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Fourth Annual Progress Report

The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines

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"Second Annual Progress Report. The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," V.R. Piatt and J.C. White, editors, NRL Report 5814, Aug. 29, 1962

"Third Annual Progress Report. The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," H.W. Carhart and V.R. Piatt, editors, NRL Report 6053, Dec. 31, 1963

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FOREWORD

The nuclear submarine fleet continues as a major arm of the deterrent system of the United States. The potentialities have been brought about by revolutionary changes in propulsion, weaponry, navigation, and atmosphere purification, with the lack of any one of these accomplishments capable of effectively neutralizing the others.

NRL Report 5465, "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," April, 1960, summarized the development of an adequate atmospheric system for submarines and covered in some detail the research at NRL through calendar year 1959. In July, 1961, August, 1962, and December 1963, NRL Reports 5630, 5814, and 6053, respectively, were issued as subsequent annual progress reports.

The present report is essentially a summary of the progress made in submarine-atmosphere control by NRL during calendar year 1963, but it also covers some of the early work of 1964. Research and development studies by other Naval laboratories or contractors are not discussed in any detail.

The Bureau of Ships Fleet Assist Project was discontinued in 1962. Nevertheless NRL has continued to enjoy considerable cooperation from the submarine fleet in permitting research and experimentation aboard the nuclear submarines. Overall during the year, fleet experience indicated numerous problems in reduction of atmospheric contamination and in monitoring and control equipment. Moreover, there has yet been little operational evaluation of the new Mark IV Atmosphere Analyzer and Mark III CO/H_2 burner.

The total atmospheric-habitability research and development effort by NRL during 1963 continued its slow decrease as planned, with about 18 man-years of direct effort at a cost of approximately $420,000.

ABSTRACT

This annual progress report supplements NRL Reports 5465 of April 21, 1960, 5630 of July 14, 1961, 5814 of August 29, 1962, and 6053 of December 31, 1963, which provided a comprehensive review of the past and present research and development effort of the U.S. Naval Research Laboratory on the atmospheric habitability of submarines. Emphasis is at present being devoted almost exclusively to nuclear-powered submarines. Considerable progress has been made in the major efforts of developing: (a) improved methods of sampling and analysis of atmospheres, (b) additives to decrease the degradation of monoethanolamine (MEA) in the CO_2 scrubber, and (c) a system for maximum utilization of the carbon in the main ventilation filter. Other topics covered in the present report include the use of algae for oxygen production and carbon dioxide absorption, a study of water-thinned, fire-retardant paints, and a differentiation scheme for look-alike carbon and catalysts.

PROBLEM STATUS

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

AUTHORIZATION

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

NRL Problems C08-32 and C08-33
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Fourth Annual Progress Report

The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines

Summary of Progress

As in the previous year, during 1963 there were numerous improvements in atmosphere purification and control equipment aboard nuclear submarines. However, it remained obvious throughout the year that a considerable amount of research and development was still required for a peacetime Navy and that an even greater effort would be required to increase reliability and decrease maintenance for the extreme situations likely to occur in a wartime Navy.

The preceding reports in this series (1-4) provided historical, status, and progress accounts on submarine air-replenishment equipment and supporting research. The present is the fourth supplementary annual progress report; and although representing generally the events in 1963, it contains much of the early research during 1964.

As a result of the increasing importance of analytical techniques for monitoring the atmosphere of operating submarines, a summary of the overall NRL organization for this portion of the R and D program and also of the principal analytical techniques and equipment involved will be found in Chapter 1.

On the basis of a long-term survey of the analytical studies on hydrocarbons and organic contaminants, a number of recommendations have been made for the use of the main filter carbon (Chapter 2). The principal objective has been to insure that the carbon is replaced prior to the time it is saturated, thus avoiding subsequent desorption of troublesome contaminants back into the submarine atmosphere. The NRL Total Hydrocarbon Analyzer has been developed for direct shipboard determination of hydrocarbons, which should also provide the necessary information as to when the main filter carbon should be replaced before it reaches saturation.

Increasing amounts of chlorinated hydrocarbons were found during 1963 in the atmospheres of some of the newer FBM submarines (Chapter 2). These results appeared related to incidence of corrosion in the auxiliary machinery spaces, which is to be expected since these materials should yield appreciable amounts of hydrochloric acid on passage through the CO/H_2 burner.

The gas chromatograph built by the Beckman Instrument Company to NRL specifications performs reasonably well for the routine analysis of the predominant submarine gases: oxygen, nitrogen, hydrogen, carbon dioxide, Freon-11, Freon-12, and carbon monoxide (Chapter 3). However, certain improvements by the manufacturer are still required, particularly in the Karmen detector for carbon monoxide. A reliable source for helium of the proper quality must also be obtained. The Bureau of Ships has let a contract for the production of six seagoing atmosphere-analyzer chromatographs based largely on this modified process gas chromatograph.

Continued difficulty has been experienced with the operation of the Mark IV Atmosphere Analyzer and especially with numerous replacements required for the radiation detectors and sources (Chapter 4). NRL and Mare Island test results have demonstrated the need for improved quality control by the manufacturer and predicted that successful operation of these units could be attained with extra care in maintenance and with replacement of components which have deteriorated in operation or in storage.

Mass spectrometry is becoming increasingly useful in conjunction with gas chromatography in the laboratory analysis of atmosphere samples (Chapter 5). However, the techniques still require considerable effort and time. An expansion of the program is anticipated in calendar year 1965 through the procurement of a rapid-scanning mass spectrometer and an associated capillary-column gas chromatograph, with resultant more complete and more rapid analysis of submarine atmosphere samples.

The original Ringrose carbon dioxide meter (Chapter 6), a British development, has been used on British submarines since 1956. Despite several exceptional advantages, chiefly its portability and self-compensation for pressure fluctuations, it proved unsatisfactory in operation on U.S. nuclear submarines. NRL made several improvements in the Ringrose meter, on the basis of which the manufacturer has recently produced a more satisfactory instrument. Five units were procured late in 1964 by NRL for laboratory and fleet evaluation.

Because of the earlier contamination of submarine atmospheres by solvents from oil-base paints, NRL had developed by 1961 a semigloss latex touch-up paint designed for application during submergence. Although it was generally satisfactory, and in fact superior in many respects, its fire retardancy was regarded by the Bureau of Ships as being inadequate. NRL has since evaluated proprietary fire-retardant paints for interim use and in early 1964 began research to increase the fire-retardancy of its earlier paint without contributing to the atmosphere toxic components normally associated with such fire-retardancy (Chapter 7).

Shipboard atmospheric problems have occasionally arisen because of confusion in installing the carbon for the main ventilation filter, the Hopcalite catalyst for the CO/H_2 burner, and the catalyst for a hydrogen eliminator. NRL has developed a procedure for shipboard discrimination among these three similar-appearing materials which should obviate further mixups and hazards, if due caution is exercised by the ships (Chapter 8). To lessen further the potential disadvantages of continuing to operate the CO/H_2 burner at a high temperature (600°F), an NRL study aboard the SCULPIN demonstrated the apparent feasibility of dropping this temperature to 500°F; additional studies by NRL are required before this can be formally recommended.

An investigation of the stabilization of the monoethanolamine (MEA) used in the CO_2 scrubber has been completed and a final report issued (5). Additional shipboard evaluations are being conducted on the NRL-developed additive package of chelating agents containing the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA) and the monosodium salt of N,N-diethanol glycine (VFS) (Chapter 9). The latter ingredient used alone had been recommended several years ago by Mare Island Naval Shipyard. NRL has urged elimination of any copper-containing metals and any other source of copper contamination in the CO_2 scrubber and hence has recommended use of potable, battery-grade water in MEA makeup solutions; the Bureau of Ships appears convinced that the NRL additive package will be adequate and is relying upon the shipboard evaluations to confirm predictions.

The sulfate-cycle system for oxygen generation and carbon dioxide absorption (1-4) has received no further study at NRL other than an evaluation of the Ionics, Inc., electrolytic cell containing a cation-exchange membrane and a diaphragm (Chapter 10). The Ionics cell appears simpler than the NRL diaphragm cell, should be more rugged, and

should permit improved control of sodium hydroxide concentrations. Further study of problems which arose during intermittent operations would be desirable if the sulfate-cycle system is to be reconsidered. In the meantime, Ionics, Inc., is continuing to develop under Bureau of Ships contract a prototype ion exchange system for both oxygen generation and carbon dioxide absorption.

As reported previously (4), the NRL studies of algae for carbon dioxide absorption and oxygen generation have been completed insofar as the Polaris-supported feasibility study is concerned. The currently reported long-term studies (Chapter 11) relate culture conditions to the composition of cells and oxygen production to light intensity, illuminated area, and pressure.

Although either discussed in specific chapters of this report or mentioned as continuing problems, separate attention is devoted in this report to two problems for which NRL is not directly responsible, shipboard operation of the CO_2 scrubber and of the oxygen generator. Despite frequent attempts by the Bureau of Ships to improve both of these equipments through minor modification or design changes, maintenance and parts supply problems continue to plague the ships. Valving is a major item for both equipments, with the ships often having to manufacture new components as a result of spare parts shortages. In addition, the CO_2 scrubber continues to require repairs to the seawater pump; faulty design or faulty operation is frequently blowing MEA throughout the scrubber compartment, and the CO_2 concentrations in the FBM submarines remain excessive. NRL initiated a small-scale study early in 1964 to improve the efficiency of desorption in the scrubber and has stepped up a surveillance of the scrubber and generator operating problems. The Bureau of Ships also took the initiative in early 1964 of obtaining a new supplier for the oxygen generator in an effort to improve the logistics picture as well as to decrease the maintenance required. Improvements in all areas continue to be in demand.

Mutual exchange of information about the atmospheric habitability program and problems continues primarily through the quarterly progress reviews at NRL, to which are invited bureau, fleet, medical, Supervisor of Ship Building, and Naval shipyard personnel, and also through the NRL quarterly and annual progress reports. The Bureau of Ships held its second meeting of shipyard air-conditioning engineers late in 1964 as a delayed supplement to such a meeting in 1961; the planned conversion of this to an annual meeting is expected to prove valuable.

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Chapter 1
The Status of Submarine Atmosphere Sampling and Analysis

L. B. Lockhart, Jr., and V. R. Piatt

INTRODUCTION

With the emphasis of the early chapters in this report on analytical techniques and problems, it is appropriate to place these techniques in a proper perspective, along with the NRL organization involved in this aspect of the habitability program. The analytical techniques have been reported previously but not summarized (1-4). Analytical chemistry is but a minor part of the Chemistry Division research effort; it is the great depth and breadth of the overall research program which has made possible the diversion of enough highly qualified personnel to man the habitability program adequately.

The Chemistry Division at NRL has no single unit or group responsible for analyzing solids, liquids, or gases submitted to the Division for analysis. Each of the branches of the division is responsible for conducting research in its own field and for performing those chemical analyses for which it is especially qualified. The Analytical Chemistry Branch of the Metallurgy Division often has assisted the Chemistry Division with spectrographic analysis of solids for metallic elements.

DIVISION ANALYTICAL RESPONSIBILITIES

The Physical Chemistry Branch performs research in different forms of spectroscopy: mass, infrared, Raman, ultraviolet, nuclear magnetic resonance, and electron spin resonance. Of these, infrared and mass spectroscopy have played an important role in determining the identities and amounts of most of the compounds found to date in nuclear submarine atmospheres (Chapter 5). It was a logical extension, with far-reaching results, to add gas chromatography as an associated technique, primarily to separate the gaseous components for more positive identification by spectroscopic techniques (Chapter 5).

The Inorganic and Nuclear Chemistry Branch has an all-around background in inorganic analysis and has contributed to the submarine atmosphere program by developing the monoethanolamine (MEA) tubes, improving the Ringrose CO_2 detector (Chapter 6), and analyzing the oxygen produced by the chlorate candle and the corrosion products (from acids and from MEA).

The Protective Chemistry Branch is especially qualified in aerosol sampling and analysis and in measurements on atmospheric ions. It also conducts filtration research and supplies expert consultants on air filtration problems and electrostatic precipitator operations on submarines. Chemical analyses are performed, where necessary. This group has developed an ozone detector which is the best monitor of submarine ozone to date; and if the need could be demonstrated, the branch could assist in the production of these detectors for the submarine fleet.

The Electrochemistry Branch developed, manufactured, and installed the Mark I and Mark II Atmosphere Analyzers aboard the first four nuclear submarines. It has since monitored the commercial production of the Mark III and Mark IV Atmosphere Analyzers; but this has become more difficult with the increase in numbers of nuclear submarines, with the lack of quality control by the manufacturer, and with the different standards of maintenance among the nuclear submarine crews (Chapter 4). The branch originated the thermal conductivity leak detector which in a transistorized form is the basis of the present NRL Thermistor-Bridge Leak Detector, soon to become standard equipment on all nuclear submarines. The branch also performs special chemical analyses related to the operation of the CO/H_2 burner, the Mark III and Mark IV Atmosphere Analyzers, and submarine batteries.

The Surface Chemistry Branch performs research in colloid, surface, and lubrication chemistry; it was in connection with its antioxidant research that the branch became involved in MEA oxidation studies, currently nearing completion (Chapter 9). The branch's analytical responsibility has been limited to the MEA studies.

The Fuels Branch performs combustion research on fuels and hydrocarbons, the latter research leading a few years ago to the laboratory catalytic combustion studies with Hopcalite which have contributed so much to our detective work on the possible sources of deleterious products from the CO/H_2 burner. The branch has developed an extensive background and capability in gas chromatographic analysis and research and has applied that know-how in many important ways to further our knowledge of the composition of submarine atmospheres. It is developing gas chromatography as a monitor for the principal submarine gases (Chapter 3) and is applying gas chromatography to the development of the NRL Total Hydrocarbon Analyzer (Chapter 2). The branch monitored the carbon sampling program designed by NRL and administered initially at the Navy Applied Science Laboratory and later at the Marine Engineering Laboratory; it is also responsible for the main filter carbon sampling program involving ships of Squadron 14.

In addition to, or as part of the above specific areas of analytical research, NRL has invited personnel of nuclear submarines (usually the medical officer) to collect and submit specific samples of atmospheric gases or other materials for analysis, together with pertinent data as to date, time, location, and method of sampling, and unusual operations or conditions which might be useful in interpretation of the results. The samples are then turned over to the appropriate branch for analysis and evaluation; the results are reported to the submarine as soon as possible, although some of the tests require considerable time and may delay individual reports.

The above analytical program is augmented by occasional field trips by NRL scientists aboard nuclear submarines, in which new techniques for shipboard analysis are investigated, special analyses are made, and additional samples aboard nuclear submarines are collected for later laboratory analysis.

SAMPLING AND ANALYTICAL TECHNIQUES

As indicated in the previous section and the following chapters, the principal analytical techniques used in the NRL habitability program are infrared spectroscopy, mass spectroscopy, and gas chromatography. Of these, only infrared spectroscopy is employed routinely in shipboard analysis, comprising the CO_2, CO, and Freon channels in the Mark III and Mark IV Atmosphere Analyzers. However, these analyzers utilize nondispersive infrared optics, whereas laboratory research normally employs dispersive optics. For shipboard analysis, submarine air can be compressed directly into the infrared cell; but for laboratory analysis, the air sample must be compressed into cylinders, usually at about 100 psi, and carefully sealed for transmittal to the laboratory.

These pressurized air samples in the laboratory can also be analyzed by gas chromatography and mass spectrometry, depending on the concentrations and types of the contaminants involved.

Air can also be sampled by passage through activated carbon which retains the contaminant material. Such samples are obtained by shipboard personnel, either with the exposure of activated carbon, contained in flat, pancake-type cartridges in a sampler-blower apparatus, or from used main filter carbon that is being replaced. In the recently discontinued carbon sampling program, the contaminants were steam desorbed from the canister carbon, with the oil desorbate then being analyzed by gas chromatography to determine total hydrocarbons. Infrared spectroscopy and mass spectrometry have been used to analyze individual fractions obtained by gas chromatography, and gas chromatography itself has been useful for identification or further analysis of some of these fractions. The Fluorescent Indicator Adsorption (FIA) technique has been used to determine the hydrocarbon types in liquid samples. The organic material can also be recovered from the carbon by vacuum heating. The main filter carbon samples can be analyzed with similar techniques, utilizing steam or vacuum desorption with subsequent chromatographic separation and analysis by the above techniques.

Shipboard analysis by the crew largely consists of supplemental or backup use of the Dwyer CO_2 analyzer, the Model D2 Oxygen Analyzer, and various colorimetric gas detection devices such as Kitagawa, Draeger, MSA, the CO Monoxor, and the NRL NH_3-MEA tube. Except for the last two, the colorimetric tubes can be considered of qualitative value only and individually suspect because of uncertain effects of storage and the almost indeterminate effects of the numerous other contaminants in submarine atmospheres. An evaluation of most colorimetric tubes has been reported by the Taft Sanitary Engineering Center of the Public Health Service (5). An excellent evaluation of seven detection tube devices for carbon monoxide has been made by the Navy Toxicology Unit, with the Bacharach Monoxor appearing the best (6). There is some question, however, as to the behavior of the Monoxor in the presence of small amounts of hydrogen.

Other special analytical techniques have been developed at NRL for aldehydes (4), stibine (2), arsine (2), and ozone (2). The Marine Engineering Laboratory has been developing several special techniques for atmosphere analysis, but to date there has been no need for evaluation or comparison by NRL of their techniques.

From the toxicological standpoint, increased accuracy and sensitivity of analytical techniques are becoming more necessary as the threshold limit values (maximum acceptable concentrations) are decreased in a gradual trend. For example, the industrial threshold limit value for ammonia was decreased from 100 parts per million (ppm) to 50 in 1964, and that of methyl chloroform from 500 to 350; methane was assigned a tentative value of 1,000 ppm (7). Further concern should also possibly be felt about the components of tobacco smoke in the atmosphere, as evidenced by the Surgeon General's report of early 1964 (8). At least the obvious need continues for greater sensitivity in the detection of these trace components.

SUMMARY AND CONCLUSIONS

Despite the basic simplicity and adequacy of present shipboard analytical equipment, operating problems continue, largely the result of the following factors: lack of proper quality control or workmanship by manufacturers, lack either of proper training or of stimulation of interest in maintenance by operating personnel, and a natural shakedown period in modification of equipment to adjust to the operational and atmospheric extremes in the nuclear submarine environment. Research and development continue to be necessary to improve on present equipment, to develop new equipment, and to extend the sensitivity of instrumentation for trace contaminants.

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Chapter 2
Organic Contaminants - Sources, Sampling, and Analysis

J. E. Johnson

INTRODUCTION

Organic compounds in nuclear submarine atmospheres continue to warrant special attention for a number of reasons:

- Because of their possible toxicological effects
- To determine the decomposition reactions of organic compounds in the catalytic combustor in terms of toxic or corrosive products
- To determine any direct deleterious effects of such compounds on equipment or materials
- To determine the sources of these contaminants
- To determine the effectiveness of various means of removal.

Identification of individual compounds present in the atmosphere and estimation of their concentrations have been difficult because of the many hundreds of individual compounds and the very low concentrations of each compound usually found (1). In addition, it is invariably necessary to bring samples back to NRL for analysis, except for special field trips in which NRL scientific personnel have operated analytical instruments such as gas chromatographs on board the nuclear submarines during submergences. Further, it has been customary and necessary to concentrate the contaminants in some way on shipboard before shipment to the Laboratory. Adsorption of organic compounds from the atmosphere on activated carbon followed by desorption and analysis in the laboratory has been a very powerful tool (2-5). Until the recent acquisition of extremely sensitive detectors, it had rarely been possible to make analyses for organic compounds on compressed atmosphere samples taken on shipboard and returned to the Laboratory.

The total hydrocarbon analyzer mentioned in last year's annual progress report (5) has undergone further development (6). Using this instrument, a detailed study of organic contaminants was made by NRL chemists during a cruise aboard SCULPIN (7). The total hydrocarbon analyzer, a backflush gas chromatograph of a new design, was used very successfully for the determination on shipboard of methane, Freon-12, and "total hydrocarbons."

Chlorinated organic solvents have been increasingly important because of their contribution to corrosion problems and their high toxicity. Evidence has been obtained which indicates that these solvents are in more common usage than formerly.

HYDROCARBONS

Carbon Sampling and Analysis

Semiroutine sampling of atmospheric hydrocarbons on activated carbon by means of the NRL Carbon Sampler is continuing as a limited program, and the desorption-analysis work on these samples has continued at the U.S. Naval Marine Engineering Laboratory, Annapolis, Maryland. The data reported from this program (8) indicate that the contamination by hydrocarbon vapors generally continues to hold at fairly low values in the submarines of Squadron 14. Occasionally, the data show that fairly high concentrations of hydrocarbons were present. These highs were almost invariably shown to be due to release into the atmosphere of solvents during activities such as oil-base painting or "field days."

Main Filter Carbon Analysis and Efficacy

The main carbon filter is an important component of the atmosphere purification system in each nuclear submarine. Samples of used carbon taken from the main filters have been useful sources of information in regard to identification of organic contaminants, the amounts present, and their removal from the atmosphere. On the basis of data accumulated during this program, it is possible to make certain general statements. For example, as shown by typical data given in Table 1, the hydrocarbon content of main filter carbon in many instances remains less than 5 to 10% even during a full patrol of 60 days or longer. This is the case with FBM submarines which have been in service with the squadron for at least several months. Occasionally, the contamination level in a given ship has shown a decided increase after a period of low contamination (Samples 252A and 259). Such events have been shown to be caused by excessive use of solvents in some form. On the other hand, it has been found that for the early months of operation

Table 1
Main-Filter Carbon Data, Seasoned Submarines (Squadron 14)

Submarine	Sample No.	Log Date	Exposure (Days)	Grams Hydrocarbon per 100 g Carbon
WASHINGTON	239	11-62	23	1.9
WASHINGTON	240A	4-63	45	0.1
HOUSTON*	252A	7-63	65	4.4
EDISON*	253A	7-63	62	8.0
LEE	254A	7-63	–	0.8
LEE	255A	7-63	–	1.8
HENRY*	256A	7-63	90	8.0
LINCOLN	258A	8-63	31	3.2
MARSHALL	257A	8-63	78	22.6
HOUSTON	259	8-63	56	15.5

*Carbon known to be inserted before refit period.

Table 2
Main Filter Carbon Data, New Submarines

Submarine	Sample No.	Log Date	Exposure (Days)	Grams Hydrocarbon per 100 g Carbon
JEFFERSON	C-249	7-63	*	18.9
JEFFERSON	C-250	7-63	*	18.9
HAMILTON†	C-251	7-63	36	27.8
HAMILTON†	C-251A	7-63	36	28.3

*Carbon installed during construction and removed following second sea trial.
†Carbon installed a few days before sea trials began.

of a newly commissioned ship, the hydrocarbon loading runs very high (20 to 25%) if exposed for a period as short as 30 days (Table 2). This means that the carbon has become saturated because of a high level of contamination which is prevalent in the atmospheres of new submarines.

A number of recommendations concerning the use of the main filter carbon were made based on the information gained during this study. One important recommendation was that a program should be established for the routine sampling of main filter carbon in all FBM submarines. This sampling should include used carbon beginning with the first installation of main filter carbon. These samples will give a good picture of the overall atmospheric contamination and, in addition, will permit the analysis for specific organic compounds which are suspected of having caused the difficulty.

It was recommended that carbon should not be installed in the main filters of submarines under construction until just before closed-boat operation. The carbon seemed to serve no useful function during early installation and soon became saturated with organic vapors during the construction period. Such saturated carbon cannot remove additional contaminants (except by the process of replacing lower-boiling compounds by the higher) and may, in fact, contaminate the atmosphere with chlorinated solvents or other compounds which had been adsorbed earlier. It should be noted also that carbon saturated with hydrocarbons is a fire hazard because of its susceptibility to ignition by a spark or hot source like a welding torch used during construction or overhaul.

It was also recommended that fresh carbon be installed in the main filter immediately before a period of prolonged submergence such as an FBM patrol. Some FBM submarines have installed fresh carbon immediately after returning from a patrol, while other ships install the fresh carbon shortly before departing on patrol. The latter practice is preferable, because otherwise solvents used during upkeep will accumulate on the carbon and lower its efficiency as well as provide a potential source of contamination of the atmosphere.

This investigation has demonstrated that, when properly used, the main filter carbon bed is an effective means for removing organic contaminants from the atmospheres of nuclear submarines. It also has the capability of rather rapidly reducing the atmospheric contamination which would be occasioned by spillage of volatile materials. If an effort is made to limit the contamination by controlling the sources of organic vapors, the main filter beds in FBM submarines have adequate capacity for removing these contaminants during full patrols of 60 days or longer.

TOTAL HYDROCARBON CONTENT BY DIRECT ANALYSIS

For many years there has been a need for a method suitable for the direct shipboard determination of the total hydrocarbon content in nuclear submarine atmospheres. Because the total contamination is made up of hundreds of individual hydrocarbons, it is more suitable for some purposes to determine this contamination as a single composite entity. It is desirable to exclude methane and Freons from this total because these latter two compounds often individually amount to several hundred parts per million, more than the total of all other organic contaminants combined. The goal is, therefore, to find a method which can give the total hydrocarbon content in a few minutes on shipboard but eliminate the interference by methane and Freon.

The successful development of an instrument having such capabilities is described in a recent NRL report (6). It is based on a gas chromatographic method known as the "backflush" technique. A sample of submarine air (about 5 cc) is injected into the chromatograph, and the sample is swept along in the separation column by the stream of carrier gas until the peaks for methane and Freon-12 emerge. The column is then backflushed and the total hydrocarbon content, exclusive of methane and Freon-12, is measured as a single peak. The concentrations of methane and Freon-12 are obtained as a bonus during the separation step.

In this instrument the usual inert carrier gas is replaced by purified air. Since air is needed for burning the hydrogen in the flame ionization detector, this results in a two-gas system rather than the usual three-gas system. To further simplify the supply problem for shipboard use, a catalytic purifier has been developed which permits the use of the ship's compressed air supply for the chromatograph and hence eliminates the need for carrying pure air in cylinders.

The developmental models of the NRL Total Hydrocarbon Analyzer have been successfully used by NRL chemists during submerged cruises in SCULPIN (7) and SCAMP. Further refinements are being built into an analyzer now under construction, which will improve performance and simplify packaging.

CHLORINATED HYDROCARBONS AND THE CORROSION PROBLEM

During 1963, severe corrosion in the auxiliary machinery spaces of several FBM submarines was reported. Analyses of samples of air and of main filter carbon taken from several of these submarines were made at NRL to help determine the cause of the corrosion (9).

Considerable corrosion occurred in ALEXANDER HAMILTON, SSB(N)617, during the first few sea trials. Subsequently, samples of the ship's atmosphere were collected in stainless steel bottles at 60 psig during the fifth sea trial. Two samples were taken from the CO/H_2 burner inlet and two from the burner outlet. The Freon-12 concentration determined with the Mark IV Atmosphere Analyzer varied from 8 to 13 ppm, which is very low. The analyzer indicated no Freon-11, and none was detected in the bottled samples which were analyzed by gas chromatography at NRL. However, considerable quantities of two chlorinated hydrocarbons were found in the bottled samples: methyl chloroform (1,1,1-trichloroethane) and vinylidene chloride (1,1-dichloroethylene). The analytical results are given in Table 3. In both instances the data show that the methyl chloroform was almost completely destroyed by passage through the CO/H_2 burner. The concentrations of vinylidene chloride on the other hand were somewhat higher in the burner effluent, i.e., the concentration increased in passing through the burner.

These phenomena can be explained in terms of a previous NRL study of the decomposition of halogenated compounds over Hopcalite catalyst (10,11). It was shown in this

Table 3
Chlorinated Compounds in the Atmosphere of USS ALEXANDER HAMILTON

Sample No.	CO/H_2 Burner Location	Submergence (Hours)	Methyl Chloroform		Vinylidene Chloride	
			mg/m^3	ppm	mg/m^3	ppm
1	Inlet	15	33	6.1	6.5	1.6
2	Outlet	15	0.6	0.1	8.2	2.1
3	Inlet	20	12	2.2	2.0	0.5
4	Outlet	20	0.2	0.04	4.3	1.1

study that methyl chloroform is almost completely destroyed by Hopcalite at 600°F, with vinylidene chloride and acid vapors, probably HCl, as major decomposition products. This may be pictured as HCl splitting off from methyl chloroform, leaving vinylidene chloride as a residue which is stable enough to escape from the burner for the most part intact.

In Table 3 it is noted that the concentrations of both methyl chloroform and vinylidene chloride dropped as the submergence continued from 15 hours to 20 hours. This shows that vinylidene chloride, a decomposition product of methyl chloroform, is in turn eventually destroyed by the burner.

Two samples of main filter carbon from ALEXANDER HAMILTON were obtained during the same period and analyzed at NRL. The carbon had been in place for 36 days. Steam desorption of the two samples yielded 27.9 ml and 27.2 ml of hydrocarbon per 100 g of sample, respectively. This means that the activated carbon was saturated. Both methyl chloroform and vinylidene chloride were found in the desorbate, as had been the case for the bottled atmospheric samples.

THOMAS JEFFERSON, SSB(N)618, also experienced damaging corrosion during sea trials. The Freon levels were generally low for both Freon-12 and Freon-11 during this period. Two samples of main filter carbon were obtained from SSB(N)618. Analysis showed that this carbon contained about 15 wt-% of organic compounds, 0.5% being methyl chloroform as determined by gas chromatography and infrared analysis. Chromatographic examination of the air above this carbon in a closed container showed methyl chloroform and vinylidene chloride to be major contaminants.

It is apparent that recent practices have resulted in relatively high concentrations of methyl chloroform and other chlorinated solvents in the atmospheres of some new nuclear submarines. It has been indicated that these solvents are decomposed in the CO/H_2 burners, yielding corrosive acids. In one instance it was reported by Electric Boat Company personnel that acid concentrations as high as 8 ppm were detected in the burner effluent (9) of SSB(N)617.

SOURCES OF CHLORINATED HYDROCARBONS

Chlorinated hydrocarbons are often used to impart flammability resistance to solvent formulations, and in addition they are good solvents for polymeric materials. For example, Saunders (12) analyzed the solvent from a contact adhesive used for fastening heat-resistant plastic sheets to submarine bulkheads. This adhesive sample was

submitted to NRL by the Medical Officer of POLLACK, SSN603. The major volatile component of this mixture was found to be methyl chloroform; other components were sym-dichloroethane and minor amounts of p-dioxane and toluene.

In addition, it is known that relatively large amounts of commercial methyl chloroform have been used as a degreasing solvent to prepare surfaces for painting in submarine interiors.

Most of the usage of chlorinated solvents in nuclear submarines appears to occur during construction and in-port upkeep work. However, there are three potential reservoirs of these solvents which are more or less available during submerged operation as follows:

1. The location of primary application. For example, methyl chloroform that is present in the solvent system of a contact cement is likely to continue to evaporate from the point of application for a considerable time. Also, any free chlorinated solvents used during submergence will be direct contributors to atmospheric contamination.

2. The main filter carbon. Fresh activated carbon will adsorb large quantities of chlorinated solvents. However, the continued passage of air through the carbon bed and the adsorption of heavier molecular species will result in the gradual desorption of the methyl chloroform and other volatile chlorinated hydrocarbons. Consequently, any carbon in use in the ship's ventilation system during a time when significant amounts of chlorinated solvents have been used should be replaced to prevent these solvents from reappearing in the atmosphere.

3. Other organic coatings and materials. It was tentatively concluded after analyzing data accumulated in a study of atmospheric contaminants during a cruise aboard SCULPIN, SSN590, that painted surfaces, plastics, insulation, and other organic materials were acting as reservoirs for solvents (7). It was theorized that, during periods when volatile solvents were being used, these organic materials would dissolve and absorb the solvents, which would later be released over a long period of time. Work is planned with the aim of establishing the magnitude of this effect.

FUTURE WORK

New instances of severe local corrosion in nuclear submarines have been reported during the past year. Since it is strongly indicated that chlorinated hydrocarbons are major contributors to this corrosion, a greater effort will be devoted toward establishing the incidence and amounts of such compounds in the submarine atmospheres. In addition, it is planned to confirm beyond doubt the principal sources of chlorinated hydrocarbons which appear in submarine atmospheres.

It is also planned to devote more attention to the aqueous phase obtained during steam desorption of activated carbon, especially in regard to acidic components. There is some evidence that organic acids are present.

Further development of the Total Hydrocarbon Analyzer is being actively pursued in an effort to provide several units for further shipboard evaluation.

A report is in preparation which discusses in detail the occurrence of aromatic hydrocarbons in nuclear submarine atmospheres.

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Chapter 3
The Development of a Gas Chromatograph for Submarine Atmosphere Analysis

M. E. Umstead

INTRODUCTION

Gas chromatography is being explored as a means of monitoring the predominant gases and a few of the trace gases in the atmospheres of nuclear submarines. It is hoped that this technique will provide a more reliable and maintenance-free atmosphere analyzer (1,2) than the present instruments. The predominant gases to be measured are hydrogen, oxygen, nitrogen, and carbon dioxide; the trace gases, carbon monoxide, Freon-11, and Freon-12. Chromatography has been shown to be both precise and dependable for monitoring hydrogen, oxygen, nitrogen, carbon dioxide, and Freon-12, at least under laboratory conditions and by the manual measurement of peak heights (2). Carbon monoxide has been the most difficult gas to measure because of its low concentration and long retention time.

About three years ago, two gas chromatographs with thermal conductivity detectors were purchased from different manufacturers and were intended to demonstrate the feasibility of using gas chromatography for this application. One instrument was a commercial process or industrial chromatograph designed for carrying out routine analyses automatically in industry. Though its column system was designed specifically for the gases to be monitored in submarines, the performance of this instrument was not satisfactory. It did not separate some of the gases properly, was subject to excessive base-line drift, and did not have the needed sensitivity. Its return to the manufacturer for modification did not result in sufficient improvement, and no further work has been carried out with this instrument.

The second chromatograph (Fig. 1) was specially built for this application and used a high-sensitivity thermistor detector. It was semiautomatic in operation; sample injection and column switching were done automatically, peak attenuation manually. It performed well for those gases present in high concentrations: oxygen, hydrogen, nitrogen, and carbon dioxide. Satisfactory sensitivity and reproducibility were obtained for Freon-12 also, if the height of the peak was measured manually, since the peak was elevated from the base line by a tail on the air peak. This incomplete base-line return before appearance of a new peak makes the use of an automatic readout system difficult and could lead to serious errors in readings. Moreover, the sensitivity of this chromatograph to carbon monoxide was not adequate. It was concluded that the presently available thermal conductivity detectors were not capable of delivering the desired sensitivity for carbon monoxide while maintaining the required stability under shipboard conditions.

Because of the inadequate response of thermal conductivity detectors to the traces of carbon monoxide to be monitored, the use of an ionization detector developed by Karmen (3) was explored. This detector, one of the few ionization detectors that are highly sensitive to gases of high ionization potential such as carbon monoxide, functions by measuring changes in the electrical breakdown potential of helium as traces of other

Fig. 1 - Semiautomatic gas chromatograph designed for submarine atmosphere analysis

gases pass through the detector. The semiautomatic chromatograph was returned to its manufacturer, and the thermal conductivity detector was replaced by one of the Karmen type.

Studies at NRL confirmed that this detector was indeed highly sensitive to the fixed gases. Its sensitivity was more than adequate for carbon monoxide; a full-scale deflection on a one-millivolt recorder could be obtained readily for less than 100 ppm with no detectable noise. However, it was found to drift badly, and its response to the same sample injected at different times was not constant.

Although the use of this detector is desirable from the standpoint of sensitivity, it has two serious inherent disadvantages. First, it is not linear over a wide range. With an increasing concentration of a foreign gas in the detector, the breakdown voltage first decreases until it reaches a minimum and then increases with a different slope. A component in low concentration thus produces a simple negative peak, but one in moderate or high concentration yields a W-shaped curve. This minimum in the breakdown voltage versus concentration curve makes it difficult to measure all the components in a sample such as submarine air that contains a wide range of concentrations of components of interest, particularly if an automatic readout device is used.

The other disadvantage of the Karmen detector is the adverse effect of impurities in the carrier gas on the response of the detector. Its sensitivity decreases drastically with increasing concentrations of impurities in the helium. Even moderate contamination of the helium makes this detector useless for monitoring low levels of carbon monoxide. Column carryover from a partition column continuously contaminates the carrier gas, making it impossible to obtain high sensitivity to many gases if the partitioning liquid has any appreciable vapor pressure.

Because of these limitations of the Karmen detector, it was concluded that the most practical approach to an atmosphere analyzer chromatograph should be the use of the Karmen detector for carbon monoxide only, where its high sensitivity is required, and use of the well-proved thermal conductivity detector for the other components to be monitored.

PRESENT STATE OF DEVELOPMENT

Karmen Detector

One of the initial, more serious problems in using the Karmen detector in an atmosphere analyzer chromatograph was its tendency to drift excessively and its inconsistent response to the same sample injected at various times. It has been found that the elution of carbon dioxide from the molecular sieve column was the major cause of both the drift and the varying sensitivity. Although carbon dioxide is presumed to be irreversibly adsorbed by a molecular sieve column, actually it is eluted slowly by the carrier gas. Under the conditions used in this chromatograph, carbon dioxide began to emerge from the column after about 50 hours as a broad peak that was several hours in width. Thus the drift was actually a series of partially overlapping carbon dioxide peaks from samples simulating submarine air that were injected two days previously. The helium supplied to the detector was effectively contaminated with varying amounts of carbon dioxide that altered the response of the detector, causing nonreproducible results for the other gases.

The semiautomatic chromatograph was modified so that all the gases except carbon monoxide were measured by thermal conductivity. At the proper time in the analysis cycle, the carbon monoxide fraction was diverted to a second molecular sieve column followed by a Karmen detector. The second column had the added function of further separating the carbon monoxide from the tail of the nitrogen peak. In order to keep the molecular sieve columns free of carbon dioxide, a silica gel column was added to the precut column. The silica gel held back the carbon dioxide until the other components had entered the molecular sieve column; it was subsequently backflushed to clean it up prior to the next sample injection. Keeping the molecular sieve column free from carbon dioxide markedly improved the performance of the Karmen detector. During a run of over a month's duration in which a sample simulating submarine air was injected at half-hour intervals, the Karmen detector showed good reproducibility and less drift than the thermal conductivity detector, while producing a full-scale response for 50 ppm of carbon monoxide at a retention time of 20 minutes.

The problem of obtaining helium of adequate purity for use with the Karmen detector requires attention. This detector does not demand helium of exceptional purity; a good commercial grade is satisfactory. However, in a test of a considerable number of Navy cylinders of "Grade A" helium as received at NRL, about half were found not suitable for use. Analyses of a few samples of unsatisfactory helium have shown that they contained air as the major impurity, undoubtedly resulting from careless refilling of the cylinders. If the Karmen detector is to be used successfully as a shipboard carbon monoxide monitor, helium of adequate purity must be supplied to the fleet. A study is planned to determine the maximum level of impurities that can be tolerated with this detector.

Process Chromatograph with Karmen Detector

Concurrently with the work at the Laboratory on the Karmen detector, a second chromatograph (Fig. 2) was built by Beckman Instrument Company, the manufacturer of the semiautomatic chromatograph. In addition to the gases previously mentioned, the new instrument was to measure Freon-11. The basic instrument was a process gas chromatograph, manufactured commercially by that company, that contained a column

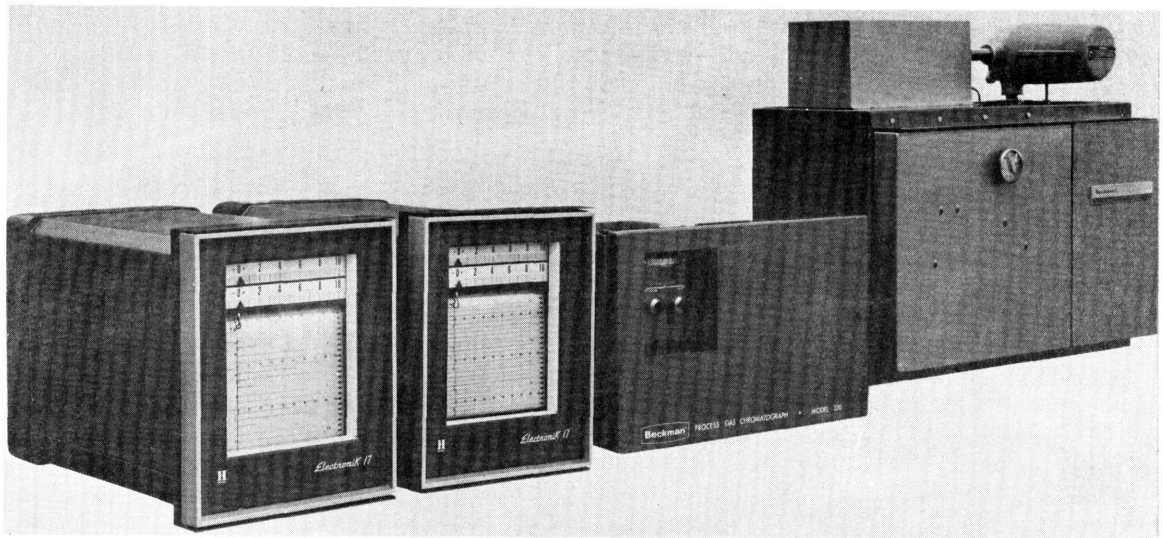

Fig. 2 - Process gas chromatograph with Karmen detector

system tailored for this application. It contained a Karmen detector for monitoring carbon monoxide and a hot filament thermal conductivity detector for the other gases. The chromatograph was completely automatic in operation; its readout consisted of bar graph presentation on two potentiometric recorders.

An evaluation of the chromatograph at the Laboratory showed its performance to be satisfactory except for carbon dioxide and carbon monoxide and, at best, marginal for Freon-12. The separation of carbon dioxide from the unresolved oxygen-nitrogen peak was not adequate and caused readings of almost 0.5% carbon dioxide for samples of pure nitrogen. The column system was modified prior to delivery of the instrument to further separate Freon-12 from the tails of the oxygen-nitrogen and carbon dioxide peaks; but it is felt that with the particular columns used, the timing between the peaks is too critical to be satisfactory for shipboard operation. Additional work on columns to separate these components cleanly is needed.

In an attempt to eliminate drift, the Karmen detector was coupled to the amplifier by means of a capacitor. In this way, the amplifier was to respond to the fast changes in detector voltage produced by a peak and not to slow changes due to drift. It was found, however, that certain tanks of helium caused the circuit to oscillate, making the detector useless. The helium that caused oscillation proved to be the helium that contained the least amount of impurities. With this circuit, the Karmen detector will not work either with moderately contaminated helium or with helium that is too pure. The instrument was returned to its manufacturer for the installation of a circuit similar to that used with the earlier detector.

Seagoing Atmosphere Analyzer Chromatographs

A contract has been awarded to Beckman Instrument Company by the Bureau of Ships for the production of six seagoing atmosphere analyzer chromatographs, based largely on the previously described process chromatograph. A Karmen detector is to be used for carbon monoxide and a thermal conductivity detector for the other gases. Test results conducted on a preproduction model are to be submitted in March 1965. Delivery of production units will commence on Aug. 1, 1965.

CONCLUSIONS AND FUTURE PLANS

The use of a Karmen detector for monitoring carbon monoxide and of a thermal conductivity detector for the other gases of interest looks very promising as the basis for an atmosphere analyzer chromatograph. The Karmen detector has been shown to yield excellent stability and reproducibility when it is used only where its high sensitivity is needed and a helium supply of adequate purity is employed. A study of the effect of other variables, such as pressure and flow rate, on the performance of this detector is planned.

Upon the return of the modified process chromatograph by the manufacturer, a long-term study of the reliability of the component parts is planned. Further work to develop columns that will separate carbon dioxide and Freon-12 cleanly from the oxygen-nitrogen peak and still not retain Freon-11 excessively long is needed. Also the long-term effects of certain trace contaminants in submarine air on the molecular sieve column and the Karmen detector must be determined.

Because of the adverse effect of helium contaminants on detector sensitivity, a supply of sufficiently pure helium must be made available to the fleet if the Karmen detector is to be used in an atmosphere analyzer chromatograph. A study is planned to determine the effect of varying quantities of contaminants on detector response and to establish the limits of helium contamination that can be tolerated.

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Chapter 4
The Mark IV Atmosphere Analyzer

F. S. Thomas

INTRODUCTION

The Mark IV Atmosphere Analyzer is a limited-objective service apparatus intended to provide a determination of the concentration in nuclear submarine atmospheres of the principal components which require surveillance and control. The development of the several models of this series of analyzers leading up to the Mark IV and the early NRL experience with the Mark IV have been previously reported (1-4).

MARE ISLAND NAVAL SHIPYARD TESTS

The findings of the preservice operation of five Mark IV units at the Mare Island Naval Shipyard have been previously reported (4). Additional units were subsequently run at Mare Island for various periods of time in a continuation of this test, with a total of 23 units accumulating about 35,000 hours of operation, or an average of about 1500 hours each. The objective was to accumulate longer instrument experience, so that the manufacturer could institute any program of corrective measures necessary to attain satisfactory shipboard operation, which was not assured with the short-time acceptance tests previously passed. All results, information, and replaced parts were made available to the manufacturer for his study and diagnosis. For the most part, component replacements or repairs were one or two of a kind and, although undesirable, were not considered serious because of their nonrecurrent nature.

Radiation Sources and Detectors

The most common cause of equipment failure involved the radiation detectors and sources. About one-fourth of the 92 detectors required replacement during the test period; the remaining detectors were still giving satisfactory service after 600 to 4000 hours of operation. Detector replacement was generally caused by the development of crossover sensitivity, i.e., the CO units became sensitive to water and the Freon units became sensitive to CO_2. Another cause of failure was an excessive zero drift leading to loss of sensitivity, apparently resulting from gas leakage. The application of optical filters, which essentially completely remove these crossover sensitivities, was achieved by the manufacturer in 1963. More recent production of radiation sources for Freon and radiation detectors for CO makes use of these filters. The presence of the filter can be recognized by the metallic luster of the window. About 30% of the original radiation sources, predominantly the Freon units, required replacement during this operation. In these units the phenomenon observed was an increase in resistance with ultimate burnout of the filaments in the source. Again gas leakage was the apparent basic cause.

It is significant that most of the radiation sources and detectors were still operating satisfactorily after the entire test. Of those that failed, some drifted slowly out of the usable range, whereas other units failed quickly despite having just passed acceptance tests. Two different types of failures appear to be involved: a slow drift of characteristics and a sudden and catastrophic failure. During and after the preparation of these units, they were subjected to extensive aging and testing procedures such as heat cycling, vacuum leak testing, etc., in the attempt to eliminate all units which would prematurely fail. It would appear that these test procedures and the acceptance tests did not apply some particular service condition which will cause trouble later, or else that a presently acceptable test value, such as the maximum zero drift, is indicative of future failure and needs to be drastically reduced before a unit is accepted.

During and following the Mare Island test, the manufacturer carried on an in-house program of detector and source improvement. This program was primarily aimed at improving sealing and leak testing procedures as well as the consistency of performance under acceptance testing. The large area in which progress can already be seen is in the reduction of crossover sensitivities by application of the optical filters; improvement in the ability to attain the hermetic seals is also reported.

As of the end of 1963 the follow-on Mark IV testing at Mare Island had shown that the detectors supplied with the newer units, above serial number 15, were not of better quality than those previously supplied. The radiation sources, especially those for Freon, in these same newer units appeared to be showing additional untimely failures.

Oxygen Indicators

Inspection of the data accumulated in the Mare Island test has shown that when all the usual corrections were applied, the oxygen analysis channel of some units gave indicated values in excess of the oxygen content of the sample gas. The cause of this was found to be a decrease in the operating temperature of the magnetic element which had occurred after the indication scale had been prepared. In the three units available for trial, this temperature had dropped by about 12°F. Readjustment of the temperature back up to 140°F would appear to be the most desirable corrective action. However, with the present thermostat this has been shown to initiate a new period of temperature drift downward. The test results indicate that the thermostats now installed have reached an essentially stable operating temperature, so that a suitable correction chart could be prepared based on a careful calibration at the present operating temperature. Such a chart should remain applicable for a relatively long period of use with infrequent checks. A less accurate but more easily applied correction would be to set the oxygen indication to be correct at the air point (156 mm, normally) and then to neglect the small incremental error arising as the indication diverges from that value.

Pump Leakage

Some of the test operations of these units have shown that the sample pumps used on the early units (those having the Electric Indicator Company Motor) have a leakage of ambient air from around the pump into the sample when sampling from a long or restricted sample line. The pump modification supplied for these units reduces this leakage so that for normal usage the results obtained should not be significantly affected. This leakage makes the units unsuitable for determination of sample line tightness. The advisability of further remedial measures remains to be determined.

CONCLUSIONS

On the basis of the Mare Island test results it can be predicted that when these units are put into service after the usual prolonged storage period, some of the radiation sources and detectors will not operate satisfactorily. A considerable proportion of these, both installed and spares, will probably need to be returned for replacement as a result of the development of crossover sensitivity, since they are of early manufacture without the optical filter. Possibly some will also need replacement because of the effects of gradual changes occurring during the long idle period. Unfortunately, determination of the characteristics of these units requires actual operation in the units.

It is obvious that the critical areas in these units still needing improvement, especially as regards performance consistency, are the detectors and sources. The manufacturer is carrying on improvement studies on these as an in-house development program; but the effectiveness, as applied to Mark IV, is essentially unassessable without actual trials such as in the Mare Island testing.

FUTURE PLANS

The manufacturer is continuing studies of ways to improve both quality control and design of the critical analyzer components. NRL will continue to monitor the operational problems with BUSHIPS and will use the serial 4 unit at NRL as a basis for checking the manufacturer's modifications.

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Chapter 5
Improved Methods for the Detailed Analysis of Trace Contaminants in Submarine Atmospheres

R. A. Saunders and F. E. Saalfeld

INTRODUCTION

As indicated earlier in this report, the mixture of organic constituents in the atmosphere of a nuclear submarine is exceedingly complex. This complexity has discouraged attempts at anything but a token identification of the multiplicity of components of the mixture; hence, potentially highly toxic compounds could be present in a submarine atmosphere but escape detection by existing physical methods of analysis.

Recent developments at NRL of methods for analysis of the simpler range of contaminants in spacecraft atmospheres (1) are also applicable to the analysis of compounds eluted from activated carbon samplers exposed on submarines. Although such an analysis has been attempted in the past with the identification of over 50 specific compounds (2-4), the analysis was far from complete. The list of identified contaminants in a nuclear submarine atmosphere could be extended considerably by means of the analytical techniques presently available, although such analysis would be lengthy and tedious. It is estimated that with present equipment a detailed analysis of a single sample of submarine atmospheric contaminants would require about 30 man-days of highly skilled scientific manpower and the use of a well-equipped laboratory for infrared and mass spectral analysis. Such analyses would be costly, therefore, and far from practical on a routine basis.

PROCEDURES

A description has been given elsewhere (1) of the instrumentation required for analyses of atmospheric contaminants and the procedures whereby microquantities of complex mixtures of organic compounds can be separated into their components and identified. Briefly, these steps involve concentrating the contaminants, which usually occur in the atmosphere in the parts-per-billion to parts-per-million concentration range, by separating them from the large volume of air in which they are dispersed. This can be accomplished in a number of ways, but the most convenient and frequently used method is to pass the air through activated charcoal which retains the contaminant material. The organic material can be recovered later in the laboratory by very slowly heating the charcoal in an evacuated system over a period of several hours, and retaining the desorbate in liquid-nitrogen-cooled traps. This desorbate is generally a very complex mixture, comprised of as many as 60 different contaminants in the case of a Project Mercury spacecraft or three to four hundred in the case of a nuclear submarine.

The amount of contaminant material recovered obviously depends upon the volume of air sampled and the contaminant load. Typical closed-atmosphere samplings produce a few milligrams of desorbate. The concentrations of the various components in the desorbate mixture vary widely, by a factor of a thousand or more, depending on the

composition of the original atmosphere. Before very many of the components of such a mixture can be identified or measured quantitatively, it is necessary to separate them from one another. This can be accomplished rather conveniently with a gas chromatograph. Fortunately, the chromatograph functions best with a microquantity of sample, which often is all that can be recovered from atmosphere samplers.

The efficacy of the chromatograph depends on the fact that various compounds require different periods of time to pass through a given chromatographic column. In a homologous series of compounds each individual compound would have a different retention time on a suitable column, the time increasing progressively with molecular weight. For any given column and set of column conditions, however, many compounds can have the same retention time. It often happens, therefore, in the case of a completely heterogeneous mixture, such as that recovered from submarines or spacecraft, that more than one component of the mixture has the same retention time, and these components are eluted together from the chromatographic column.

The emergence of each component or group of components from the column is indicated by a suitable detector. Obviously, if the input sample is 100 $\mu\ell$ or less of a 50 to 400 component mixture, the amount of any single component eluted from the column will be exceedingly small. The components of the desorbate mixture are recovered from the effluent stream of the column in microquantities, usually singly but sometimes in mixtures of two or more, by means of a unique fraction collector developed at NRL (1). These components are then transferred to a suitable infrared gas or liquid microcell or to the inlet system of a mass spectrometer and their identity established spectrally.

Spectral methods of identification are highly specific and unambiguous, whereas chromatographic identification by retention time is not. When the spectrum of a fraction recovered from the column effluent indicates it to be a mixture, some components of which cannot be identified because of spectral complexity, the fraction can be reintroduced onto a second chromatographic column employing a different column substrate and further resolved into its components. Usually compounds which have the same retention time on one column will have different retention times on a judiciously chosen second column.

The overall sensitivity of this analysis is sufficient to permit spectral identification of all components giving rise to observable peaks on a chromatogram when 1/4-in. packed columns and thermal conductivity detectors are used. This type of column and detector is a prerequisite imposed by the relatively insensitive spectral equipment currently allocated to this project.

MERCURY SPACECRAFT RESULTS

These analytical methods, when applied to desorbates from spacecraft atmospheres, have been highly successful in spite of the fact that desorbate mixtures of 30 to 60 components are often encountered (5). Each fraction must be recovered from the column effluent, refractionated when necessary on a different column, and its infrared and/or mass spectrum recorded, all in an 8 to 10 hour period. It is difficult to hold microquantities of relatively low-molecular-weight organic compounds for longer periods under the conditions imposed. In spite of the complexity of the mixture of contaminants recovered from the spacecraft atmosphere, the very low concentrations at which these contaminants occur, their widely varying relative concentrations, the small amounts of sample mixture which can be introduced onto a chromatographic column, and the still smaller quantities which are recovered therefrom, all of the chromatographically apparent contaminants from Project Mercury spacecraft atmospheres have been identified. There are no unknowns! Moreover, a number of contaminants which were not chromatographically apparent have been detected spectrally and identified; that is, the components were

eluted in relatively small quantity simultaneously with larger quantities of other components. It should not be inferred, however, that there were not other unidentified contaminants in Mercury spacecraft atmospheres. Such contaminants were either present at concentrations below the present level of detection, were not adsorbed on or desorbed from the carbon sampler, had unreasonably long retention times on the chromatographic columns chosen for resolving the mixture, or were chromatographically and spectrally obscured by larger quantities of other contaminants with the same retention time.

SUBMARINE PROBLEMS

Relatively speaking, these analytical methods have not been as successful when applied to desorbates recovered from carbon exposed to nuclear submarine atmospheres, although approximately the same number of contaminants have been identified in mixtures from each source. The astounding complexity of the contaminant mixture recovered from the submarine atmosphere (300 or 400 components), the wide range of concentrations, and the large number of contaminants with the same retention time on any given column render the detailed analysis of such a mixture by the methods described incredibly involved, time consuming, and impractical.

Naturally, some current effort is directed towards circumventing these difficulties. The problem of poor resolution could be avoided by taking advantage of the greater resolving power afforded by capillary chromatographic columns. More sensitive chromatographic detectors are also available which would improve the present limits of detection. The price to be paid for these improvements, however, is an approximate 100-fold decrease in column capacity. As a result, the quantity of any single contaminant in the effluent of such a column would be insufficient for infrared spectral identification, at least at the present state of the art. More modern mass spectrometers than the one currently being used are available, however, with ample sensitivity to give recognizable spectra of components at concentrations of less than 10^{-5} mole percent in helium. The approximate lower limit of concentrations identifiable in a typical capillary effluent stream is, fortunately, of this same order of magnitude. In addition to the increased sensitivity, there are mass spectrometers available with very rapid response, requiring only a fraction of a second, under optimum conditions, to scan a mass "octave" (a doubling of mass units).

This combination of circumstances means it is now practical to utilize a capillary chromatographic column—with its greatly increased resolving power—and more sensitive chromatographic detectors and pass a portion of the column effluent directly into the inlet system of a rapid-scanning mass spectrometer. In the several seconds or longer required for a component to be eluted from the column, it will then be possible to record a mass spectrum over an appropriate mass interval.

RAPID-SCANNING MASS SPECTROMETER RESULTS

Preliminary experimental evaluation of this analytical system looks very promising. An example of the type of information that has been obtained is given in Fig. 3 and Table 4. The contaminant mixture used for this exploratory analysis was recovered from a charcoal exposed several years ago aboard the NAUTILUS during a long-duration dive. The data was obtained with an F and M Model 720 gas chromatograph employing a 0.250-in.-diameter packed column (Carbowax) in combination with a CEC Model 21-130 rapid-scanning cycloidal mass spectrometer. The data were obtained in cooperation with Dr. O. P. Tanner, Central Research Labs., Monsanto Chemical Corp., St. Louis, Missouri, whose assistance is gratefully acknowledged.

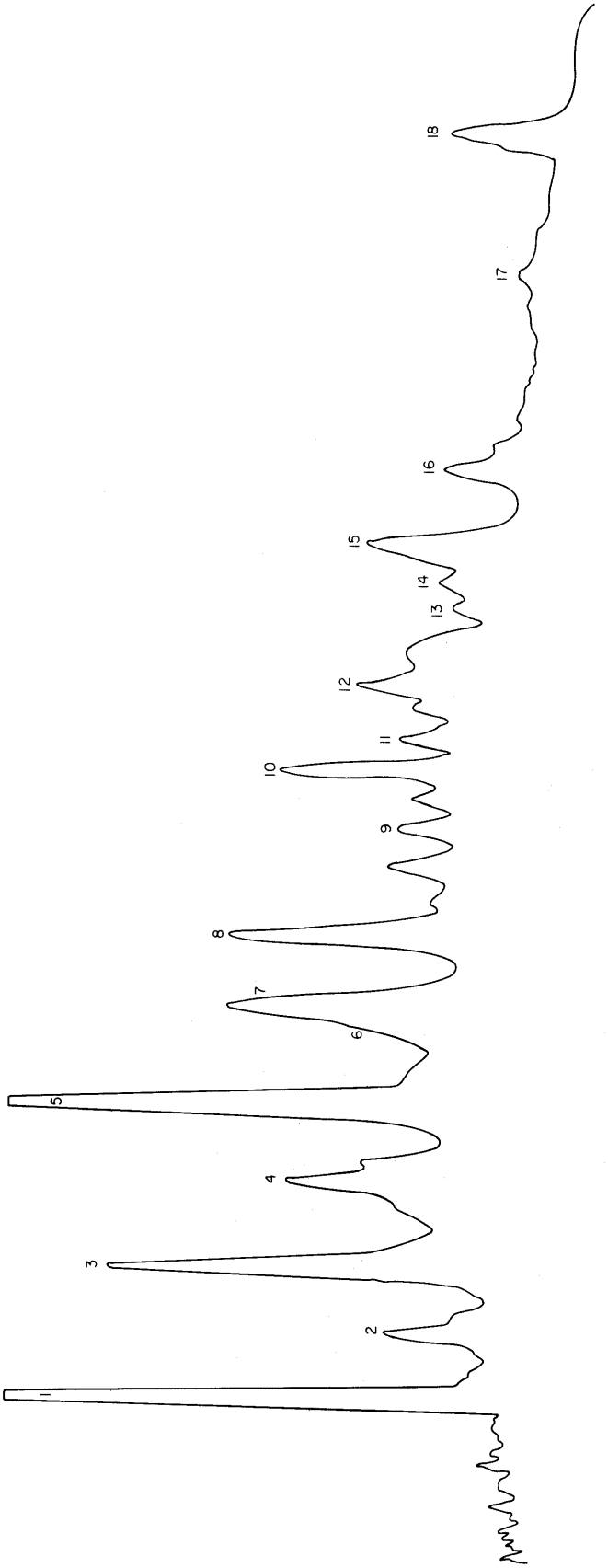

Fig. 3 - Chromatogram of hydrocarbon fraction in USS NAUTILUS atmosphere sample. For identification of peaks, see Table 4.

Table 4
Organic Compounds Identified in a Contaminant Mixture Collected from the Atmosphere of a Nuclear Submarine

Chromatograph Peak Number*	Compounds Identified from Mass Spectral Data†
1	n-Nonane
2	Branched C_{10}-paraffins, benzene
3	n-Decane, n-decene
4	Toluene, n-decane
5	n-Undecane, n-undecene
6	Xylene, n-undecane, $C_{10}H_{20}$, C_9H_{18}, $C_{11}H_{22}$
7	$C_{11}H_{22}$, xylene, $C_{12}H_{26}$, $C_{11}H_{24}$
8	Xylene, $C_{11}H_{22}$, several compounds not uniquely identifiable
9	Propylbenzene, $C_{11}H_{18}$
10	Branched C_5-alkylbenzenes, propylbenzene
11	Butylbenzene, branched C_5-alkylbenzenes
12	Isobutylbenzene, diethylbenzene, ethyltoluene
13	$C_{12}H_{24}$
14	Isopropylbenzene, $C_{12}H_{24}$
15	$C_{10}H_{18}$, pentylbenzene, $C_{12}H_{24}$
16	Pentylbenzene, $C_{11}H_{20}$
17	Phenol, indane
18	Naphthalene

*Temperature programmed F and M Model 720 gas chromatograph employing an 0.250-in. packed column (Carbowax). Numbers refer to peaks in chromatogram in Fig. 3.

†Obtained with a CEC 21-130 rapid-scanning mass spectrometer. Compounds are listed in order of abundance within each group. Identified compounds have been named; where formulas are given, a number of isomers of this formula may be present.

Eighteen mass spectral scans were obtained of the column effluent at the positions indicated by number in the chromatogram shown in Fig. 3. It was obvious from the spectral data obtained that, except in two cases, several components were being eluted from the column simultaneously at the time each spectral scan was made. Only two compounds, n-nonane and naphthalene, were eluted singly. The eighteen mass spectra indicated the presence of 28 distinct compounds, not including the large number of isomers of each that were present but not identified specifically. Experimentally, these data were obtained with a single 2-$\mu\ell$ liquid sample and required only 30 minutes, exclusive of the time spent in spectral interpretation.

Though the successful application of a capillary-column gas chromatograph/mass spectrometer system to this problem has not yet been demonstrated, it is anticipated that the much greater resolution of the capillary column would have permitted the identification of many more individual contaminants by increasing the elution time and reducing the number of components eluted at any instant. The latter effect would appreciably simplify the interpretation of the mass spectral data.

CONCLUSIONS

These preliminary results show the great potential of the combination of gas chromatograph and rapid-scanning mass spectrometer systems for identifying the components of certain complex organic mixtures. The increased rapidity with which an analysis can be made now makes feasible a serious attempt to identify more completely the large number of components that are known to exist in the submarine atmosphere. The greater sensitivity of this instrumentation and the improved condition of the atmosphere of nuclear submarines which has resulted from better housekeeping should make possible easier identification of exotic contaminants that might be released to the atmosphere through degradation of mechanical or electronic components or from other sources in the submarine.

FUTURE PLANS

As a result of its feasibility studies, NRL has already initiated the purchase of equipment to facilitate the analysis of complex mixtures of volatile organic compounds through use of the tandem operation of a capillary-column gas chromatograph and a rapid-scanning mass spectrometer with the necessary auxiliary equipment. This equipment can serve to analyze and identify the components isolated from the atmospheres of nuclear submarines, spacecraft, or other closed systems or, equally well, to study the evolution under various conditions of volatile products from the materials and components which are introduced into the closed system.

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Chapter 6
The Ringrose Co_2 Analyzer

S. H. Smith, Jr.

INTRODUCTION

The Ringrose CO_2 Indicator is an instrument manufactured by International Gas Detectors, Ltd., Leeds, England, for indicating the quantity of CO_2 in the surrounding air. Its range is 0% to 5% CO_2, its accuracy is about ±10% of the reading, and its response time is about five minutes. This instrument is well suited for submarine use, since it is self-compensated for the magnitude and rapidity of pressure fluctuations one encounters on a submarine. It was placed in service on British submarines in 1956.

This CO_2 meter (Fig. 4) consists basically of a manometer with a cylindrical chamber on each end. These chambers are sealed from the atmosphere except for a permeable ceramic membrane on each. The chamber at the low-pressure end of the manometer contains a carton of CO_2 absorbent (soda lime), and the chamber at the high-pressure end contains a carton of cotton batting impregnated with calcium chloride ($CaCl_2$). All of the gaseous constituents of the surrounding air are free to diffuse in and out of the sealed chambers through the ceramic membranes. However, when CO_2 enters the soda lime chamber, it is absorbed, and a partial vacuum is developed which is proportional to the CO_2 content of the atmosphere; this pressure difference is indicated by the manometer which is calibrated to read directly in volume percent CO_2. Since soda lime exerts a water vapor pressure, this must be balanced by an equal water vapor pressure over the impregnated cotton in the other chamber. Also, it is the presence of equal-sized chambers at each end of the manometer that compensates for ambient pressure changes.

The U.S. Navy has been interested in the Ringrose CO_2 meter since 1959. At that time NRL was asked to evaluate an instrument that had been purchased by BUSHIPS. The evaluation (1) showed that the instrument functioned quite well but was sensitive to rapid or large changes in relative humidity. The service life of cartons and the pressure compensation were not checked at that time. However, when the instrument was later tested on two nuclear submarines, it was found that CO_2 readings began to fall below the correct value after only two days of use. It was thought that the soda lime was being dried by the low ambient relative humidity (ca. 40%) in the boats, and lithium hydroxide was suggested as a substitute, since it is not affected adversely by dry air as readily as soda lime.

At this time NRL started a study of lithium hydroxide (LiOH) behavior in the Ringrose meter. Since it was believed that a more compact and lightweight instrument was possible, the first step was to proceed with the design and construction of an NRL model of the Ringrose meter. It was determined with the NRL unit that LiOH was more difficult to use than soda lime because of the moisture compensation requirement. Fresh lithium hydroxide comes in a specially prepared anhydrous form in order to have high efficiency as a CO_2 absorbent, but moisture is generated by reaction with CO_2 just as it

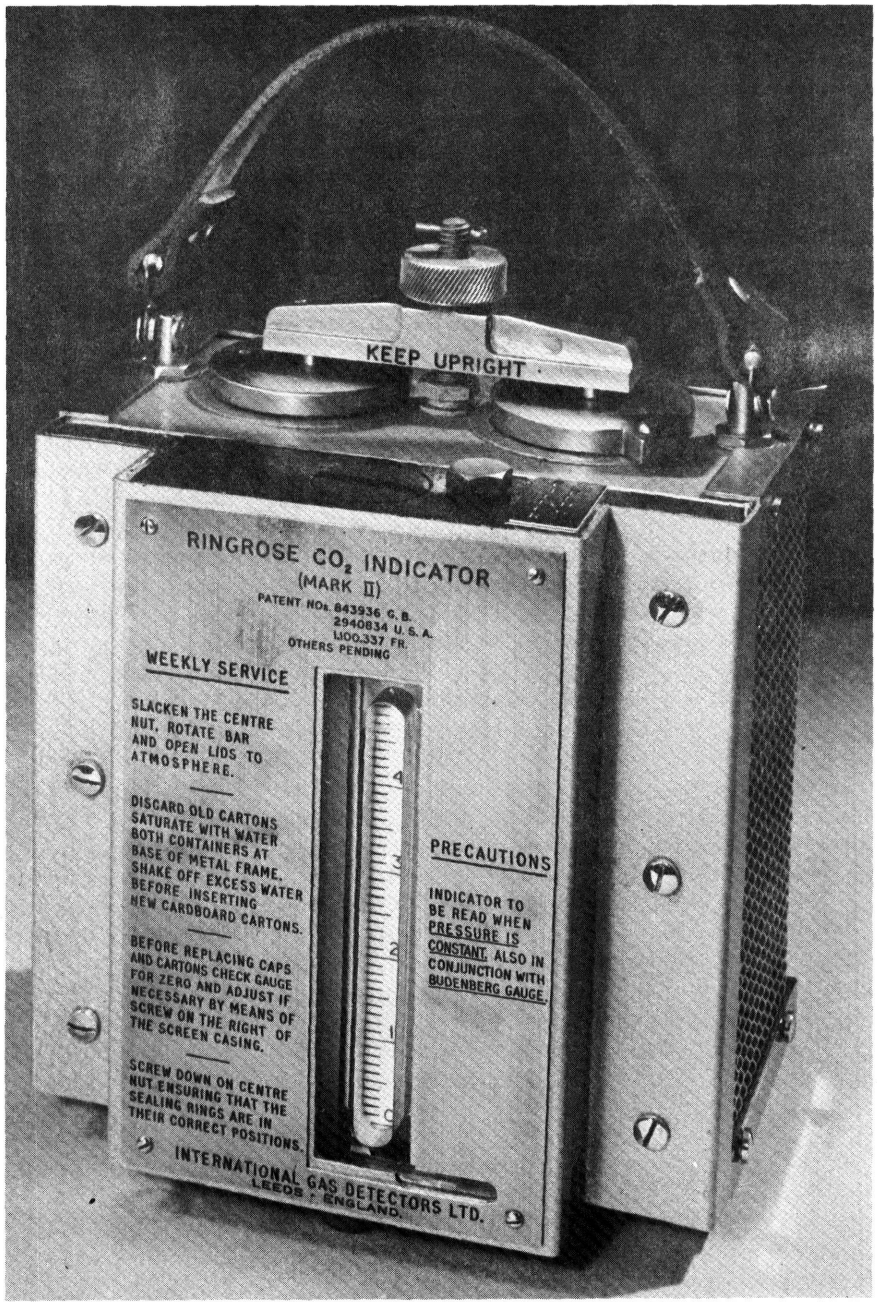

Fig. 4 - The Mark II Ringrose CO_2 Indicator

is with soda lime. This variation from initial dryness to a moist condition when spent is more troublesome than the potentially constant humidity situation with soda lime.

Through correspondence with the English manufacturer, IGD, concerning the problems with the Ringrose meter, it became apparent that they were most willing to cooperate in its redesign. During a visit with the company in England, the NRL version of their instrument was demonstrated; and in the discussion it was decided that IGD would redesign their production model in such a way as to combine the best features of the NRL

instrument with those of an experimental model they had recently constructed. Their designing of a new model had been instigated by a report on performance tests at the Royal Naval Physiological Laboratory at Alverstoke, in which many of the same faults found at NRL were enumerated.

An important fact discussed with IGD in England was that the malfunction of the instrument in air of 40 to 50% relative humidity occurred because the water vapor pressure over the soda lime increased as a result of water generated by the carbonation reaction. This overpowered the ability of the compensator to balance, and the resultant manometer reading was forced down. The NRL group had realized that such might be the trouble only a week before this visit.

During the year following this conference, little work was done at NRL other than the design and construction of a mechanical pressure differential gage to eliminate the oil-filled manometer—an effort that was unsuccessful. IGD proceeded with design and construction of their Mark II Ringrose meter, and company representatives submitted a prototype in April 1963 (Fig. 4). It had already passed performance tests at the Alverstoke Laboratory (2) and was left on loan for evaluation by NRL.

The subsequent testing of this instrument at NRL demonstrated several difficulties. The manometer leaked oil at the O-ring seal of the zero adjustment screw and at the closure of the oil reservoir. The rate of response to changes in CO_2 level was a bit slow. The cartridge holders tended to bind with the hold-down nut upon their removal. The angle through which the manometer could be observed was limited by the machining for application of the scale. But all of these are minor items. A more troublesome difficulty proved to be the still remaining inability of the compensator to balance increasing moisture pressure over the soda lime as it reacted with CO_2.

The change that had been made between the Mark I and Mark II meters to take care of the moisture compensation problem had been to increase the depth of the chambers by about one inch and add a cartridge of water-soaked cotton in this space. The same cartons of soda lime (with about 9% moisture content) and compensators with $CaCl_2$-impregnated cotton were being used as had been provided for the Mark I. NRL proceeded with corrective action based on the premise that anything further one could do to increase the relative humidity existing in the chambers toward 100% would tend to alleviate the problem. The moisture content of the soda lime was raised to 17%, the usual amount for soda lime marketed in this country, and the compensator loading was changed to cotton soaked with a saturated solution of zinc sulfate, which seemed to balance the moist soda lime quite well.

Tests performed with this system showed it to be a considerable improvement over the low moisture soda lime-$CaCl_2$ system. However, under the extreme condition of days of exposure to CO_2 levels of 4% or higher, the compensation problem still existed. Since the instrument would virtually never be called upon to indicate CO_2 as high as 4%, the best action may be simply to reduce the scale range to about 2-1/2%.

The Mark II instrument has been subjected to service conditions under the supervision of NRL personnel on two cruises of the nuclear submarine SCAMP (SS(N)588). Performance under rapidly changing conditions of boat pressure and CO_2 level were judged entirely satisfactory for both carton systems. Only the IGD cartons were subjected to a prolonged exposure to CO_2 at 1-1.8%; in this case slightly low readings were noticed initially, and they became still lower during the six days of exposure. Acceptance of the instrument by the ship's crew was good.

CONCLUSIONS

This instrument has proved itself eminently suited for the proposed use on nuclear submarines. It is simple, reliable, and requires little servicing. The necessity for training crewmen in its use will be practically nil. The cost is moderate and the service life indefinitely long. The weekly replacement of chemical cartons in the instrument should not pose any supply problem. There are several alternative ways in which the instrument might be used. An instrument could be carried from place to place on the ship where it is desired to read CO_2 levels, a separate instrument could be provided for each station, or one could place an instrument in a sealed chamber fitted with valved sample lines and a pump, as is used with the present Atmosphere Analyzer.

FUTURE PLANS

An order has been placed for five Mark II Ringrose meters with any improvements that have been devised since the prototype was made. Four of these instruments will be distributed among different nuclear submarines for longer term evaluation. If the performance is satisfactory, a recommendation will be made for issuance as a stock item for submarines.

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Chapter 7
Development of Paints for Nuclear Submarines

D. E. Field and T. R. Walton

INTRODUCTION

The use of paint on a Navy vessel is essential for protecting the hull and machinery from corrosion. Almost equally important is the use of paints for sanitary and decorative purposes. With the advent of nuclear submarines, prolonged undersea voyages became commonplace, and atmospheric habitability became of paramount importance. The interior paints attracted particular attention when in late 1958 extensive research had proved that much of the hydrocarbon contamination in a submarine atmosphere could be traced to solvent-base paints (1). The establishment and growth of a large FBM submarine fleet has brought increasing demands on the development of paints for both the interior and exterior of submarines. Our national defense requires these ships to operate in remote seas and from bases in the proximity of their operations where upkeep periods are short and the weather may not be conducive to exterior painting. To cope with these troublesome paint problems, the Bureau of Ships requested NRL to develop nontoxic, nonflammable, interior coatings and also exterior shipboard paints for application in cold, damp weather. The latter paints are not concerned with habitability and will be discussed in other reports (2).

EARLY WORK ON INTERIOR PAINTS

In early 1959 after NRL researchers had proved that much of the hydrocarbon contamination in a submarine atmosphere could be traced to paints which had been applied weeks and months before (1), the Bureau of Ships issued an instruction to all Submarine Force Commands to cease all interior submarine painting 30 days prior to departure for sea (3). Meanwhile work had been initiated at NRL to evaluate proprietary latex paints for toxic components and to develop a touch-up paint which would be nontoxic and which could be used during periods just prior to departure for sea or even during sealed-ship conditions. This problem was discontinued by mid-1961 after a satisfactory touch-up paint was developed (4-6).

In the following two years latex paints were being used more extensively on the interior of submarines, especially on elastomeric, unicellular, plastic foam insulation (which was replacing molded cork hull insulation) where the conventional nonflaming alkyd paints were cracking. During this period NRL worked intermittently on evaluating several proprietary, fire-retardant, latex paints and on measuring the evaporation rate of paint solvent from the interior fire-retardant paint. The latex paints had been submitted to the Bureau by several manufacturers for evaluation as interior paints for nuclear submarines, and samples were forwarded to the U.S. Navy Toxicology Unit at the National Naval Medical Center and to NRL for testing.

At NAVMEDCTR the paints were subjected to infrared analysis, measurement of volatile organic components in a "comparison device," and toxicity tests exposing mice to saturated vapors in a painted chamber. Results of the tests showed the paint samples contained several volatile combustible organic components and ammonia, which varied in amounts and evaporation rates; however, only minor distress signs were noted in the mice exposed to the saturated vapors from these samples (7).

At NRL the samples of paint were tested for paint-film quality. Included were tests for fire retardancy, freeze-thaw stability, gloss, leveling, viscosity, hiding power, cleansability, and scrubbability. These paints had sufficient fire retardancy and flexibility to be used on nonflammable, resilient surfaces, but they did not have sufficient gloss or leveling for good appearance and soil hold-out (8,9). Although these paints left something to be desired, three of them were authorized for limited use on the interior of nuclear submarines pending the development of a formula specification of a nontoxic, interior submarine paint (10).

The drying rate of a specified solvent-base paint used on the interior of nuclear submarines is shown in Table 5. The drying rate was measured on the apparatus shown in Fig. 5. Although this paint gains weight from oxidation of its vehicle while losing weight from solvent evaporation, it can be calculated to have lost about 95% of its solvent in four days under these conditions. The remaining solvent evaporates very slowly unless conditions are changed. After 14 days the paint was heated to evaporate the remaining 5% of the solvent. These results show that all but a small percentage of solvent has evaporated from the paint three or four days after application, but painted surfaces which are heated even after two weeks of drying could rapidly release over two pounds of solvent for each ten gallons of applied paint (11).

Table 5
Drying Rate of Interior, Fire-Retardant Paint

Elapsed Time	Weight of Paint (g)	Unevaporated Solvent (%)
0	62.0	100
1 hour	57.5	80.5
4 hours	51.45	54.2
7 hours	48.32	40.6
4 days	40.031	4.6
5 days	40.013	4.6
6 days	40.007	4.5
10 days	40.083	4.9
14 days	40.105	5.0
64 hours at 100°C	38.964	0

Specification: MIL-P-17971A (SHIPS) Paint, Nonflaming (Dry) Alkyd-Chlorinated Rubber, Pastel Green, Semigloss, Formula No. 125/57
Average Film Thickness: 14 mils (dry)
Surface Area of Film: 95 in.^{2}
Temperature: 73°F
Relative Humidity: 40-50%
Air Flow: 4 changes per hour

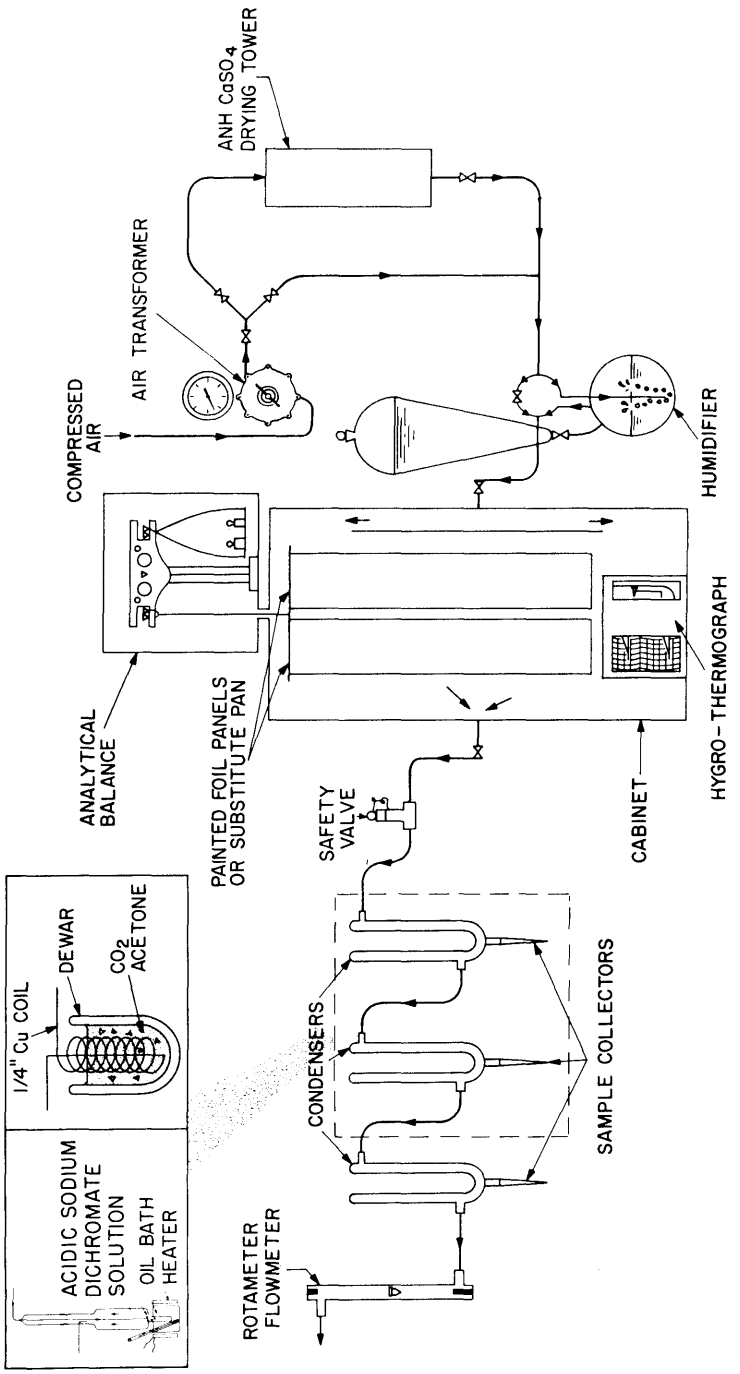

Fig. 5 - Apparatus for measuring evaporation rates of solvents from paint films

These results and increasing alarm at what the Bureau of Ships considered the extensive use of flammable latex paints on the interior of submarines led the Bureau in July 1963 to issue a Change Transmittal (10) to their Instruction (3) which restricted further the use of latex paints but which changed the deadline for use of specified nonflaming paints to five days prior to departure for sea. Moreover, the change order contains the following requirements: (a) during and for at least 24 hours after this painting period, exhaust ventilation to the weather shall be maintained; (b) subsequent to this ventilation period while still maintaining the exhaust ventilation, painted thermal surfaces shall be activated (heated); and (c) the main carbon filters shall then be changed prior to submergence. With the increasing demands for paints of both the protective and decorative type which would be nonflaming during, as well as after, application, a new research program was initiated at NRL in March 1964 to develop such coatings.

DISCUSSION

The present state of the art leaves only three avenues open for development of a paint which does not contain volatile or toxic solvents. These are: (a) the use of water as the solvent, (b) the use of liquid resins which convert to solids by chemical reaction(s), or (c) a combination of the two. Any of these systems may be made fire retardant by either physical or chemical addition of fire-quenching reagents. The water-base paints have disadvantages such as the poor wetting, leveling, and corrosion protection while the two-package systems (100% solids) are characterized by high viscosity, limited application time after mixing, and complexity of use.

The interior of a nuclear submarine has a variety of surface materials with individual requirements for coating performance. These surfaces include rigid and resilient insulations as well as bare and painted steel surfaces and might have only average wear or be subject to the severe conditions found in bilges or showers and on hot piping or treadways. In addition to the physical requirements of the paint, it also must be a noncomplex system which can be used by inexperienced painters in a ship's force and still result in a satisfactory coating.

FUTURE PLANS

Research will be conducted using various combinations of fire-quenching techniques with nontoxic systems to develop first a decorative paint and secondly an anticorrosive primer or protective paint. Initial studies are underway to develop a fire-retardant acrylic latex paint formulation by the addition of halogenated plasticizers in combination with antimony oxide. Halogenated materials in this study will include chlorinated biphenyls and polyphenyls, chlorinated paraffin esters of tetrachlorophthalic anhydride or tetrabromophthalic anhydride, and halogenated diol. In future work, the development of fire-retardant paint vehicles will be attempted by synthesis of polymers containing halogen atoms. These polymers will be water soluble, convertible resins or emulsions. It is anticipated that formulations will be developed that, while they may not completely satisfy all the requirements established for the final paint, will offer considerable improvement over the presently used formulations. For example, it would be helpful to reduce the five-day deadline on painting to only one or two days before a ship's departure for sea. When such improvements are made, they will be specified for use, since each improvement gives the fleet better operational capabilities.

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Chapter 8
The Carbon Monoxide/Hydrogen Burner

F. S. Thomas

INTRODUCTION

The development of the jury-rig CO burner for use on the earliest nuclear-powered submarines, the several models in the Mark series of CO/H_2 burners, and various studies of the oxidation processes occurring in the operation of this equipment have been reported earlier (1-4).

About two-thirds of the operational burners are the Mark II units. These have a flow rate of 250 cfm and contain a rotary heat exchanger of good efficiency. Most of the remaining operational burners are Mark III units. These are basically the same as the Mark II and also use a rotary heat exchanger but are modified to give a 500-cfm flow rate. The Mark IV burners are now coming into operational use. These have the same 500-cfm flow rate as the Mark III but use a flat-plate heat exchanger with no moving parts.

The Bureau of Ships and the several manufacturers of these units have handled the mechanical problems which have arisen with the later units. NRL has been essentially concerned only with the chemical aspects of the catalytic reaction relative to the various components in the submarine atmosphere.

CATALYST CONTAMINATION

There is only one proper catalyst for use in these burners, Hopcalite, FSN PN6850-605-7854. As contained in the supply system, this material is adequately identified by labeling of the containers. As the material is finally available for use on the submarine, however, there is the possibility that the container markings may become obliterated or that, as a result of repackaging for the ship's convenience, the material may have lost its identifying markings. The burner system cannot operate efficiently if the hydrogen eliminator catalyst (FSN P6850-547-0673) is used instead of Hopcalite. The installation of either carbon or a carbon-catalyst mixture into the burner must absolutely be avoided since fire or other hazard could result. To aid in identifying the correct catalyst several chemical tests have been devised which indicate whether a questionable sample contains Hopcalite.

The following physical and chemical test procedure illustrates an effective method for detecting catalyst contamination (5). Addition of a portion of the material in question to 85% phosphoric acid provides an indication if any carbon is present in the catalyst. Carbon floats on this liquid, whereas both catalysts sink. After a short time in the acid the Hopcalite turns the liquid a bright purple, whereas hydrogen eliminator catalyst gives no color. Appreciable hydrocarbon contamination of the catalyst produces a readily recognizable combustion upon rapid heating of a small amount of the material on a

preheated hot surface. Similarly, used carbon containing appreciable hydrocarbon contamination when placed on a hot surface will give off copious fumes. In any situation where misapplication of these materials might occur, the use of adequate identification and purity tests appears well justified.

OPERATING PROBLEMS

The reaction desired from this burner equipment is the complete oxidation of the carbon monoxide, hydrogen, and hydrocarbons contained in the submarine atmosphere to carbon dioxide and water. This has been attained by operation of the burner units at a high enough temperature to assure maximum oxidation. There are, however, other components in these atmospheres which on oxidation produce undesirable products. Such components are mainly halide-containing materials. From the beginning of nuclear submarine operation there has been a continuing effort to keep these materials out of the submarine atmosphere, which has resulted in their normal atmospheric concentrations being quite small. Accidental occurrences, of course, can cause sudden and large increases in the ambient concentrations. In the effort to minimize the effect of these materials, the possibility of operating the burners at lower temperature has been studied. In a period of submerged operation of SCULPIN (SSN590), it was possible to examine some aspects of this. The CO burners were operated at 600°F long enough to give a base line, then run for a short time at 550°F, and finally for several days at 500°F. It was determined that the atmospheric hydrocarbons were satisfactorily burned throughout this temperature range (6). Catalyst samples taken showed no evidence of hydrocarbon accumulation. No deterioration of the carbon monoxide removal ability was seen on lowering the temperature. No reason became apparent during this period of study to indicate that the burner could not be successfully operated at a temperature as low as 500°F. Although this desirable change to lower operating temperature appears feasible from the SCULPIN operation, it should be given additional study with longer periods of operation in several units of the fleet before its general application can be recommended.

In early 1963 there were reports that in the operation of newly completed FBM submarines, corrosion and electrical groundings were occurring in the space surrounding the CO/H_2 burners and CO_2 scrubbers. Two separate factors contributing to this were found in an inspection of the THOMAS JEFFERSON (SSB(N)618) and in related studies (7). One factor was the decomposition of halogen-containing atmospheric contaminants on passage through the burners to form halogen acids. The second factor was that excessive monoethanolamine was being spread into the surrounding space from the CO_2 scrubber equipment. Atmospheric Freon-12 concentrations were low. Samples of such surface deposit and corrosion materials formed were taken by JOHN MARSHALL (SSB(N)611) and on examination showed, as in the previous case, the presence of MEA and halide. This halide was found to be essentially all chloride with little or no fluoride and hence was again apparently not a result of the decomposition of Freon-12 (8). The Marine Engineering Laboratory (MEL) reported on the inspection and study of similar materials on the SAM HOUSTON (SSB(N)609), concluding that the corrosion present was the result of burner decomposition of halide contaminants which were not Freons (9). The extent and effect of this was not considered serious at that time. Later, NRL studies of samples from THOMAS JEFFERSON (SSB(N)618) and ALEXANDER HAMILTON (SSB(N)617) showed (a) that the main ventilation carbon bed absorptive capacity was rapidly exhausted by the large quantity of solvents in the atmospheres of newly commissioned ships, (b) that the used carbons from these ships contained a chlorinated solvent, methyl chloroform, (c) that the submarine atmosphere also contained this solvent, and (d) that methyl chloroform is readily converted to reactive halogen compounds by the CO/H_2 burner (10,11).

By the end of 1963 alterations had been or were being made to the ventilation system in a number of these ships to reduce the dissemination of MEA into the surrounding

space. Several control measures for limiting the amount of and effect of halide materials in these atmospheres were known, and it appeared that adequate control of the corrosion could be attained by applying these. Application of such measures on the JAMES MONROE (SSB(N)622) indicated that they could produce effective control of the corrosion (12).

FUTURE PLANS

Operational problems of the CO/H_2 burners will continue to be monitored. Investigation of the corrosion problems will be continued, whether applicable to methyl chloroform, Freons, or other contaminants. Further studies will be made on the possibility of lowering the burner operating temperature from 600°F to 500°F.

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Chapter 9
Monoethanolamine Stability Studies

H. Ravner and C. H. Blachly

INTRODUCTION

Carbon dioxide is the major contaminant of nuclear submarine atmospheres, and the agent used for its continuous removal must be efficient and reliable. The regenerative absorbent monoethanolamine (MEA) as now formulated meets these requirements in large part, but its stability under operating conditions is not as great as is desired. As a result (a) oxidative breakdown of the amine triggers the generation of ammonia, a toxic nuisance which cannot be tolerated in a ship's atmosphere, (b) the necessity of carrying adequate replacement stocks of MEA adds to the overall logistics burden, and (c) the darkening of the solution which accompanies oxidative breakdown interferes with shipboard normality determinations based on color indicator titrations.

A major contribution to the stabilization of MEA was made by the Mare Island Naval Shipyard with the discovery that certain chelating agents, notably the monosodium salt of N,N-diethanol glycine (abbreviated VFS, the initials of a common commercial trade name for this material), markedly improved the useful life of the amine (1,2). The procurement specification for scrubber MEA (3) now requires incorporation of VFS; it also imposes a limit on iron content because this metal has been considered a serious catalytic contaminant.

In the previous annual report (4), preliminary information was given on the generation of peroxide, ammonia, and nonbasic nitrogen-containing compounds in unstabilized amine solutions; on the adverse effect on MEA stability of copper in any form even in the presence of VFS; and on the roles of VFS and EDTA (the tetrasodium salt of ethylenediaminetetraacetic acid) as antioxidants and metal deactivators. The present chapter describes the completion of these studies.

SCOPE OF EXPERIMENTAL WORK

The majority of the dynamic oxidation experiments were conducted on 4N MEA solutions in glass cells under reflux conditions. Air containing 1% CO_2, to simulate submarine atmospheres, was passed through the solutions at a rate of 1 cc per ml solution per minute. The term MEA will hereafter refer to the carbonated form of the amine, unless otherwise specified.

The test temperatures were rather arbitrarily selected, since no one test temperature could adequately describe the scrubber environment; solution temperatures vary from about 90°F in the absorber to 280°F in the stripper and may approach 300°F next to the electrical heaters.

The majority of the experiments were conducted at 131°F (55°C), at which temperature the oxidation rate permitted convenient measurement of the degradation products. At higher temperatures stainless steel test cells were employed, because of excessive attack by the amine on glass and to simulate scrubber conditions more realistically. Static tests were conducted in stainless steel cells at 280° and 300°F either with no air or with only limited amounts present.

VFS-PEROXIDE REACTION

In both aqueous and nonaqueous media, many oxidations proceed by a chain reaction autocatalyzed by peroxide decomposition. The presence of peroxides in oxidized MEA solutions and their absence in VFS-stabilized solutions suggested the possibility of such a mechanism for the present system; the role of VFS would be the classic one of reacting with and destroying peroxides, thus interrupting the reaction chain (4). A series of experiments was set up to determine whether VFS did, in fact, destroy peroxides.

The reaction of equimolar quantities of VFS and tertiary butyl hydroperoxide in aqueous solution was studied at 80°, 108°, and 131°F by following the changes in peroxide concentration with time. These changes were adjusted for the small amount of peroxide which decomposed in the absence of the additive.

Figure 6 shows that peroxides are reduced by VFS, the calculated activation energy of the reaction being 16.5 kcal.

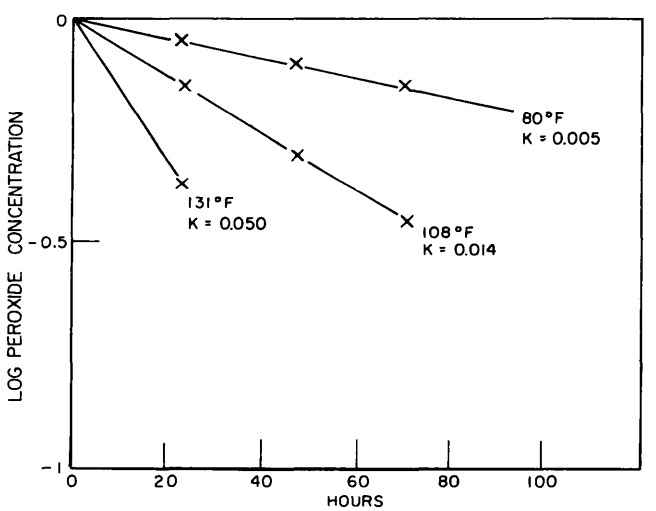

Fig. 6 - Reaction of VFS with tert-butyl hydroperoxide

EFFECT OF METALS WITH VFS PRESENT

Samples of makeup water, base stock amine, and used scrubber solutions with known prior histories were obtained from Submarine Squadron 10 and analyzed for their metal content. About a dozen metals were found in the amine, some of which could adversely affect the stability of operating solutions. Four of these metals—iron, copper, chromium, and nickel—were selected for detailed study because of their known catalytic

activity in other applications. Of these, only copper was present in the makeup water samples. Some typical analyses are shown in Table 6.

Table 6
Metal Content of Scrubber Solutions and Makeup Components

Submarine	Source	Amount of Metal (in ppm)			
		Copper	Nickel	Chromium	Iron
NAUTILUS	Potable water	5.0	None	None	None
	Storage MEA	2.5	-	-	-
	Scrubber (400 hr)	8.5	-	-	-
	Scrubber (800 hr)	13.5	-	-	-
SCULPIN	Potable water	2.0	None	None	None
	Lean MEA	8.0	10.0	-	-
SEAWOLF	No. 1 Storage	5.0	2.0	0.4	8.0
	No. 2 Storage	3.5	1.8	-	5.0
	Potable water	3.5	None	None	None
	No. 1 Scrubber (200 hr)	9.0	3.0	0.4	15.0
	No. 2 Scrubber (168 hr)	10.0	3.7	0.4	43.0
	No. 2 Scrubber (246 hr)	13.0	3.0	0.6	50.0

A dash signifies that no analysis was performed.

Reference has already been made to the adverse effects of copper in any form on MEA stability; the effects of chromium and nickel are described below. MEA formulations were oxidatively stable in the presence of chromium, both as bulk metal and as the chromate, and of nickelous ion in 3.7 ppm concentration. As shown in Fig. 7, however, significant deterioration occurred when the concentration of nickelous ion was increased tenfold or when the metal was present in bulk form. The pattern of ammonia evolution shown in Fig. 7 and in subsequent figures, i.e., a rapid rise to a peak value followed by a decrease, is generally typical of MEA oxidative decomposition. It appears probable that ammonia is the initial decomposition product of the amine but that as the reaction with oxygen proceeds, other degradation products form at the expense of ammonia.

The increased generation rate of nonbasic nitrogen-containing compounds from uninhibited MEA as a function of time is shown in Fig. 8.

EFFECT OF EDTA

Several water-soluble amines, phenols, and metal deactivators were investigated for their ability to stabilize MEA solutions; a primary criterion was that they, like VFS, be antioxidants for MEA in their own right. Of the dozen or so materials investigated, only EDTA fulfilled this condition (4). In addition, this compound reacted with peroxides in the same manner as did VFS, thereby lending additional support to, but by no means establishing, the theory that these chelates function in part by interrupting peroxide-catalyzed chain reactions.

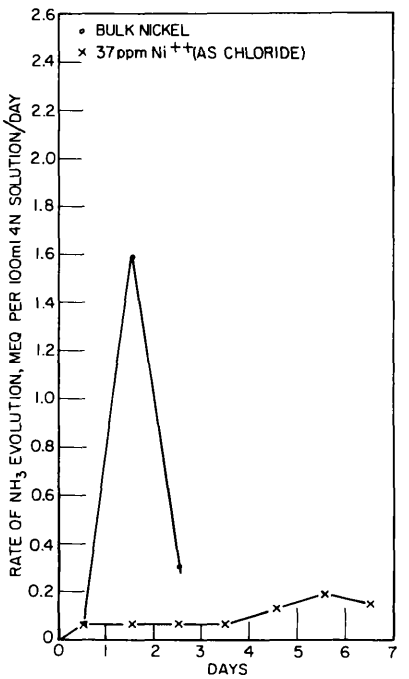

Fig. 7 - Effect of nickel on the stability of MEA + VFS (dynamic test at 131°F, 1% CO_2 in air, 1.5% VFS)

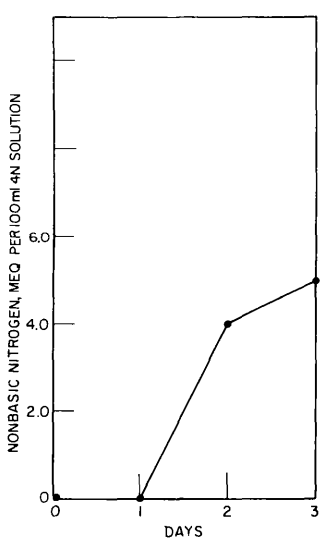

Fig. 8 - Generation of nonbasic nitrogen-containing compounds in 4N MEA (dynamic test at 131°F, 1% CO_2 in air)

The outstanding inhibitory activity of EDTA with copper present has been reported (4); its effect in the presence of ferrous, nickelous, and chromate ions is shown in Fig. 9. The EDTA additive offered no improvement over VFS when large quantities of nickelous or ferrous ions were present and provided somewhat less protection with chromate ions. Since, to a large extent, the activities of VFS and EDTA complemented each other, their combined effectiveness was of interest. Accordingly, 1.5 percent each of the two additives was added to a solution containing 15 ppm cuprous, 3.7 ppm nickel, 30 ppm ferric, and 10 ppm chromium as chromate ion; to increase the severity of the test, stainless steel cells were employed. During the two-week test period at 131°F, there was no evidence of degradation, and the performance of the additive package was considered to be highly satisfactory.

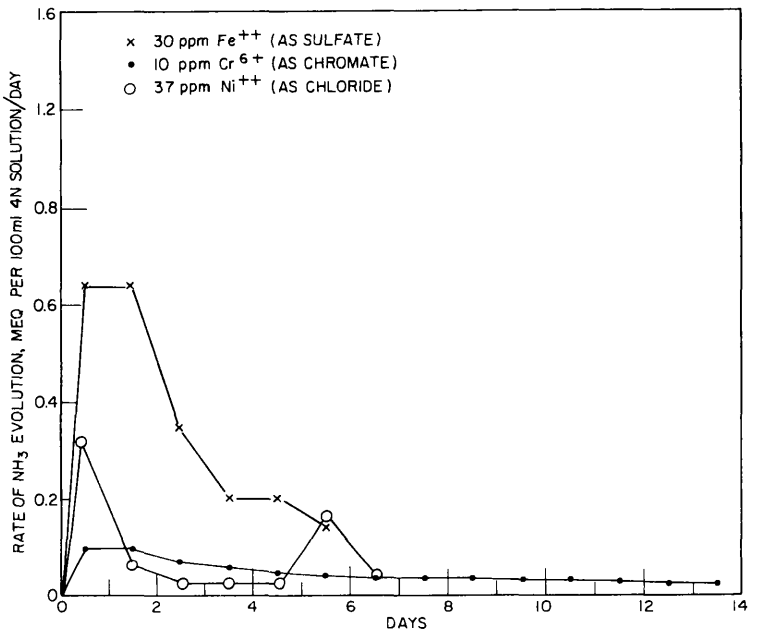

Fig. 9 - Effect of iron, nickel, and chromium on the stability of MEA + EDTA (dynamic test at 131°F, 1% CO_2 in air, 1.5% EDTA)

AERATION-OXIDATION EXPERIMENTS AT 160° AND 208°F

The effects of oxidative degradation of the amine-VFS system in stainless steel cells but in the absence of metal ion activators are shown in Figs. 10 and 11. Oxidation at 160°F (Fig. 10) resulted in only minor evolution of ammonia with no further improvement being obtained by the addition of EDTA. During a four-day test at 208°F (Fig. 11), the amine suffered substantial degradation in the absence of additives and even more in the presence of EDTA. Significant improvements in stability were imparted by VFS and VFS-EDTA. In another series of runs carried out at 208°F in the presence of salts of iron, copper, nickel, and chromium (Fig. 12), VFS was totally ineffective as a stabilizer. In view of the lack of efficacy of EDTA when no metals were added, it was presumed to be equally ineffective when the metals were present. The combination of VFS and EDTA, on the other hand, was highly effective for three days. Thus, EDTA, although ineffective as an antioxidant at this temperature, is able to neutralize the procatalytic effect of copper so that optimum inhibition can be provided by the VFS. It is of interest to note that there was no metal pickup from the cells by the amine under these rather severe test conditions.

STATIC TESTS AT HIGH TEMPERATURES

Engineering consideration is being given to the possibility of raising stripper temperatures in order to increase scrubber efficiency. In the stripper, the scrubber solution is subject to possible degradation by reaction with dissolved oxygen and by thermal breakdown. To determine which, if either, of these processes do in fact occur, 50-ml portions of ca. 4N MEA free of metal salts were treated as described below, transferred to stainless steel cells of 90-ml capacity, rendered air tight with neoprene stoppers, and autoclaved at 280° and 300°F for three and two days respectively. These times were determined by the life of the stoppers. At the conclusion of the tests, high-purity nitrogen gas was passed through the solutions, and any ammonia in the effluent was trapped in a boric acid solution for later analysis.

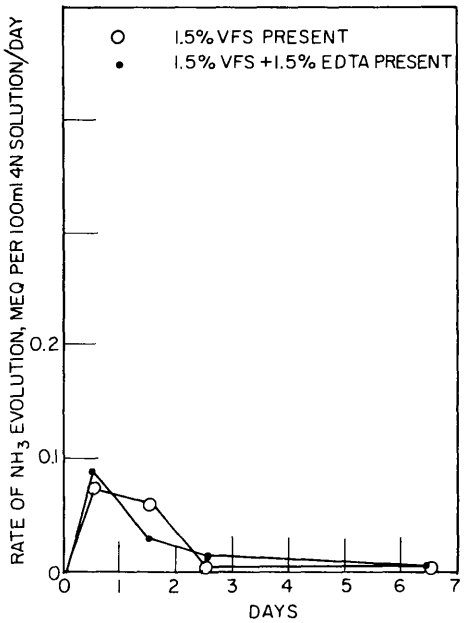

Fig. 10 - Effect of VFS and EDTA on the stability of 4N MEA (dynamic test at 160°F, 1% CO_2 in air, stainless steel cells)

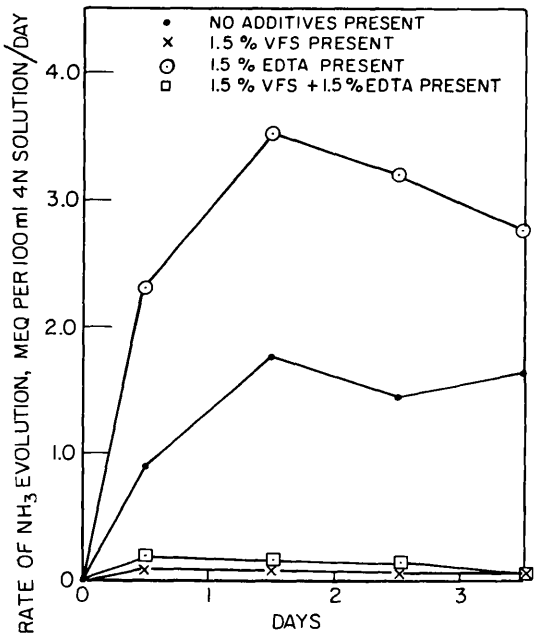

Fig. 11 - Effect of VFS and EDTA on the stability of 4N MEA (dynamic test at 208°F, 1% CO_2 in air, stainless steel cells)

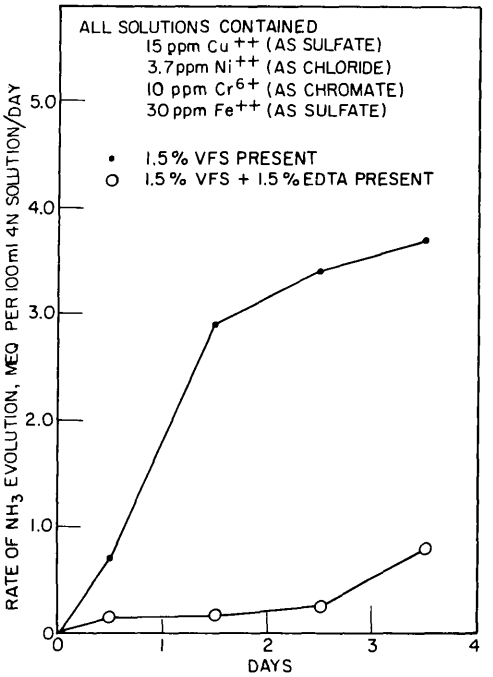

Fig. 12 - Effect of additives and metals on the stability of 4N MEA (dynamic test at 208°F, 1% CO_2 in air, stainless steel cells)

Run 1—Solution saturated with high-purity nitrogen containing one percent CO_2

Run 2—Same as above but air substituted for nitrogen

Run 3—Same as Run 2 but with 1.5 percent each of VFS and EDTA added

Run 4—Solution saturated with oxygen containing one percent CO_2; VFS and EDTA added.

In the tests at 280°F the least quantity of ammonia was generated in the absence of oxygen (run 1) during the three-day test period. A second run made for a period of six days under the same conditions revealed a 75% increase in the quantity of ammonia but no significant change in the rate of evolution. The quantity of ammonia evolved and its linear relation to the exposure time would suggest that thermal degradation occurs, but only to a limited extent.

It should be understood, however, that the effect on MEA stability of three days of continuous exposure at 280°F may not be equivalent to that which would result from intermittent exposure of the solution to 280°F for the same aggregate length of time during scrubber operation.

Runs 2 and 3 indicated that a relatively slight reaction occurred between the oxygen component of the air originally present and MEA and that the additive package imparted no additional stability. When oxygen replaced air in run 4, ammonia evolution increased, and a significant quantity of nonbasic nitrogen-containing compounds was generated.

The results of two days at 300°F (runs 1A to 4A, Table 7) were about the same as for three days at 280°F. While the results of operating the stripper at 300°F, with concomitant heater skin temperatures of 325°F or greater, cannot be predicted from the data, it seems safe to expect the usual doubling in rate of degradation for a 20°F rise in temperature. The results might be even more severe than this.

CURRENT STATUS OF VFS-EDTA ADDITIVE PACKAGE FOR MEA

The useful life of CO_2 scrubber solutions as now formulated with VFS is materially decreased by copper and to a much lesser degree by nickel and iron in the concentrations normally found in these solutions. This discovery is of obvious practical significance. One approach to extending the life of the solutions would be to eliminate known sources of copper contamination. Accordingly, recommendations have been made that battery-grade water replace potable water for makeup purposes and that a limit on copper content be incorporated into the procurement specification for the amine (5). An additional approach is to employ EDTA in an additive package with VFS to reduce the adverse effect of copper (6). The present position of BUSHIPS is that since an additive package can probably minimize adequately the effect of copper, it appears unnecessary to use battery-grade water for makeup purposes (7). The VFS-EDTA additive package is now undergoing sea trials.

FUTURE WORK

The MEA stability study was essentially completed at the end of Fiscal Year 1964, and a final report on this phase of the NRL Habitability Program has been issued (8). Some additional work remains to be done in evaluating the current sea trials of the VFS-EDTA additive package. The research personnel responsible for the MEA study will be available for future consultative services as required.

Table 7
Static Test of MEA Stability at High Temperature

Solution and Treatment	280°F for 3 days						300°F for 2 days					
	Run	Test Duration (Days)	Meq. MEA/ml			Meq. NH_3 Evolved Per ml	Run	Test Duration (Days)	Meq. MEA/ml			Meq. NH_3 Evolved Per ml
			Start	Finish	Change				Start	Finish	Change	
MEA-CO_2^*-N_2	1	3	4.23	4.23	none	3.2×10^{-4}	1A	2	4.28	4.28	none	4.8×10^{-4}
		6	4.23	4.23	none	5.6×10^{-4}						
MEA-CO_2-Air	2	3	4.16	4.16	none	5.0×10^{-4}	2A	2	4.28	4.28	none	5.6×10^{-4}
MEA-CO_2-Air-EDTA-VFS†	3	3	4.25	4.25	none	3.8×10^{-4}	3A	2	4.26	4.26	none	8.0×10^{-4}
MEA-CO_2-O_2-EDTA-VFS	4	3	4.25	4.21	-0.04	13×10^{-4}	4A	2	4.24	4.18	-0.06	14×10^{-4}

*CO_2 in 1% concentration.
†VFS and EDTA each in 1.5% concentration.

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Chapter 10
The Ionics Electrolytic Cell for the Sulfate-Cycle System

S. T. Gadomski

INTRODUCTION

Interest in the sulfate cycle for O_2 generation and CO_2 removal has diminished somewhat with the current construction of a ten-man prototype system which incorporates ion-exchange resins and cation- and anion-exchange membranes to provide both O_2 generation and CO_2 removal within a single cell (1). Any unforeseen shortcomings in such a cell, however, would require renewed consideration of the sulfate cycle, particularly if the sulfate-cycle system as described by NRL (2) could be improved. A possible modification would be the replacement of the NRL electrolytic cell with one containing both a cation-exchange membrane and a diaphragm. Considerable work on such a cell has been reported by Ionics, Inc. (3), and several test cells were procured by NRL from that company some time ago.

This chapter summarizes the NRL evaluation of the Ionics test cells and includes a comparison with the NRL two-diaphragm electrolytic cell. This chapter also completes the reporting of the NRL studies on the sulfate-cycle system.

TEST CELL

The Ionics test cell, of their own design and construction, contains a porous anodic diaphragm and a cation-exchange membrane adjacent to the cathode. Membrane properties permit the active areas of the cell to operate submerged. The catholyte is prevented from diffusing from the cathode compartment into the center feed compartment by the membrane's impermeability toward neutral and negatively charged particles. The membrane's permselectivity, however, allows sodium ions to migrate toward the cathode in response to an applied voltage. The cathode compartment, therefore, requires a separate feed input; the rate of flow of this feed at a given current density determines the concentration of sodium hydroxide (NaOH) produced. The flow of feed into the center compartment and then through the diaphragm to the anode prevents or minimizes acid diffusion toward the center compartment.

The construction details of the Ionics test cell include a Lucite body, a nickel-screen cathode, and an anode of expanded metal (platinized titanium). The diaphragm material is microporous polyvinylchloride. An insulator of Saran screen separates the membrane and diaphragm by one-eighth inch, the thickness of a gasket forming the center feed compartment. The distance between electrodes is about one-fourth inch. These dimensions require the center feed to be located at right angles to the thickness of the center compartment. The active area of the cell is about 42 sq in.

Catholyte and anolyte levels are determined by overflow tubes which are located to provide some space for gas and liquid disentrainment.

ION-EXCHANGE MEMBRANES

Ion exchangers are insoluble solid materials which carry exchangeable cations or anions. They consist of a three-dimensional crosslinked framework of hydrocarbon chains carrying fixed ionic groups whose electric charge is balanced by mobile ions of opposite charge, the counter ions. In cation exchangers the counter ions are cations. The crosslinked network provides resin insolubility, but the degree of crosslinking must be properly adjusted to enable the resin to absorb to some extent the solvent in which it is placed. The ion exchange resins of interest here are constructed to be swelled only to a limited extent by aqueous solutions. Polymers which are too highly crosslinked are not sufficiently swelled, which restricts the mobility of the counter ions to such an extent that ion exchange no longer occurs.

The Ionics CR-70 membranes consist of a copolymer of divinylbenzene and acrylic acid, which provides carboxylic acid groups for the ion-exchange function. The membranes which were evaluated at NRL had been stored for at least two years in a sealed polyethylene envelope containing an aqueous solution of 10% NaOH to prevent drying out and cracking of the resin.

CELL OPERATION

The assembled cell was operated with an aqueous solution of 18% Na_2SO_4 to compare its operation with that of the two-diaphragm cell (2). At a current density of 100 amp/sq ft, 2N NaOH was produced with a cathode feed rate of about 9 cc/min, while 1N H_2SO_4 was generated with a center feed rate of about 19 cc/min. Concentrations as high as 4N NaOH were obtained. Such alkali concentrations, however, required a very clean system to avoid foaming difficulties. Cell temperatures were usually around 50°C, and the lowest cell voltage required was 4.65 v. The current efficiency for O_2 ranged from 94 to 99%, while the current efficiency for NaOH was 92%.

Difficulties appeared after several short runs, and the membrane ruptured after a total service time of 15 hr. During these intermittent operations the cell had been secured with about a liter each of alkali and acid in their respective compartments after each run. In this standby condition the acid could enter the center compartment by back-diffusion through the porous diaphragm. No alkali was present to neutralize this acid since it was restrained in the cathode compartment by the membrane. The acid attack developed a white and uneven surface on the membrane, whereas the resin on the cathode side still retained its normal brown color. The white material proved to be asbestos used for reinforcement of the resin. It was, therefore, necessary to keep the central feed compartment neutral or slightly basic at all times, not only to prevent deterioration of the asbestos backing, but also to maintain the efficiency of the resin. A basic condition is required to keep the resin in the Na^+ form. Reversion to the H^+ form decreases the electrical conductivity of the membrane because the carboxylic acid group, a weak acid, does not ionize to any appreciable extent.

Two other membranes of the same type as the first were tried, and these gave similar results, with the exception that membrane deterioration by acid attack was prevented.

TEFLON-BACKED MEMBRANES

Teflon-backed membranes with CR-70 resin had been used in the original 2800-hr tests which had resulted in the recommendation of the Ionics cell for use in the sulfate-cycle system (3). Two of these membranes were ordered from Ionics, but they proved to be available only in experimental quantities. According to Ionics a different process had been used in the manufacture of the earlier membranes, so that the newly supplied

Teflon-backed membranes had a water content of perhaps only 2% to 3%, which was much lower than that present in the asbestos-backed membranes. The company suggested a pretreatment using strong caustic solution and heat for prolonged periods to condition the resin structure to a conductive state. One suggested method called for soaking the membranes in an aqueous solution of 20% NaOH at 60°C for 30 days. An alternative conditioning method required three days. The membranes were to be immersed in a methanol solution containing 2% NaOH at room temperature for one day, then transferred to an aqueous solution of 20% NaOH at room temperature for another day. Each membrane was then to be placed between two electrodes in an aqueous solution of 20% NaOH, and a dc voltage was to be applied gradually to allow the current to increase to a value of 2 amp/sq in. of membrane area over a period of two hours. This current density was to be maintained for another four hours.

It was decided to use the electrical conditioning method, although power requirements were considerable for a membrane area of 42 sq in. The conditioning method appeared to be succeeding, since the voltage decreased with increasing current until the specified current density was achieved, but there was very little change in the voltage during the four-hour holding period. When these membranes were tried in a test cell with 18% Na_2SO_4, however, the improvement in conductivity was both disappointing and temporary. The feed solution at this time was slightly basic, so that the trouble could not have been in reversion from the Na^+ to the H^+ form. Other attempts were made in conditioning the membranes at 2 amp/sq in. for longer periods than four hours, but to no avail.

MEMBRANE CONDUCTIVITY

The electrical conductivity of an ion-exchange membrane is essentially determined by the concentration of its mobile ions. Factors which yield high specific conductivity are as follows (4):

1. High concentration of the fixed ionic groups, which determines the concentration of the mobile ions
2. Low degree of crosslinking of the ion exchanger
3. Small size and low valence of the counter or mobile ions
4. High concentration of the solution which is in equilibrium with the ion exchanger
5. Elevated temperature.

Comparison of the conductivities shown under similar conditions by the same ion-exchange resin on the two different backing materials, asbestos and Teflon, eliminates all but the first two factors as pertinent items in the conditioning problem.

The degree of crosslinking is indicated by the nominal DVB content, which refers to the mole percent of pure divinylbenzene in the polymerization mixture. Lower DVB crosslinkage permits greater swelling and increased ionic activity but weakens the structure. Higher crosslinkage improves physical properties and chemical resistance but interferes with ion exchange. As water content varies inversely with crosslinkage, the Teflon-backed membranes must have been highly crosslinked. In conditioning, the membranes were first soaked in methanol, since weak acid resins in the H^+ form swell more strongly in methanol than in water (4). (This is an exception to the general rule that structural similarity of the solvent molecules and the organic constituents of the resins favors swelling.) The H^+ form was then converted to the Na^+ form by soaking in the strong caustic solution. In the Na^+ form swelling is more pronounced in polar solvents

with higher dielectric constants such as water ($\varepsilon = 81$) than in less polar solvents (for pure methanol $\varepsilon = 32$).

In the conditioning process some swelling was apparent, since conductivity did improve to some extent, but this either was not enough or was only part of the problem. The source of difficulty in conditioning could not be readily determined because the membranes might have been damaged by being subjected to a relatively high voltage (20 v) before it was known that conditioning was required; such notification was not furnished with the membrane shipment. Further effort in conditioning these membranes was, therefore, not justified. In addition, other membranes were not readily available from Ionics; and since the delivery time for the two Teflon-backed membranes had been prolonged, further tests were discontinued.

CELL COMPARISON

The submerged operation of the membrane-and-diaphragm cell would tend to make it sturdier and more shock resistant than the two-diaphragm cell (2). Its most important contributions would be the removal of the difficult requirement of constant-porosity diaphragms and the ability to obtain higher concentrations of alkali in a more convenient manner.

Membranes appear to have the desired life and stability in continuous operations. Intermittent operations, however, could be troublesome. Both types of cells need a system of feed purification either to maintain porosity or to prevent a decrease in the ion-exchange rate by the preferential retention of polyvalent ions. The ion-exchange resin must also be kept in its Na^+ state, not only during the time the cell is secured but also during cell operation, to maintain membrane conductivity.

CONCLUSIONS AND FUTURE WORK

The sulfate-cycle system for oxygen generation and carbon dioxide removal aboard nuclear-powered submarines is a feasible system which can incorporate either the NRL two-diaphragm cell or the Ionics membrane-and-diaphragm cell. The membrane cell appears to be more favorably situated in regard to ruggedness, removal of critical diaphragm porosity, and control of NaOH concentrations. Membrane deterioration during cell operation can be minimized by providing the center compartment with a basic feed solution which could be the byproduct of a feed-purification system. The prevention of acid back-diffusion during cell down time requires the removal of all acidity. This could presumably be arranged through proper cell design to require minimum time and effort.

No further work appears profitable on the Ionics electrolyte cell pending the outcome of the ten-man prototype ion-exchange system for O_2 generation and CO_2 absorption.

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Chapter 11
Studies of Oxygen Production by Algae

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

INTRODUCTION

Factors affecting oxygen production by the alga, Chlorella pyrenoidosa, have been studied at NRL for several years; the principal results are contained in NRL Report 5954 (1). The algae system is sufficiently reliable for submarine use, and the expected volume requirements for the equipment needed would be competitive with existing systems, but its major disadvantage is the high power requirement of approximately 32 kw per man. A breakthrough in lighting technology is needed to change the prospects for adoption of the algae system by the submarine fleet.

Research on Chlorella pyrenoidosa (Sorokin strain) is being continued for several reasons: (a) the high growth rate of the strain used lends itself well to many basic studies of photosynthesis, (b) equipment available at NRL provides facilities for useful studies not likely to be made elsewhere, and (c) the Navy's interest in photosynthesis reflects its increasing awareness that more must be known of the biological aspects of oceanography. Some of the experimental data presented in this report will have application for the latter use as well as for problems in photosynthetic gas exchange.

The major areas investigated during the report year have been:

1. Chemical analyses of cells grown under different conditions
2. Effects of pressures up to 50 psi
3. Effects of magnetic fields
4. Development of equations relating O_2 production to light intensity, suspension depth, etc.

EXPERIMENTATION AND RESULTS

Inorganic Content of Cells

Suspensions which were cultured under greatly varied conditions in the six-lamp unit were centrifuged and washed, then analyzed for N, P, Mn, Cu, Fe, and K. Only slight differences in concentrations of each element from the control conditions to the test conditions were found, despite the extreme culture conditions employed, e.g., exposing a culture to a light intensity of 25,000 ft-c while only air, but no CO_2, was being bubbled through for two hours. One common effect was noted, however: culture conditions which were inhibitory to oxygen production produced cells which were slightly enriched in phosphorus, 2.10 to 2.23%, compared with 1.65 to 1.68% for the controls.

Effect of Pressure

It was reasoned that an increase in CO_2 solubility, obtainable by imposing pressure on an algal suspension being fed with an air-CO_2 mixture, would provide an increase in O_2 production by the culture. An apparatus was designed therefore (Fig. 13) to impose pressures up to 50 psi on a mass culture of algae. In order to detect any interactions between pressure and degree of CO_2 saturation (in this context, CO_2 saturation is that rate of CO_2 input sufficient to give maximum O_2 production at a given light intensity), three input rates were used, corresponding to CO_2 saturation, 60% CO_2 saturation, and 30% CO_2 saturation. Only one light intensity, 11,000 ft-c with 175 v on the lamp, was used in this study. Details of the procedure are contained in a recent report (2).

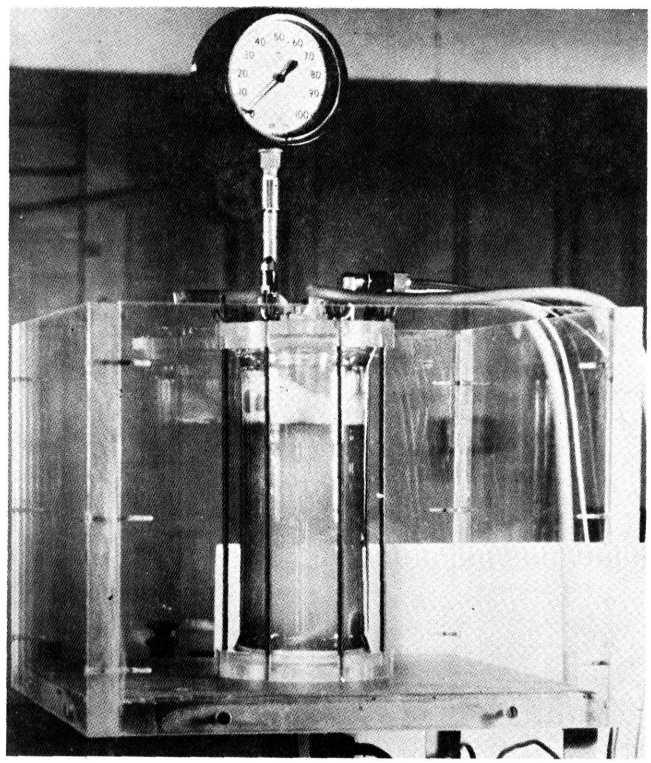

Fig. 13 - Apparatus used in pressure studies of Chlorella

Figures 14 through 18 represent O_2 production as a function of CO_2 input rate and the time exposed at various pressures. The first point on each curve denotes the O_2 production of the unit at atmospheric pressure, and succeeding points show O_2 production versus time at the pressure indicated. Two conclusions are apparent: (a) at the two lower CO_2 input rates, pressure increased O_2 production, temporarily at least, and (b) when the system was CO_2 saturated, at the highest input rate, pressures above 10 psi progressively inhibited O_2 production.

In these experiments with CO_2-air mixtures, the algae may be responding to changes in CO_2 tension, O_2 tension, pH, and pressure itself. It was possible to rule out pH as a

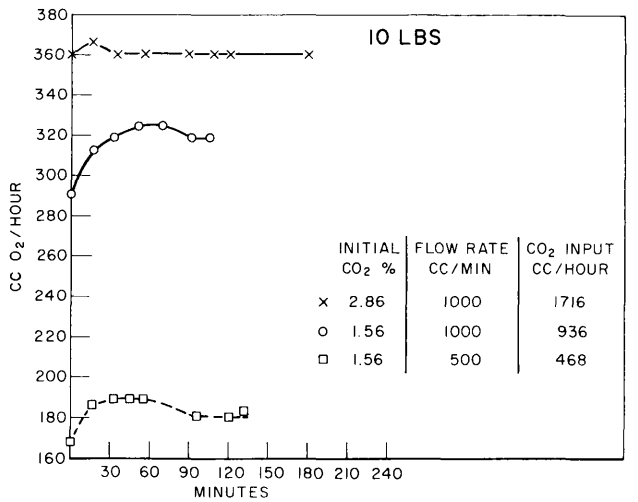

Fig. 14 - Effect of pressure on O_2 production by Chlorella, 10 lb gage pressure

factor in the experiments described because the pH was shown to remain constant even at the highest CO_2 input rates used. Individual effects of O_2 tension and CO_2 tension are being resolved by a series of experiments in which gas mixtures containing various amounts of CO_2 and O_2 with N_2 are used to aerate algal cultures.

Effect of Culture Depth

In the previous report of this series (3) preliminary work was described concerning the influence of culture thickness on O_2 production by cultures in the linear phase of growth. (A culture is in the linear phase of growth when the mass of the cells increases linearly with time.) A cylindrical unit in which the depth of the annular culture chamber

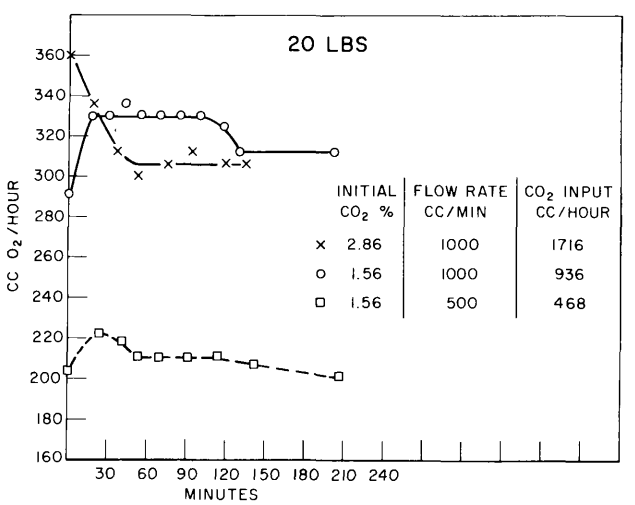

Fig. 15 - Effect of pressure on O_2 production by Chlorella, 20 lb gage pressure

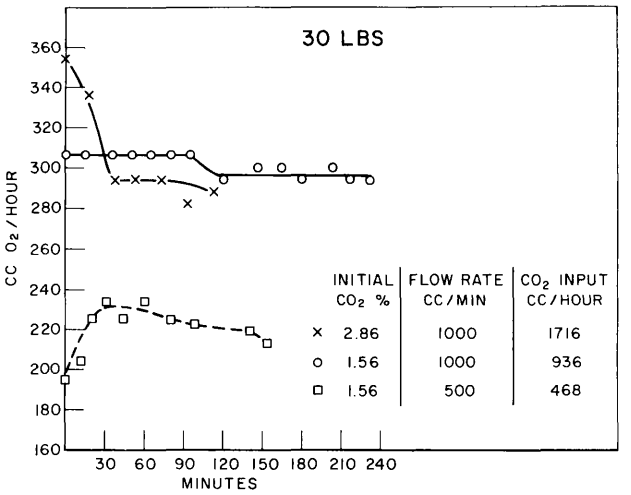

Fig. 16 - Effect of pressure on O_2 production by Chlorella, 30 lb gage pressure

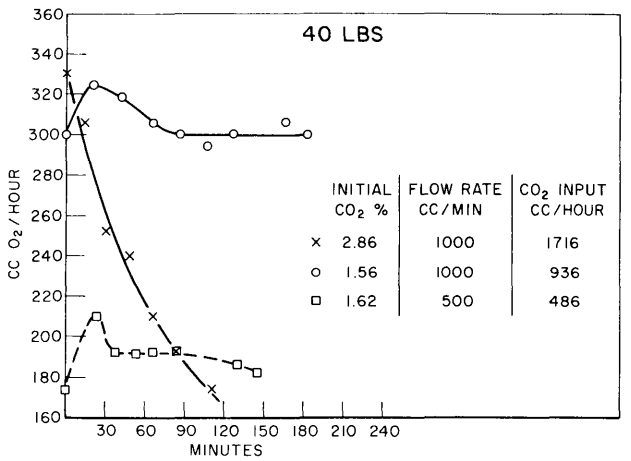

Fig. 17 - Effect of pressure on O_2 production by Chlorella, 40 lb gage pressure

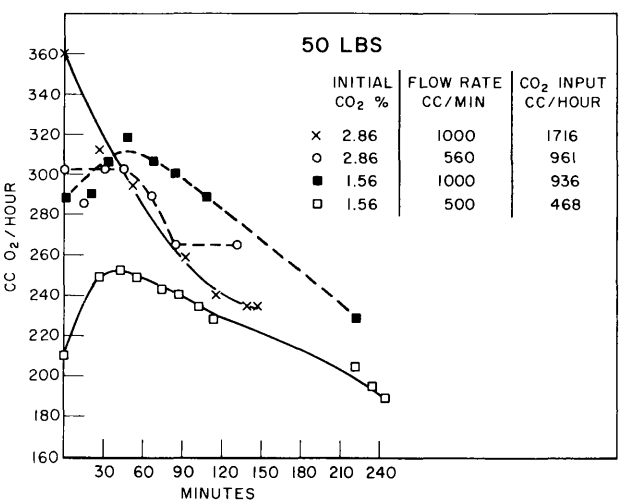

Fig. 18 - Effect of pressure on O_2 production by Chlorella, 50 lb gage pressure

can be varied from 1.0 to 2.9 cm has been used. For the three culture thicknesses considered, the O_2 output of the culture unit increased logarithmically with light intensity and decreased with culture thickness. However, a definite relationship could not be established between O_2 production and culture thickness because of the limited data available. To determine this relationship, O_2 production measurements have been made at several light intensities for two additional intermediate culture thicknesses.

The O_2 production of the five culture chambers has been calculated on the basis of a liter of suspension, and the results (Fig. 19) have been plotted against the logarithms of the light intensities. The rate of O_2 production is seen to be higher, the thinner the culture chamber. In order to relate O_2 production to culture thickness, the rates taken from the graph were plotted against the reciprocal of the culture thickness for four light intensities. Figure 20 shows that the curve is almost a straight line over the range of culture thicknesses and light intensities.

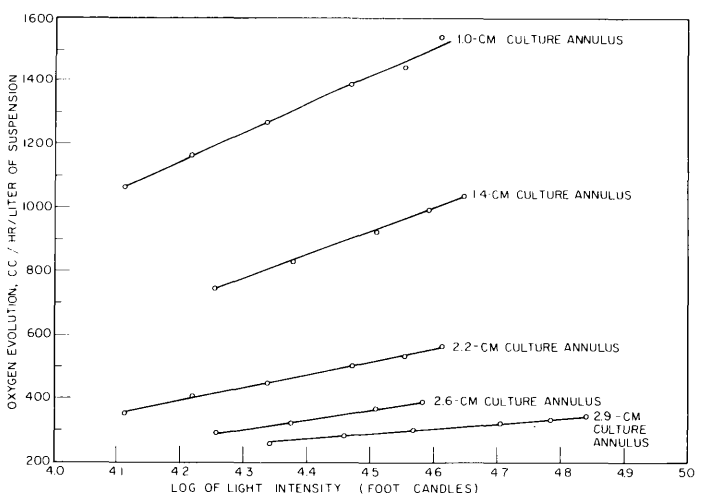

Fig. 19 - Effect of light intensity on O_2 production at five culture thicknesses

An explanation for the inverse relationship between O_2 production per liter of suspension and culture thickness is as follows: for a given culture volume, the illuminated area (the inner surface of the culture annulus) decreases with increasing culture thickness; consequently the average illumination of each cell is decreased. If the O_2 production of the culture unit were determined solely by the extent of the illuminated area, the O_2 evolution rate per liter of suspension would vary with culture thickness in the same way that an illuminated area per liter of suspension changes with culture thickness. The shape of the curve obtained by plotting illuminated area of suspension against the reciprocal of the culture thickness is very similar to those shown in Fig. 20 where O_2 production is plotted against the reciprocal of suspension depth for four light intensities. This demonstrates the importance of illuminated area in the O_2 production of any culture unit.

An empirical relationship, the derivation of which will be given in a forthcoming report, has been obtained which summarizes the experimental observations in this study and gives the expected O_2 yield of this culture unit at a given light intensity, culture thickness, and culture volume. This equation was tested on the six-lamp culture vessel used at NRL by comparing the predicted O_2 production with experimental values. In this unit the light sources are arranged symmetrically, but the light path (culture thickness)

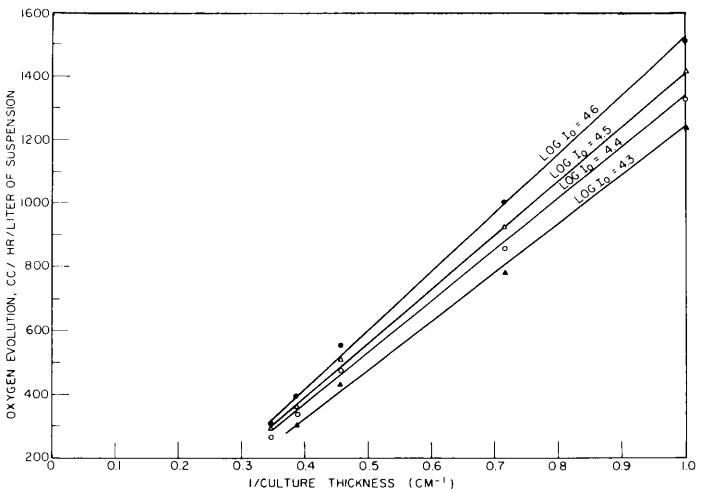

Fig. 20 - Effect of culture thickness on O_2 production at various light intensities

varies from about 1.6 to 4.5 cm so only an average culture thickness can be estimated. However, by inserting this value into the empirical expression aforementioned, excellent agreement between predicted and experimental values was obtained as shown in Table 8.

Table 8
Comparison of Experimental and Calculated
O_2 Production for Six-Lamp Culture Unit

Lamp Voltage	Intensity (Foot-Candles*)	O_2 Production (cc/hr)	
		Calculated	Observed
170	9,000	2290	2350
200	15,000	3310	3300
228	23,000	3940	4000
245	30,000	4240	4240
260	34,000	4450	4500

*As measured by G.E. Light Meter.

The excellent agreement between the observed and calculated O_2 production rates suggests that the equation derived has general applicability because the configuration of the six-lamp unit differs greatly from the one-lamp culture unit which provided the basis for the calculations.

Estimated Space and Power Requirements for One-Man Unit

If one assumes that the culture depth used in a one-man unit would be 1 cm, it is possible to estimate the space and power requirements of that unit when various voltages are applied to the incandescent light sources. In arriving at these estimates it was assumed that one man consumes 25 l of O_2/hr (STP). Table 9 contains a summary of these calculations.

Table 9
Estimate of Electrical Power and Space Requirements for One-Man Gas Exchanger

Power (w)	O_2 Output (cc/hr/l suspension)	Volume* (cu ft)	Power (kw/man)
846	740	2.69	29
900	825	2.58	27
1023	885	2.41	29
1225	965	2.19	32
1370	1005	2.11	34
1520	1076	1.98	35

*Volume includes culture volume and cooling space between light source and culture, but does not include auxiliary equipment such as stirring motors, blowers, etc.

The Treadwell electrolytic O_2 generator, capable of providing O_2 for a 100-man crew, occupies 175 cu ft of space and requires 75 kw. Table 9 shows that the space required for a 100-man algal unit would be competitive with that required by the Treadwell generator, but the power demands of the algal unit would be 40 times greater. The most obvious way to reduce the power and space requirements would be to use a lesser culture thickness, but it is difficult within a narrow annulus to provide sufficient agitation for the suspension to prevent the cells from sticking to the walls.

Effect of High Magnetic Fields

In recent literature, the effects of magnetic fields on snails and worms (4) and plant seedlings (5) have been described. More pertinent was the demonstration of the presence of free radicals in illuminated chloroplasts (6), suggesting that some effect of magnetic fields should be detectable in the performance of green plants. To determine the extent of such an effect, an algal culture apparatus was designed to fit inside the bore of a large electromagnet, which is a facility of the Solid State Division at NRL. The equipment has been fully described elsewhere (7); it consisted of a G.E. Quartzline lamp suspended through the center of the culture chamber, an algal suspension circulated through the chamber by a centrifugal pump, and a constant CO_2-air supply was provided by a large cylinder of compressed gas.

Respiration measurements were made at 100,000 gauss, and photosynthesis measurements were made at 10,000 gauss. Because of the vibration induced in the filament of the light source by the interaction of the magnetic field and the ac of the filament, it was not possible to measure photosynthesis at field strengths above 10,000 gauss. Even at this level the filament snapped after 40 min; at 25,000 gauss the filament broke after only 3 min. However, the results with both the photosynthesis and respiration measurements showed no relation between magnetic field and O_2 production. These experiments were brief, so no estimate of any long-term effects is possible. The demands on the magnet facility at NRL are so great that no extension of the studies is now planned.

DISCUSSION

Composition of Cells

Extreme changes in culture conditions result in only minor changes in the inorganic composition of cells, but several generalizations may be made: (a) low O_2 production

correlates well with a relatively high P content, (b) cells exposed to high light intensities and air, but no CO_2, have a low Cu content and a K content 50% above normal, and (c) while the cells were becoming adapted from a concentrated culture medium (devised by the Army laboratories at Natick, Mass.), there was a gradual increase in Mn content from 0.004% to 0.007%. This latter trend is interesting because Mn has been shown by Tanner (8) to play a key role in the photosynthesis process.

The significance of these observations is not understood at present, but further correlations between cell performance and cell composition are being sought.

Oxygen Production as a Function of Suspension Depth

The inverse relationship found between O_2 production and suspension depth (despite a corresponding increase in suspension volume) seemed paradoxical and, indeed, was questioned by some capable research men. It is now apparent that O_2 production is a function of the light intensity and the illuminated area, and an increase in suspension depth results in a lesser exposure of cells to the light source. This results in a lower photosynthetic rate per cell.

Another consequence of an increase in depth of the suspension is the increase in the number of cells in the dark which are absorbing oxygen in a respiration process. It has been found here that the photosynthetic rate and the respiration rate vary greatly according to the culture conditions; the more favorable culture conditions increase both the photosynthetic rate and the respiration rate, and the O_2 production of the culture is the difference between these factors. Research on the quantitative determination of respiration rates is continuing, the intent being to define the respiration rate while cells are photosynthesizing as well as when they are in the dark. Literature references to this problem are often contradictory.

Pressure

The variable effects of pressure on O_2 production are interesting for several reasons. For example, the beneficial effect of pressure when the system is CO_2-deficient may have a bearing on the design of a gas exchanger for submarine use. In order to provide maximum O_2 production from a minimum of algal suspension, the light sources must be operated at high intensities which necessitate a high CO_2 input rate. But if the atmosphere of the submarine contains 1% CO_2 or less, an extremely high gas flow rate would be necessary to satisfy the CO_2 requirement. Under these conditions of CO_2 limitation, pressures as low as 10 psi would be helpful.

A relevant aspect of the pressure effect on algae concerns the natural growth of phytoplankton in the sea. It has been assumed generally that the growth rate of aquatic plants is limited by nutrient and light availability, but the results obtained in this study indicate that pressure also might be a factor in their growth. Twenty pounds of hydrostatic pressure are reached at a depth of approximately 40 ft, and the photic zone is said to extend to approximately 300 ft. It is reasonable to assume, therefore, that pressure may be a factor in the growth of phytoplankton. Laboratory experiments under conditions found in the sea would clarify the point.

FUTURE PLANS

Changes in the respiration rate under various culture conditions are of interest because they affect the net O_2 production of the culture. Therefore, preliminary studies on

the factors affecting respiration are underway with the hope that a better understanding of this process will enable us to improve the O_2 productivity of a culture.

The effects of pressures as slight as 10 psi have been so evident that studies in this area are being continued. For example, other investigations on the effects of pressure have shown that the temperature optimum of an organism may be changed, with pressures of hundreds of atmospheres effecting a change of several degrees in the temperature optimum. It is not likely that the small changes in pressure used here would make a significant change in the temperature optimum, but the point should be investigated.

Some of these experiments with pressure should be run at a different light intensity to determine the importance of this variable on the effects already studied. For example, it would be interesting to know whether growth under low light intensities, such as those found at 20 to 30 ft below the sea surface is affected by pressure. Probably the natural growth of algae under such conditions is limited predominantly by light and nutrient availability, but this has not been established.

Light sources rich in the red region of the spectrum have been of interest because of the efficiency of algae in using red light. There was no intense red light source available, however, to provide the energy for mass cultures until Vitro Laboratories developed an arc lamp of pressurized neon. One of these units has been ordered for use at NRL for two purposes: (a) to determine the efficiency of algae in using intense red light and (b) to provide much higher intensities than have been available in the past, regardless of wavelengths used.

Two problems directly concerned with mass cultures of algae for shipboard use are to be studied. The first concerns the sticking of algal cells to glass walls; a laboratory method to determine the relative effectiveness of various glass coatings in preventing such sticking has been satisfactory in preliminary trials. If the method is sufficiently reliable, a study will be made of the effect of various culture conditions on the sticking characteristic of the cells. The second area of study concerns the effect of culture depths less than 1 cm on O_2 production. Undoubtedly O_2 production will increase as the culture depth is decreased, but the practical problems of providing sufficient turbulence within such a narrow annulus remain to be solved.

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Recommendations

Each year the major recommendations contained in this annual report are implemented by the respective activities to a degree, but the major atmospheric problems of the following year can inevitably be traced to slowness or incompleteness in implementation of these recommendations. Undoubtedly much of the delay is due to normal time-consuming processes and to the size of the tasks, coupled with shortages of funds and qualified personnel, but possibly these recommendations should be taken more seriously. To accent the repetition in these recommendations to the Bureau of Ships, all of last year's recommendations are herewith repeated, with appropriate remarks and with the major items first.

1. A specific program initiated at the Marine Engineering Laboratory was aimed at determining the degradative effect of nuclear submarine atmospheres on materials. This continues as but a minor program and falls far short of the needed determination of composition specifications required for materials used in construction of or going aboard nuclear submarines. With the coming procurement of a rapid-scanning mass spectrometer and auxiliary equipment, NRL will be able to perform a portion of this requirement but cannot commit personnel and resources to do more than monitor the program.

2. The Habitability Data Book should be revised and more complete information should be disseminated to all shipbuilders to assist them in modification of equipment and procedures to minimize atmospheric contamination.

3. Proper quality control should be required in the initial production of the Mark IV Atmosphere Analyzer and in replacement parts, and ships and shipbuilders should be required to return faulty components to the manufacturer for replacement, and should improve training of shipboard personnel in operation and upkeep.

The following recommendations, also for Bureau of Ships action, although possibly not so urgent, acquire more importance with the passage of time:

4. The development of the ion-exchange system for O_2 generation and CO_2 absorption, by Ionics, Inc., should be continued as long as the system demonstrates its earlier promise.

5. Major design improvements are required in the CO_2 scrubber, including better quality valves and sea water pumps, avoidance of MEA ejection into the atmosphere, and provision of battery-quality makeup water.

FURTHER ACTION BY NRL

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

1. All research and development will continue to be performed with the view of applicability toward an integrated air-purification system (an objective which should also be furthered by the Bureau of Ships).

2. Studies on the causes of MEA degradation, although essentially completed, will be discontinued as soon as an adequate degradation inhibition system is obtained and the causes can be ameliorated by Bureau of Ships action.

3. Investigations should continue on: (a) refinements on the Mark IV Atmosphere Analyzer, (b) methods of air sampling and analysis, including infrared and mass spectroscopy and gas chromatography, (c) the chromatographic atmosphere analyzer, (d) the CO_2-H_2 reaction which might eliminate the need for pumping these gases overboard, (e) innovations on manufacturer-furnished chlorate candles (near completion) and improved filters for the candles, and (f) a satisfactory water-thinned, nonflammable paint for application while submerged.

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

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

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (BuShips, BuWeps, and Special Projects Office)

13. ABSTRACT

This annual progress report supplements NRL Reports 5465 of April 21, 1960, 5630 of July 14, 1961, 5814 of August 29, 1962, and 6053 of December 31, 1963, which provided a comprehensive review of the past and present research and development effort of the U.S. Naval Research Laboratory on the atmospheric habitability of submarines. Emphasis is at present being devoted almost exclusively to nuclear-powered submarines. Considerable progress has been made in the major efforts of developing: (a) improved methods of sampling and analysis of atmospheres, (b) additives to decrease the degradation of monoethanolamine (MEA) in the CO_2 scrubber, and (c) a system for maximum utilization of the carbon in the main ventilation filter. Other topics covered in the present report include the use of algae for oxygen production and carbon dioxide absorption, a study of water-thinned, fire-retardant paints, and a differentiation scheme for look-alike carbon and catalysts.

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Security Classification

14. KEY WORDS		LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Submarine	CO_2 meter						
Atmosphere purification	Latex paints						
Carbon filter	CO/H_2 burner						
Organic contaminants	Monoethanolamine (MEA) stabilizers						
Chlorinated solvents	Ion-exchange membrane						
Gas chromatography	Chlorella pyrenoidosa						
Thermal conductivity detectors	Photosynthetic gas exchanger						
Karmen ionization detector	Oxygen generation						
Mark IV Atmosphere analyzer	Gas analysis						
Capillary-column chromatograph							

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