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**U. S. NAVAL SUBMARINE
MEDICAL CENTER**

Submarine Base, Groton, Conn.

REPORT NO. 452

**CONTROL OF THE CHEMICAL CONSTITUENTS OF
THE SUBMARINE ATMOSPHERE (U)**

by

Richard F. Schillaci

LT MC USN

Bureau of Medicine and Surgery, Navy Dept.,

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ERRATA SHEET NO. 1 FOR SMC REPORT 452

- Page v - List of Tables - delete "(17)" in Table D
- Page 1 - Col. 2-Par. 1-line 3 - seven instead of eight
- Page 2 - under BOYLE'S Law - $P_1V_1 = P_2V_2$ instead of $P_1V_1 = P_1V_2$
- Page 2 - Col. 2-Par. 3-line 4 - delete "This aspect of atmosphere control is considered in greater detail in Pages 32-34"
- Page 2 - Col. 2-Par. 5-line 6 - minus instead of minor
- Page 8 - Col. 2-line 3 - feet instead of foot
- Page 13 - Col. 2-formula - Li_2CO_3 instead of Li_2CO_2
- Page 13 - Col. 2-last sentence - delete "(1)" after "weight)" and add "in the available manifolds determine the operating cycle required to maintain an atmospheric CO₂ concentration of 1% (1)."
- Page 17-Col. 1-Par. 1-SubPar. 1 - contaminants instead of containinants
- Page 17 - Col. 2-Par. 4-line 4 - in instead of is
- Page 19 - Table B-Item 5 - Particulate instead of Particular
- Page 25 - Table E-Col. 2-line 3 - AsH₃ instead of A_sH_2
- Page 26 - Table F-Col. 1-line 1 - Acetaldehyd~~e~~ instead of acetal dehyde
- line 12 - tert-Butylbenzene instead of tert-Buthylbenzene
- Page 27 - Table G-Col. 1-line 6 - Furfuraldehyde instead of Fur Fur aldehyde
- Page 28 - Col. 1-Par. 1-line 7 - acute instead of actute
- Page 28 - Col. 2-Par. 1-line 12 - is instead of in
- Page 31 - Col. 1-Par. 3-line 1 - Beckman instead of Bechman
- Page 31 - Col. 1-Par. 4-line 6 - other instead of outer
- Page 34 - Col. 2-Par. 1-line 17 - alkali instead of alkaki

Page iv - Table of Contents:

- iv should be Page 1
- 1 should be Page 2
- 3 should be Page 4
- 4 should be Page 5
- 5 should be Page 6
- 6 should be Page 7
- 12 should be Page 13
- 14 should be Page 15
- 16 should be Page 17

Page v - List of Figures

- Figure 1 - should be Page 9
- Figure 2 - should be Page 10
- Figure 3 - should be Page 11
- Figure 4 - should be Page 12
- Figure 5 - should be Page 14
- Figure 6 - should be Page 16

- Table A - should be Page 18
- Table B - should be Page 19
- Table C - should be Page 21
- Table D - should be Page 23
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**U. S. NAVAL SUBMARINE MEDICAL CENTER REPORT NO. 452
Bureau of Medicine and Surgery, Navy Department
Research Project MR005.14-3002-9.02**

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SUMMARY PAGE

THE PROBLEM

To present a summary of current principles and methods utilized to evaluate and control the chemical constituents of the submarine atmosphere.

FINDINGS

The general principles and problems involved in maintaining a habitable closed space environment (submarine) are reviewed. The chemical constituents of the submarine atmosphere are presented with regard to their sources, methods of evaluation, and methods of control.

APPLICATIONS

It is intended that this paper serve as a general summary to be used by medical officers and hospital corpsmen in acquainting themselves with the problems of submarine atmosphere control.

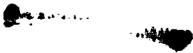
ADMINISTRATIVE INFORMATION

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ABSTRACT

The author presents a summary of the current principles and methods used to monitor and control the chemical constituents of nuclear submarine atmospheres. The paper includes discussion of applicable gas laws, units of measure, oxygen supply, CO₂ removal, removal of gaseous and particulate contaminants. The principles of operation of the atmosphere analyzer, portable gas analyzers, CO/H₂ burner, electrostatic precipitator, and carbon filtration are discussed. This monograph is of interest to all concerned with 'closed space' atmospheric control, and is of especial interest to the submariner. (U)

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CONTROL OF THE CHEMICAL CONSTITUENTS OF THE SUBMARINE ATMOSPHERE

LT Richard F. Schillaci, MC, USN

INTRODUCTION

The prolonged periods of submergence which characterize current submarine operations make mandatory strict monitoring and rigid control of the atmosphere within these vessels. While they are operating on the surface of the sea or when snorkeling, a fresh supply of air can be drawn from outside the ship while removal of 'stale' or contaminated air can be accomplished simultaneously via the diesel(s) and/or the outboard ventilation exhaust system.

When completely submerged, however, the submarine crew must live and work within a sealed environment of varying composition for continuous periods of several hours to several months' duration. During these periods, the volume of air within the submarine is constantly recirculated by large fans located in the ventilation system. Except for certain overboard machinery exhausts, all contaminants must be released

into this volume of air and subsequently removed from it by atmosphere purification equipment. Similarly, oxygen must be continually added to the atmosphere in order to support life.

A discussion of the components of the submarine atmosphere and the factors which affect it is contained in the eight sections which follow. There is a presentation also of the units and methods of measurement for gases and contaminants, and of the types of equipment available for control of the submarine's atmosphere.

The primary components of the submarine atmosphere, and most of the contaminants within it, are gases. The atmosphere, therefore, varies as the results of the interrelated effects of temperature, volume, and pressure. The laws which govern these effects are stated and discussed in the section which follows.

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TEMPERATURE, VOLUME, AND PRESSURE

The various laws which describe the behavior of gases are listed below:

BOYLE'S LAW - If the temperature of a fixed mass of gas is held constant, its volume will vary inversely with the absolute pressure.

$$P_1 V_1 = P_2 V_2$$

Where: P_1 = Initial pressure
(Absolute)

V_1 = Initial volume

P_2 = Final pressure
(Absolute)

V_2 = Final volume

GAY-LUSSAC'S LAW - If the pressure of a fixed mass of gas is held constant, its volume will vary directly with the absolute temperature:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Where: V_1 = Initial volume

T_1 = Initial temperature
(Absolute)

V_2 = Final volume

T_2 = Final temperature
(Absolute)

DALTON'S LAW - The total pressure exerted by a fixed volume of a mixture of gases is the sum of the individual pressures that would be exerted by each of the gases if it alone occupied the same volume. Stated more simply; the pressure exerted by a mixture of gases is the sum of the partial pressures of the component gases.

GENERAL GAS LAW - Combines the principles stated by Gay-Lussac's and Boyle's laws.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

HENRY'S LAW - The amount of a gas that will dissolve in a liquid at a given temperature is almost directly proportional to the partial pressure of that gas. (This tells us that as the partial pressure of a gas increases, its physiological effect will increase because its solubility in the blood increases.)

Current atmosphere control equipment effectively maintains the temperature of the submarine atmosphere within habitable limits. This aspect of atmosphere control is considered in greater detail in Pages 32-34.

The volume of air within which the submarine crew lives and works is approximately equal to the floodable volume of their ship. Depending upon the class of ship, this volume may be from about 35,000 to over 160,000 cubic feet. Since this volume is contained within the rigid pressure hull, it does not change significantly and variations in temperature and/or pressure affect the atmosphere in accordance with the gas laws.

An attempt is made to maintain the pressure within the submarine as near to normal atmospheric pressure as possible. In most instances this can be achieved with occasional and gradual pressure changes on the order of plus or minus two to three inches of mercury.

Relatively rapid pressure build-up may result from the venting of various tanks inboard (fuel tanks, depth control tanks, etc.) or extensive use of the torpedo tubes. This condition is correctable via use of the ship's air compressors to pump air from the interior to the high pressure air banks.

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Decreased pressure may result during snorkeling evolutions when the snorkel induction valve ("head valve") closes. This occurs automatically whenever the head valve is submerged due to high waves in rough weather or loss of depth control. Air for combustion is then drawn from the interior of the ship and a relative vacuum is produced. The head valve reopens when it again clears the surface and there is then a rapid equalization of pressure with the outside. Although a low pressure cutout will automatically shut down the diesel(s) if too great a vacuum is produced, rapid opening and closing (cycling) of the head valve occurs frequently. The ensuing transient pressure fluctuations produce little significant physical damage, but can be extremely annoying to the crew;

especially when occurring for prolonged periods and/or during the hours of sleep.

A local area of low pressure may be produced rapidly in an individual compartment as the result of an improper ventilation line-up during a drill calling for emergency ventilation of the compartment. This is a transient situation which is extremely hazardous when unrecognized, and can result in personnel casualties should a water-tight door be opened carelessly.

Decreased pressure may also result from the use of air compressors to charge the ship's air banks while submerged. This is a controlled pressure decrease, usually of low magnitude, and rarely presents any habitability problem.

UNITS OF MEASURE

Various units of measure are employed when considering the chemical constituents of the atmosphere. The choice of a unit of application to a specific constituent is usually based upon the desire to express the acceptable limit or commonly encountered concentration as a small whole number. Conversion from one unit to another may be utilized when comparative concentration data are required.

The following are the units of measure most often employed:

PARTIAL PRESSURE: The physiologic gases are frequently discussed in terms of their partial pressures expressed as millimeters of mercury (mm Hg). This term is derived from the absolute percentage and the ambient pressure. For example, air at atmospheric pressure (760 mmHg) containing 20.5% oxygen would have an oxygen partial pressure (pO_2) of:

$$0.205 \times 760 = 155.8 \text{ mm Hg } pO_2$$

It will be seen that as the ambient pressure changes, the pressures exerted by the constituent gases change in the same direction. This is important in that the degree of physiological effect produced by a gas is a function of the partial pressure of the gas.

PARTS PER MILLION (ppm): This unit expresses the actual number of parts of the subject gas present in one million parts of the total mixture under consideration. Conversion from this unit to percentage can be made, as in the following examples:

$$\begin{aligned} 1 \text{ ppm} &= 0.000001 = 0.0001\% \\ 10 \text{ ppm} &= 0.00001 = 0.001\% \\ 100 \text{ ppm} &= 0.0001 = 0.01\% \\ 1000 \text{ ppm} &= 0.001 = 0.1\% \end{aligned}$$

PERCENTAGE (%): This is an expression of the number of parts of the subject gas present in one hundred parts of the total mixture. When referring solely to the actual amount of a gas present, without regard to the physiological effect, the expression is defined as absolute percentage. However,

since the pressure exerted by a component gas (and, hence, its physiological effect) varies as the pressure of the total mixture varies, a term which takes the physiological effect into account is needed. The term effective percentage defines that percentage of the gas under consideration which would, at atmospheric pressure, (760 mm Hg = 30" Hg) produce the same degree of physiological effect as the observed concentration does at ambient pressure. The following equations illustrate the relationship between absolute and effective percentages:

$$\begin{aligned} \text{Effective \%} &= \frac{\text{Observed partial pressure}}{\text{Normal atmospheric pressure}} \\ \text{Absolute \%} &= \frac{\text{Observed partial pressure}}{\text{Ambient atmospheric pressure}} \end{aligned}$$

For example, given an oxygen partial pressure of 130 mm Hg at an ambient pressure of 615 mm Hg:

$$\text{Effective \%} = \frac{130}{760} = 17.1\%$$

$$\text{Absolute \%} = \frac{130}{615} = 21.1\%$$

An understanding of these two terms and the ability to convert from one to the other is essential, since absolute values must be expressed as effective values, if the physiological effects are to be accurately evaluated.

MILLIGRAMS PER LITER (mg/L): This unit, which relates weight to volume, is most useful when considering dispersed liquids or solids (e.g., mists, fumes, dusts). It facilitates the calculation of body uptake data and assessment of hazard, since toxicity data are also frequently reported in terms of weight per volume or weight per weight. The following formula defines the relationship between mg/L and ppm and permits conversion from one unit to the other:

$$\text{mg/L} = \frac{24.45 \times 1000 \times \text{ppm}}{\text{Molecular weight}}$$

Milligrams per cubic meter (mg/M^3) and millions of particles per cubic foot are related terms which are occasionally used.

MAXIMUM ACCEPTABLE CONCENTRATION (MAC): The MAC theoretically represents the greatest concentration of a contaminant to which a person may be exposed for prolonged periods without suffering ill effects. A related term, sometimes used interchangeably with MAC, is "Threshold Limit Value" (TLV). These concepts were developed in the field of industrial hygiene and the values assigned to various contaminants are primarily based on exposure patterns encountered in industry (eight hours per day, five days per week). Many of the levels purported to be maximum limits are, in fact, based on prima facie evidence that no deleterious effect on workers has been noted at concentrations lower than the value cited. In addition, industrial MAC's and

TLV's are usually determined for the situation in which only one toxic agent is of concern. Possible additive or synergistic effects resulting from the simultaneous presence of several toxic substances are not usually taken into account. Nor are values cited for those substances which present no hazard in the industrial setting, but may be deleterious when present as one of several contaminants in the submarine atmosphere.

Industrial MAC's and TLV's, therefore, have limited applicability in the field of submarine atmosphere control where continuous long-term exposure to a complex atmosphere is the rule. They serve as general guides, but are not to be interpreted as absolute limits or unquestionably non-hazardous levels.

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OXYGEN

An average oxygen consumption rate per man of 0.9 to 1.0 standard cubic foot per hour (SCFH) is used to calculate the amount of oxygen required for routine revitalization of the submarine atmosphere, assuming normal crew activity. Addition of oxygen to the atmosphere may be begun immediately upon diving, if a long-duration submergence is anticipated, or may be delayed until a later time when revitalization is indicated by a decreased oxygen level or increased carbon dioxide level in the atmosphere. The calculated amount of oxygen required (number of personnel aboard x average oxygen consumption per man) may be added to the atmosphere from one or a combination of the following sources:

OXYGEN CYLINDERS: Cylinders containing aviator's breathing oxygen (Grade A), located in various compartments, are the primary source aboard conventional submarines. Each cylinder has a volume of 1.63 cubic feet and contains approximately 244 SCF of oxygen at 2200 psig, when full. The Bureau of Ships currently requires that sufficient cylinders be carried to provide 37 SCF of oxygen for each man aboard plus three additional cylinders for emergency use.

Oxygen is released from the cylinders directly to the atmosphere at a rate based upon the decrease in cylinder pressure required to supply enough oxygen for one hour. The required pressure drop may be computed using the formula:

$$P = 13.2 \frac{N}{V}$$

Where: P = Decrease in cylinder pressure (psig) required to release a one hour oxygen supply

N = Number of personnel to be supplied

V = Volume of cylinder (1.63 SCF)

13.2 = Constant (14.7 psia x 0.9 SCFH/man)

OXYGEN BANKS: Large cylindrical flasks located outside the pressure hull comprise the oxygen banks which serve as the routine source of oxygen for most SSN class submarines. Oxygen from shore sources or from electrolytic oxygen generators is stored in these flasks at pressures up to 3000 psig.

When revitalization of the atmosphere is required, oxygen is released from the banks via two bleed stations, one located in the engine room and one in the bow compartment. The oxygen passes through a pressure reducer to a flowmeter calibrated in standard cubic feet per hour, thence into the atmosphere via a diffusing nozzle located adjacent to a ventilation supply outlet. This location assures dispersion of the gas in the compartment and eliminates the hazard of fire or explosion which might occur if "pockets" of oxygen were to accumulate. Normal recirculation of the atmosphere then distributes the oxygen uniformly through the ship.

The size and number of flasks comprising the oxygen banks vary with the class of ship. If these values and the pressure in the banks are known, however, the standard volume (SCF) of the banks can be calculated using the formula:

$$\text{Standard volume (SCF)} = \frac{V \times P}{14.7}$$

Where: V = Volume of the bank (ft³)

P = Pressure in the bank (psia)

14.7 = Normal atmospheric pressure (psia)

Using this value, we can also determine the duration of the oxygen supply present in the banks:

$$\text{No. of days O}_2 \text{ remaining} = \frac{\text{Stand. vol. (SCF)}}{N \times 21.6}$$

Where: N = Number of personnel aboard

21.6 = O₂ consumption/man/day (24 hrs/day x 0.9 SCFH/man)

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ELECTROLYTIC OXYGEN GENERATORS:

The primary source of oxygen aboard fleet ballistic missile submarines (FBM) and some SSN class ships is the monopolar electrolytic oxygen generator which produces oxygen by the electrolysis of distilled water using 30% potassium hydroxide (KOH) as the electrolyte (Figure 1). The generator consists of sixteen electrolysis cells connected in series and is capable of producing 120 SCFH at 3000 psig when the maximum electrolysis current is employed. The oxygen which is generated is pumped to the ship's oxygen banks. Hydrogen is also evolved and is pumped directly overboard, however leakage into the atmosphere does occasionally occur and hydrogen explosions have been reported (1).

In an effort to improve reliability, and to decrease weight and space requirements, several other oxygen generation systems have been evaluated. The bipolar electrolytic generator (Figure 2) is similar to the monopolar type in operation and capacity, but consists of a single large electrolytic cell. It offers the advantages of lower weight and volume, lower power requirement, and lower cost. It also has an integral nitrogen generator, eliminating the need for an external source of nitrogen for routine purging or inerting of the system in the event of a casualty. At present, developmental work by the contractor is continuing, but no anticipated date for service-evaluation aboard an operating submarine has been announced.

The split-cell generator (Figure 3), developed by the United States Naval Research Laboratory, operates on the principle of the battery. The present design consists of 66 nickel-cadmium half cells connected in series and employs potassium hydroxide as the electrolyte. This unit also costs less and requires less power than the monopolar generator. Construction difficulties have been encountered, however, they are not considered to reflect defects in the principles involved. Installation and evaluation of two such units (each with an oxygen generation capacity of 75 SCFH) on two future SSBN class submarines is anticipated (2, 3).

Other systems, capable of generating oxygen and removing carbon dioxide from the atmosphere simultaneously, are currently being developed and evaluated (vide infra).

SODIUM CHLORATE CANDLES:

Compressed chemical candles composed of sodium chlorate (NaClO_3), barium peroxide (BaO_2) and steel fiber provide a compact supplementary source of oxygen. They are employed to extend submergence beyond the capacity of other oxygen sources and in emergency situations. When burned in a specialized furnace (Figure 4) each 26.4 pound candle yields 117-119 SCF of oxygen via the thermal decomposition of sodium chlorate. The following equation depicts the basic process:



Some chlorine is evolved, but the majority of it is absorbed by the barium peroxide ($\text{BaO}_2 + \text{Cl}_2 \longrightarrow \text{BaCl}_2 + \text{O}_2$). Carbon monoxide, iron oxides, and heat are also produced. Analysis of the oxygen produced has revealed the following contaminants in the amounts indicated (4):

Chlorine: None detectable to 3 ppm

Carbon monoxide: 10 to 20 ppm

Water vapor: 3 to 30 mg/L

The sodium chloride by-product is liberated as an aerosol which must be removed from the evolved oxygen. At present the most efficient method for this would seem to be a washable glass-fiber blanket filter developed by the U.S. Naval Research Laboratory and recommended for service-evaluation in submarines (4).

These candles represent a safe and stable source of supplementary oxygen having an indefinite shelf-life and no danger of leakage.

AIR BANKS: Another source of oxygen which may be used in the event of emergency is the air contained in the ship's air banks. By pumping air from the interior of the submarine to an air bank selected to receive contaminated or oxygen-depleted air, the pressure is lowered within the ship. "Clean" air is then bled into the ship from another air bank to revitalize the atmosphere temporarily. The degree of pressure decrease which must be produced hourly, and then restored with "clean" air, may be calculated with the following formula:

$$K = 25 \frac{NP}{V}$$

Where: K = Degree of pressure decrease produced and restored each hour (inches of Hg)

N = Number of personnel aboard

P = Pressure in ship at start of pumping (inches of Hg)

V = Floodable volume of the ship (ft³)

25 = Number of cubic foot of air to be exchanged per man

The amount of oxygen supplied by this technique is relatively small and it should be reserved for the emergency situation.

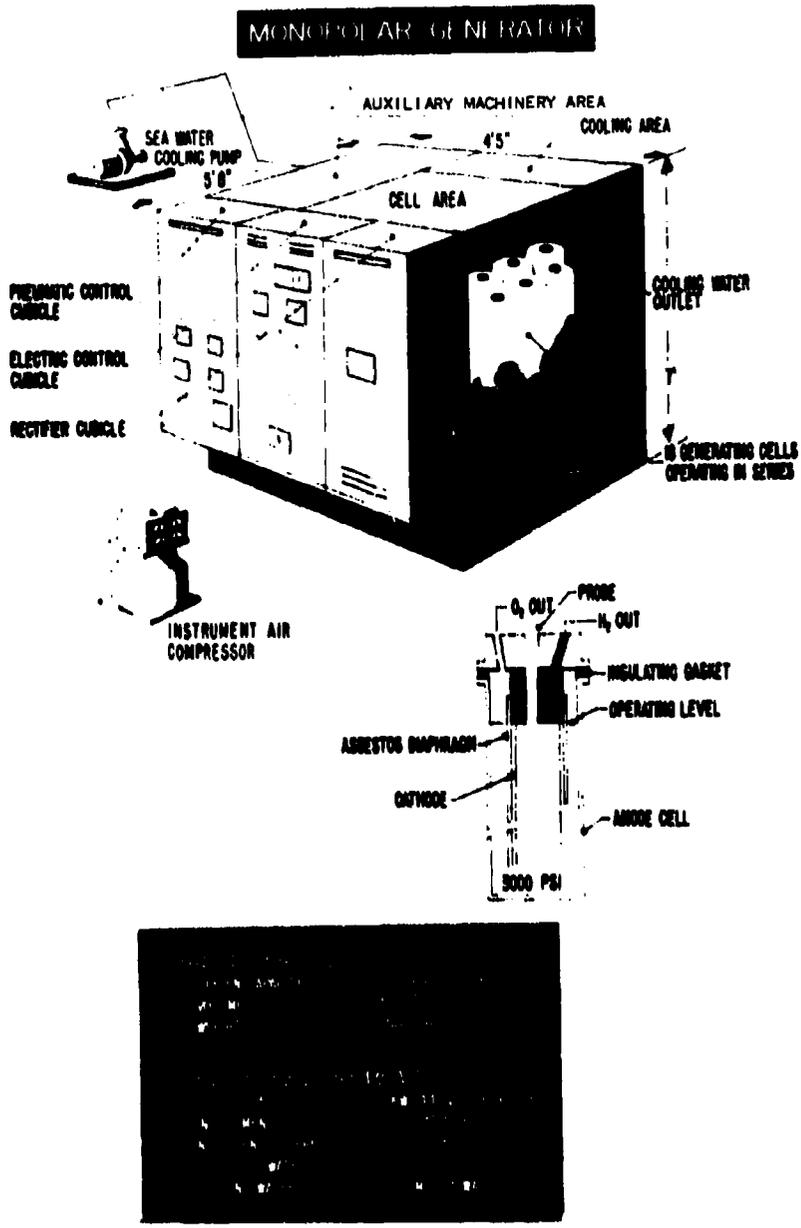
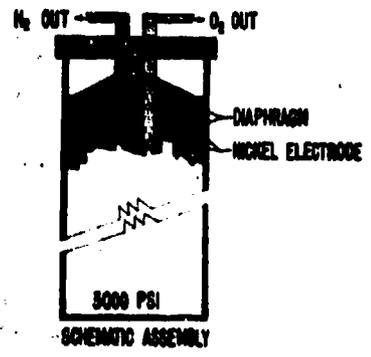
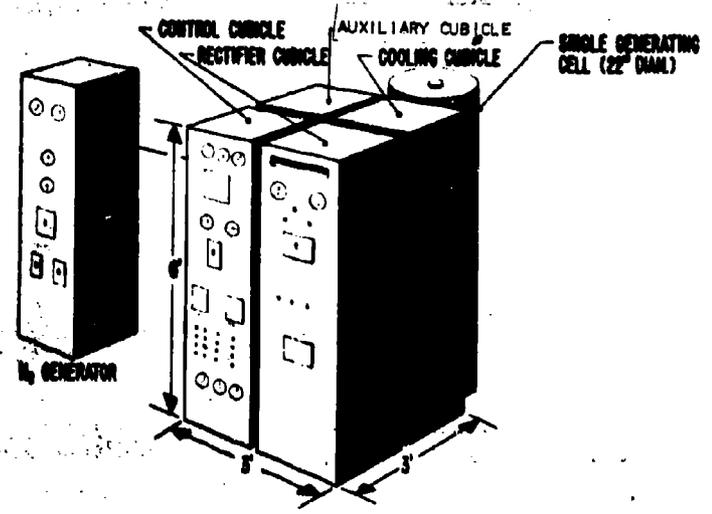


Fig. 1. Monopolar Generator

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BIPOLAR GENERATOR



The bipolar generator is a self-contained unit which produces hydrogen and oxygen gases. It is designed for use in a space environment and is capable of operating at pressures up to 3000 PSI. The generator consists of a control circuit, a rectifier circuit, an auxiliary cubicle, a cooling circuit, and a single generating cell. The generating cell is 22 inches in diameter and contains a diaphragm and a nickel electrode. The generator is rated for a maximum output of 1000 SCFH of hydrogen and 500 SCFH of oxygen. The maximum operating pressure is 3000 PSI. The generator is designed to operate on a 28VDC power source. The maximum current draw is 100A. The generator is designed to operate at a temperature range of -55°C to +55°C. The maximum relative humidity is 95%. The generator is designed to operate on a 28VDC power source. The maximum current draw is 100A. The generator is designed to operate at a temperature range of -55°C to +55°C. The maximum relative humidity is 95%.

Fig. 2. Bipolar Generator

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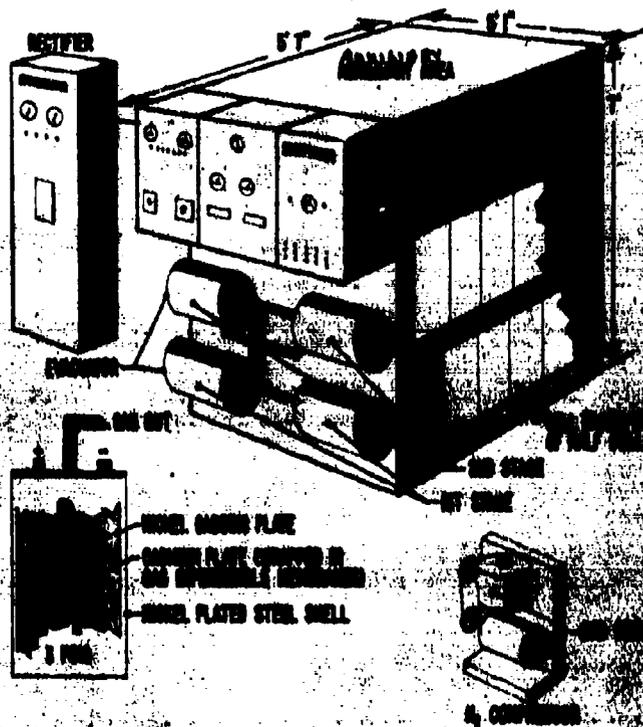


Fig. 3. Split-Cell Generator

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Fig. 4. Oxygen Candle Burner

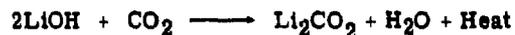
CARBON DIOXIDE

Carbon dioxide is continually liberated into the atmosphere as the result of respiration, smoking and oxidation of contaminants in the CO/H₂ burner. The rate of carbon dioxide build-up in the atmosphere is variable, depending primarily upon crew activity, but experience has shown that for the normal patrol routine an average CO₂ production per man of 0.85 SCFH (0.1 pounds/hour) may be assumed. The acute effects of exposure to CO₂ concentrations in excess of 3% are well established, and this level has been observed for years as the limit for CO₂ in the atmosphere aboard submarines. With the advent of nuclear submarines, however, the effects of continuous exposure to lower CO₂ concentrations have gained increasing interest and importance. Schaefer, et al (5-9) demonstrated that men exposed to 1.5% CO₂ underwent adaptive changes resulting in a period of uncompensated respiratory acidosis during the first 23 days, followed by a compensated respiratory acidosis which lasted until exposure was terminated on the 42nd day. Recovery from acid-base and electrolyte changes was still not complete 28 days after removal from the atmosphere containing 1.5% CO₂. They concluded that the following three tolerance levels for chronic exposure to CO₂ could be delineated:

- 3% and above: Deterioration of performance, alteration of basic physiological functions, and pathological changes.
- 1.5%: Slow respiratory, acid-base, and electrolyte adaptive changes which might produce pathological states on greatly prolonged exposure.
- 0.5% to 0.8%: Probably no significant physiological, psychological or adaptive changes occur.

As the result of information gained from these and similar studies, and the development of equipment capable of removing CO₂ from the atmosphere, the limit for CO₂ in the continuous 90-day exposure situation has been revised downward to the present value of 1%.

LITHIUM HYDROXIDE (LiOH): Earliest attempts to develop an efficient and reliable system for CO₂ removal dealt primarily with the use of solid alkali compounds. Sodium hydroxide in various forms (e.g., soda lime) was evaluated and used for emergency CO₂ removal from 1919 to 1954, but was considered unsuitable because of its highly caustic nature and tendency to produce an irritating dust. Lithium hydroxide was noted to have the same shortcomings, but to a lesser degree; and due to its greater efficiency as a CO₂ absorbent became the mainstay of CO₂ control. When CO₂ removal was necessary, 15 pound cans of crystalline LiOH were opened and their contents spread on mattress covers. The recirculated air within the submarine was thus cleansed of CO₂ via the reaction:



Continued investigation to improve efficiency and minimize such problems as dusting led to the development of the pelletized form of LiOH currently in use. This form is issued in 6.4 pound canisters of compressed LiOH pellets. For routine CO₂ removal, the canisters are opened at both ends and installed in a manifold containing a blower which circulates air through the canisters at a rate of 60 cubic feet per minute (Figure 5). Some dusting does occur with the pelletized form and the manifold contains a mechanical filter through which effluent air is routed during the first few minutes of operation. After this, the filter can be by-passed to permit maximum air flow through the manifold. The number of personnel aboard and the CO₂ absorption capacity of LiOH (1 to 1 ratio by weight) (1).



Fig. 5. Lithium Hydroxide Manifold

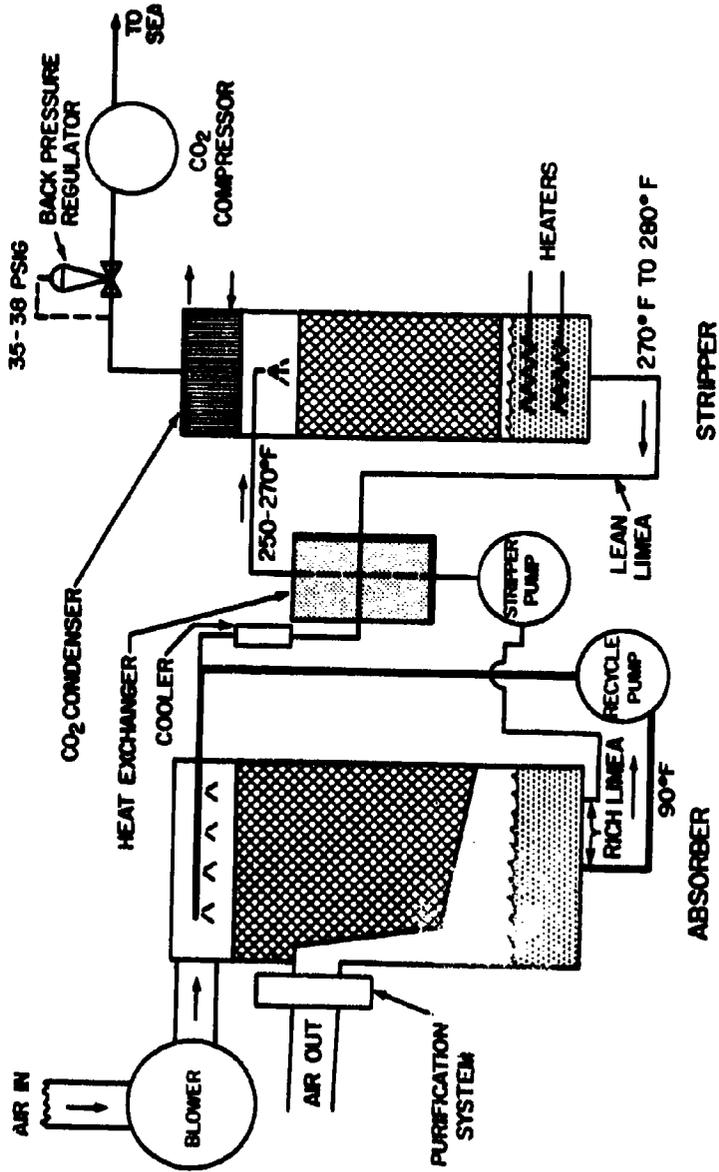
The pelletized form can also be spread. It is routinely employed in this fashion in submarines not equipped with LiOH manifolds or in casualty situations where no power is available to operate the manifold blower.

THE MONOETHANOLAMINE SCRUBBER: The primary means of carbon dioxide removal in SSBN class submarines is the monoethanolamine (MEA) scrubber. This unit operates on the principle that an alkaline amine solution (MEA) will absorb CO₂ when cool and liberate it when heated (Figure 6). The MEA solution is sprayed into a scrubber tower, through which CO₂-laden air is blown, and forms a weak chemical bond with the CO₂. The CO₂-rich MEA is then pumped to a stripper tower where it is heated, liberating the CO₂ which is compressed and discharged overboard. After being cooled, the MEA is again available for passage through the scrubber tower.

Several problems have been encountered beyond the normal increase in maintenance problems as current units age. Trace metallic contaminants (e.g., iron, copper) in the MEA solution have been shown to catalyze the oxidative degradation of MEA, resulting in greatly decreased CO₂ removal efficiency and the formation of peroxides and ammonia (10, 11, 12). Increased MEA stability has been achieved

through the use of a low-iron-content amine compound (LIMEA) and the addition of a chelating agent, the monosodium salt of N, N-diethanol glycine (VFS) (13). Investigation has shown, however, that although VFS acts as a conventional antioxidant to stabilize MEA in the absence of contaminants, it loses its effectiveness when catalytic metals are present (11). The tetrasodium salt of ethylene-diamine tetracetic acid (EDTA), another chelating agent, has been found to be efficient as both an antioxidant and a copper deactivator in MEA solutions (11). Its properties in the presence of other catalytic metals are still being studied, as are other prospective regenerative CO₂ absorbents (14, 15).

Another major problem is the inefficiency inherent in the basic design of the current scrubber. Evaluation has indicated that CO₂-rich MEA leaving the scrubber section contains approximately 46 volumes of CO₂ per volume of MEA (maximum saturation for the 4N MEA employed), whereas the ratio in the solution leaving the stripper section is lowered only to about 37:1(16). Significant reduction of the CO₂ saturation of MEA leaving the stripper section, and concomitant increase in overall scrubber efficiency, is anticipated as the result of an improved stripper design developed at the United States Naval Research Laboratory.



**CO₂ SCRUBBER
SIMPLIFIED FLOW DIAGRAM**

Fig. 6

Fig. 6. CO₂ Scrubber Simplified Flow Diagram

ATMOSPHERE CONTAMINATION

Certain basic assumptions may be made about the dynamics of contaminants in a sealed environment. The following are particularly germane to submarine atmosphere control:

1. The contaminants in a sealed atmosphere derive from endogenous sources.
2. The rate of generation and elimination of commonly occurring contaminants (not those produced in special or casualty situations) can be predicted with reasonable accuracy.
3. With a normal ventilation line-up, contaminants are dispersed almost uniformly through the atmosphere ("one-volume" concept).
4. Removal of contaminants must be accomplished by means within the environment. (Subsequent discharge outside the environment may occur.)
5. The level of a given contaminant in the atmosphere is a function of two variables: rate of contaminant generation and rate of contaminant elimination.
6. The primary route of entry into the body for atmosphere contaminants is via the respiratory system. Therefore, uptake and physiological effects at a given concentration may be influenced by pulmonary and circulatory parameters.

Classification of atmosphere contaminants is usually made on the basis of their chemical composition (Table A), physiological action (Table B), or physical state (Table C). The chemical and physiological properties of many contaminants vary widely with differences in concentration, conditions of exposure, or the aspect of chemical

composition to be emphasized, and reliable data concerning these properties are lacking for many substances. Therefore, classifications based on these characteristics are not considered suitable for submarine atmosphere control application. Physical characteristics, however, provide a more uniform basis for classification when considering the problems of contaminant source, detection, and elimination. At present, this system is the one most used in the field of submarine atmosphere control.

GASES AND VAPORS: Generation of gaseous contaminants occurs via evaporation, volatilization, thermal decomposition, or high level irradiation of some substances. The possible sources of these contaminants are many. For example, Table D lists those substances identified as actual or potential sources of one major group of contaminants known to exist in nuclear submarine atmospheres--the aromatic hydrocarbons, constituting 25-30% of the total hydrocarbon content (17).

Over 200 gaseous compounds have been identified or suspected in the submarine atmosphere (1, 18). Table E lists pertinent data for those compounds which have been quantitatively identified. Table F lists those compounds qualitatively identified in varying amounts. Compounds suspected as present in the submarine atmosphere, but not yet identified, are listed in Table G. No attempt is made here to enumerate the many and diverse physiological effects which may result from exposure to these contaminants under various conditions. Much of this information may be obtained from references (19), (20), and (21).

The broad spectrum of contaminants in the submarine atmosphere is readily apparent. The possibilities of several contaminants acting in conjunction to enhance or reduce their individual physiological effects are numerous. A well documented example is the additive effect of the asphyxia-producing poisons, carbon monoxide (CO) and hydrogen cyanide (HCN). Although several investigators (22, 23, 24) have shown

TABLE A
CHEMICAL CLASSIFICATION OF CONTAMINANTS

(As used in reference 21)

1. Halogens
2. Alkaline Materials
3. Arsenic, Phosphorus, Selenium, Sulfur, and Tellurium
4. Inorganic Compounds of Oxygen, Nitrogen, and Carbon
5. Lead
6. The Metals (excluding Lead)
7. The Aliphatic (Open Chain, Acyclic) Hydrocarbons
 - a. Saturated Aliphatic Hydrocarbons
 - b. Specific Paraffin Hydrocarbons
 - c. Hydrocarbon Mixtures
 - d. Unsaturated Aliphatic Hydrocarbons
8. The Alicyclic Hydrocarbons
9. The Aromatic Hydrocarbons
10. Halogenated Hydrocarbons
 - a. Aliphatic
 - b. Cyclic
11. Phenols and Phenolic Compounds
12. Alcohols
13. Glycols
14. Derivatives of Glycols
15. Epoxy Compounds
16. Ethers
17. Ketones
18. Organic Acids and Their Derivatives
19. Esters
20. Organic Phosphates
21. Aldehydes and Acetals
22. Cyanides and Nitriles
23. Aliphatic and Alicyclic Amines
24. Aliphatic Nitro Compounds, Nitrates, Nitrites
25. Aromatic Nitro and Amino Compounds
26. Heterocyclic and Miscellaneous Nitrogen Compounds

TABLE B
PHYSIOLOGICAL CLASSIFICATION OF CONTAMINANTS

(Adapted from reference 21)

1. Irritants

Characterized by their corrosive or vesicant action when in contact with moist or mucous surfaces. This class may be subdivided into:

- a. Irritants affecting primarily the upper respiratory tract.
- b. Irritants affecting both the upper respiratory tract and lung tissue.
- c. Irritants affecting primarily the terminal respiratory passages and air sacs.

2. Asphyxiants

Exert their effects by interfering with oxidative metabolism. Further classification is usually made as follows:

- a. **Simple Asphyxiants:** physiologically inert gases that act principally by dilution of the atmospheric oxygen below the partial pressure required to maintain an oxygen saturation of the blood sufficient for normal tissue respiration.
- b. **Chemical Asphyxiants:** contaminants which, through chemical action, either prevent the blood from transporting oxygen from the lungs or prevent normal tissue oxygenation, even though the blood is well oxygenated.

3. Anesthetics and Narcotics

This group exerts its principal action as simple anesthesia without serious systemic effects, and the members have a depressant action on the central nervous system governed by their partial pressure in the blood supply to the brain.

4. Systemic Poisons

- a. Materials that cause organic injury to one or more of the visceral organs.
- b. Materials damaging the hematopoietic system
- c. Nerve poisons
- d. Toxic metals
- e. Toxic nonmetal inorganics

5. Particular Matter Other Than Systemic Poisons

- a. Fibrosis-producing dusts
- b. Inert dusts
- c. Dusts causing allergic reactions
- d. Irritants
- e. Bacteria and other microorganisms

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TABLE C
PHYSICAL CLASSIFICATION OF CONTAMINANTS
(Adapted from reference 21)

1. Gases and Vapors

Gases and vapors consist of dispersed molecules, ranging in size from 0.00003 to 0.01 microns, which are diffused rather than suspended in air. In general the term "gas" is applied to any substance that is in the gaseous state at 25°C and 760 mmHg, whereas "vapor" refers to the gaseous phase of a substance which exists as a liquid or solid at 25°C and 760 mmHg.

2. Particulate Matter

- a. **Aerosol:** a dispersion of solid or liquid particles of microscopic size in a gaseous medium; e. g., smoke, fog, and mist.
- b. **Dust:** loosely applied to solid particles predominantly larger than a colloid and capable of temporary suspension in a gaseous medium.
- c. **Fog:** loosely applied to visible aerosols of liquid particles dispersed in a gaseous medium. Formation by condensation is implied.
- d. **Fume:** Solid particles generated by condensation from the gaseous state, generally after volatilization from melted substances and often accompanied by a chemical reaction, such as oxidation.
- e. **Mist:** loosely applied to dispersed liquid particles many of which are large enough to be individually visible without visual aid.
- f. **Smog:** a term derived from smoke and fog and applied to extensive atmospheric contamination by aerosols arising from a combination of natural and man-made sources.
- g. **Smoke:** small gas-borne particles resulting from incomplete combustion and consisting predominantly of carbon and other combustible materials.

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TABLE D
ACTUAL OR POTENTIAL SOURCES OF AROMATIC HYDROCARBONS
FOUND IN NUCLEAR SUBMARINE
ATMOSPHERES (17)

Mineral spirits
Diesel fuel
Paint thinners
Paints
Solvents in waxes, cements, glues, adhesives, etc.
Special cleaning solvents
Lighter fluids
Tobacco smoke
Decomposition of lubricating and hydraulic oils
Cooking
Mastics and sealing compounds
Plastic compositions (solvents and plasticizers)
Adhesive sealers (used for lagging)
Rubber compounds
Insulation compounds

[REDACTED]

[REDACTED]

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TABLE E

COMPOUNDS QUANTITATIVELY IDENTIFIED IN SUBMARINE
ATMOSPHERES IN VARYING AMOUNTS

Compound	Chemical Formula	Suspected Source	MAC in ppm (ACGIH)*	90-day Limit (ppm)*
Acetylene	C_2H_2	Smoking, welding gases	-	2.5% \perp
Ammonia	NH_3	CO_2 scrubbers	50	25
Arsine	AsH_3	Battery gassing	0.05	0.01
Benzene	C_6H_6	Solvents, smoking	25	-
Carbon Dioxide	CO_2	Respiration, smoking, burners	3-5,000	6-10,000
Carbon Monoxide	CO	Engine exhausts, smoking, missile launch system	100	25
Chlorine	Cl_2	NaCl in battery, chlorate candles	1	0.5
Ethylbenzene	$C_6H_5C_2H_5$	Fuels, solvents	200	-
m, p-Ethyltoluene	$CH_3C_6H_4C_2H_5$	Fuels, solvents	-	-
Freon 11 and 12	CCl_xF_y	Air conditioning and refrigeration plants	1,000	500
Hydrocarbons, total (excluding methane)	Various	Various	-	10
Hydrogen	H_2	Battery gassing	-	3% \perp
Hydrogen Chloride	HCl	Methyl chloroform and freon decomposition	5	0.1
Hydrogen Fluoride	HF	Freon decomposition	3	0.1
Mesitylene	1,3,5- $(CH_3)_3C_6H_3$	Paints	-	-
Methane	CH_4	Cigarette smoke, sanitary tanks	1,000 \oint	5.3% \perp
Methyl Alcohol	CH_3OH	Cigarette smoke, mimeograph fluid	200	3
Methyl Chloroform	CH_2Cl_2	Adhesives, solvents	350	-
Monoethanolamine	$HOCH_2CH_2NH_2$	CO_2 scrubbers	3 \oint	1
Nitrogen	N_2	Normal constituent	-	-
Nitrogen Dioxide	NO_2	Burners, smoking	5	0.5
Nitrous Oxide	N_2O	Burners, smoking	-	-
Oxygen	O_2	Normal constituent	-	17% min.
Ozone	O_3	Precipitators, electrical arcing	0.1	0.05
iso-Propylbenzene	$C_6H_5CH(CH_3)_2$	Paints	-	-
n-Propylbenzene	$C_6H_5(CH_2)_2CH_3$	Paints	-	-
Pseudocumene	1,2,4- $(CH_3)_3C_6H_3$	Paints	-	-
Stibine	SbH_3	Battery gassing	0.1	0.05
Toluene	$C_6H_5CH_3$	Fuel, solvents, paints	200	20
Vinylidene Chloride	$CH_2=CCl_2$	Methyl chloroform decomposition, plastics	-	-
Water vapor	H_2O	Normal constituent	-	-
m, p-Xylene	$(CH_3)_2C_6H_4$	Fuels, solvents, paints	200	3
o-Xylene	1,2- $(CH_3)_2C_6H_4$	Fuels, solvents, paints	200	1

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

 \perp Based on explosive limit \oint Tentative value

References (1), (2), (3), (17), and (18).

TABLE F
COMPOUNDS QUALITATIVELY IDENTIFIED IN SUBMARINE
ATMOSPHERES IN VARYING AMOUNTS

Compound	Chemical Formula	MAC in ppm (ACGIH)*
Acetaldehyde	CH ₃ CHO	200
Acetic Acid	CH ₃ COOH	10
Acetone	CH ₃ COCH ₃	1,000
iso-Butane	(CH ₃) ₂ CHCH ₃	-
n-Butane	CH ₃ (CH ₂) ₂ CH ₃	-
iso-Butene	(CH ₃) ₂ C=CH ₂	-
1-Butene	CH ₃ CH ₂ CH=CH ₂	-
2-Butene (trans)	CH ₃ CH=CHCH ₃	-
2-Butene (cis)	CH ₃ CH=CHCH ₃	-
n-Butylbenzene	C ₆ H ₅ (CH ₂) ₃ CH ₃	-
sec-Butylbenzene	C ₆ H ₅ CH(CH ₃)C ₂ H ₅	-
tert-Butylbenzene	C ₆ H ₅ C(CH ₃) ₃	-
n-Decane	CH ₃ (CH ₂) ₈ CH ₃	-
1,3-Dimethyl-5-ethylbenzene	1,3-(CH ₃) ₂ -5-C ₂ H ₅ C ₆ H ₃	-
n-Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	-
Ethane	C ₂ H ₆	-
Ethyl Acetate	CH ₃ COOC ₂ H ₅	400
Ethyl Alcohol	C ₂ H ₅ OH	1,000
Ethylcyclohexane	C ₂ H ₅ C ₆ H ₁₁	-
Ethylene	C ₂ H ₄	-
o-Ethyltoluene	1-CH ₃ -2-C ₂ H ₅ C ₆ H ₃	-
Formaldehyde	HCHO	5
Freon 114B2	CF ₂ BrCF ₂ Br	1,000
n-Heptane	CH ₃ (CH ₂) ₅ CH ₃	500
n-Hexane	CH ₃ (CH ₂) ₄ CH ₃	500
Isoprene	CH ₂ =C(CH ₃)CH=CH ₂	-
Isopropyl Alcohol	CH ₃ CHOHCH ₃	400
Methylcyclohexane	CH ₃ C ₆ H ₁₁	500
Methyl Ethyl Ketone	CH ₃ COCH ₂ CH ₃	200
Methyl Isobutyl Ketone	CH ₃ COCH ₂ CH(CH ₃) ₂	100
n-Nonane	CH ₃ (CH ₂) ₇ CH ₃	-
n-Octane	CH ₃ (CH ₂) ₆ CH ₃	500
iso-Pentane	(CH ₃) ₂ CHCH ₂ CH ₃	-
n-Pentane	CH ₃ (CH ₂) ₃ CH ₃	1,000
Propylene	CH ₂ =CHCH ₃	-
Sulfur Dioxide	SO ₂	5
n-Undecane	CH ₃ (CH ₂) ₉ CH ₃	-

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

References (1), (2), (3), (17), and (18).

TABLE G
COMPOUNDS SUSPECTED AS PRESENT BUT NOT IDENTIFIED
IN SUBMARINE ATMOSPHERES

Compound	Chemical Formula	Suspected Source	MAC in ppm (ACGIH)*
Acrolein	CH_2CHCHO	Cooking fats and greases	0.1
1,3-Butadiene	$\text{CH}_2 = \text{CHCH} = \text{CH}_2$	Cigarette smoke	1,000
Diacetyl	$\text{CH}_3\text{COCOCH}_3$	Cigarette smoke	-
Diethyl Ketone	$\text{C}_2\text{H}_5\text{CO C}_2\text{H}_5$	Cigarette smoke	-
Furan	$\text{C}_4\text{H}_4\text{O}$	Cigarette smoke	10
Fur Fur aldehyde	$\text{C}_4\text{H}_3\text{O CHO}$	Cigarette smoke	-
Hydrogen Cyanide	HCN	Cigarette smoke	10
Mercury	Hg	Thermometers, batteries, instruments, fluorescent lights	0.01
Methyl Chloride	CH_3Cl	Cigarette smoke, solvents	100
2-Methyl Furan	$\text{C}_4\text{H}_3\text{O CH}_3$	Cigarette smoke	-
Phosgene	COCl_2	Freon decomposition	0.1 β
Propion aldehyde	$\text{C}_2\text{H}_5\text{CHO}$	Cigarette smoke	-
Triaryl Phosphates	-	Hydraulic fluids, compressor lubricants	0.06
Trichloroethylene	$\text{CHCl} = \text{CCl}_2$	Methyl chloroform decomposition	100

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

β Tentative value.

References (1), (2), (3), (17), and (18).

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the synergistic effects of mixed toxic gases to be greater than their individual effects, little reliable information is available as yet concerning the results of many such possible interactions.

In almost all cases the limit for a continuous 90-day exposure is below the industrial MAC. However, no established 90-day limit or MAC data exist for a great number of the compounds encountered. Also lacking are reliable data concerning permissible levels for the acute exposure situation (exposure to high concentrations for relatively short periods) and the toxicology of hydrocarbon compounds. Until more reliable data are available, the expedients of exclusion from, or controlled admittance to the submarine environment must remain the primary methods of control for many of these substances.

PARTICULATE CONTAMINANTS:

Particulates (aerosols) are discrete solid or liquid particles larger than molecules, but small enough to remain airborne. They are produced either mechanically (e.g., grinding, atomization), thermally (e.g., condensation of gases), or chemically (e.g., solid or liquid particles formed by reaction of gases or vapors). They are usually reported in terms of number of particles or weight per volume. These terms are not completely satisfactory, however, as they do not compensate for differences in individual particle size. This difference is especially important for contaminants below 5 microns in size. Equal number or weight concentrations of 1 and 3 micron size particulate contaminants represent different degrees of hazard because of differences in alveolar deposition and inherent toxicity. Valid comparisons, therefore, must incorporate knowledge of particle size, particle density, and basic toxicological characteristics.

Early studies conducted aboard nuclear submarines have shown that the average

aerosol concentration reaches a steady-state level of 0.4-0.5 microgram per liter after approximately 100 hours of submergence (25). About 75 percent of the aerosol derives from cigarette smoke, with a high hydrocarbon content and a median particle size of 0.45 micron--a size permitting penetration of the respiratory tract to the level of the alveoli. The aerosol concentration has also been shown to be related to crew activity and/or the type of patrol operation in which the ship is participating. Recurring fluctuations of the aerosol content have been observed which correspond with variations in personnel activity during different periods of the day, and sharp rises occur during operations requiring the recirculation fans to be run at half-speed or secured (26).

Although the adverse effects of aerosols on electronic equipment and delicate instruments have been acknowledged, little is known about the physiological effect on man of long-term exposures. Exact assessment of the problem is made especially difficult in the case of submarine atmosphere aerosols due to the presence of numerous hydrocarbons. Many of these have been detected by chromatography, but few specifically identified.

The values quoted above concerning aerosol concentrations were obtained in submarines having purification equipment capable of processing approximately 1200 cubic feet of air per minute and reflect conditions existing at present in conventional submarines and some nuclear submarines. Equipment capable of processing 11,000 cubic feet of air per minute with particle removal efficiencies of 80 to 99.98 per cent has subsequently been installed in most nuclear submarines. Studies conducted aboard one of these ships indicated an aerosol concentration of 0.07 microgram per liter (27). Variations related to crew activity were again noted, but initial build-up and subsequent equilibration were not observed.

DETECTION AND MEASUREMENT

Various instruments are employed for the detection and measurement of gaseous constituents in the submarine atmosphere. Portable devices for the determination of carbon monoxide and carbon dioxide concentrations have been in use since World War II. The need for equipment capable of use in repeated monitoring over prolonged periods with increased accuracy and dependability has resulted in the development of several new instruments and the adaptation of some existing units for submarine application. At present, no device for aerosol monitoring has been found suitable for routine submarine application.

THE ATMOSPHERE ANALYZER:

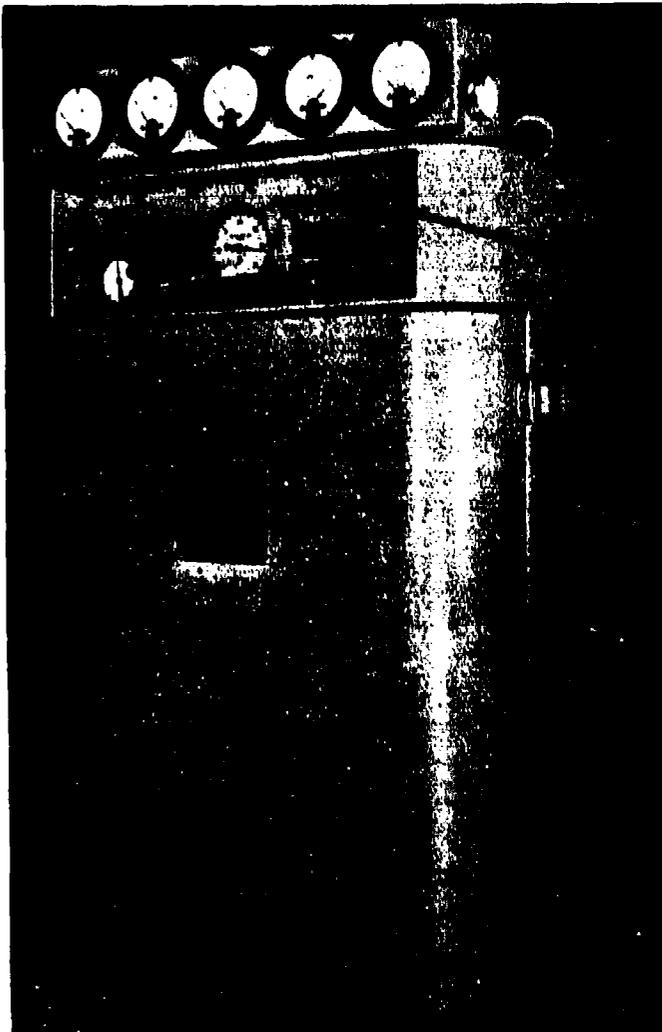
The atmosphere analyzer (either the Mark III or Mark IV - see Figure 7) is the principal instrument for atmosphere monitoring in nuclear submarines. The unit utilizes an installed system of sampling lines and mechanical filters, each of which originates in a different area of the ship. All lines connect to a selector switch which has a single outflow path to the analyzer, permitting analysis of an atmosphere sample from a specific selected location. The instrument is capable of determining the concentrations of carbon monoxide, carbon dioxide, oxygen, hydrogen and Freon, and provides visual readout indication of the levels detected.

Infrared analysis channels are used for the determination of carbon dioxide, carbon monoxide and Freon. These gases absorb infrared radiation, with maximum absorption occurring at specific characteristic wavelengths. The difference in heat energy between a chamber containing the atmosphere sample and a reference chamber devoid of the gas being measured creates a pressure differential which is converted to an electrical potential. This potential, after amplification and rectification, is used to produce needle deflection on a meter, indicating the concentration of the subject gas in the sample. Crossover sensitivity does occur in these channels to some extent, especially between nitrous oxide (N_2O) and carbon monoxide in the Mark III analyzer.

Operation of the hydrogen analysis channel is based upon the thermal conductivity of hydrogen gas. The atmosphere sample to be analyzed is brought into contact with a heated filament which is one element of a balanced Wheatstone bridge. Hydrogen in the sample conducts heat away from the filament, cooling it and thereby increasing its resistance to electrical current flow. This change in current flow is measurable and, with proper calibration, is proportional to the amount of hydrogen present. The channel is non-selective, being affected by any thermally conductive gas (e.g., helium). In the range of concentrations usually encountered in the submarine atmosphere, however, only hydrogen significantly alters the thermal conductivity of the sample.

Analysis of the sample for oxygen takes advantage of the paramagnetic property of this gas, i.e., the fact that it is the only common gas which is strongly attracted in a magnetic field. The sample to be analyzed is introduced into a chamber in which a glass dumbbell test body is suspended on a thin quartz fiber in a magnetic field. Oxygen in the sample is attracted to the strongest part of the magnetic field, tending to displace the test body with a force proportional to the amount of oxygen present. In the Mark III analyzer, an electrostatic potential is generated to counteract this displacing force and maintain the test body in the "at rest" position. This potential is amplified to provide visual indication of oxygen concentration on a meter. In the Mark IV analyzer, displacement of the test body is permitted to occur and a beam of light is reflected by a mirror mounted on the test body, at an angle proportional to the amount of oxygen present. The reflected beam falls on a linear scale to provide visual readout.

The Mark IV analyzer incorporates several improvements over the Mark III. Nitrous oxide sensitivity of the carbon monoxide channel has been eliminated. All channels of the Mark IV operate at ambient pressure, whereas the Freon and carbon monoxide channels of the Mark III require pressurization of the sample to 100 psig and



Meter
Indicator
Housing

Control
Panel

Console

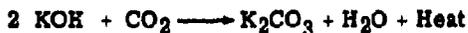
Fig. 7. Atmosphere Analyzer Mark III

subsequent reduction to ambient pressure for analysis in the carbon dioxide, oxygen and hydrogen channels. The Mark III will analyze only for Freon-12, but the Mark IV contains a fourth infrared channel permitting individual analysis for Freon-11 and Freon-12, a requirement imposed by the increasing use of Freon-11 equipment. The Mark IV also includes provision for the addition of a long-optical-path ultraviolet photometer capable of selectively analyzing for mercury, ozone, and a wide variety of aromatic and substituted hydrocarbons. Despite these improvements, drift and crossover sensitivity continue to be problems with the infrared channels, especially sensitivity of the carbon monoxide and Freon-12 radiation detectors to water vapor (28).

PORTABLE GAS DETECTING INSTRUMENTS: Compact portable instruments requiring only simple mechanical cleaning and maintenance are utilized for atmosphere analysis in ships not having an atmosphere analyzer, and as backup monitors in ships equipped with this unit.

The Bechman Oxygen Analyzer (Model D2) is a portable device operating on the same principle as the oxygen channel of the Mark IV analyzer. Sampling is achieved via a hand-operated rubber bulb. Prior to entry into the analysis chamber, the sample is exposed to a desiccant to remove water vapor which would produce a false low reading.

The Dwyer Carbon Dioxide Indicator, capable of measuring CO₂ in concentrations from 0 to 5%, uses 30% potassium hydroxide to remove CO₂ from an air sample of known volume via the following reaction:



The reaction takes place in one side of a U-shaped, KOH filled, chamber with the pressure equalized initially. As CO₂ is removed from the sample, a vacuum is created in that side. Subsequent venting of the outer side to the atmosphere results in a fall of the KOH column in that side proportional to the amount of CO₂ in the sample. The CO₂ concentration may be determined by the point at which the meniscus of this column comes to rest on a calibrated scale.

A Mine Safety Appliance Explosimeter is used as a portable monitor for hydrogen. This unit uses a platinum filament to cause the catalytic combustion of hydrogen. The resulting change in filament temperature creates an alteration of electrical resistance, proportional to the amount of H₂ present, which is used to produce a meter indication. The unit is non-discriminatory, indicating the presence of any combustible gas, but the concentrations encountered in submarine atmospheres are not sufficient to cause significant interference.

Two basic types of Freon detectors have been employed to identify leaks and local high concentrations. A flame - type ("Halide Torch") indicates the presence of Freon by the change in color of a flame to which the sample is exposed. The NRL Thermistor-Bridge and NRL Wire-Bridge units compare the thermal conductivity of the sample with that of a reference gas. Problems of low sensitivity, response time lag, and lack of specificity of response exist with current leak detectors, and none is considered completely suitable for submarine application. Interest and investigation in this area continue.

Another group of portable analysis devices utilizes glass tubes containing specific reagents supported on some inert absorbent (e.g., silica gel or alumina gel). This group includes the Draeger, Kitagawa, Bacharach Monoxor, MSA, and Saf-Co-Meter instruments. These units are compact kits consisting of a hand-operated pump designed to draw an air sample of a known volume at a reproducible, fixed rate through a glass detector tube. The presence and concentration of the contaminant are determined visually by the color change of the reagent (colorimetric method) or by the amount of reagent affected by the color change (length of stain method). In many instances the color change is ill-defined, especially when other reactive gases are present. In such cases the accuracy of the determination may vary considerably, but can be improved by thorough training of the operator. Interference does occur, the most notable example being the invalidation of Monoxor determinations in the presence of hydrogen concentrations above about 0.4%.

ATMOSPHERE CONTROL EQUIPMENT

Installations provided for the individual removal of carbon dioxide and generation of oxygen have been discussed. Additional methods are employed for the control of other gaseous and particulate contaminants.

THE CARBON MONOXIDE/HYDROGEN BURNER: Aboard nuclear submarines, carbon monoxide, hydrogen, and hydrocarbons are removed from the atmosphere by CO/H₂ burners which remove these contaminants by catalytic oxidation. Air drawn from the atmosphere, after being filtered and preheated, is heated to approximately 600°F. (Figure 8). It then passes through a bed containing Hopcalite catalyst (copper oxide and manganese dioxide) where oxidation to carbon dioxide and water vapor occurs. Subsequent removal of the CO₂ is accomplished by the scrubbers.

Breakdown of certain other substances which do not undergo complete oxidation during passage through the burner results in the generation of additional contaminants. Chief among these substances are the Freons, which yield halogen acid vapors, methyl chloroform, which yields hydrochloric acid, trichloroethylene, and vinylidene chloride; and nitrogenous compounds such as MEA and morpholine which yield nitrous oxide (29, 30, 31). When present in sufficient amounts, acid vapors thus produced cause irritation of the respiratory tract and corrosion of metal structures in the vicinity of the burners. The use of lithium hydroxide, either added to the catalyst in the ratio of one part LiOH to ten parts Hopcalite or in an absorber bed containing only LiOH, and the placement of metal waster screens, with which acid vapors can react, in the outflow path significantly reduce the level of acid vapors in the burner effluent. Study of these problems is continuing.

Shipboard studies have shown the burner to oxidize hydrocarbons with an average efficiency of about 80%, even at temperatures as low as 500°F (31). Efficiency appeared to be a function of molecular weight, with about 80% efficiency for

compounds in the decane range and higher, but 90-95% efficiency for those in the pentane and hexane range.

THE ELECTROSTATIC PRECIPITATOR: Aerosols are removed from the atmosphere by two-stage, plate-type electrostatic precipitators located in various areas aboard nuclear submarines. Air is circulated through a high-voltage electrical field in the ionizing section (first stage) where an electrical charge is imparted to particulate matter in the air. Approximately 20% of these charged particles are collected on the grounded plates of the ionizer. The remaining particles are carried by the air stream into the collector section (second stage) where another strong electrical field causes the particles to deposit on a group of parallel grounded plates. The air stream, cleansed of particulate matter, is then returned to the ship's atmosphere. Removal of collected particulate matter from the precipitator is accomplished periodically by flushing with a hot detergent solution through an integral system of hose connections and nozzles.

Precipitator efficiency is primarily a function of ionizing voltage, but it is also affected by air velocity, particle size and mass, collector voltage, and collector plate length. Removal efficiency in excess of 95% has been attained (27). Ozone formation secondary to electrical arcing occurs to some extent, but is minimized by using a negative ionizing potential due to its higher arcing voltage.

Mechanical (impingement) filters located in ventilation lines and precipitator intakes are used to remove large particles from the atmosphere.

CARBON FILTRATION: Removal of odors and trace contaminants, particularly hydrocarbons, is accomplished by coconut shell charcoal filtration of the atmosphere aboard nuclear submarines. Coconut shell charcoal has an internal structure characterized by microscopic capillary pores

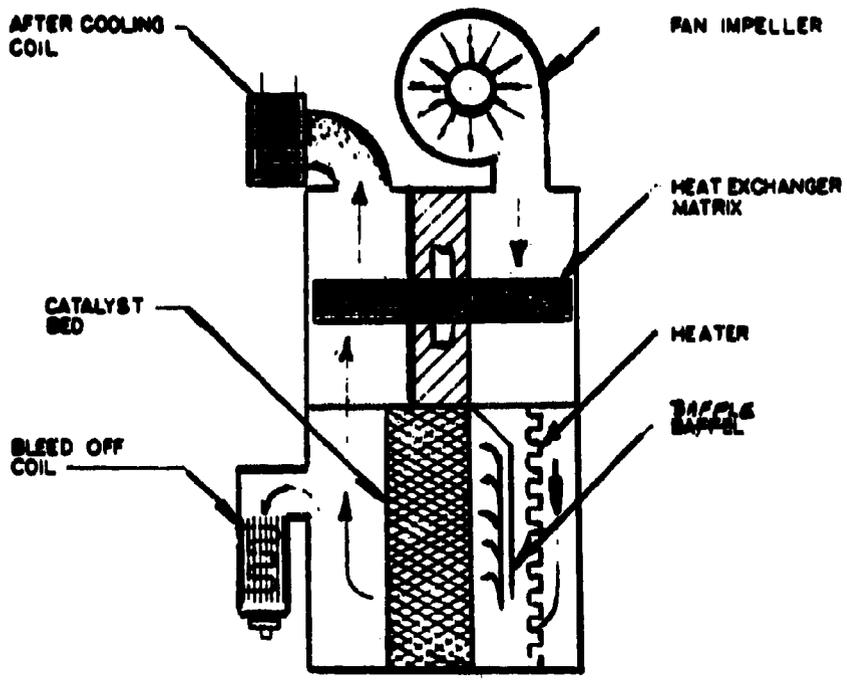


Fig. 6. CO/H₂ Burner Simplified Flow Diagram

enabling it to adsorb most vapor contaminants, even though present in extremely low concentrations. Charcoal is used variously in small canister filters in heads, on sanitary tank vents, in galley exhaust systems, and in a main carbon bed associated with the ventilation fan room through which a portion of the atmosphere is continually filtered.

Adsorption of hydrocarbons is a function of molecular weight. Low molecular weight contaminants (e.g., methane, Freons) are adsorbed rapidly and efficiently at first, but are subsequently displaced by higher molecular weight substances. Therefore activities contributing large amounts of heavy molecules to the atmosphere, such as painting with oil based paints, can drastically shorten the functional life of the carbon filter bed. An additional and potentially more hazardous problem is the low flash-point temperature of some hydrocarbons found adsorbed on submarine carbon samples (33).

METHODS UNDER INVESTIGATION:

Several additional methods for the control of atmosphere contaminants have been investigated (16, 33, 34, 35). Four of these

would perform the dual function of O₂ generation and CO₂ removal. The sulfate cycle system generates O₂ by the electrolysis of H₂O using sodium sulfate (Na₂SO₄) as the electrolyte. Sodium hydroxide formed in this process is used to remove CO₂ from the atmosphere, and is subsequently reclaimed to regenerate Na₂SO₄. An ion-exchange resin system absorbs CO₂ on resin particles continually activated by electrolysis. The electrolysis of water generates O₂ and the evolved H₂ is collected and pumped overboard, as is the CO₂. Alkali metal peroxides and superoxides have been evaluated as O₂ sources since the early 1940's. Comparison with other O₂ generation systems, however, reveals the alkali oxides to be relatively less efficient and more expensive. The use of algae to generate O₂ and remove CO₂ from the atmosphere by the process of photosynthesis has been extensively investigated by the U. S. Naval Research Laboratory. Due to the inefficiency of currently available light sources, however, the power required to operate this system is considered too high to permit submarine application in the foreseeable future.

SUMMARY

The general principles and problems involved in maintaining the submarine atmosphere are reviewed. Specific chemical constituents of the atmosphere are presented with regard to their sources. Current and proposed methods for their detection, measurement and control are discussed.

A continuing research effort should be made to discover the effects of atmospheric contaminants on submarine personnel and to find ways of providing a more normal atmosphere within our operating submarines.

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13. ABSTRACT The Author presents a summary of the current principles and methods used to monitor and control the chemical constituents of nuclear submarine atmospheres. The paper includes discussion of applicable gas laws, units of measure, oxygen supply, CO ₂ removal, removal of gaseous and particulate contaminants. The principles of operation of the atmosphere analyzer, portable gas analyzers, CO/H ₂ burner, electrostatic precipitator, and carbon filtration are discussed. This classified monograph is of interest to all concerned with 'closed space' atmospheric control, and of especial interest to the submariner. (U)			

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