 indicate the possibility that partially hydrolyzed esters do remain in the residue, as signified by the large difference in concentration in the two species of hydrogen ion. The presence of free phosphoric acid is indicated by symmetrical titration curves of water extracts as shown in Fig. 59.

Calculations based on titration of the residues indicate that as much as 50 percent of the TAP has been hydrolyzed within 24 hours at 500° F. Because relatively little phenolic distillate was collected, it seems likely that most of the phenolic hydrolysate has polymerized or reacted in other ways to remain in the tarry residue. Examination of residues by infrared spectroscopy also points to the presence of such polymers in the liquid residue.

Other preliminary information shows the addition of a considerable amount of oxygen to the system. The occurrence of extensive oxidation is confirmed by the gain in weight during the thermal exposure to air, by the considerable hydrolysis in the absence of any significant amount of added water, and by the collection of more water distillate than was supplied with the air.

All of the observations to date indicate very strongly that all three of the expected chemical degradation processes–oxidation, hydrolysis, and pyrolysis–are taking part in the attack on the TAP. This causes deterioration of the esters to yield acidic, tarry residues, and volatile mixtures of phenols and water.

A laboratory study has shown that o-cresol is very effectively consumed by catalytic combustion in a Hopcalite burner to yield the theoretical amount of carbon dioxide (4). Thus, the catalytic-combustion units can be expected to keep the concentration of phenols to a minimum should these materials enter the submarine atmosphere system from the air compressors.

This investigation is being extended in several directions to determine (a) the effect of water content of the air on TAP degradation, especially with regard to volatile products, (b) the volatile deterioration products which are not condensable with the trapping systems used thus far, (c) the effect of long-term exposure at lower temperatures, and (d) more detailed data on the phenolic distillates.

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RECOMMENDATIONS

It is noteworthy that many of the recommendations contained in NRL Report 5465 have been implemented. Practically all have received careful attention, and the only items on which progress has been slow have been the redesign of the CO_2 scrubber to incorporate a less toxic absorbent, and the ready availability of funds in the Bureau of Ships to expedite provising developments. That the latter has not been too serious is indicated by the success of the backfit program of electrostatic precipitators on the NAUTILUS and SEAWOLF, and the provision of "split-cell" electrolytic oxygen generators on two forthcoming submarines. That the former has not been too serious is indicated by the fact nobody has yet been poisoned by MEA, and current work to improve MEA and the scrubber itself may yet obviate a replacement absorbent.

Nevertheless, a restatement of the still-pressing problems (which incidentally means all of them to varying degrees) is advisable. The following recommendations are addressed primarily to the various bureaus and offices of the Navy Department.

1. The Bureau of Ships should sustain its aggressive course of developing and installing the most modern techniques and habitability equipment on existing and planned nuclear submarines. It is imperative that budgets for such action be adequate to take advantage of recent experiences and rapidly increasing knowledge of atmospheric control and purification.

2. The Bureau of Ships is urged to expedite installation of both backfit and new electrostatic precipitators on all nuclear submarines.

3. The Bureau of Ships should continue to support development programs on both the "split-cell" electrolytic oxygen generator and the sulfate-cycle method of generating oxygen and absorbing carbon dioxide.

4. The Bureau of Ships should continue the routine sampling program covering the "fingerprinting" of the atmosphere for each nuclear submarine until operational procedures are standardized sufficiently at safe atmospheric concentrations to require only occasional monitoring.

5. The Bureau of Ships should rapidly promulgate the necessary specifications for water-thinned paints so that oil-base paints can legitimately be forbidden.

6. The Bureau of Ships should expedite the redesign of the CO_2 scrubber to eliminate excessive loss and degradation of MEA solution.

7. The Special Projects Office should continue to act as the "Watchdog" on atmosphere habitability for the FBM submarine, pointing out areas in which it believes the bureaus or NRL should increase their efforts, assiting the bureaus and Navy laboratories with priorities or financial support as necessary, and urging full application in the FBM submarine of recommended techniques and practices.

8. Both the Special Projects Office and the Bureau of Medicine and Surgery should continue to support the Bureau of Ships in the latter's effort to monitor all of the materials appearing on nuclear submarines and to question all materials known or suspected to be toxic, to have high vapor pressures, or to form aerosols in the submarine atmosphere.

9. The Office of Naval Research should be available to assist the Bureau of Ships, the Special Projects Office, the Bureau of Medicine and Surgery, and NRL in establishing and defending the necessary financial support and priorities for the atmosphere habitability program as a whole, in keeping the Navy aware of the need for a sustained research effort in this field, and in providing support for basic or long-term research on various aspects of the problem.

10. The Chieft of Naval Operations is urged to continue the support for the Bureau of Ships of the Fleet Assist Project, under which arrangements are made for participation by research and development specialists in submarine cruises for analyses, obtaining essential data to guide research and development of new or improved equipment, and for observation of reported troubles involving specific equipment or excessive atmospheric contamination.

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

1. NRL will continue research on the promising sulfate-cycle system of oxygen generation and carbon dioxide absorption. In order to establish feasibility and freedom from hazards, a small-scale, cycling sodium sulfate plant has been constructed and will be operated continuously for at least a month before a final report is prepared.

2. NRL will continue its study of algae utilization in an air-purification process for long submergences.

3. Improvements in the utilization of MEA in the CO_2 scrubber will be studied until the toxicity and degradation problems diminish to a reasonable level.

4. Investigations will continue on: (a) methods of air sampling and analysis, (b) refinements on the Mark III and Mark IV Atmosphere Analyzer, (c) the completion of the fleet testing of the NRL leak detector, (d) the composition and concentration of submarine aerosols, (e) the measurement and control of ion concentrations in the air, (f) methods for improving the catalytic combustion properties of the CO/H_2 burner, and (g) problems relating to the establishment of specifications for water-thinned paints.

5. 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.

6. Equipment-development projects will be terminated on which sufficient data have been obtained to permit the Bureau of Ships either to incorporate the results immediately into the fleet or to arrange for a contractor to construct prototype equipment. In the latter case, if the need is urgent and the assignment within out capabilities, NRL may undertake the design, construction, and installation of the first few items.

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

8. NRL will continue to direct all of its research and developmental effort in this area toward an integrated air-purification system.

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