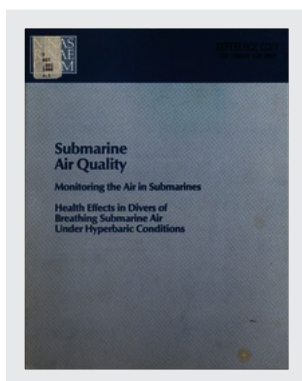


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## Submarine Air Quality: Monitoring the Air in Submarines: Health Effects in Divers of Breathing Submarine Air Under Hyperbaric Conditions (1988)

### DETAILS

168 pages | 8.5 x 10 | PAPERBACK

ISBN 978-0-309-31981-2 | DOI 10.17226/19146

### CONTRIBUTORS

Panel on Monitoring; Panel on Hyperbaric and Mixtures; Subcommittee on Submarine Air Quality; Committee on Toxicology; Board on Environmental Studies and Toxicology; Commission on Life Sciences; National Research Council

### SUGGESTED CITATION

National Research Council. 1988. *Submarine Air Quality: Monitoring the Air in Submarines: Health Effects in Divers of Breathing Submarine Air Under Hyperbaric Conditions*. Washington, DC: The National Academies Press. <https://doi.org/10.17226/19146>.

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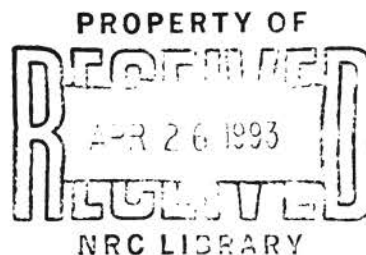
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# **Submarine Air Quality**

## **Monitoring the Air in Submarines**

## **Health Effects in Divers of Breathing Submarine Air Under Hyperbaric Conditions**

Panel on Monitoring *and*  
Panel on Hyperbarics and Mixtures  
Subcommittee on Submarine Air Quality  
Committee on Toxicology  
Board on Environmental Studies and Toxicology  
Commission on Life Sciences  
National Research Council



NATIONAL ACADEMY PRESS  
Washington, D.C. 1988

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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This report was prepared under Contract DAMD-17-86-C-6151 between the National Academy of Sciences and the Department of the Army.

Limited number of copies available from:

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## PREFACE

In July 1985, J. K. Summitt, Commodore of the U.S. Navy Medical Corps, asked the Board on Toxicology and Environmental Health Hazards, now the Board on Environmental Studies and Toxicology (BEST), of the National Research Council to assess the quality of the air in the enclosed environment of a nuclear submarine. The Navy also asked BEST to examine the possible health effects of breathing mixtures of submarine contaminants at increased pressure, as would be experienced by divers, and to review analytic techniques for monitoring submarine contaminants.

BEST, through its Committee on Toxicology (COT), has responded to the request by setting up the Subcommittee on Submarine Air Quality. The objectives of the study by the Subcommittee were as follows:

- To develop emergency exposure guidance levels (EEGLs) and continuous exposure guidance levels (CEGLs) for compounds of high interest to the U.S. Navy, namely, ammonia, hydrogen chloride, lithium bromide, toluene, trichloroethylene, and lithium chromate.

- To review the analytic techniques used in monitoring submarine contaminants, to recommend alternative methods when applicable, and to suggest which compounds it would be most useful to monitor.

- To study the possible health effects in divers of breathing commonly encountered airborne contaminants at increased pressures (up to 6 atmospheres absolute), considering possible interaction of substances encountered as mixtures.

The objectives were met by the three panels of the Subcommittee on Submarine Air Quality: the Panel on Emergency Exposure Guidance Levels, the Panel on Monitoring, and the Panel on Hyperbarics and Mixtures.

This volume contains the reports of the Panel on Monitoring and the Panel on Hyperbarics and Mixtures. Each report was prepared separately, so that it could be used independently. Much of the background material is therefore presented in both reports, but with a different orientation in each.

The first report of the Panel on Emergency Exposure Guidance Levels, *Emergency and Continuous Exposure Guidance Levels for Selected Airborne Contaminants, Vol. 7--Ammonia, Hydrogen Chloride, Lithium Bromide, and Toluene*, has been published separately. That panel's second report, on lithium chromate and trichloroethylene, will be published shortly.

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## ACKNOWLEDGMENTS

Presentations and written materials were provided to the Panel on Monitoring by a number of individuals to whom the Panel wishes to express its sincere gratitude:

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The Panel acknowledges the assistance of the British Royal Navy and French Navy for providing written material or consultation pertaining to this project.

Presentations and written materials were provided to the Panel on Hyperbarics and Mixtures by a number of persons to whom the Panel wishes to express its sincere gratitude:

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**Francis N. Marzulli**, **Kulbir S. Bakshi**, and **Richard D. Thomas** of the National Research Council's Committee on Toxicology provided staff assistance. The Panels wish to commend the technical assistance provided by **Mireille G. Meslas**, **Jean Dent**, and **Erik A. Hobbie**.

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# CHAPTER 1

## INTRODUCTION

This report addresses atmospheric monitoring on board a submarine and examines the capability of current monitoring instrumentation to measure the concentrations of gases for 90-day continuous exposure guidance levels (CEGLs) and for 1-hour and 24-hour emergency exposure guidance levels (EEGLs). The current analytic techniques are also assessed for such limitations as inadequate sensitivity and specificity. Where current methods are considered inadequate or where new technology might add needed sensitivity or reliability, alternative methods are suggested. The report suggests new monitoring methods for newly identified monitoring needs on the basis of analyses of submarine air and information on contaminants of potential importance for which no measurements are available. Such information includes reports of accidents, equipment failures, shipboard activities, and materials used or allowed on submarines. Throughout the study by the Panel on Monitoring, the toxicity of atmospheric substances was considered in making recommendations for changes in allowed concentrations of currently monitored substances or for concentrations of substances newly proposed for monitoring. Laboratory and field tests should precede the adoption of new monitoring techniques.

The monitoring system on submarines has been designed primarily to provide information on the major gases normally present in the normal atmosphere, such as  $O_2$ ,  $CO_2$ , and  $N_2$ . The monitoring equipment and procedures provide information on the performance of control

equipment and on overall air quality, including the presence of some toxic and corrosive contaminants. Current monitoring methods are based on the identity and concentration of the components to be measured, the overall composition of the submarine atmosphere, and the intended application of the data. The monitoring system tracks the concentrations of specific contaminants; there is no universal air monitoring device. All monitors are limited in their sensitivity, and many have well-known interferences. Therefore, to develop a monitoring strategy, information is needed on what hazardous substances might be present and at what concentrations.

The procedures followed on submarines for monitoring the atmosphere are described in the *Submarine Atmosphere Control Manual of the U.S. Naval Sea Systems Command* (1979). The Panel considered the frequency of monitoring the various gases and suggests alternative frequencies where the potential danger of the gas could dictate immediate action. The Panel's study also generated some anecdotal information that suggested that procedures other than those described in the *Submarine Atmosphere Control Manual* are followed on occasion, perhaps because of the inadequacy of monitoring equipment. The Panel commented on these procedures as appropriate in the hope that deficient practices and instrumentation will be recognized and corrected.

The atmosphere control equipment in a submarine maintains a livable atmosphere by adding  $O_2$  and by removing  $CO$ ,  $H_2$ ,  $CO_2$ , and

various hydrocarbons and particles that otherwise would increase to physiologically undesirable concentrations. One design requirement for nuclear submarines is to maintain a breathable atmosphere for 90 days without surfacing. Prolonged submergence of submarines is complicated by their small absolute volume, the small volume per person, and the vapor and aerosol emissions from machinery, equipment, shipboard activities, and supplies. In addition, gases build up in the atmosphere as the result of life processes and equipment use.

Monitoring of contaminants in submarine air is also of concern because the air is compressed and used to fill diver's self-contained underwater breathing apparatus (SCUBA) tanks. This use of submarine air presents special hazards that are not present at 1 atmosphere absolute (ATA). The work of the Panel on Monitoring was preliminary to that of the Panel on Hyperbarics and Mixtures, which has evaluated the effects of breathing various submarine contami-

nants under hyperbaric conditions and considered possible interactions of substances present as mixtures.

The primary sources of data used for this study were the 1979 Submarine Atmosphere Control Manual (the manual is being revised), reports of unclassified studies provided to the Panel by the Navy, publicly available published documents and data bases, and consultations with naval personnel of the United States, France, and the United Kingdom and their contractors. The sparseness of air analysis data to which the Panel had access and the lack of full information on specifications and current practices are serious limitations; important contaminant substances might have been overlooked.

The following chapters of this report discuss sources of air-quality degradation, methods of air purification, and measurement of air quality. The final chapter presents the Panel's conclusions and recommendations.



## CHAPTER 2

# SOURCES OF AIR-QUALITY DEGRADATION

### OVERVIEW OF SUBMARINE ATMOSPHERE DATA

There are many sources of contaminants of submarine air. Most sources release only small amounts of material into the air, but there is always a potential for contaminants to build up during operation of a closed vessel. Recognition of the many sources of atmospheric contamination has helped in the elimination of major sources of contaminants and in the development of methods to control and decrease contamination from any one source.

The major sources of air contamination are cigarette smoking, which accounts for 40-50% of the total particulate emission and most of the CO (Rossier, 1984); the human body, which produces CO<sub>2</sub> and methane in flatus; and cooking. Other sources of contaminants are control equipment (O<sub>2</sub> and NO<sub>2</sub> come from improperly functioning electrostatic precipitators, HF and HCl from the breakdown of fluorocarbons [FCs] in the CO-H<sub>2</sub> burner, NH<sub>3</sub> from breakdown of monoethanolamine, oxides of nitrogen [NO<sub>x</sub>] from NH<sub>3</sub> oxidized in contact with the CO-H<sub>2</sub> burner, and H<sub>2</sub> and KOH from the O<sub>2</sub> generator); the power train (oil mist, diesel fuel vapors, and diesel exhaust from snorkeling [snorkeling is the exchange of interior submarine air via the gas intake called the snorkel], including NO, CO, hydrocarbons, and particulate emissions); weapons systems (missile exhaust and Otto fuel, which contains propylene glycol dinitrate); batteries (off gases and leaks of hydrogen and small amounts of arsine and

stibine); sanitary tanks (gases and aerosols); air-conditioning and refrigeration systems (leaks of FC-12 from refrigeration system and FC-114 from the ship's air-conditioning plant); FC-113 used as a cleaning solvent; and a variety of maintenance and repair activities that involve the use of arc welding, burning of volatile chemicals, FCs, and outgassing from paints. Many small sources of emissions are associated with the use of personal-care products, medical supplies, hobby materials, cigarette lighters, and office activities. Minor contaminants associated with the air monitoring equipment include phosgene from the leak detector and substances released from the detector tubes. Smoldering fires and overheated insulation can produce CO. Some sources of contamination may be difficult to identify, such as materials inadvertently left on board, gases and vapors adsorbed onto clothing, and materials brought on board.

The catalytic burner aboard submarines converts some organic chemicals to H<sub>2</sub>O and CO<sub>2</sub> and in some cases forms acid gases (such as SO<sub>2</sub>, HCl, and HF) from sulfur and halogen compounds. When acid gases are not adequately removed by the submarine's air purification system, they degrade air quality. One also needs to be aware of the potential impact of these substances and their decomposition products on instrumentation and the air control equipment.

A full description of submarine air quality monitoring must include information on aerosols. Aerosols are suspensions of liquid and solid particles in air. Particles that are in the



respirable size range (smaller than  $5\text{ }\mu\text{m}$ ) are of concern, because they can be inhaled deep into the lungs. They can be of microbiologic origin, as well as of chemical and mineral origin, and some are inherently infective or toxic. Solid particles can adsorb toxic gases and vapors and carry them deep into the lungs. Some of those substances might not otherwise reach the deep lung in their gaseous phase; for example, highly soluble gases might normally be trapped in the upper airways. Liquid particles can behave similarly, by absorbing and incorporating gases. Organic compounds associated with particles have been shown to be cleared from the lung more slowly than those not associated with particles (Bond et al., 1986).

Sources of particles include tobacco smoke, condensable vapors from cooking, foaming and bubble formation in human-waste tanks, oil droplets from lubricated machines, flaking of paint, cleaning-compound residues, and personal-care products. Some of the particles found in submarine air originate in the life-support systems themselves; for example, the monoethanolamine (MEA) scrubber for  $\text{CO}_2$  internally generates caustic liquid drops, and thus MEA at concentrations of 1-2 ppm escapes with the scrubber effluent.

Little is known about the toxic properties of aerosols of high-boiling-point vapors that originate from lubricants, cooking, and human bodies and that tend to be in the size range that is deposited deep in the lungs.

Appendix A contains a list of substances that might be present in U.S. submarines, as assembled by the Panel on Monitoring. Some abnormal conditions, such as fires and major spills of volatile materials like solvents or fluorocarbons (FCs) can rapidly produce hazardous air contamination. The risks presented by many of those materials are well recognized, and monitoring methods have been established, as shown in Table 1. Most of the substances listed in Table 1 have been studied for health hazards, and guidance levels for exposure to them have been recommended by the National Research Council's Committee on Toxicology and other groups.

The information in Appendix A was obtained from published reports, including submarine logs, analyses of adsorbents used in submarines, analyses of exhaled air of submarine personnel, and information on accidents. Much of the information is not quantitative, because many substances were reported only as present, without concentration data. A full analysis of the

submarine atmosphere was not available to the Panel.

Various parts of the control and monitoring system can be used to collect samples for detailed on-shore analysis. For example, phosphorus-containing lubricant-based aerosols will decompose in contact with the catalyst in the  $\text{CO-H}_2$  burner, and the phosphorus will be left on the catalyst. Information on the atmospheric content of lubricant-source aerosols obtained by analyzing used Hopcalite catalyst might be combined with information on airflow through the catalyst and the duration of catalyst use. The high efficiency (about 100%) of the catalyst in decomposing lubricant-based compounds has been documented (Christian and Johnson, 1963). Water samples taken from locations of condensation and periodic drainage can be analyzed to determine which substances are being removed. The filter used to remove water and particles from diver's air is another possible source of useful samples.

The Panel requested and received, in addition to data collected during the last 2-3 decades by the U.S. Navy, an extensive list of substances detected (but not quantified) in British Royal Navy submarines (Appendix B). A list of substances for which maximal permissible concentrations in British Royal Navy submarines have been set was also received, but the actual concentrations themselves are classified and were not revealed. The British Royal Navy adheres to the limits through real-time monitoring of some substances and through on-shore analysis of samples taken at sea. Several substances on the list are not monitored on U.S. submarines, and their pertinence to U.S. boats requires evaluation. The Panel suggests that the U.S. Navy request quantitative information from the British Royal Navy and explore the reasons for the differences in monitoring, so that it can determine whether additional limits and monitoring are necessary for U.S. submarines.

The Panel believes that the Navy needs to do a thorough survey of trace contaminants for various classes of submarines. Carefully controlled sampling procedures should be established for the use of sorbents, such as Tenex, which would be followed by on-shore analysis. Compounds of concern that have been detected or are thought to be present, but on which no concentration data are available, should be measured. Although current monitoring methods measure the concentrations of specific compounds, contaminants of physiologic significance that are outside the capability of the

**TABLE 1**  
**Classification of Submarine Atmospheric Measurement Requirements<sup>a</sup>**

<u>Category</u>	<u>90-d Limit<sup>b</sup></u>	<u>24-h Limit<sup>b</sup></u>	<u>1-h Emergency Limit<sup>b</sup></u>	<u>Current Measurement Methods<sup>c</sup></u>
<b>Category I:</b> <b><u>Essential for Life Support</u></b>				
Oxygen	140-160 torr	140-160 torr	140-220 torr	C,P
Carbon dioxide	0.8%	4%	4%	C,T
Carbon monoxide (toxic)	15	200	200	C,T
<b>Category II:</b> <b><u>Explosive, Acutely Toxic, or Irritating</u></b>				
<b>a. Common or Occasional Contaminants</b>				
Acrolein (irritant)	0.1	0.1	0.2	--
Ammonia (irritant)	25	50	400	T
Chlorine (irritant)	0.1	1	3	T
Hydrogen chloride (irritant)	1	4	10	T
Hydrogen cyanide (toxic)	--	--	--	T
Hydrogen fluoride (irritant)	0.1	1	8	T
Nitrogen dioxide (irritant)	0.5	1	10	T
Ozone (irritant)	0.02	0.1	1	T
Refrigerants (decompose to irritant)				
FC-11	5	20	50	C,THA
FC-12	200	1,000	2,000	C,THA
FC-114	200	1,000	2,000	C,THA
Hydrogen (explosive)	10,000	10,000	10,000	C
Hydrocarbons (total aromatics, without benzene)	10 mg/m <sup>3</sup>	--	--	T,THA,PID
Hydrocarbons (total aliphatics, without methane)	60 mg/m <sup>3</sup>	--	--	T,THA,PID



TABLE 1 (contd)  
Classification of Submarine Atmospheric Measurement Requirements<sup>a</sup>

<u>Category</u>	<u>90-d Limit<sup>b</sup></u>	<u>24-h Limit<sup>b</sup></u>	<u>1-h Emergency Limit<sup>b</sup></u>	<u>Current Measurement Methods<sup>c</sup></u>
<b>Category II:</b>				
<b>b. Contaminants from Abnormal Releases</b>				
Fire may release acrolein, CO, HCl, HCN, HF, NO <sub>2</sub>	--	--	--	--
Hydrocarbons (solvents, etc.)	--	--	--	--
Monoethanolamine (irritant)	0.5	3	50	T
Sulfur dioxide (irritant)	1	5	10	T
Spills (solvents, refrigerants, Otto fuel, etc.)	--	--	--	--
Sulfuric acid mist (irritant)	d	d	d	--
<b>Category III:</b>				
<b>Known or Suspected Chronic or Carcinogenic Toxicity</b>				
Tobacco smoke products	--	--	--	--
Benzene	1	100	None	THA, T
Methyl chloroform	2.5	10	25	THA, T
Vinylidene chloride	2	10	25	THA

<sup>a</sup>Limits from *U.S. Naval Sea Systems Command* (1979, Tables 3-6 and 3-7). The Panel on Monitoring arranged material into categories.

<sup>b</sup>Limits in parts per million unless otherwise noted.

<sup>c</sup>C = central system (CAMS-I); T = detector tube; THA = total hydrocarbon analyzer; PID = photoionization detector; P = portable paramagnetic analyzer. THA is no longer in operation on submarines.

<sup>d</sup>limits based on SO<sub>2</sub>.

current monitoring equipment and are not currently monitored might also be present. The recommended survey should include sampling from all locations where contaminants might be found, especially those where contaminants might be highly concentrated.

The enclosed, controlled environment of a submarine provides a unique opportunity to study relationships between prolonged exposure to atmospheric contaminants and health effects. Current monitoring on submarines does not provide quantitative analysis of all submarine air contaminants and provides only sparse data on exposure. Future health-effects studies will require quantitative monitoring of the submarine atmosphere for a wide range of contaminants and a fuller epidemiologic approach.

## BACKGROUND

U.S. Navy studies on the habitability of submarine atmospheres that are pertinent to the work of the Panel date from the early 1950s, when life-support systems necessary to enable nuclear submarines to stay submerged for many weeks began to be developed (Carhart and Johnson, 1980). The research and development work was most intense in the 1960s, when the problems associated with long submergence became apparent. New systems for life support were developed, new monitors and detectors were introduced to establish the sources of contaminants, methods for removing contaminants were upgraded, and controls were established for materials brought on board. Current interest in the contaminant content of the submarine atmosphere is related to the use of submarine air for diver's air. The gas of greatest interest is CO<sub>2</sub>, because the normal CO<sub>2</sub> content in submarines is too high for diver's air (Weathersby et al., 1987).

The U.S. Naval Research Laboratory has had an extensive research program on the submarine atmosphere for many years. Work begun in the 1960s to support prolonged submergence was charted in numerous progress reports (Miller and Piatt, 1960, 1968; Piatt and Ramskill, 1961, 1970; Piatt and White, 1962; Carhart and Piatt, 1963; Lockhart and Piatt, 1965; Alexander and Piatt, 1967). Carhart and Thompson (1975) have briefly summarized the composition of the submarine atmosphere and the contaminant control methods. Data generated during testing and sea trials of atmosphere monitoring and control equipment make up a large fraction of the sub-

marine data available to the Panel. Those tests and others led to recognition of the sources of hydrocarbons in the submarine atmosphere and to the adoption of measures that greatly decreased hydrocarbon concentrations. Furthermore, it was recognized that, although a given compound might not be toxic, its decomposition over the CO-H<sub>2</sub> burner might produce toxic products.

On-shore analyses of samples collected during submergence have been the source of detailed information on the identity of contaminants in the submarine atmosphere. Several detailed studies have addressed organic contaminants. The identification of individual organic contaminants and the estimation of their concentrations are difficult, because hundreds of compounds are present at very low concentration in submarines. But the identification of each organic contaminant or group of contaminants has long been recognized as of prime importance if their toxic effects are to be evaluated. Studies that make use of the collection of submarine air samples on activated carbon have led to the identification of major contaminant sources, such as paints, diesel fuels, mineral spirits, and solvents (Johnson, 1963; Christian and Johnson, 1963; Johnson et al., 1964). Diesel fumes are a source of NO<sub>2</sub> (Bondi et al., 1983), and cigarette smoke is a source of CO and numerous hydrocarbons (Carhart and Piatt, 1963; Bondi, 1978; National Research Council, 1986a). The electrostatic precipitators were identified as a source of high ozone concentrations (Piatt and Ramskill, 1970). Some emphasis has been given to identifying chlorinated hydrocarbons on board submarines. Chlorinated hydrocarbons found included FCs (FC-11, FC-12, FC-113, FC-114, FC-114B2), methyl chloroform, vinylidene chloride, chloroform, trichloroethylene, and tetrachloroethylene (Williams and Johnson, 1968, 1970).

Comprehensive atmosphere studies conducted on submerged submarines during cruises have produced information on contaminant concentrations during operation of the atmosphere control system. The studies have produced more direct information on suspected contaminant sources than carbon sampling followed by analysis on shore (Umstead et al., 1964; Smith et al., 1965; Rossier, 1984).

Information on the submarine atmosphere is collected in the submarine logs. These logs contain data on the concentrations of the gases routinely monitored--e.g., H<sub>2</sub>, CO, O<sub>2</sub>, CO<sub>2</sub>, FC-12, and FC-114--as well as atmospheric



pressure. The data are not routinely analyzed retrospectively.

Knight et al. (1984) studied the hydrocarbon content of the expired breath of submariners and found an average of 486 compounds per sample. Of the 17 compounds found in highest concentrations, 13 were those of  $C_7$ - $C_{11}$  alkanes.

A serious interest in aerosols in submarine atmospheres began in 1958 with a recognition that aerosols might accumulate in the atmosphere during prolonged periods of submergence (Anderson and Ramskill, 1960). During a respiratory habitability cruise, it was learned that average aerosol concentrations increased during the first 100 h of submergence and stabilized thereafter, although there were daily increases that reflected heavy patrol operations (Anderson and Ramskill, 1960). Daily aerosol concentrations ranged from 0.1 to 0.9  $\mu\text{g/L}$ , and the median particle size was 0.45  $\mu\text{m}$ . Tobacco smoke was identified as a major constituent. The effect of aerosols on equipment, as well as on health, was noted; as a consequence, a recommendation was made to upgrade the electrostatic precipitators (ESPs) to a minimal efficiency of 99% by changing from a low-voltage two-stage design to more efficient high-voltage single-stage units of greater airflow capacity (Anderson and Ramskill, 1960). However, the Navy continues to use two-stage units.

In 1961, an experiment was conducted aboard the U.S.S. Triton during a round-the-world cruise. With the cooperation of the crew, smoking was banned for 72 h while aerosol concentrations were monitored. During the unlimited-smoking period before the experiment, aerosol concentrations of 0.3-0.4  $\mu\text{g/L}$  were observed. They decreased to 0.11  $\mu\text{g/L}$  soon after the smoking ban went into effect (Anderson, 1961). The importance of the on-board aerosol purification systems is demonstrated by the fact that concentrations increased rapidly under "patrol quiet" (ventilation at half speed) and even more rapidly under "ultraquiet" (ventilation off).

By 1972, with the introduction of increased numbers of ESPs on board, the average aerosol concentration was reduced by half, i.e., to 0.15-0.2  $\mu\text{g/L}$  (Rossier, 1984); for the Trident submarine, a normal-operation limit of 0.1  $\mu\text{g/L}$  was adopted, with an allowable maximum of 0.2  $\mu\text{g/L}$ .

Despite the 1961 recommendation that ESPs be redesigned for an efficiency of at least 99%, the Trident ESPs ranged in efficiency from 70

to 95%; the most reliable number was 89%. Although that 89% does not seem very different from 99%, the penetration of an ESP with 89% efficiency is 11 times that of an ESP with 99% efficiency.

The engine room continues to be a major producer of aerosols, despite installation of local unit ESPs referred to as vent fog precipitators. With the addition of tobacco smoke, the engine-room aerosol generation rate was 4.5 g/h (Rossier, 1984).

In summary, only a few studies have attempted to define the nature of the equilibrium aerosol, and they have not gone much beyond crude measurements of total particle concentration and the division of particle sizes into less than and greater than 0.4  $\mu\text{m}$ . In addition, submarine ESPs, the principal aerosol purification devices, are no more efficient in 1987 than they were 30 years ago, although more capacity has been installed. Several principal sources of vapors and aerosols are described below.

## SMOKING

Approximately half of the 500  $\mu\text{g/m}^3$  of aerosol particles found in the submarine were traced to tobacco smoke (Rossier, 1984). It should be noted that approximately 40% of submarine crew members are smokers (Rossier, 1984). To understand the potential environmental effects of smoking, we need to know something about the characteristics of tobacco smoke, which are briefly discussed below.

Mainstream smoke (MS) is the vapor and aerosol that is drawn into the smoker's mouth from a cigarette, cigar, or pipe (National Research Council, 1986a). The vapor and aerosol from burning tobacco that are released to the surrounding air are termed sidestream smoke (SS). SS is the main contributor to environmental tobacco smoke (ETS). The exhaled fraction of MS also contributes to ETS (National Research Council, 1986a).

Combustion of tobacco yields many reaction products whose distribution is a function of the region of the tobacco product where combustion is occurring. For example, SS is generated in a strongly reducing atmosphere and thus contains a larger number of chemicals that represent a greater level of incomplete oxidation than does MS (National Research Council, 1986a; Grob, 1966). Reactions in SS also produce higher quantities of nitrosated chemicals. Differences



in physicochemical properties between SS and MS are shown in Table C-1 (Appendix C).

Approximately 3,800 chemicals have been identified in tobacco smoke but only 300-400 have been quantified (National Research Council, 1986a; Higgins et al., 1983, 1984; Grob, 1963). Table C-2 (Appendix C) lists the amounts of a few chemicals measured in MS and SS from nonfilter cigarettes. In general, these are present at higher concentrations in SS than in MS. CO and CO<sub>2</sub> occur at much higher concentrations than other chemicals. CO is generated at 0.026-0.07 g/cigarette (Rossier, 1984). Many other hazardous chemicals are also produced during smoking, e.g., acrolein.

Table C-3 (Appendix C) shows substances measured in MS from high-, medium-, and low-tar nonfilter cigarettes (Higgins et al., 1984). Because of a rich oxygen environment for combustion, many oxygenated chemicals occur in MS.

ETS consists of smoke that has been diluted by air and has undergone physicochemical changes (National Research Council, 1986a). The concentration of ETS aerosol in a submarine is expected to depend on the air-exchange rate and the scrubbing efficiency of the control equipment. During suspension in air, the median diameter of particles decreases from 0.32 to 0.14  $\mu\text{m}$  or smaller.

The major oxide of nitrogen in SS is NO, which can react further to form NO<sub>2</sub>. As a constituent of the inhaled air, NO<sub>2</sub> could contribute to increased susceptibility to upper respiratory tract infections (Jakab, 1980, 1987). NO<sub>2</sub> causes respiratory tract irritation, bronchiolitis, and edema.

Volatile carbonyl compounds, such as acrolein and acetone, in ETS affect mucociliary functions, however, these two compounds probably do not survive the catalytic burner in a submarine.

The presence of tobacco smoke yields a respiratory environment that contains measurable quantities of many toxic agents, including carcinogens. The concentrations of ETS chemicals in submarines will depend on smoking rate (tobacco burned), air dilution or ventilation rate, volatility of agents, and efficiency of the catalytic burner. The Panel believes that there is a need for monitoring to determine the contribution of ETS to submarine air quality. However, in view of currently available information on tobacco smoke and smoking on board submarines, the Panel recommends that smoking be eliminated to improve air quality. The Panel

is concerned that contaminants introduced by smoking increase the load on air control, air monitoring, and other equipment.

## BIOLOGIC AEROSOLS

Investigations of health effects associated with biologic aerosols were in vogue during the 1930s and 1940s but then lost their public health urgency. It was possible to demonstrate the presence of viable microorganisms in indoor air, but it proved difficult to identify disease-producing types. Even when disease-producing types were identified, little evidence was developed to verify that they retained their virulence after exposure to the potentially denaturing effects of the air environment.

Submarines provide a confined environment for the spread of microbiologic aerosols, although there are few recorded studies of this phenomenon in submarines. It is generally believed that during the first few days of a voyage there is a general exchange of respiratory illnesses, but after that the incidence decreases to near zero and remains there until new contacts with outsiders occur. That belief has come into question, and there is little documentation to support it. A National Research Council report (1986b) discussed biologic aerosols as related to commercial aircraft cabins; that discussion is a good starting point for looking at the topic of biologic aerosols in submarines, where contact conditions are similar, although of longer duration.

Wastewater aerosols seem not to have been a matter of concern in submarines, although the wastewater systems are known to produce droplets during flushing and during storage (as a result of gas production). The National Research Council report mentioned above cited two submarine studies. Watkins (1970) reported "as many as 30,000 bacteria/ft<sup>3</sup> of air were isolated during sewage handling procedures", and Morris (1972) reported a mean concentration of about 20 bacteria-carrying particles per cubic foot in Polaris submarines. The numbers and nature of biologic aerosols on operating submarines do not appear to be well characterized although such information might have health importance for submarine crews.



## CONSUMER PRODUCTS

Another source of vapor-phase chemicals in submarine air is the wide variety of consumer products that may be used during construction and maintenance of a submarine (e.g., painting, lubricants) and in personal activities (Knight et al., 1984). Sources of chemicals are difficult to identify or predict solely on the basis of materials used in routine operations. Nevertheless, it is instructive to examine a data base on chemical emissions from a variety of products, some of which can be used in submarines. Chemicals with important toxicologic consequences might later be eliminated by placing restrictions on particular materials or uses of some consumer products.

Direct determination of emissions from liquid and solid materials used in submarines provides necessary information for predicting air quality. Demas and Greenberg (1986) have compiled chemical procedures for determining aliphatic and aromatic hydrocarbons, halocarbons, alcohols, ketones, aldehydes, amines, ethers, esters,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}$ ,  $\text{NH}_3$ , oxides of nitrogen, and several other inorganic chemicals present in materials used in nuclear submarines. Appendix C (Table C-4) categorizes materials that have been certified for use in nuclear submarines. Materials are not evaluated according to toxic emissions in fire under current procedures.

Information was available to the Panel from a NASA data base on vapor emissions from coating materials, rubber products, plastics, insulation, wire, cables, and personal-hygiene items. Appendix C (Tables C-5 through C-9) lists chemicals emitted at over 1 mg/m<sup>2</sup> per minute under testing conditions (generally, 40–70°C and standard atmospheric pressure). The tables indicate the release of many organic chemicals—halocarbons, aliphatic and aromatic hydrocarbons, alcohols, esters, aldehydes, and siloxanes.

## COOKING

Odors are often detected during the preparation of foods, and airborne emission of vapors and aerosols is expected to occur from cooking on submarines. The Panel examined the literature to obtain information on the chemical composition of emission during the cooking of foods, especially from deep-fat frying, because

relatively little is known about emission from cooking on submarines.

Pan frying and deep-fat frying are the most common procedures for the preparation and manufacture of foods. During deep-fat frying, oxidation and heat can form volatile and non-volatile decomposition products (Chang et al., 1978; Krishnamurthy and Chang, 1967; Kawada et al., 1967; Mancini-Filho et al., 1986; May et al., 1983; Mounts, 1979; Paulose and Chang, 1973; Paulose and Chang, 1978; Reddy et al., 1968; Thompson et al., 1978; Yasuda et al., 1968). Liquid cooking oils constitute a substantial portion of the common cooking media for pan and deep-fat frying. Refined and properly deodorized frying fats are initially odorless, regardless of their source or their degree of unsaturation. Vegetable oils have their own characteristic odors when heated to frying temperatures (Mounts, 1979).

The volatile decomposition products (VDPs) of corn oil, hydrogenated cottonseed oil, trilinolein, triolein, and oleic acid under simulated commercial frying conditions have been collected, fractionated, and chemically identified (Chang et al., 1978; Krishnamurthy and Chang, 1967; Kawada et al., 1967; Mancini-Filho et al., 1986; May et al., 1983; Mounts, 1979; Paulose and Chang, 1973; Paulose and Chang, 1978; Reddy et al., 1968; Thompson et al., 1978; Yasuda et al., 1968). Some 211 compounds have been identified (Table C-10).

Controlled cooking studies have been conducted that might yield clues to potential volatile chemicals from cooking of different foodstuffs. For example, volatile materials associated with meat aroma generated in a *d*-glucose, hydrogen sulfide, and ammonia model system (Shibamoto and Russell, 1976) formed a variety of chemicals, such as thiols, sulfides, thio-phenes, thiazoles, and furans (Table C-11). Some nitrogen-containing heterocyclic compounds, such as pyrroles, oxazolines, and pyrazines, have been detected and associated with the aroma of roasted or cooked foods (Table C-12) (Shigematsu et al., 1972).

On the basis of the sparse data on VDPs from cooking, it appears that quantitative information on VDPs in the cooking and dining areas of submarines is needed. Many of the VDPs previously identified during cooking are polar substances and would be adsorbed on to the stainless-steel lines leading to the Central Atmosphere Monitoring System (CAMS) and thus go undetected. A pilot study might reveal whether toxic chemicals are present at

concentrations likely to cause health problems. The Navy might also investigate the pollution generation from various fats considered for use.

A report (Carson, 1986) on the nutrient intake of crew members of the USS Florida suggested that, in addition to possible health benefits, elimination of the deep-fat fryer would reduce fire hazards and reduce an important source of contaminants on submarines. Menus for 5 weeks showed deep-fried foods were served on 18 of 35 days and a grilled breakfast every day. In consequence, the Navy might wish to follow up on the possibility that dietary changes could provide a three-fold benefit.

### CONTAMINANTS IN DIVER'S AIR

Divers operate from nuclear submarines for several purposes (inspection of the submarine hull, deployment of combat swimmers, etc.). Diving can extend to a pressure of 6 ATA for up to 12 h. During a dive, divers are away from monitoring equipment and sometimes out of communication with anyone; thus, the context for toxicology questions is different from that of other submariners. In addition, compressed submarine air with reduced  $\text{CO}_2$  content might be the source of diver's air for diving. The contaminants in diver's air are therefore potentially the same as those in general submarine air, unless special procedures are adopted to reduce contamination. Nonetheless, because diver's air is stored in air banks after compression of submarine air, it does not necessarily contain the same concentrations of contaminants as does submarine air.

A simplified submarine air system is shown in Figure 1. This figure illustrates how air is drawn to fill SCUBA bottles from the air system.

### EMERGENCIES

Emergencies of many kinds can occur in a submarine under operating conditions that can cause air-quality degradation. Failure of vital life-support systems ( $\text{O}_2$  generator and  $\text{CO}_2$  scrubber) is guarded against by redundancy, whereby a single unit has sufficient capacity to prevent serious distress. In the event of total collapse of vital life-support systems, emergency air and oxygen are available. The use of backup life-support systems, however, can be the source of additional air contaminants (e.g.,  $\text{Cl}_2$  and  $\text{CO}$  from chlorate candles used to generate  $\text{O}_2$  and dust from  $\text{LiOH}$  used to scrub  $\text{CO}_2$ ).

Emergencies that affect the submarine atmosphere can originate from total failure of all redundant units of one or more life-support systems, from dire events on the submarine that do not directly affect vital life-support systems (e.g., fires in appliances, machinery, deep-fat fryers, instruments, control equipment, or submarine structures), from catastrophic explosions inside or outside the submarine, and from flooding. Table 2 lists various emergencies that release contaminants to the submarine atmosphere.

Emergencies that adversely affect the submarine atmosphere call for donning air-supplied respirators or self-contained breathing units, devices that are ubiquitous in submarines. However, there does not appear to be a well-defined policy for measuring air quality after an event like a fire, to ascertain when the air is safe to breathe, except for instructions in the *Submarine Atmosphere Control Manual* to monitor atmosphere contaminants with the central monitor. This subject needs additional consideration to ensure that crews are adequately trained to handle emergencies.

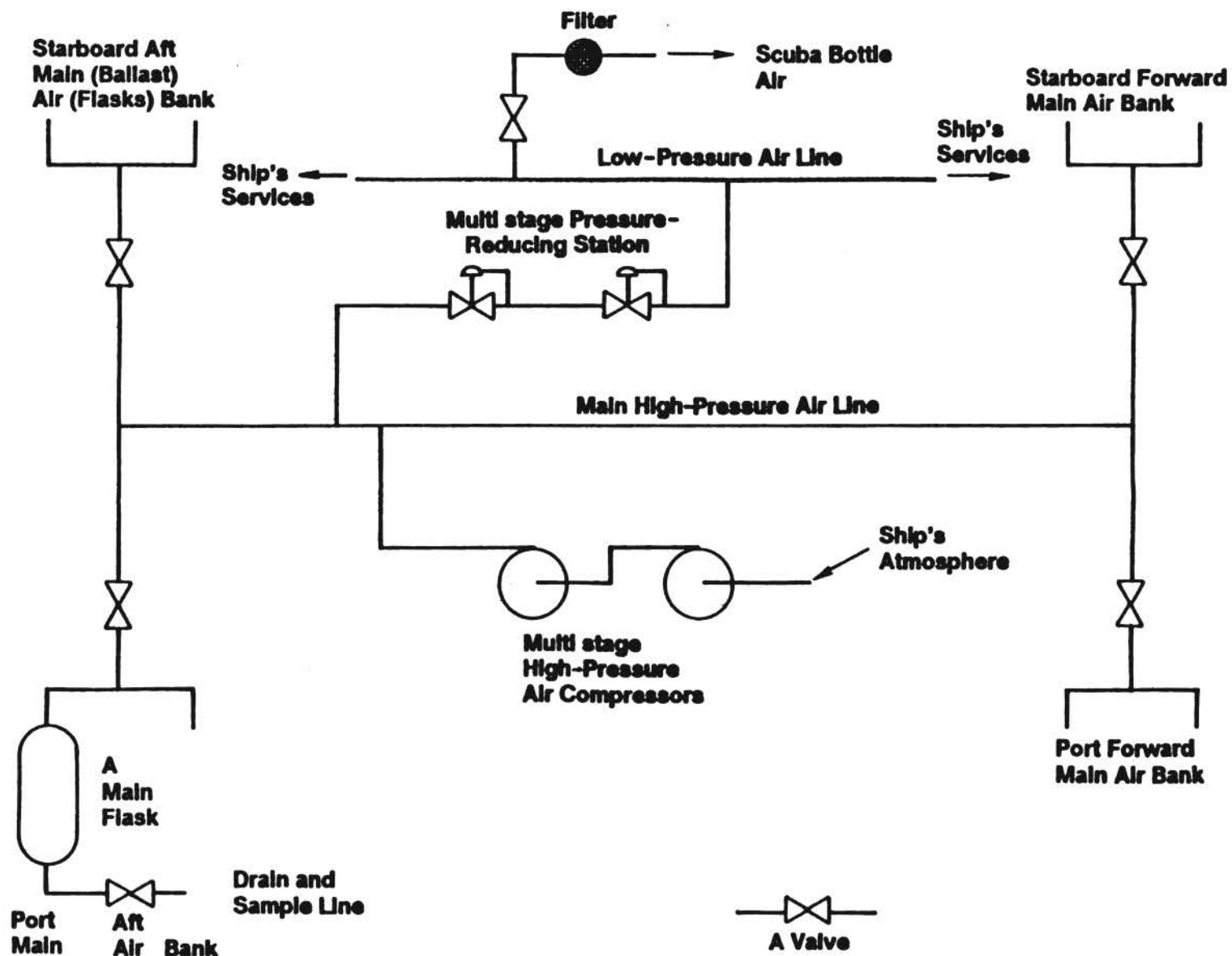


FIGURE 1 Simplified submarine air system.



TABLE 2

**Emergencies That Lead to Contamination**

**Generation of acutely toxic or irritating airborne contaminants**

- (a) Fire (HF and HCl from FCs; CO, CO<sub>2</sub>, NO<sub>2</sub>, and HCN from Otto fuel)
- (b) Releases from ruptured life-support systems (e.g., KOH from O<sub>2</sub> generator, monoethanolamine from CO<sub>2</sub> scrubber)
- (c) Leaks and spills of FC-12, FC-114, hydraulic fluids, Otto fuel (propylene glycol dinitrate), and radioactive water
- (d) Leaks from other equipment malfunctions (e.g., LiBr from air-conditioner)

**Failure of critical life-support systems**

- (a) O<sub>2</sub> generator
- (b) CO<sub>2</sub> scrubber (leads to increased CO<sub>2</sub>)
- (c) CO-H<sub>2</sub> burner (leads to increased H<sub>2</sub> and CO) and acid-gas absorber (leads to increased HF and HCl)

**Explosive damage (not addressed)**

**Flooding (sea water in battery evolves H<sub>2</sub> and Cl<sub>2</sub>)**



# CHAPTER 3

## METHODS OF AIR PURIFICATION

### OVERVIEW OF SUBMARINE AIR CONTROL

The purposes of air control systems on submarines are to provide enough oxygen to replenish that consumed and to keep contaminant gases and particulate material at concentrations below those at which adverse effects occur. Three techniques are used to provide control: shipboard air can be replaced with outdoor air, which has sufficient oxygen and is low in contaminants; restrictions can be placed on materials and activities permitted on board ship (this provides no oxygen, but does prevent release of some contaminants); and engineered systems can provide oxygen and remove contaminants.

Performance objectives for the control system vary with atmospheric constituents. Table 1 lists pollutant concentrations that are not to be exceeded and the range of oxygen concentrations permitted. All three approaches are discussed briefly below.

Fans circulate air rapidly, so shipboard concentrations of oxygen and pollutants are nearly uniform. The concentration of each constituent can be calculated from a mass-rate balance, given information on rates of generation and removal. The assumptions implicit in the balance are that concentration is uniform throughout the ship and that removal efficiency is independent of pollutant concentration.

Shipboard contaminant concentrations will increase slowly even if the removal system fails. For example, with a  $\text{CO}_2$  generation rate of 10

lb/h (100 men, 0.1 lb/h per man) and a floodable volume of 100,000  $\text{ft}^3$ , it will take about 6 h for the  $\text{CO}_2$  concentration to increase from 0.5% to 1% if the  $\text{CO}_2$  control and backup systems both fail. That situation, even if tolerable for some hours, will ultimately lead to unacceptably high  $\text{CO}_2$  concentrations. In an emergency situation, such as a fire, in which a contaminant generation rate is high, an unacceptable concentration might be reached very quickly.

In a ship with a floodable volume of 100,000  $\text{ft}^3$  that carries 100 sailors who each remove oxygen at 1  $\text{ft}^3/\text{h}$ , with no other oxygen sinks, 26 h will pass before oxygen concentration falls from 160 to 140 torr.

### Control by Exchange of Shipboard Air with Outdoor Air

Ventilating by exchanging shipboard air with outdoor air ensures that the concentrations of all contaminants are low. Although the control systems remove some contaminants efficiently, they might be ineffective for other contaminants, such as some fluorocarbons (FCs), whose concentrations will increase with time. Contaminants not removed by the control systems can be removed from ship air only by ventilation.

In port, the Navy's standard procedure calls for ventilating the ship daily for at least an hour (U.S. Naval Sea Systems Command, 1979). At sea, standard procedures call for ventilating the ship at least once a week, tactical considerations

permitting, until the concentration of contaminants is half the original concentration (U.S. Naval Sea Systems Command, 1979).

### Control by Restriction of Materials and Activities

Some materials release undesirable substances, and others decompose to undesirable substances with time or when passed through a control system. The intent of restricting materials is to reduce contaminant generation rates and thereby to minimize the resulting contaminant concentrations.

Restrictions are managed by dividing materials into four categories: "permitted," "limited," "restricted," and "prohibited" (U.S. Naval Sea Systems Command, 1979). "Permitted" materials have no use restrictions. "Limited" materials might contain toxic materials, but may be used for a specific purpose because there is no nontoxic substitute; these materials should not be carried on board in excess of quantities required. "Restricted" materials contain substantial amounts of toxic materials and are not allowed on board while a submarine is under way, except in the case of specific exemptions, although they may be used in small quantities in port while ventilating. "Prohibited" materials are not allowed on submarines, except in the case of specific exemptions. The Navy maintains lists of permitted, limited, restricted, and prohibited materials organized by uses. Items in these categories are listed in Table C-4 (Appendix C).

Restrictions are also placed on activities that generate contaminants (U.S. Naval Sea Systems Command, 1979). For example, welding, brazing, and metal-burning operations are prohibited unless absolutely essential. Deep-fat fryers must operate at temperatures below 425°F. Although nontoxic paints have been the subject of research for years, the Panel is not aware that any have been adopted for use in submarines. The Panel recommends that nontoxic paints be developed and used in submarines.

Good housekeeping can reduce the rate of generation of organic materials (U.S. Naval Sea Systems Command, 1979). For example, rags used to wipe spilled fuel should be stored in airtight containers and disposed of as soon as possible.

The Navy maintains lists of products whose use is restricted on submarines to minimize use

of materials that could degrade air quality. The lists enable sailors to know what substances they *cannot* use for some tasks, but they do not disclose all the products they *can* use. Submarine officers with whom the Panel discussed this matter would welcome a list of products that *could* be used without restrictions for various tasks.

The Navy should give continued attention to reducing air contaminants at their sources. For example, better seals should be developed for air-conditioning and refrigeration equipment to decrease the release of FCs to the submarine atmosphere. FC control at the source is essential, inasmuch as there is no significant removal, except for some decomposition in the CO-H<sub>2</sub> burner. Measures should be taken to eliminate cigarette-smoking to lower aerosol and CO emission.

## ENGINEERED SYSTEMS

### Oxygen

Oxygen consumption varies with activity, but averages 1 ft<sup>3</sup>/h per man. A continuous supply of O<sub>2</sub> is provided by electrolysis of water at 2,100 to 3,000 psi in multiple cells (U.S. Naval Sea Systems Command, 1979); 16 cells constitute one O<sub>2</sub> generator. An O<sub>2</sub> reserve is maintained in tanks at high pressure until needed; H<sub>2</sub> produced during the electrolysis of water is discharged overboard. The O<sub>2</sub> generators can be purged with N<sub>2</sub> at high pressure. Difficulties with the electrolytic O<sub>2</sub> generators are generally mechanical and associated with the high pressure required, and they do not generate airborne contaminants.

A backup O<sub>2</sub> supply can be provided by burning chlorate candles--a mixture of sodium chlorate, about 5% iron, and small quantities of other materials. Each candle is 6.5 in. in diameter and 12 in. long and weighs about 26 lb. When lit, iron in the candle burns and produces enough heat to liberate O<sub>2</sub> from the chlorate and produce NaCl.



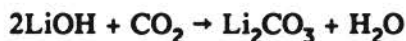
Burning takes place in a canister that holds two candles and a fibrous glass filter through which liberated O<sub>2</sub> passes. Each candle generates about 115 ft<sup>3</sup> of O<sub>2</sub> and burns for about 45 min.

A candle contains a small quantity of barium peroxide, which reacts with chlorine products such as free chlorine and hypochlorite to form barium chloride,  $O_2$ , and water vapor. While burning, the candle produces chlorine at about 10 ppm and CO at about 25 ppm. Concentrations that result from generation of these pollutants are low, because generation rates are low.

### Carbon Dioxide

The rate at which  $CO_2$  is generated varies with  $O_2$  consumption rate, but averages about 0.1 lb/h per man (U.S. Naval Sea Systems Command, 1979).  $CO_2$  is continuously removed by absorption in a monoethanolamine (MEA) scrubber (U.S. Naval Sea Systems Command, 1979) shown schematically in Figure 2. Air at 250-700 ft<sup>3</sup>/min (cfm) flows concurrently with 25-30% MEA solution at 0.25-3.0 gal/min through a column packed with Goodloe woven mesh packing, which removes about 70% of the entering  $CO_2$ . Flow is manually adjusted according to the flow rate of air and inlet  $CO_2$  concentration. The MEA solution flows at about 1 gal/min through a heat exchanger to a heated stripping column, where  $CO_2$  is liberated from the solution to be discarded overboard. Hot,  $CO_2$ -lean solution circulates through the heat exchanger and then back to the scrubber. A ship carries two scrubbers, each of which can remove  $CO_2$  from submarine air at 8-22 lb/h.

The MEA solution degrades with time and must be replenished. Its lifetime increases if it is passed through an activated-carbon bed. Backup removal of  $CO_2$  is accomplished by reaction of  $CO_2$  with granular lithium hydroxide (U.S. Naval Sea Systems Command, 1979).



If power is available, a fan blows  $CO_2$ -rich air at 12 cfm through each of five canisters that contain LiOH pellets. If power is not available, the pellets can be spread on an open surface. Some dust is generated when these pellets are handled. Each 31.5-lb charge of five canisters can remove about 28 lb of  $CO_2$ . At least a 3-day supply of LiOH canisters must be carried on board for emergency situations. The  $CO_2$  absorption rate by LiOH canisters decreases from nearly 5 lb/h when fresh to about 1 lb/h after 8 h. If a canister is used for 6 h, the average absorption rate is 4 lb/h; for 12 h of

use, the average is 2.3 lb/hr (U.S. Naval Sea Systems Command, 1979).

British Royal Navy submarines have used molecular sieves to remove  $CO_2$ . Problems with this technique include dusting of the molecular sieves and the high energy required to heat the molecular sieves to desorb the  $CO_2$ . Wastewater must be removed from the air before  $CO_2$  removal. The technique has the advantage that it removes some FCs.

### Carbon Monoxide and Hydrogen

Burning cigarettes produce CO; charging shipboard batteries produces  $H_2$ . Both are removed by catalytic oxidation to  $CO_2$  and water with a CO- $H_2$  burner (Figure 3) which oxidizes some other hydrocarbons at the same time.

Air passes through a filter and a heat exchanger and then to a catalyst bed at 600°F that contains about 75 lb of Hopcalite, a mixture of copper oxide and manganese dioxide. From the catalyst bed, air flows through the heat exchanger, where 75% of the heat is transferred to the incoming air, and then to a final cooling coil. Airflow is either 250 cfm (MK II) or 500 cfm (Mk III, Mk IV). The CO- $H_2$  burner generally operates at 80-90% efficiency for hydrocarbons and in one test (Rossier, 1984) removed  $H_2$  with an efficiency of 96% at an inlet concentration of 0.2%  $H_2$ . In another test, removal efficiency for CO was 98-100% at an inlet partial pressure of 3 millitorr (Rossier, 1984).

When FC-12 passes through the bed, less than 1% decomposes; however, about 30% of FC-114 decomposes (Carhart and Johnson, 1980). Significant fractions of nitrogen-bearing compounds, such as ammonia and monoethanolamine, from the  $CO_2$  scrubber that enter the burner decompose to form  $NO_x$  (Carhart and Thompson, 1975).

The CO- $H_2$  burner can generate acidic materials when FCs decompose. These are removed by passing the air downstream of the burner through a bed that contains lithium carbonate (U.S. Naval Sea Systems Command, 1979). Some air can bypass the lithium carbonate bed if a condensate trap in the line feeding the bed becomes clear and thus allows some corrosive gases that should be collected to escape. The concentration of HCl in gas passing from a functioning lithium carbonate bed was

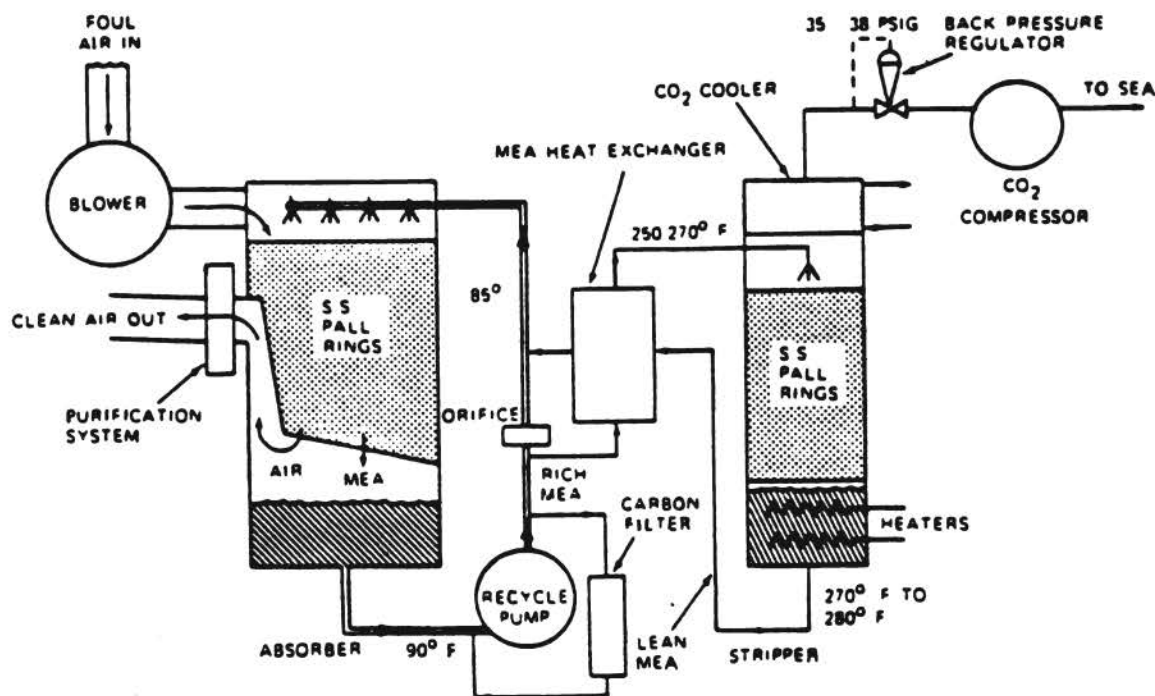


FIGURE 2 Schematic drawing of monoethanolamine scrubber for  $\text{CO}_2$ . Reprinted from U.S. Naval Sea Systems Command (1979).

measured in one case at 0.2-0.5 ppm (Rossier, 1984).

#### Fluorocarbons (FCs) and Other Nonreactive Compounds

Nonreactive compounds are not readily removed from ship's air. Some FCs form acidic compounds while passing through the  $\text{CO-H}_2$  burner, although burner efficiency for FCs and other nonreactive hydrocarbons is low.

#### High-Molecular-Weight Hydrocarbons and Odors

Some organic contaminants are removed near their points of generation by adsorption onto activated carbon (U.S. Naval Sea Systems Command, 1979) in half-filled cotton bats measuring 12 x 8 x 5 in. Beds of activated carbon are in several places on a ship. A main bed is in the fan room. Other beds in the galley, in

washroom and watercloset spaces, and above sanitary tanks are used to control odors.

Carbon is replaced according to a time schedule, rather than after tests that indicate bed saturation (U.S. Naval Sea Systems Command, 1979). For submergence longer than 45 d, the carbon in the main bed is changed at the approximate midpoint of the period, but not earlier than 30 d after submergence. Otherwise, the carbon is changed after 45 d. Carbon in the beds used to control odors is changed before prolonged submergence or when odors persist. Some FCs and other nonreactive hydrocarbons will be adsorbed onto the activated-carbon bed, although the same compounds might not be retained strongly by activated carbon. Clearly, the carbon beds will retain some contaminants better than others, and, as the beds become loaded with contaminants, the possibility of displacement of previously adsorbed compounds becomes more important. Such displacement is likely to occur in a catastrophic event, such as a major spill or a fire, when the carbon bed would be exposed to a high concentration of



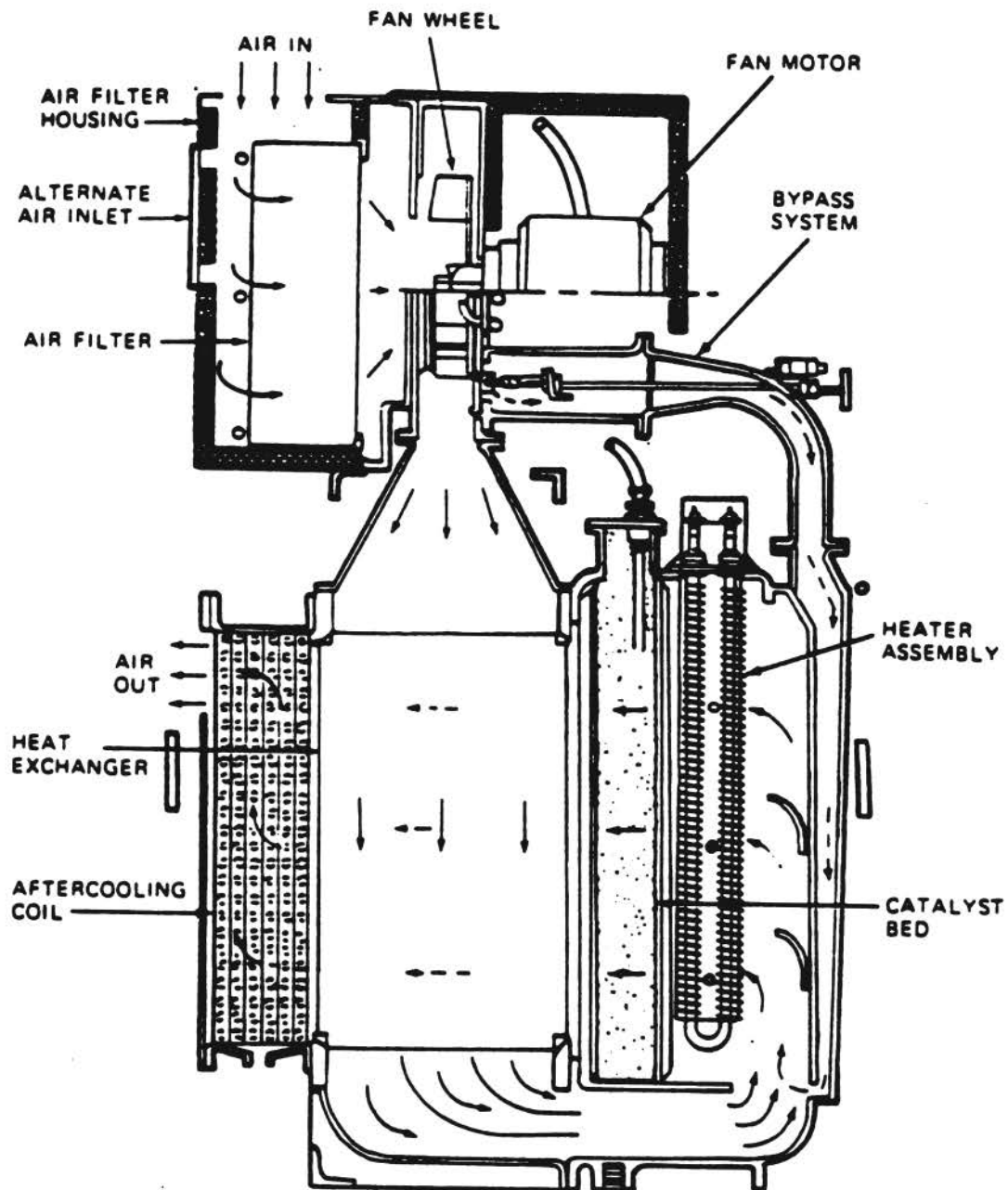


Figure 3 Schematic drawing of CO-H<sub>2</sub> burner. Reprinted from U.S. Naval Sea Systems Command (1979).



contaminants. In this case, the CO-H<sub>2</sub> burner might be unable to dispose of the displaced materials fast enough to prevent high concentration of contaminants from building up in the submarine air.

The Panel recommends that the Navy undertake research to measure the breakthrough of toxic contaminants as a function of bed loading by other, more strongly retained contaminants. Of particular concern should be the toxic contaminants that are not easily sensed by people.

On a long cruise or if several events occur that load the beds, insufficient carbon might be aboard to ensure adequate adsorption capacity. The Panel recommends that the Navy investigate the possibility of regenerating some carbon beds in place. Regeneration would obviate the carrying of replacement carbon and would ensure that adequate carbon is aboard, regardless of the travails of submarine life.

At present, activated carbon is contained in half-filled cotton bats. This arrangement makes the carbon easy to handle, but leads to an inhomogeneous bed with the possibility of substantial air bypass between the bats. The Navy should consider alternative ways to package the carbon, such as placement in canisters or in sealed elements that can be emptied and recharged ashore. That arrangement would reduce the probability of leaks through the carbon beds.

### Particles

Particles are produced on board from sources that include burning cigarettes, cooking, and vents in lubrication oil sumps and gear casings as outlined previously. Over half the particle mass comes from cigarettes; the total particle generation rate from cigarettes on one submarine was estimated to be about 2.5 g/h (Rossier, 1984). In general, 40-50% of the particles are smaller than 0.4  $\mu\text{m}$  in diameter (Rossier, 1984).

Two-stage electrostatic precipitators are installed in the ventilation system. The first stage charges incoming particles, which are collected in the second stage. On Trident submarines, three two-stage precipitators in the engine room provide a combined flow of 8,250 cfm. In addition, one precipitator is installed in each of five fan rooms, and one is in the galley exhaust. All these precipitators collect aerosols from lubricants, as well as those generated in the laundry, berthing lounges, and galley spaces. In addition, oil mists from lubricating oils are

collected by five "vent fog" Precipitators on lubrication oil sumps. The vent fog precipitators are of the wire-in-tube design and are mounted directly on the sump breather pipe (T. Daley, personal communication, 12 Jan. 1987). Precipitator efficiency is 70-95% on an overall-mass basis (Rossier, 1984). In addition, the navigation center electronics and missile control center electronic cabinets have a ventilation system that includes absolute filters for supply air (Rossier, 1984).

The Panel believes that particle concentration on ships can be reduced and that the Navy should investigate means to reduce it. The investigation should consider improving the efficiency of the particle removal equipment and increasing the flow of air through particle removal equipment.

The Navy might wish to consider the use of filters, instead of precipitators. Although an efficiency increase from 90% to 98% is an improvement of only 8%, it would constitute an 80% decrease in particles that pass through collectors. If high-efficiency particle-absorbing (HEPA) filters (99.97% efficiency) were used, concentration of respirable aerosols could be lowered significantly.

The Panel understands that maintenance of the present precipitators may be inadequate, because they are difficult to service, and that efficiency therefore is probably seldom at design specifications. Any new precipitator design should give ample attention to reliability and to ease of maintenance. Improved efficiency might not suffice to reduce the concentration of particles in shipboard air adequately, so the investigation should also consider whether the flow of air through the precipitators is sufficient. If necessary, additional precipitators should be installed.

### Emergency Procedures

*The Submarine Atmosphere Control Manual* (U.S. Naval Sea Systems Command, 1979) describes emergency procedures to be followed if harmful contaminants are released to the atmosphere. These procedures include securing the CO-H<sub>2</sub> burner, putting out the smoking lamp, and replacing the carbon filter bed. After an emergency, the ventilation system is run in the normal submerged mode; the ship is ventilated and portable blowers are used, if permitted by the tactical situation.

In a fire during submergence, pollutant generation rates might be much higher than removal rates of the engineered control systems and their backups. This situation would cause pollutant concentrations to increase quickly and to an undesirable extent.

If ventilation by exchange with outdoor air is impossible, as would occur in submergence under ice or in some tactical situations, personnel can breathe air from the emergency air breathing (EAB) system. Compressed air is drawn from the ship's air banks through regulators at many points throughout the ship (U.S. Naval Sea Systems Command, 1979). Sufficient air is available for 24-48 h, during which it is anticipated that the problem can be fixed and air quality restored.

Submarines also carry portable, self-contained oxygen breathing apparatus (U.S. Naval Sea Systems Command, 1979). One of these units consists of a mask connected to a canister that contains chemicals sufficient to remove  $\text{CO}_2$  and provide  $\text{O}_2$  for about an hour.

The air cleaning system is designed to clean air and provide  $\text{O}_2$  under normal operating conditions. Under some emergency conditions, such as a fire, the rate at which these systems could remove contaminants would be low, compared with the contaminant generation rate; that might result in an unacceptably rapid buildup of contaminants in submarine air.

The Panel believes that the Navy should consider installation of a one-pass, small, seawater, pressure-powered venturi scrubber in the air handling system for use in emergencies. The scrubber could use cold seawater to clear air rapidly of particles and water-soluble toxic materials. Because the air handling system is designed to recirculate the total volume of air in the submarine every few minutes and many of the most toxic materials produced in a fire involving plastics are either particles (soot) or water-soluble compounds ( $\text{HCl}$ ,  $\text{HF}$ ,  $\text{HCN}$ , acrolein, and other aldehydes and acids), an efficient seawater scrubber could rapidly make the air breathable again, once the fire is controlled. The used seawater could be pumped overboard. The Panel recognized that failure of the air control system to perform optimally could produce additional monitoring needs. Indeed, a major function of the air monitoring system is to help in recognizing malfunctions that are not immediately detected by some other means.

### Failures of Control Systems

The primary air control units on a submarine are the  $\text{O}_2$  generators, the  $\text{CO}_2$  scrubbers, the  $\text{CO-H}_2$  burner, the electrostatic precipitators, the fans, the carbon adsorbent beds, and the temperature and humidity control units. The malfunctions considered here are in two general categories: the electric or mechanical malfunction, defined as a malfunction that is made immediately obvious to the operator by an alarm; and the performance malfunction defined as a malfunction that is *not* made immediately obvious to an operator by an alarm. A performance malfunction can occur as a result of an electric or mechanical malfunction that is not monitored by sensors, interlocks, and alarms on the air control unit; as a result of physical or chemical deterioration of the active agents in an air control unit; or simply as a result of formation of an undesired reaction product. Three examples of performance malfunctions are elution of hydrocarbons from the carbon adsorbent beds as a result of displacement by other compounds or saturation of the bed, chemical deactivation of the catalyst in the  $\text{CO-H}_2$  burner, and formation of an undesirable air contaminant over the catalyst.

Each air control unit currently has sensors, interlocks, and alarms that notify an operator immediately in the event of a major electric or mechanical malfunction. The sensors, interlocks, and alarms ensure that the subsystems in the unit are supplied with the correct electric power and are operating at the correct temperature and pressure (where appropriate). For example, the  $\text{CO-H}_2$  burner has built-in minimal and maximal temperature sensors and a sensor that indicates when the fan is not supplied with correct power. The manufacturer of each unit is responsible for providing appropriate interlocks and alarms for the unit it manufactures, with simple instructions that identify the action that the operator must take for various combinations of situations.

Alarms will not indicate whether a unit is actually performing the desired air control function. For example, the  $\text{CO-H}_2$  burner could fail to provide adequate conversion of  $\text{CO}$  with a deactivated catalyst, even with the fan operating properly and the catalyst bed at the desired temperature.

Air is currently analyzed by a Central Atmosphere Monitoring System, CAMS-I, which has mass spectrometer monitoring of several fixed mass-to-charge ratios and an infrared  $\text{CO}$

analyzer. Air can be drawn from the sample location through a filter and through tubing to a manual selector valve near the analyzer. Air in the main fan room is analyzed continuously and readings logged several times each day, and air from the other stations is analyzed on a rotating basis such that each sample point is monitored at least once a day.

The air sample inlet ports in submarines are arranged primarily to ensure that the air in each section is of good quality and that pockets of contaminants do not build up. The ports might not be placed optimally or in sufficient number to monitor the performance of individual air control units. Some ports, however, allow determination of local addition of contaminants to the atmosphere. For example, there are air ports at both the inlet and the exhaust of the battery compartment.

#### Possible Improvements In Current Air Control Systems

In current submarines, a performance malfunction of an air control unit that is used intermittently would be detected if an operator noticed that the concentration of a contaminant in the submarine's atmosphere did not decrease when the unit was turned on. Detection of a performance malfunction of an air control unit will be delayed, because of the large reservoir of air in a submarine. Even though the air circulates rapidly and is reasonably well mixed throughout the submarine, the large volume slows the rise or fall in concentration of any gas. The large volume provides time for corrective action, but it also has the deleterious effect of slowing detection of malfunctions. That slowing of detection can be minimized by using the CAMS-I to provide direct measurements of the performance of each air control unit. The air moving into and out of atmosphere control equipment is not routinely monitored in submarines. Monitoring is now accomplished with jumper hoses and performed only for troubleshooting. Implementing routine monitoring would require installation of air sample ports (preferably with airflow sensors, if they are not already present) at points before and after each air control unit. The air monitoring protocol would be modified for the operator to monitor the performance of the air control units. This monitoring could be automated in future CAMS designs equipped with microprocessor control.

Current submarines do not have enough air sample lines for direct monitoring of the performance of air control units. Installation of additional sample lines and data communication cables would be difficult in an existing submarine, but installation during new submarine construction should involve minimal additional expense.

The number of air sample inlet ports required in a submarine would increase if performance monitoring were implemented. The exact increase cannot be determined without a detailed analysis of the airflow in each class of submarine. For example, Figure X in the *Trident Atmosphere Control Sea Trial Final Report* (Rossier, 1984) indicates that one sample intake would be at the intake to the "air revitalization room" and one would be at the discharge of each of the two CO-H<sub>2</sub> burners and two at CO<sub>2</sub> scrubbers--a total of five air sample inlet ports to monitor the performance of the four units in the air revitalization room.

The Panel recommends that, during design and construction of new submarines, the Navy prepare for future implementation of performance monitoring of air control units and automatic control of the submarine atmosphere. That preparation would involve placement of air sample lines and data communication cables between the air control units and the CAMS. The current protocol for air control could be used when the submarine was first made operational, but the hardware would be present for future implementation of advanced air control.

The Panel envisions three possible levels or stages in the implementation of direct performance monitoring. These are listed below in order of increasing number of measurements and increasing automation.

- Two manual selector valves--a primary valve used regularly by the air control operator to measure air quality, as is done now, and an auxiliary valve to measure the performance of individual air control units, either regularly or when malfunctions are suspected. This level of implementation would require installation of additional air sample lines during submarine construction, but would require no substantial change in crew procedures.

- A single selector valve through which all sample lines are selected by an automatic valve sequencer (with backup manual operation). Implementation of this type of sample valve



requires use of the microprocessor capabilities of the proposed CAMS-II. An electric signal from each air control unit would inform the CAMS-II unit when an air control unit was activated. The CAMS-II unit would calculate a performance rating for each air control unit and activate an alarm if an activated air control unit were not performing according to specifications or if a rapid decay in the performance of the unit occurred over a period of several days.

- Automatic control of the submarine atmosphere. The second level of implementation described above is close to providing for completely automatic control of the submarine atmosphere. Such complete control has been proposed by Naval Research Laboratory and has been named "CAMS-IIB, an integrated life support system" (Saalfeld and Wyatt, 1976). Figure 7 of NRL Memorandum Report 3432 (dated December 1976), entitled "NRL's Central Atmosphere Monitor Program," (Saalfeld and Wyatt, 1976) showed a block diagram of this level of control. Although the diagram was referred to primarily in the context of automatic control, the report did mention air control unit performance monitoring--specifically that "the CAMS-II unit will be able to monitor the status of the carbon filter bed by monitoring the hydrocarbon concentration input and comparing it to the output concentrations and alert the crew when the carbon should be changed."

Below are suggestions as to how major modes of air control unit malfunctions could be detected by CAMS-II with the microprocessor programed for performance monitoring.

**CO-H<sub>2</sub> Burner:** Chemical deactivation (poisoning) of the Hopcalite catalyst can cause reduced conversion of CO and H<sub>2</sub>. CAMS-II could analyze the air before and after the unit during operation and compute the fractional conversion of CO and H<sub>2</sub> by the unit. The operator would be informed only if conversions dropped below minimal allowable values or if a rapid decay were detected by the computer over a period of several days. Another potential problem with the burner can occur when hydrocarbons undergo partial oxidation over the catalyst or when halocarbons undergo decomposition to produce HCl and HF. The computer could provide an alarm when unacceptable amounts of hydrocarbons or halocarbons enter the burner or when partially oxidized hydrocarbons or the acid gases are detected at the outlet of the burner.

**CO<sub>2</sub> Scrubber:** The computer could provide an alarm if CO<sub>2</sub> removal efficiency became unacceptable, if rapid decay in CO<sub>2</sub> removal efficiency were detected over a period of several days, or if emission of NH<sub>3</sub> or monoethanolamine (MEA) were detected at the outlet of the unit.

**Carbon Beds:** The computer could provide alarms if hydrocarbon removal efficiency became unacceptable, if rapid decay in hydrocarbon removal efficiency were detected over a period of several days, or if net production of CO or CO<sub>2</sub> were detected (an indication of fire in the carbon beds).

**Oxygen Generator Battery Compartments:** The computer could activate alarms if H<sub>2</sub> emission from any of the units became unacceptable.

#### Diver's Air

Nuclear submarines have hardware provisions to charge SCUBA flasks from the submarine compressed-air banks and to allow divers to leave the submarine under water. The five or six separate air banks are sometimes charged with outdoor air before a diving operation is scheduled, but that original state cannot be maintained. The air banks are needed for many routine purposes (e.g., pneumatic control systems) and emergency purposes (e.g., rapid emptying of ballast tanks) and so cannot be reserved for diver use.

Interior submarine air is compressed by the ship's oil-lubricated pumps, so the gas purity in the banks approaches that of the submarine interior. The gas is routed from the 4,500-psi compressor through a drier and particle filter and then through a series of pressure-reducing valves before it is breathed. Direct use of the submarine compressed air is allowed and indeed practiced in submarine emergency procedures. However, because of concern over the purity of this air, most divers use SCUBA flasks compressed with standard diving compressors on shore before the submarine deploys. A recent report has recommended, for purification of submarine air for divers, that a pressure-swing molecular-sieve adsorbent be placed in-line on existing submarines between the submarine air banks and the diver SCUBA charging port (Fargo, 1985).

A program called the Dry Deck Shelter (DDS) has recently started, with diving-air

requirements so stringent that use of shore-compressed air is logistically impossible (Cohen, 1981). Gas from the submarine air banks is routed through a special LiOH adsorbent bed to remove CO<sub>2</sub> before use by divers. A particle filter (Cuno Model 1H1; pore size, nominal 18  $\mu$ m) is installed after the adsorber-scrubber. An interim monitoring requirement established for this operation calls for use of the CAMS-I, a photoionization detector, and a number of detector tubes (U.S. Naval Sea Systems Command, 1986). The procedure is designed to verify that about 30 substances are below the OSHA permissible exposure limits (PELs) with a pressure-adjustment factor of 4. That factor assumes that most diving will be at 4 ATA or less, and it is not adjusted for different dive depths. Laboratory analyses of some air-bank samples from DDS operations reportedly (Weathersby et al., 1987) have shown concentrations below the DDS standards and the presence of compounds not on the list (Appendix A).

Before divers use a particular air bank, gas is taken downstream from the LiOH scrubber and tested by the CAMS-I or detector tubes for the eight gases listed in Table 3. If these DDS limits are met, a reading is taken with the photoionization detector. If the photoionization detector shows under 2 ppm (as isobutylene), the gas is declared acceptable. If the reading is

over 50 ppm (as isobutylene), the gas is declared unacceptable. Intermediate readings require the use of additional detector tubes, listed in Table 4, to see whether individual gases exceed the DDS limits. It is noted that the DDS limit is below the detector tube range for cyclohexane, ethylbenzene, methyl ethyl ketone, nonane, and trichloroethane. Also, there is no tube for heptane, naphthalene, and trimethylbenzene. Unacceptable breathing gas is a cause for the submarine to change air banks or to purge a dirty bank with fresh air. Only CO<sub>2</sub> is analyzed for repeatedly (at 30-min intervals) to check the adequacy of the LiOH adsorber. The Panel noted that capability is needed for continuously monitoring diver's air more precisely for CO<sub>2</sub>. It also noted the absence of analysis of particle contamination. Measurements should be made to determine the effectiveness of the particle filters.

Panel members who visited a submarine at Groton expressed concern that procedures that have been described as in place might not in fact be commonly used. The submarine that the Panel members toured had no LiOH scrubber to remove CO<sub>2</sub> from diver's air. The submarine personnel on board were not aware of the potential problem associated with high CO<sub>2</sub> concentrations but the submarine was not being used for DDS operations.

**TABLE 3**  
**Compounds Always Requiring Regular Analysis for DDS Operations<sup>a</sup>**

<u>Compound</u>	<u>DDS limit, ppm</u>	<u>CAMS-I<sup>b</sup></u>	<u>Detector Tubes<sup>c</sup></u>	<u>Tube range, ppm</u>
Ammonia	12.5	No	M-92115 D-CH 20501 K-8014-105Sc	10-400 5-700 10-260, 5-130
Carbon monoxide	12.5	Yes	M-47134 D-CH 25601 K-8014-106Sb	10-1,000 5-700 5-50
Carbon dioxide	1,250	Yes	M-85976 D-CH 23501 K-8014-126Sb	200-120,000 0.01-6 vol% 0.05-1.0%
FC-113	250	No	M-92030	100-4,000
FC-114	250	Yes	M-88536	200-2,000
FC-12	250	Yes	M-88536	25-3,000
Hydrazine	0.25	No	D-CH 31801 M-460425	0.25-3 0.5-40
Vinyl chloride	1.3	No	M-462534 D-67 28061 K-8014-132Sc	0-100 0.25-6 0.5-10

<sup>a</sup>Data from U.S. Naval Sea Systems Command (1986).

<sup>b</sup>The CAMS has a CO<sub>2</sub> accuracy of 1.25 torr (1,645 ppm), but usually operates better. On the first sample of the day, the CAMS should be checked with a detector tube. If the measurements agree, the CAMS alone can be used for later monitoring. Exception: If the CAMS has had a reading of 4 torr or higher (e.g., from another compartment), the next DDS CO<sub>2</sub> sample should be checked with both the CAMS and a detector tube.

<sup>c</sup>D, from National Draeger, Inc.; M, from MSA; K, from Kitigawa.



TABLE 4  
Compounds Sometimes Requiring Analysis for DDS Operations<sup>a</sup>

Compound	PEL, <sup>b</sup> ppm	DDS Limit, ppm	PID <sup>c</sup> Sens.	Maximum <sup>d</sup> Acceptable PID Reading	Detector <sup>e</sup> Tubes	Tube Range, ppm
Chlorobenzene	75	19	2.4	46	D-67 28761 M-85834 K-8014-178S	5-200 10-200 5-140
Cumene (isopropyl benzene)	50	12.5	2.0	25	M-460422	0-1,000
Cyclohexane	300	75	0.3	23	D-67 25201(H) K-8014-115S(H)	100-1,500 100-6,000
Ethyl benzene	100	25	1.8	45	D-6728381(H) M-463202 K-8014-179S	30-600 10-500 10-500
Heptane	500	125	0.3	38	No tube	--
Hexane	500	125	0.2	25	M-463838 D-67 28391(H) K-8014-113Sb	25-5,000 100-3,000 3-150
Isopropyl alcohol	400	100	0.2	20	K-8014-150S	100-20,000
Methyl bromide	20	5	4.2	21	D-67 28211 M-462135 K-8014-157Sb	3-100 2.5-90 2.5-80
Methyl chloride	100	25	0.12	3.0	M-92030	25-1,000
Methyl chloroform	350	88	0.04	3.5	D-CH 21101 M-88536(H) K-8014-160S	50-600 100-700 15-400
Methyl ethyl ketone	200	50	0.5	25.0	K-8014-139Sb(H)	100-14,000
Methyl isobutyl ketone	100	25	0.9	18.0	K-8014-155S(H)	50-10,000
Naphthalene	10	2.5	3.2	8.0	no tube	--

TABLE 4 (contd)

Compound	PEL, <sup>b</sup> ppm	DDS Limit, ppm	PID <sup>c</sup> Sens.	Maximum <sup>d</sup> Acceptable PID Reading	Detector <sup>e</sup> Tubes	Tube Range, ppm
Nonane	200 <sup>f</sup>	50	0.4	20.0	D-67 30201	200-5,000
Octane	500	125	0.4	50.0	D-67 30201	100-2,500
Phenol	5	1.25	1.7	2.0	D-CH 31501(H) K-8014-183U	5 0.5-25
Styrene	100	25	1.6	40	M-461781 D-67-23301 K-8014-158s	0-500 10-200 5-300
Toluene	200	50	1.8	90	M-93074 D-CH 23001 K-8014-124S	10-800 5-400 10-500
1,1,2-Trichloro- ethane	10	2.5	0.17	0.4	M-85834(H)	50-700
Trichloro- ethylene	100	25	1.6	40	M-460328 D-67 28541 K-8014-134S	25-600 2-200 5-300
1,2,4-Trimethyl- benzene	25 <sup>f</sup>	6.3	2.0	12.5	No tube	--
1,3,5-Trimethyl- benzene	25 <sup>f</sup>	6.3	2.0	12.5	No tube	--
Xylenes (o, m, p isomers)	100	25	1.9	48	M-463201 D-67 33161 K-8014-143S	10-800 10-400 5-1,000

<sup>a</sup>Data from U.S. Naval Sea Systems Command (1986).

<sup>b</sup>Occupational Safety and Health Administration's (OSHA) permissible exposure limits (PELs) for 8-h workday; except where noted.

<sup>c</sup>The number to divide the PID reading to determine the concentration of the substance of interest after the PID has been calibrated with a known concentration of isobutylene.

<sup>d</sup>PID reading less than value shown is below threshold toxic concentration of this compound; detector tubes are then unnecessary.

<sup>e</sup>D, from National Draeger Inc.; M, from MSA; K, from Kitigawa. An entry of (H) under detector tube means that the tube normally is used for higher concentrations than DDS limit. It may still be used by drawing additional gas through the tube (consult product sheet with the tube).

<sup>f</sup>American Conference of Governmental Industrial Hygienists (ACGIH) time-weighted average for 8-h workday.





## CHAPTER 4

# MEASUREMENT OF AIR QUALITY

The submarine atmosphere is monitored to determine whether life gases are within prescribed limits, to prompt corrective action as necessary to bring the gases within the limits, and to ensure that contaminant concentrations do not exceed safe limits. This chapter addresses the methods of monitoring submarine atmospheres currently in use.

The major instrumental method for atmosphere monitoring is the Central Atmosphere Monitoring System (CAMS-I). Each submarine also has portable analytic monitoring equipment and colorimetric detector tubes. The portable devices include a photoionization detector for total hydrocarbons, a fluorocarbon (FC) leak detector, an O<sub>2</sub> detector, an H<sub>2</sub> detector, and a torpedo fuel leak detector.

The development of atmosphere analyzers has been the focus of submarine atmosphere research and development at the U.S. Naval Research Laboratory during the last 25 years. The present CAMS-I was preceded by a series of analyzers that lacked reliability, were not versatile, or monitored only a few compounds. A prototype of the present CAMS-I system was installed in 1972 in the USS Hawkbill. By 1976, the CAMS-I was installed in more than 30 nuclear submarines. All nuclear submarines are now equipped with the CAMS-I system.

Research and development have recently focused on a new monitoring system, the CAMS-II, which has a scanning mass spectrometer and a microprocessor (Wyatt, 1984; DeCorpo et al., 1980). The CAMS-II, like the CAMS-I, monitors preselected compounds. The

Navy has not yet decided whether the CAMS-II will be adopted for use on all submarines.

### CENTRAL ATMOSPHERE MONITORING SYSTEMS

#### CAMS-I

The CAMS-I is a combination mass spectrometer and nondispersive infrared spectrometer with the capacity to monitor the atmosphere in various submarine locations. A dual-isotope, fluorescence, nondispersive, infrared spectrophotometer measures CO, and a fixed-collector mass spectrometer monitors O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, water vapor, and three FCs (FC-11, FC-12, and FC-114). The results are displayed continuously in a digital format for the crew. The atmosphere throughout the submarine can be analyzed rapidly (within a few minutes) by obtaining air samples from various submarine locations through a compartment selector valve. The CAMS-I activates an alarm system if out-of-tolerance conditions exist for any of the compounds being monitored. The CAMS-I can only monitor eight ions of preselected mass-to-charge ratios ( $m/z$ ), which are characteristic of the gases listed, and has no flexibility for adding new collectors for monitoring additional contaminants or for removing any of the eight existing collectors. The addition of materials, weapons systems, and operational requirements can result in changes in the type and concentration of contaminants in the submarine

atmosphere that cannot be monitored with the CAMS-I.

Readings are taken every hour with the CAMS-I during submersion, so that the fan room is monitored each hour, and each measurement station is monitored at least once every 24 h.

### CAMS-II

The CAMS-II is under development (Wyatt, 1984; DeCorpo et al., 1980). It has a micro-processor control system, the same infrared spectrometer as the CAMS-I (to measure CO), and a scanning mass spectrometer ( $m/z$ , 0-300). The mass spectrometer in the CAMS-II can monitor a greater number of contaminants than the CAMS-I, although the minimal detection limit for the atmospheric components currently measured by CAMS-I remains the same (Table 5). The CAMS-II scans its entire mass range according to a predetermined schedule and records the information on tape. The entire data base will be used only for later, on-shore laboratory analysis. On board the submarine, the CAMS-II will continuously monitor at least 12 preselected atmosphere components and, like the CAMS-I, activate an alarm system if any out-of-tolerance conditions exist. The mass spectrometer cannot identify all the various hydrocarbons, but rather "characterizes" them by the following technique. The ion-current intensities at mass-to-charge ratios of 43, 57, 85, 99, and 113 are summed to indicate the aliphatic hydrocarbon concentration. The sum of the ion currents at  $m/z$  of 91, 105, 119, 133, and 147 is used to indicate the aromatic hydrocarbon concentration, and the ion current at  $m/z$  78 is a measure of the benzene concentration.

On the whole, the CAMS-II offers greater flexibility than the CAMS-I, in that it is a scanning mass spectrometer and can detect more ions. If needed, changes can be made in the species detected and in the analysis and presentation of the data. The CAMS-II could allow the monitoring of new compounds added to the atmosphere of the submarine. In addition, it could be used to analyze trace compounds in the atmosphere of the submarine whose concentrations exceed minimal detection limits. The limit of sensitivity of the CAMS-II varies as a function of mass range (at  $m/z$  0-50, sensitivity of 1 ppm; at  $m/z$  50-300, sensitivity of 100 ppb). However, if these compounds do not exhibit

ions at the preselected mass-to-charge ratios, the information will not be available to the submarine crew and could be obtained only on shore. Current plans do not include analysis of archived data.

Several compounds can produce fragment ions with the same nominal mass-to-charge ratios, so it will be necessary to use a sophisticated method of analysis called probability-based matching (McLafferty, 1974) to determine which compounds might be contributing to the mass spectrum produced by the CAMS-II. The mass spectra and a table of probability values of compounds encountered in the submarine atmosphere could be stored in the CAMS-II, and an unknown compound identified by probability-based matching. A limitation of the probability-based-matching technique should be noted here. Probability-based matching is a useful technique for pure compounds, so it is used extensively, for example, in GC/MS. It is far less reliable if used when a mixture of gases is input to the spectrometer without prior separation. After each spectrum in the library has been tested, a table of compounds selected as being present in the submarine atmosphere could be established. Each entry would contain the name of the compound, its concentration, and the probability that the selection is correct.

The operator of the CAMS-II must be well trained to assess the validity of the analysis of the trace constituents in the submarine atmosphere, if the unit is to be used to its fullest potential as a trace-gas analyzer, especially for nonroutine analysis. The CAMS-II is the same size as the CAMS-I, and it can be installed in the submarine without major modification.

The decision to go forward with the CAMS-II needs to address questions of the future need for greater flexibility in atmosphere monitoring. The Navy should consider that the need for greater monitoring capability might be currently masked by the sparse monitoring data available. On the basis of the quantitative monitoring data available to the Panel (Appendix A), no new compounds were identified as present in high concentration and thus warrant routine monitoring.

TABLE 5

Detection Range Specifications for Current  
Mass-Spectrometric Monitoring Devices

<u>Substance</u>	<u>Range, CAMS-I and CAM-II</u>
H <sub>2</sub>	0.5-5.25% ± 10%
H <sub>2</sub> O	0.5-5.25% ± 10%
N <sub>2</sub>	26.3-92.1% ± 1.3%
O <sub>2</sub>	7.9%-26.3% ± 0.6%
CO <sub>2</sub>	0.16-3.29% ± 0.1%
<sup>a</sup> CO	13-131 ppm ± 10%
FC-11	6.6-65.8 ppm ± 6.6 ppm
FC-12	13.2-329 ppm ± 13.2 ppm
FC-114	13.2-329 ppm ± 13.2 ppm

Additional Specifications for CAMS-II

Total aliphatics	0.1-100 ppm ± 10%
Total aromatics	0.05-100 ppm ± 10%
Benzene	0.1-5 ppm ± 2 ppm

<sup>a</sup>Monitored with a nondispersive infrared spectrophotometer.

**PORTABLE ANALYTIC MONITORING  
INSTRUMENTS****Photoionization Detector (PID)  
for Total Hydrocarbons**

The instrument used to monitor the hydrocarbon content of the submarine atmosphere is the HNU PI 101 detector, a trace-gas analyzer that uses photoionization for detection (Spain et al., 1980). The process is termed photoionization because the absorption of ultraviolet radiation (photons) by molecules leads to ionization. The sensor consists of a sealed ultraviolet-radiation source that emits photons that are energetic enough to ionize some of the trace components of air. A chamber next to the ultraviolet source contains a pair of electrodes. When a positive potential is applied to one electrode, the field created drives any ions and electrons formed by absorption of UV light to the collector electrode, where the current (proportional to concentration) is measured. The analyzer can operate either from a rechargeable battery or from an AC charger. The useful range of the

instrument is from less than 1 ppm to about 2,000 ppm (isobutylene equivalents). Because most paraffins give a PID signal below that of an olefin at equal concentration, the total hydrocarbon concentration could be higher than 50 ppm before the PID indicates a potential hazard.

Photoionization detection is useful for classes of compounds, but not for specific compounds. Monitoring of atmospheric contamination is possible, but only if some assumptions and predictions can be made about the types of contaminants present.

The Panel found that the monitoring of hydrocarbons was inadequate. The photoionization detector is intended for use as a hydrocarbon monitor with the CAMS-I, but it is being introduced only now, and most submarines do not have it. Its use and operation are described in the *Dry Deck Shelter Manual* (U.S. Naval Sea Systems Command, 1986). The Panel recognizes a need for a stable photoionization instrument that is capable of continuous monitoring and can be moved about to establish the source of a leak.



### Fluorocarbon Detector

A submarine is equipped with a portable fluorocarbon (FC) detector that is used to determine the origin of suspected FC leaks, if the CAMS-I activates the alarm that indicates an out-of-tolerance concentration of FC vapors. Commercial air-conditioner FC leak detectors currently in use are not sensitive. The magnitude of the FC concentration is reflected by the frequency of a flashing light. The action of the instrument is based on thermal oxidation of FC to phosgene. The monitor responds to phosgene. More advanced detector systems are now commercially available and should be investigated.

### Oxygen Detector

In case the CAMS-I is not operational, the submarine is equipped with a portable instrument (Beckman D-2) that monitors  $O_2$  concentration on the basis of oxygen's paramagnetism. The oxygen analyzer is used to sample the atmosphere weekly, except when used for backup to the CAMS-I. Various membrane electrochemical  $O_2$  sensors are being evaluated by the Navy to replace the Beckman D-2; there is a need for a monitoring method that has greater sensitivity and reliability than the Beckman D-2.

### Hydrogen Detector

Submarines carry portable  $H_2$  monitors that are used to detect  $H_2$  in the battery compartment during charging. Various monitors are currently in use.

### Torpedo-Fuel Detectors

Submarines carry portable monitors that are used to detect fuel leaks from torpedoes in the torpedo room. The detectors thermally oxidize or reduce the torpedo fuels to oxides of nitrogen ( $NO_x$ ) or to hydrogen cyanide, which can then be monitored with colorimetric detector tubes (Musick and Johnson, 1967).

### Detector Tubes

Detector tubes are sealed glass vials containing chemical reagents and colorimetric indicator substances that develop a stain or color whose length or intensity depends on contaminant concentration when the indicator is exposed to a stream of air produced with a hand pump designated by the tube manufacturer as adequate for the purpose. *The Submarine Atmosphere Control Manual* (U.S. Naval Sea Systems Command, 1979) requires a battery of analyses with detector tubes at least once a week when the submarine is submerged. Indicator (or detector) tubes have found wide application as direct-reading industrial-hygiene air analysis instruments, because they are small, light, hand-operated, and safe in all atmospheres and give an immediate readout. In addition, an indicator tube is the simplest and most economical air analysis method available for many common air contaminants, including CO (ACGIH, 1983). Nevertheless, many industrial hygienists believe that detector tubes are inaccurate and unreliable for measuring environments potentially dangerous to life.

## ALTERNATIVE MONITORING METHODS

### Overview

On the basis of available information (Thompson, 1973; U.S. Naval Sea Systems Command, 1986; Williams and Johnson, 1968; Umstead et al., 1964; Eaton, 1970; Weathersby et al., 1987; Rossier, 1984; Saalfeld et al., 1971; Bondi, 1978; Saunders and Saalfeld, 1965; Kagarise and Saunders, 1962), currently unrecognized contaminants in the atmosphere of nuclear submarines might constitute new health hazards to submariners that require new monitoring methods. The Panel understands that current monitoring methods on submarines are not designed for complete analyses of submarine atmospheres and recognizes that detection of contaminant concentrations of physiologic significance might be beyond the capability of the equipment. The submarine atmosphere data presented elsewhere in this report (Appendix A) have been consolidated and combined with the Dry Deck Shelter (DDS) limits, 90-d Navy limits, and 90-d NRC continuous exposure guidance levels (CEGLs) (U.S. Naval Sea Systems Command, 1979; U.S. Naval Sea Systems

Command, 1986; National Research Council--1984a,b,c; 1985a,b; 1986c; 1987), and the detection limits of the various monitors, (personal communication with J. Wyatt, 1986; personal communication with T. Daley, 1986) to produce Table 6. The table clearly shows the advantage of the CAMS-II for measuring a large number of compounds, compared with the CAMS-I; the photoionization detector (PID), which will respond to any compound that can be ionized by 10.2-eV radiation; and the FC detector, which will respond to any compound that contains chlorine atoms.

The PID will respond to compounds on the basis of their ionization efficiencies. Sensitivities have been expressed relative to sensitivity to benzene (Table 7) (Spain et al., 1980). The PID has a detection limit of 1 ppm for isobutylene (0.5 ppm for benzene and 25 ppm for  $\text{NO}_2$ ), so it could be used to establish whether the total concentrations of airborne contaminants in submarines that are detectable are unsafe. That general statement must be qualified, because the PID limits of detection for some toxic contaminants are above the DDS limits, the 90-d Navy limits, and the 90-d CEGs and the PID must therefore not be used to establish safe concentrations of these contaminants (Table 6). Furthermore, the reading of a combination of contaminants at toxic concentrations might not equal the sum of the readings for the separate contaminants and thus might lead to misinterpretation in some cases.

Purer et al. (1983) described an alkali ionization-based FC detector that is not currently in use. Its relative responses were determined, and the data are in Table 8. The detector responds to halogenated hydrocarbons and has a detection limit of 1 ppm for methyl chloride (0.4 ppm for chlorobenzene and 5.8 ppm for FC-113), so it could be used to establish whether the total concentrations of airborne halogenated hydrocarbon contaminants in submarine atmospheres that are detectable with the FC detector are unsafe. That is, if the total concentration measured is below the allowed concentration for any particular FC, then a safe concentration for all can be assumed.

Such uses of those detectors are comparable with the use of the CAMS-II to monitor the total concentrations of aliphatic or aromatic hydrocarbons.

Although it is possible to identify newly recognized contaminants in submarine atmospheres by analyzing samples of spent activated-charcoal filters, results cannot be quan-

tified. It is recommended, therefore, that carefully controlled air sampling procedures be established that use organic adsorbents, such as Tenex, to collect the contaminants in the air of nuclear submarines. That approach should be adopted as a routine, and additional samples should be taken if contamination is suspected. Routine sampling and analysis of Tenex samples should be performed by land-based laboratories that use capillary gas chromatography with high-resolution mass spectrometry. Other techniques should be used for inorganic and small organic substances. The sampling and analysis protocol will provide a data base to establish the identities and concentrations of newly recognized contaminants and will allow responsible decisions to be made on the need for and design of monitors to measure newly recognized contaminants.

Several unquantified contaminants have been reported in the literature (Appendix A) for which the DDS limits, 90-d Navy limits, and 90-d CEGs concentrations (U.S. Naval Sea Systems Command, 1979; U.S. Naval Sea Systems Command, 1986; National Research Council--1984a,b,c, 1985a,b, 1986c, 1987) are lower than the detection limits of the available monitoring devices; these contaminants are listed in Table 9. Clearly, the introduction of the CAMS-II will not provide measurement and identification of these contaminants. Substances that currently cannot be measured can pose problems in the submarine environment. Additional monitoring devices (possibly Fourier-transform infrared spectroscopy, FTIR) must be designed for their analysis.

Other sampling procedures must be developed for the analysis of inorganic contaminants (e.g., mercury, lithium bromide, and lithium chromate), because Tenex is not the optimal sampling medium for these agents. Monitors for the oxides of nitrogen and sulfur must also be developed for use in nuclear submarines.

Monitors for ozone might become necessary as smoking decreases. Tobacco smoke rapidly combines with ozone produced by electrostatic precipitators. At present, there is unlikely to be a buildup of ozone with approximately 40% of the crew smoking. Studies are therefore needed to find out whether a reduction in smoking would result in an increase in ozone concentration. If so, HEPA filters could be used instead of the electrostatic precipitators for the control of particles in the submarine atmosphere.

TABLE 6

Summary of Concentrations Reported with Detection Limits as  
Function of Monitor

Substance	Concentration Reported <sup>a,b</sup>	Lowest of <sup>a,c</sup> DDS Limits, 90-d Navy Limits, 90-d CEGLs	CAMS-I <sup>a,b</sup>	CAMS-II <sup>a,b</sup>	PID <sup>b,d</sup>	FC <sup>a,b,e</sup> Detector
Acetone	nd	200	nd	100	f	nd
Acid gases	nr	--	nd	nd	nd	nd
Acrolein	nd	0.01	nd	nd	f	nd
Aerosols	57-218 $\mu\text{g}/\text{m}^3$	--	nd	nd	nd	nd
Ammonia	nd	12.5	nd	nd	f	nd
Asbestos	nd	--	nd	nd	nd	nd
Benzene	0.01	0.25	nd	0.02	f	nd
Butane	nd	g	nd	0.1	f	nd
Butylbenzene	0.7-1.1	h	nd	0.05	f	nd
Carbon dioxide	0.02-0.59%	1,250	5	5	nd	nd
Carbon monoxide <sup>i</sup>	1.2-2.9	12.5	0.5	0.5	nd	nd
Chlorinated H/C	nr	--	nd	na	nd	f
Chlorine	nd	0.1	nd	nd	nd	nd
Chlorobenzene	nr	19	nd	0.05	f	f
Chloroform	<0.1	1	nd	0.05	nd	f
Cigarette smoke	25-109 $\mu\text{g}/\text{m}^3$	--	nd	nd	f	f
Cumene	nr	12.5	nd	0.05	f	nd
Cyclohexane	nr	g	nd	0.1	f	nd
Decane	3.6	g	nd	0.1	f	nd
Dimethylheptane	2	g	nd	0.1	f	nd
Dimethylpentane	3	g	nd	0.1	f	nd
Dodecane	0.4	g	nd	0.1	f	nd
Ethane	0.18	g	nd	nd	nd	nd
Ethylbenzene	5	h	nd	0.05	f	nd
FC	5	100	na	na	nd	f
FC-11	nr	100	6.6	6.6	nd	f
FC-12	0.5-100	250	13.2	13.2	nd	f
FC-22	nr	100	nd	13.2	nd	f
FC-113	0-26,500	250	na	1.3	nd	f
FC-114	0-14.2	250	13.2	13.2	nd	f
Heptane	nr	g	nd	0.1	f	nd
Hexane	nd-0.1	g	nd	0.1	f	nd
Hydrazine	0.5	0.25	nd	nd	nd	nd
Hydrogen	0-0.3%	0.01%	5	5	nd	nd
Hydrogen chloride	nd	0.5	nd	nd	nd	nd
Hydrogen cyanide	nr	--	nd	nd	nd	nd
Hydrocarbons, aliphatic	5	g	nd	0.1	na	nd
Hydrocarbons, C <sub>9</sub> -C <sub>12</sub>	nr	g	nd	0.1	f	nd
Hydrocarbons, C <sub>9</sub> -C <sub>13</sub>	0.05-0.5	g	nd	0.1	f	nd



TABLE 6 (contd)

Substance	Concentration Reported <sup>a,b</sup>	Lowest of <sup>a,c</sup> DDS Limits, 90-d Navy Limits, 90-d CEGLs	CAMS-I <sup>a,b</sup>	CAMS-II <sup>a,b</sup>	PID <sup>b,d</sup>	FC <sup>a,b,e</sup> Detector
Hydrocarbons, C <sub>9</sub> -C <sub>14</sub>	0.05-0.2	g	nd	0.1	f	nd
Isopropanol	nr	1	nd	10	f	nd
Lithium bromide	nr	1 mg/m <sup>3</sup>	nd	nd	nd	nd
Lithium chromate	nr	--	nd	nd	nd	nd
Mercury	nr	0.01 mg/m <sup>3</sup>	nd	nd	nd	nd
Methane	2-60	0.013%	nd	nd	nd	nd
Methyl bromide	nr	5	nd	0.05	nd	f
Methyl chloride	nr	5	nd	0.05	nd	f
Methyl chloroform	0.9	88	nd	0.05	nd	f
Methyl cyclohexane	0.05-0.1	g	nd	0.1	f	nd
Methyl ethyl benzene	nr	50	nd	0.05,	f	nd
Methyl ethyl ketone	nr	50	nd	1	f	nd
Methyl heptanol	1	--	nd	10	f	nd
Monoethanolamine	nr	0.5	nd	1	f	nd
Naphthalene	nr	2.5	nd	1	f	nd
Nitric oxide	nr	0.25	nd	nd	nd	nd
Nitrogen dioxide	1.5	0.25	nd	nd	f	nd
Nitrous oxide	nr	--	nd	nd	nd	nd
Nonane	0.22	g	nd	0.1	f	nd
Octane	50-200	125	nd	0.1	f	nd
Oil smoke	0.15-0.20 mg/m <sup>3</sup>	0.2 mg/m <sup>3</sup>	na	na	f	nd
Oxides of nitrogen	nr	0.25	nd	nd	na	nd
Oxygen	>20%	--	5%	5%	nd	nd
Ozone	0.003-0.01	0.02	nd	nd	nd	nd
Pentane	<0.12	g	nd	0.1	f	nd
Phenol	nr	1.25	nd	1	nd	nd
Propane	<0.06	g	nd	0.1	nd	nd
Propyl benzene	0.05-0.4	h	nd	0.05	f	nd
Silicone	0.5-1.1	--	nd	nd	nd	nd
Styrene	nr	25	nd	0.05	f	nd
Sulfur dioxide	nr	1.0	nd	nd	nd	nd
Tar-like aerosol	nr	--	na	na	na	nd
Tetrachloro- ethylene	0.2-0.4	--	nd	0.1	nd	f
Tetramethyl pentane	0.2-0.5	g	nd	0.1	f	nd
Toluene	0.2-0.4	20	nd	0.05	f	nd
Total by PID	10-20	5	na	na	1	na
Total by FC detector	--	--	na	na	na	1
Trichloroethane	nr	2.5	nd	0.1	nd	f
Trichloroethylene	<0.5-15.2	25	nd	0.1	nd	f
Trimethyl benzene	nr	6.25	nd	0.05	f	nd
Trimethyl heptane	2	g	nd	0.1	f	nd
Undecane	1	g	nd	0.1	f	nd
Vinyl chloride	nr	1.0	nd	0.1	nd	f

TABLE 6 (contd)

<u>Substance</u>	<u>Concentration Reported<sup>a,b</sup></u>	<u>Lowest of<sup>a,c</sup> DDS Limits, 90-d Navy Limits, 90-d CEGLs</u>	<u>CAMS-I<sup>a,b</sup></u>	<u>CAMS-II<sup>a,b</sup></u>	<u>PID<sup>b,d</sup></u>	<u>FC<sup>a,b,e</sup> Detector</u>
Vinylidene chloride	nr	0.13	nd	0.1	nd	f
Xylene	0.2-10	25	nd	0.05	f	nd

<sup>a</sup>Parts per million unless otherwise noted.

<sup>b</sup>nr = cited in documents, but concentration not reported; nd = not detectable by specified monitor; na = not applicable.

<sup>c</sup>Lowest concentration required by following limits: U.S. Naval Sea Systems Command (1979), U.S. Naval Sea Systems Command (1986), National Research Council recommendations (1984a,b,c; 1985a,b; 1986c; 1987).

<sup>d</sup>Photoionization detector with 10.2-eV lamp and calibrated with isobutylene.

<sup>e</sup>Fluorocarbon detector calibrated with methyl chloride.

<sup>f</sup>Detectable by specified monitor. In case of PID and FC detector, individual species not identifiable.

<sup>g</sup>Total aliphatic hydrocarbons (less methane), 60 mg/m<sup>3</sup>.

<sup>h</sup>Total aromatics (less benzene), 10 mg/m<sup>3</sup>.

<sup>i</sup>Monitored with infrared absorption in CAMS-I and CAMS-II.

TABLE 7

Relative Photoionization Sensitivities (Based on Benzene = 10.0)  
for Various Gases with a 10.2-eV Spectral Source<sup>a,b</sup>

<u>Functional Group</u>	<u>Relative Sensitivity</u>	<u>Examples</u>
Hydrocarbon, aromatic	10.0	Benzene, toluene, styrene
Amine, aliphatic	10.0	Diethylamine
Chlorinated, unsaturated	5-9	Vinyl chloride, vinylidene chloride, trichloroethylene
Carbonyl, saturated	5-7	Methyl ethyl ketone, methyl isobutyl ketone, methyl acetone
Carbonyl, unsaturated	3-5	Acrolein, propylene cyclohexene, allyl alcohol
Sulfide	3-5	Hydrogen sulfide, methyl mercaptan
Hydrocarbon, large aliphatics	1-3	Pentane, hexane, heptane
Ammonia	0.3	--
Nitrogen dioxide	0.02	--
Hydrocarbon, small aliphatics	0	Methane, ethane, propane, butane
Major components of air	0	Hydrogen, water, nitrogen, oxygen, carbon dioxide, carbon monoxide

<sup>a</sup>Data from Spain et al. (1980).

<sup>b</sup>Detector is 1.6 times more sensitive to benzene than to isobutylene which is the usual calibration standard.



TABLE 8

Relative Sensitivities (Based on Methyl Chloride = 1.0)  
for Various Gases with Fluorocarbon (FC) Detector<sup>a</sup>

<u>Functional Group</u>	<u>Relative Sensitivity</u>	<u>Examples</u>
Fluorocarbons (FCs)	1.9-5.8	FC-11, FC-12, FC-113, FC-114
Chlorinated, saturated	1.0-4.5	Methyl chloride, dichloromethane, chloroform, methyl chloroform, carbon tetrachloride, ethyl chloride, dichlorodifluoroethane, dichloroethane
Chlorinated, unsaturated	2.2-3.8	Trichloroethylene, vinyl chloride, dichloroethylene, tetrachloroethylene
Chlorinated, aromatic	0.4	Chlorobenzene

<sup>a</sup>Data from Purer et al., 1983.

TABLE 9

Contaminants with DDS Limits/90-d Navy Limits/90-d COT CEGL  
Concentrations Lower Than Detection Limits of CAMS-II

Substance	Concentration Reported	Lowest of DDS Limits, 90-d Navy Limits, 90-d CEGLs <sup>a</sup>	CAMS-II Detection Limit	PID, Freon detector Detection Limit
Acrolein	nd	0.01 ppm	nd	3-5 ppm
Ammonia	2 ppm	12.5 ppm	nd	3 ppm
Hydrazine	0.5 ppm	0.25 ppm	nd	nd
Hydrogen chloride	nr	0.5 ppm	--	nd
Lithium bromide	nr	1 mg/m <sup>3</sup>	nd	nd
Lithium chromate	nd	--	nd	nd
Mercury	nr	0.01 mg/m <sup>3</sup>	nd	nd
Methane	2-60 ppm	0.013%	nd	nd
Monoethanolamine	nr	0.5 ppm	1 ppm	1 ppm
Nitric oxide	nr	0.25 ppm	nd	nd
Nitrogen dioxide	0.035-1.5 ppm	0.25 ppm	nd	20 ppm
Ozone	3-10 ppb	25 ppb	nd	nd
Sulfur dioxide	nr	1 ppm	nd	nd

nd: Not detected.

nr: No concentration reported.

<sup>a</sup>Lowest concentration required by U.S. Naval Sea Systems Command (1979); U.S. Naval Sea Systems Command (1986); or National Research Council (1984a,b,c; 1985a,b; 1986c; 1987).

#### Currently Recognized Contaminants

Emergency exposure guidance levels (EEGLs) and continuous exposure guidance levels (CEGLs) for atmospheric contaminants were recommended several years ago and are being reviewed and updated by the National Research Council's Committee on Toxicology (1984a,b,c; 1985a,b; 1986c; 1987). There are also interim air purity guidelines for Dry Deck Shelter (DDS) operations (U.S. Naval Sea Systems Command, 1986). No available epidemiologic data suggest that exposure to operational concentrations of contaminants results in adverse health effects in submariners. The concentrations found in submarines seldom were as high as the recommended concentrations or standards. The proposed introduction of the CAMS-II in submarines represents an obvious extension to existing monitoring devices. According to the

current plan, analysis of CAMS-II data obtained from scanning the mass spectrum from 0 to 300 m/z will not be immediately available to submariners. The mass spectra will be stored and archived. No analysis is planned of the archived data.

New monitors have been suggested, and others might be required after further identification of additional specific contaminants found in the atmospheres of nuclear submarines. In the interim, two nonspecific monitors should be designed. They could be based on the PID and the fluorocarbon (FC) detector. The PID could use a series of spectral sources of different energies that would enable it to respond to different classes of compounds on the basis of their ionization potentials. They should be capable of being operated continuously. Safe concentrations should be set for the PID and FC detector; if these are exceeded, the detectors could be carried around the submarine to

ascertain the origin of the contamination.

Monitors must also be designed to monitor contaminants that cannot currently be measured; specific portable monitors are preferable. This approach is recommended for monitoring additional contaminants found in the routine Tenex sampling of nuclear submarine atmospheres. Decisions must be made as to the frequency of monitoring when continuous operation is not provided.

### Aerosol Measurements

Aerosol measurements are conducted routinely twice a year on diving air that has been compressed on shore. Compressed air is discharged through a preweighed Gelman all-glass fiber filter pad for a predetermined time at a specific pressure, and the particle content per unit volume is determined by filter-weight difference and total air volume sampled. Diving air is considered acceptable by the U.S. Navy (U.S. Naval Sea Systems Command, 1985) when the total aerosol content does not exceed 5 mg/m<sup>3</sup>. Samples are collected randomly after equipment repair. On-shore diving-air compressors are of the oilless type and have coarse particulate filters on the high-pressure line, so they can meet the aerosol-concentration criterion without difficulty, unless a breakdown occurs.

Diver's air produced on a submarine is compressed by an oil-lubricated pump and might have a higher particle content, especially when produced during prolonged submergence. However, there are no provisions for making similar concentration measurements, largely because it is impractical to carry or use a sensitive analytic balance on an operating submarine. A simple, but less accurate, method for aerosol measurement of submarine air, as well as submarine-generated diving air, would be to use the same technique for collecting samples on white Gelman all-glass fiber filter pads, but to analyze them for discoloration, by light reflectance, or by change in opacity to light penetration. It would, of course, be necessary to prepare calibrated color or opacity standards based on correlations with filter weight gains. For sampling the ambient submarine atmosphere, simple compressed-air ejector tube could be connected to the compressed air line and the negative-pressure leg used to draw a sample of air through the sampling filter. Automatic paper-tape samplers that collect an

air sample on white filter paper and then measure the discoloration are commercially available. That technique is particularly sensitive to black elemental carbon.

There are also simple beta gauges for measuring aerosols. That technique makes use of a source of beta particles and a filter assembly on which the sample is collected. Attenuation is measured before and after the filter is exposed, and the readout is proportional to the mass of the particles collected. A balance is not needed and the instrument is rugged and durable.

For more quantitative assessment of aerosols, total-scattering photometers, used routinely to test high-efficiency particle-absorbing (HEPA) filters associated with nuclear-plant safeguard facilities, can measure particle concentrations as low as 10 per milliliter accurately and reliably. Also available are single-particle counters that give particle-size information, as well as particle numbers. Both instruments can be operated intermittently or continuously. Routine use of these instruments on operating submarines is not recommended, but special studies with them are desirable and appropriate to define the characteristics of the submarine aerosol during prolonged submergence.

The chemical composition of submarine aerosol particles is largely unknown, except that a major fraction is associated with cigarette-smoking. Detailed analyses of the compounds collected on Gelman filters could be conducted at on-shore laboratories by extracting benzene-soluble compounds for gas chromatography and mass spectrometric examination and subjecting the inorganic residues to analysis by atomic-absorption spectrometry. Other methods could be used: measurement of solids by mass spectrometry is well advanced (MacFarlane, 1983), and serial deposition of aerosol particles on a moving tape has been used in research studies. Point-to-plane electrostatic precipitation of aerosol particles onto a solid substrate has also been documented and is used commercially in TSI (Minneapolis) instruments for total concentration analysis. The Panel is aware of no commercial instrument that collects particles on a moving tape for introduction into a mass spectrometer, but the technology for constructing such a device is at hand.

### Detector Tubes

The detector tubes carried on board, their minimum detectable concentrations, and some

of the interfering substances are shown in Table 10. Many tubes respond to more than one substance, at least at high concentration. The use of hydrazine and ammonia tubes results from different administrative requirements. The sensitivity, interferences, and limitations depend on the specific tube used. A serious limitation is that they are not capable of measuring most of the trace quantities of contaminants found in submarine air.

Detector-tube manufacturers exercise their own quality-assurance program with no agency providing an oversight function. The National Institute for Occupational Safety and Health (NIOSH) undertook this responsibility for a few years but discontinued it in 1980. The NIOSH Certified Equipment List (NIOSH, 1980) included quality assurance information for air detector tubes for CO, CO<sub>2</sub>, CS<sub>2</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, HCl, NH<sub>3</sub>, HCN, acetone, benzene, ethyl benzene, hexane, carbon tetrachloride, ethylene dichloride, methyl bromide, methylene chloride, toluene, trichloroethylene, perchloroethylene, and vinyl chloride. In addition, NIOSH was preparing to certify tubes for acrolein, aniline, formaldehyde, HF, mercury, methyl ethyl ketone, phosgene, phosphine, styrene, and xylene (American Conference of Governmental Industrial Hygienists [ACGIH], 1983). However, NIOSH has no plans to resume its detector-tube certification program. When NIOSH was operating its certification program, a short list of tubes was being verified as giving results within  $\pm 25\%$  of the correct concentration when tested at 1-5 times the TLV or  $\pm 35\%$  at half the federal standard (Federal Register, 1973). The Council of Europe adopted a resolution in 1974 calling for a deviation of not more than 30% from the TLV. It also recommended that, in every case, the user carry out at least two determinations with detector tubes (ACGIH, 1983).

Uncertified tubes are generally regarded by the industrial hygiene profession as being no more reliable than  $\pm 50\%$  under the best conditions, which include freshly manufactured tubes, air at ambient temperature, and absence of interfering chemicals. For example, the benzene tube will respond to other aromatic compounds with the same sensitivity as it does to benzene. (*Drager Detector Tube Handbook*, 1985, gives additional examples of lack of specificity.) Some indicator tubes have indefinite shelf-life--e.g., for H<sub>2</sub>S--but many deteriorate within a year or two. It is customary to extend the shelf-life of tubes by storing

them under refrigeration, but, because the speed of most chemical reactions is sensitive to temperature, the tubes must be warmed to ambient temperature before use if the calibration charts accompanying them are to be relied on.

Long storage and especially storage at unfavorable temperature can severely degrade many types of tubes, especially those depending on color reactions involving organic dyes. For example, the shelf life of a Drager CO tube is 1 day at 150°F (ACGIH, 1983). The only safe procedure is to test with known gas mixtures and to do it immediately before making measurements with a representative sample of the tubes from the batch that will be used. That is especially important after a period equivalent to a large fraction of the normal shelf-life. For gases, it means ready availability of cylinders of compressed gases of known composition in the correct concentration range; for vapors, it is likely to mean generating known concentrations from liquids. Neither calibration method is necessarily compatible with submarine space and skill. Some of the tubes generate volatile toxic reaction products that will be discharged from the hand pump into the submarine atmosphere.

Chapter T, "Direct Reading Colorimetric Instruments" (ACGIH, 1983), gives an instructive summary. It states:

- "Accuracy [of tubes] was found highly variable. In some cases, the tubes were completely satisfactory; in others, completely unsatisfactory."

- "At present, results may be regarded as only range-finding and approximate in nature."

- "Most tubes are not specific."

- "Detector tubes have been widely advertised as being capable of use by unskilled personnel."

It is true that the operating procedures are simple, rapid, and convenient, but many limitations and potential errors are inherent in this method, and it has been repeatedly demonstrated in practice that serious errors in sampler operation, in selection of sampling locations and times, and in interpretation of results occur, unless the tubes are in the hands of trained operators who are closely supervised by competent professionals. The latter point must be emphasized. The Panel believes it is inappropriate to assert (as one manufacturer did) that, "issued to a shift foreman, project



TABLE 10

Detector Tubes Required on Submarines<sup>a</sup>

<u>Contaminant</u>	<u>Drager Tube</u>	<u>No. Pump Strokes</u>	<u>Detectable Range</u>	<u>Principal Interference</u>
Acetone	CH 22901	10	100-12,000 ppm	Other ketones react like acetone; alcohols and esters cause plus errors
Ammonia	CH 20501	10	5-70 ppm	Hydrazine and dimethyl hydrazine react like ammonia; organic bases
Benzene	CH 24801	20	15-420 ppm	Toluene, xylene, naphthalene; all compounds resistant to pretreatment with acid
Carbon dioxide	CH 23501	5 1	0.1-1.2% 0.5-6%	None
Carbon monoxide	CH 20601	10 1	10-30 ppm 100-3,000 ppm	Acetylene reacts like CO; high concentrations of some halogenated hydrocarbons and hydrocarbons (propane, butane, perchloroethylene)
Chlorine	CH 24301	10	0.2-3 ppm	Bromine reacts like Cl <sub>2</sub> ; chlorine dioxide gives double Cl <sub>2</sub> reading; NO <sub>2</sub>
Hydrazine	CH 31801	10	0.25-3 ppm	Dimethylhydrazine, ethylene imine, propylene imine, and ammonia react like hydrazine; other amines
Hydrochloric acid	CH 29501	10 20	1-10 ppm 0.5-5 ppm	Chlorine, high humidity

TABLE 10 (contd)

Detector Tubes Required on Submarines<sup>a</sup>

<u>Contaminant</u>	<u>Drager Tube</u>	<u>No. Pump Strokes</u>	<u>Detectable Range</u>	<u>Principal Interference</u>
Hydrocyanic acid <sup>c</sup>	CH 25701	5	2-30 ppm	--
Nitrogen dioxide	CH 30001	5	0.5-10 ppm	Chlorine and ozone
Ozone	CH 31301	10	0.05-1.4 ppm	Nitrogen dioxide and chlorine
Sulfur dioxide	CH 31701	10	1-25 ppm	Nitrogen oxides
Toluene	CH 27801	10	25-1,860 ppm	Xylenes, ethyl benzene, and cumene react like toluene
Total hydrocarbon	CH 23001	5	Qualitative	Petroleum hydrocarbons give a (Toluene tube) pale reddish brown color
1,1,1-Trichloroethane	CH 21101	2	50-600 ppm	Other chlorinated hydrocarbons
Propylene glycol dinitrate <sup>c</sup>	MSA	--	--	--

<sup>a</sup>Data from Weathersby et al. (1987) and *Drager Detector Tube Handbook* (1985).

<sup>b</sup>Drager tube readings are by color change.

<sup>c</sup>Used in torpedo room for detection of leaking fuel.

leader, or supervisory personnel, the direct reading device is used to determine exact concentrations. This ability to quickly determine the nature and extent of a toxic gas release helps avoid unnecessary disruption of plant operations."

Many small hand-held, battery-operated instruments are available, reliable, and accurate. They are capable of giving a continuous readout when needed. Such devices would be superior to detector tubes as a CAMS backup. Alternative portable, battery-operated instruments of reasonable reliability and accuracy are described (ACGIH, 1983). Some, such as the Bacharach H<sub>2</sub>S detector, are diffusion instruments that do not require a pump. Others, such as the Ecolyser CO instrument, operate on the electrochemical oxidation principle and require a battery-operated pump. Small hand-held instruments that measure oxygen and combustible vapors are available from a number of manufacturers. ACGIH has listed and described all portable, battery-operated, direct-reading instruments for airborne gases and vapors.

Improved protocols for the use of detector tubes on submarines should be prepared for the guidance of users, and improved instructions should be issued, to assist in interpreting the implications of detector-tube readings for human health effects. Special attention needs to be given to the quality-assurance aspects of detector-tube freshness, reading correctness, storage, and use conditions. When available and as soon as possible, more accurate and more reliable instruments should be substituted for detector tubes for performing routine measurements, and simple methods for checking zero and span readings should be built into each newly adopted instrument.

In the long term, the air monitors of choice might be yet-to-be-developed biosensors. The Navy should follow future developments in this field.

#### METHODS FOR MEASUREMENT OF DIVER'S AIR

Submarine air from the air banks that is used to prepare diver's air is monitored for hydrazine, CO<sub>2</sub>, CO, FC-12, FC-114, total hydrocarbons, and other compounds before use by divers in accordance with procedures outlined in Chapter 3. The current method for monitoring CO<sub>2</sub> for diver's air involves the periodic use of

CAMS-I. The CO<sub>2</sub> concentration that is safe for diver's air is lower than the safe concentration on the submarine at 1 ATA, and the reading on the CAMS-I for CO<sub>2</sub> for diver's air is close to the detection limit of the CAMS-I. The ability to monitor CO<sub>2</sub> continuously for diver's air is necessary. To ensure greater precision, the measurements should be midrange, 0.01-2.0% (not at the detection limit of the instrument).

#### APPLICATION OF MONITORING PROCEDURES

The ultimate effectiveness of monitoring on the submarine is tied to the training of personnel, the careful execution of established procedures, and good judgment. The Panel observed that training in the use and function of the monitoring and control equipment is concentrated at the enlisted level. The responsibility for operating the equipment is distributed among several persons. The Panel recommends that methods of instruction of personnel be reviewed and updated. The Panel also recommends that the command level be given additional specific training in physiology and in the operation of the air monitoring and control equipment.

The *Submarine Atmosphere Control Manual* (U.S. Naval Sea Systems command, 1979) does not contain detailed instruction on the use of the monitoring equipment immediately after an emergency, particularly as to which gas readings are most important to monitor.

The Panel recommends that methods for determining the safe conclusion of an emergency situation be established in terms of instrumentation and setting of all-clear standards (e.g., the concentrations of HCN, HCl, CO, and NO<sub>x</sub> after a fire might be used as indexes of air purity).

The *Submarine Atmosphere Control Manual* does not contain information on the probable consequences of exceeding the guidelines, for various extents of excess exposure, or on the actions that should be taken for various exposures.

The Panel recommends that the *Submarine Atmosphere Control Manual* be revised to contain usable toxicologic information on the consequences of exceeding recommended concentration limits. Three levels of air control needs were recognized by the Panel:

- Category I substances ( $O_2$ ,  $CO_2$ , and  $CO$ ) should be monitored continuously.

- Category IIa substances ( $NO_x$ ,  $HF$ ,  $HCl$ ,  $Cl_2$ ,  $NH_3$ ,  $HCN$ ,  $O_3$ ,  $H_2$ ,  $FC-12$ ,  $FC-114$ , acrolein, tobacco-smoke constituents, total aromatics, and total aliphatics) should be monitored routinely. These are normal-release substances, in contrast with category IIb substances (fire products, spill products, monoethanola-

mine, and total hydrocarbons), which might result from abnormal release. Category IIb substances should be monitored according to need.

- Category III substances (toxic or possibly toxic substances) should be measured at set intervals, until a sufficient data base exists to determine the appropriate frequency and substances for monitoring.





## CHAPTER 5

# CONCLUSIONS AND RECOMMENDATIONS

### ATMOSPHERIC SURVEY AND CONTROL

1. Results of full analysis of the submarine atmosphere were not available to the Panel, and apparently no such analysis has been done in recent years. Therefore, the Panel was limited in its ability to answer fully the questions put to it. Without such information, detailed conclusions and recommendations that reflect the current environment cannot be offered.

The Panel recommends that the Navy thoroughly survey various classes of submarines for trace contaminants and particulate matter. Carefully controlled sampling procedures should be established to collect samples quantitatively with such sorbents as Tenex and have them analyzed in on-shore laboratories. Other techniques should be used for inorganic and small organic substances. Compounds of concern that have been detected or are suspected, but for which no concentrations are available, should be measured.

2. Studies have shown that cigarette smoking accounts for large amounts of particulate matter, CO, and some of the hydrocarbons in the submarine atmosphere. The health hazard of sidestream smoke and other problems associated with passive smoking have been discussed in recent National Research Council reports. Elimination of smoking would have a great impact on air quality in submarines under normal oper-

ations. Contaminants introduced by smoking decrease performance efficiency and increase the load on air control equipment; a result is an additional service rate for air monitoring and other equipment. (Smoking is prohibited on French submarines.)

The Panel recommends that smoking be eliminated to improve air quality under normal operations.

3. The minute-by-minute status of the performance of the air control equipment is not known. Failures of the control equipment are detected by measuring an increase in the average concentration of a gas in the atmosphere. Air monitoring can provide a late indication of an equipment failure, because of the large volume of submarine air. The air entering and leaving the control equipment is not monitored routinely on submarines (it is done with jumper hoses and only for trouble-shooting).

The Panel recommends that the number of air sampling ports going to the CAMS-I be increased to provide continuous information on the performance of the air control equipment.

4. Two-stage electrostatic precipitators are installed in the ventilation equipment. It was not clear to the Panel whether the electrostatic precipitators have adequate efficiency, whether the airflow through them is sufficient, and whether they are maintained adequately.

The Panel recommends that the effectiveness of the electrostatic precipitator system be addressed.

5. Nontoxic paints have been the subject of research for a number of years, but the Panel is not aware that any have been adopted for use on the submarine.

The Panel recommends that nontoxic paints be developed and used on board submarines with due consideration for the potential for biologic growth on such painted surfaces.

### INSTRUMENTS FOR MONITORING

6. A consensus method of satisfactorily monitoring hydrocarbons has not been established. New methods for monitoring hydrocarbons have been suggested, but no consensus method has been established. Also, new monitors might be required after further identification of additional specific contaminants in the submarine atmosphere. The CAMS-II will be used to monitor aliphatic and aromatic hydrocarbons as a group.

The Panel recommends that the Navy develop a stable photoionization instrument that is capable of continuous monitoring and can be moved about to establish the source of a leak.

7. Adequate monitoring equipment is not available for the analysis of many trace contaminants, especially inorganic substances. Many compounds with DDS limits cannot be monitored with the CAMS-I or CAMS-II. Detector tubes are not suitable for real-time at-sea monitoring.

The Panel recommends that monitors be used in place of detector tubes for the analysis of specific trace contaminants, such as oxides of nitrogen, hydrogen chloride, sulfur dioxide, and ozone. Additional monitoring equipment is needed for acrolein, mercury, and lithium salts.

8. The Panel concludes that current practice for monitoring submarine air quality is incomplete in that contaminant concentrations of physiologic importance might be outside the capability of the equipment. CAMS-II is not

more effective than CAMS-I for the currently monitored substances at low concentrations, because the lower limit of detection of the two instruments is the same. CAMS-II can detect more substances than CAMS-I, but does not add capability for trace contaminants, in that most information on additional substances will be collected on tape (no direct readout) and accessible only to personnel on shore.

The Panel recommends that monitors be developed to detect lower concentrations of gases that pose a hazard at very low concentrations (possibly Fourier-transform infrared spectroscopy [FTIR] or other instrumentation that meets performance specifications). Additional instrumentation should be used to identify various contaminant sources (e.g., nonspecific portable photoionization detectors to replace detector tubes, and a portable fluorocarbon monitor in place of current industrial leak detector).

9. Direct air sampling of submarines is needed to identify previously unrecognized contaminants that might pose health problems. The current method of analyzing spent charcoal filters provides only qualitative, not quantitative, information.

The Panel recommends that evacuated canisters and organic sorbent traps, such as Tenex, be used to make quantitative measurements of air contaminants in nuclear submarines routinely. A plan should be put in place to look periodically at the archived data from the CAMS-II.

10. Airborne particulate matter is not monitored, and it is not possible to ensure that filtration is adequate.

The Panel recommends that equipment be provided to measure particulate matter on submarines in real time and periodically by detailed shore-based methods.

11. Oxygen is routinely monitored with the CAMS-I. The instrument to back up the CAMS-I for monitoring  $O_2$  is the Beckman D-2, which lacks sensitivity.

The Panel recommends that the Navy develop alternative monitoring instruments

that have greater sensitivity and reliability than the Beckman D-2.

### DIVER'S AIR

12. Diver's air passes through a LiOH scrubber and an 18- $\mu$ m filter. There is no method for monitoring particulate matter. The Panel is concerned that diver's air is not filtered adequately to remove respirable particulate matter (<10  $\mu$ m).

The Panel recommends that the Navy ensure that diver's air is filtered adequately to remove respirable particulate matter and that limits for total particulate matter be established for diver's air on submarines. The 5 mg/m<sup>3</sup> limit should be adhered to until new studies suggest otherwise.

13. The current method for monitoring diver's air for CO<sub>2</sub> involves the periodic use of the CAMS-I. The level of CO<sub>2</sub> concentration that is safe for diver's air is lower than the concentration that is safe on the submarine at 1 ATA, and the CO<sub>2</sub> reading on the CAMS-I for diver's air is close to the detection limit of the CAMS-I.

The Panel recommends that capability be developed for continuously monitoring diver's air for CO<sub>2</sub> more precisely to ensure the quality of diver's air. The measurements should be midrange (0.01–2.0%), so that concentrations well below the safe concentrations are detectable.

### INFORMATION, TRAINING, AND RESEARCH NEEDS

14. The Panel notes that categories of atmospheric gases can be established according to hazard potential.

The Panel recommends the following air monitoring categories:

- Category I substances (O<sub>2</sub>, CO<sub>2</sub>, and CO), for which continuous monitoring is essential for life support.

- Category IIa substances (NO<sub>x</sub>, HF, HCl, Cl<sub>2</sub>, NH<sub>3</sub>, HCN, O<sub>3</sub>, H<sub>2</sub>, FC-12, FC-114, acrolein, tobacco-smoke constituents, total aromat-

ics, and total aliphatics), which are commonly or occasionally released and should be monitored routinely, in contrast with category IIb substances (fire products, spill products, monoethanolamine, and total hydrocarbons), which might result from abnormal release and should be monitored according to needs.

- Category III substances (toxic or possibly toxic substances), which should be measured at set intervals, until a sufficient data base exists to determine the appropriate frequency and substances for monitoring.

15. The deep-fat fryer used for food preparation on submarines is a source of atmospheric contaminants with possible health consequences. The deep-fat fryer adds to the burden on the atmosphere control equipment and is a fire hazard.

The Panel recommends that the Navy evaluate the impact of the deep-fat fryer in the submarine atmosphere and consider eliminating it from submarines if necessary in order to eliminate this source of atmospheric contaminants.

16. The current *Submarine Atmosphere Control Manual* does not contain information on the probable consequences of exceeding the guidelines for various extents of excess exposure or on the action that should be taken in the event of various exposures.

The Panel recommends that the *Submarine Atmosphere Control Manual* contain usable toxicologic information on the consequences of exceeding recommended exposure concentration limits.

17. The NRC Committee on Toxicology (COT) has been updating exposure guidance levels for atmospheric contaminants since 1984. The values reported are emergency exposure guidance levels (EEGLs) for 1- and 24-hour exposures and continuous exposure guidance levels (CEGLs) for 90-day (24-hour/day) exposures.

The Panel recommends that current COT EEGLs and CEGLs be cited in the *Submarine Atmosphere Control Manual*.

18. The Panel concludes that information on the concentration of contaminants in submarine air is incomplete. The Navy conducts tests on



the air-pollution consequences of materials that might be used on the submarine and catalogs the resulting information according to whether the materials are permitted, restricted, etc. This procedure is time-consuming and has not kept up with all new products as soon as they are introduced.

The Panel recommends that work on the screening of materials be continued and that the permitted-substance list for products that can be used without restrictions be expanded and kept current. Emissions under both use and storage conditions should be considered.

19. Current guidance for the use of detector tubes is incomplete. For example, instructions contained in the *Submarine Atmosphere Control Manual* on detector tubes are not sufficiently quantitative (e.g. "store in a cool, dry location"). Also, the quality assurance of detector tubes is provided currently by the manufacturer with no agency oversight. The Panel considers detector tubes to be less reliable than stated in the *Submarine Atmosphere Control Manual* ( $\pm 50\%$  vs  $\pm 30\%$ ).

The Panel recommends that improved protocols for the use of detector tubes on submarines be prepared for the guidance of users and that improved instructions be issued to assist in interpreting the implications of detector-tube readings for human health effects. Special attention needs to be given to quality assurance, with regard to detector-tube freshness, reading correctness, and storage and use conditions. High priority should be given to substitution of more accurate and more reliable instruments to replace detector tubes for routine measurements. Simple methods are needed for calibration. Span readings should be built into each instrument.

20. Carbon canisters are used to collect and store hydrocarbons from the submarine atmosphere as part of the atmosphere control system. The retention of hydrocarbons on carbon depends on temperature, pressure, and competition for adsorption sites on the surface of the charcoal. Changes in the pressure and adsorption of more strongly held compounds could result in the release of previously stored hydrocarbons to the atmosphere.

The Panel recommends that retention of hydrocarbons on carbon be investigated, to provide information on adsorption and release of toxic contaminants in a broad range of conditions. The arrangement of the carbon in the bed should be examined and optimized, to decrease breakthrough. Methods for regenerating the beds might be explored for emergency use.

21. Removal of hydrocarbons from the submarine atmosphere by carbon beds is incomplete, and operation of the CO-H<sub>2</sub> burner at temperatures high enough to oxidize additional hydrocarbons is undesirable, because of the simultaneous conversion of fluorocarbons (FCs) to acid gases.

The Panel recommends that the Navy undertake research on the selective removal of contaminants with techniques other than the use of carbon beds and the CO-H<sub>2</sub> burner, including gas separation. Methods for improving efficiency of carbon beds might also be investigated.

22. The Panel observes that training in the use and function of the monitoring and control equipment is concentrated at the enlisted level. The responsibility for operating the equipment is distributed among several persons.

The Panel recommends that methods of instruction of personnel be reviewed and updated. The Panel also recommends that the command level be given appropriate training in physiology and in the operation of air monitoring and control equipment.

23. The enclosed environment of the submarine constitutes a unique controlled environment for study of toxicologic, physiologic, and epidemiologic relationships involving prolonged exposure of submariners to atmospheric contaminants.

The Panel recommends that monitoring on submarines provide complete analysis of submarine air and data on exposure of personnel to contaminants to provide a basis for further retrospective epidemiologic health-effects studies that might be desired.

24. The British Royal Navy has set maximal permissible exposure concentrations and

established a monitoring protocol for many substances for which no limits are set and for which no monitoring is done on U.S. submarines.

The Panel recommends that the U.S. Navy explore with the British Royal Navy the reasons for the different strategies and determine whether additional exposure limits and monitoring for additional substances are necessary on U.S. submarines.

#### EMERGENCIES

25. The *Submarine Atmosphere Control Manual* does not contain detailed instructions on the use of monitoring equipment during and immediately after an emergency and in particular on whether readings of some gases might be more important than readings of others.

The Panel recommends that methods be established for determining the safe conclusion of an emergency situation, with respect to instrumentation and setting of all-clear standards (e.g., concentrations of HCN, HCl, CO, and NO<sub>x</sub> might be used after a fire as indexes of air purity).

26. Emergency situations that release large quantities of contaminants to the submarine atmosphere can place a large burden on the air monitoring and control equipment.

The Panel recommends that the Navy consider the design, development, and testing of an air-cleaning scrubber system for use in purifying the air after an emergency, such as a fire.



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# **APPENDIX A**

## **CONTAMINANTS PRESENT IN AIR**

Awareness of the possibility that some substances in submarine air have been overlooked as constituting a potential health hazard led to compilation of analytic data from various sources as Table A-1. This information was obtained from reports of substances recorded in submarine logs, of the use of adsorbents in submarines, of air exhaled by submarine personnel, and of accidents.

TABLE A-1

## Contaminants Potentially Present in Submarine Air

Substance	Concentration or Partial Pressure <sup>a</sup>	References
Acetaldehyde	NR	Saalfeld et al., 1971
	NR	Kagarise and Saunders, 1962
Acetic acid	NR	Kagarise and Saunders, 1962
Acetone	ND	USS Cavalla, 1986
	NR	Saalfeld et al., 1971
	NR	Kagarise and Saunders, 1962
Acetonitrile	NR	Saalfeld et al., 1971
Acetylene	NR	Kagarise and Saunders, 1962
Aerosols <sup>b</sup>	57-218 $\mu\text{g}/\text{m}^3$	Rossier, 1984
Aliphatics C <sub>8</sub>	0.05-0.2 ppm	Wyatt, pers. comm., 1986
Aliphatics C <sub>9</sub>	0.2 ppm	Wyatt, pers. comm., 1986
	0.2-0.5 ppm	Wyatt, pers. comm., 1986
Aliphatics C <sub>10</sub>	3.6 ppm	Wyatt, pers. comm., 1986
	0.2-0.5 ppm	Wyatt, pers. comm., 1986
Aliphatics C <sub>11</sub>	0.7 ppm	Wyatt, pers. comm., 1986
	0.2-0.5 ppm	Wyatt, pers. comm., 1986
Aliphatics C <sub>12</sub>	0.2-0.5 ppm	Wyatt, pers. comm., 1986
Aliphatics C <sub>13</sub>	0.2-0.5 ppm	Wyatt, pers. comm., 1986
Aliphatics straight chain C <sub>14</sub>	0.05-0.2 ppm	Wyatt, pers. comm., 1986
Aliphatics straight chain C <sub>15</sub>	0.05-0.2 ppm	Wyatt, pers. comm., 1986
Aliphatics branched chain C <sub>9</sub> -C <sub>13</sub>	0.05-0.2 ppm	Wyatt, pers. comm., 1986
Ammonia	ND	USS Cavalla, 1986
	2 ppm	Johnson, 1963
Aromatics C <sub>9</sub>	NR	Saalfeld et al., 1971
Aromatics C <sub>10</sub>	NR	Saalfeld et al., 1971
Aromatics C <sub>14</sub> (tertiary)	NR	Saalfeld et al., 1971
Arsine	0.015 ppm	Johnson, 1963
Asbestos	< OSHA PEL	DeCorpo, pers. comm., 1986
	ND	Rossier, 1984
Benzene	<0.01 ppm	Wyatt, pers. comm., 1986
	ND	USS Cavalla, 1986
	0.1 ppm	Johnson et al., 1964
	ND	Weathersby et al., 1987
	NR	Saalfeld et al., 1971
	NR	Kagarise and Saunders, 1962

TABLE A-1 (contd)

Substance	Concentration or Partial Pressure <sup>a</sup>	References
C <sub>3</sub> -benzene	0.4 ppm	Wyatt, pers. comm., 1986
	0.05-0.2 ppm	Wyatt, pers. comm., 1986
C <sub>4</sub> -benzene	0.6 ppm	Wyatt, pers. comm., 1986
	0.7 ppm	Wyatt, pers. comm., 1986
	0.8 ppm	Wyatt, pers. comm., 1986
	0.9 ppm	Wyatt, pers. comm., 1986
	1.1 ppm	Wyatt, pers. comm., 1986
Butane	ND	Weathersby et al., 1987
2-Butene ( <i>trans</i> )	NR	Kagarise and Saunders, 1962
2-Butene ( <i>cis</i> )	NR	Kagarise and Saunders, 1962
Butylacetate	NR	Saalfeld et al., 1971
Butylalcohol	NR	Saalfeld et al., 1971
Butylbenzene	NR	Saunders and Saalfeld, 1965
Carbon dioxide	NR	Thompson, 1973
	2.1-3.6 Torr <sup>b</sup>	USS Michigan, 1986
	2.3-7.1 Torr <sup>b</sup>	USS Daniel Webster, 1986
	0.3%	USS Cavalla, 1986
	<0.01 to 0.59%	Weathersby et al., 1987
	0.35%	Rossier, 1984
	1%	Johnson, 1963
	NR	Kagarise and Saunders, 1962
Carbon disulfide	NR	Saalfeld et al., 1971
Carbon monoxide	1-9 milliTor <sup>b</sup>	USS Michigan, 1986
	2-9 milliTor <sup>b</sup>	USS Daniel Webster, 1986
	1-3 ppm	Weathersby et al., 1987
	1-5 milliTor <sup>b</sup>	Rossier, 1984
	7 ppm	Bondi, 1978
	30 ppm	Johnson, 1963
	NR	Kagarise and Saunders, 1962
	<10 ppm	USS Cavalla, 1986
	9 ppm	USS Kamehameha, 1975
Chlorine	ND	USS Cavalla, 1986
	1 ppm	Johnson, 1963
Chlorobenzene	NR	Saalfeld et al., 1971
Chloroform	<0.1 ppm	Williams and Johnson, 1968
Cigarette smoke	NR	Thompson, 1973
Cyclohexane	NR	Saalfeld et al., 1971
Cyclopentene	NR	Saalfeld et al., 1971
n-Decane	NR	Saunders and Saalfeld, 1965
Dichlorobenzene	NR	Saalfeld et al., 1971
Difluorodichloro-methane	NR	Saalfeld et al., 1971



TABLE A-1 (contd)

Substance	Concentration or Partial Pressure <sup>a</sup>	References
Difluorochloro-methane	NR	Saalfeld et al., 1971
Dimethylheptane	2 ppm	USS Kamehameha, 1975
2,3-Dimethylpentane	3 ppm	USS Kamehameha, 1975
Dimethyl sulfide	NR	Saalfeld et al., 1971
Dioxane	NR	Saalfeld et al., 1971
Dodecane	0.4 ppm	Wyatt, pers. comm., 1986
n-Dodecane	NR	Kagarise and Saunders, 1962
Ethane	ND to 0.18 ppm	Weathersby et al., 1987
Ethylacetate	NR	Kagarise and Saunders, 1962
	NR	Kagarise and Saunders, 1962
Ethylalcohol	NR	Saalfeld et al., 1971
	NR	Saalfeld et al., 1971
Ethylbenzene	5 ppm	Kagarise and Saunders, 1962
	NR	USS Kamehameha, 1975
	0.3 ppm	Saalfeld et al., 1971
	NR	Wyatt, pers. comm., 1986
Ethylene	NR	Johnson et al., 1964
	NR	Saalfeld et al., 1971
Ethylene glycol	NR	Kagarise and Saunders, 1962
Ethyl nitrile	NR	Saalfeld et al., 1971
Fluorocarbon TF	NR	Saalfeld et al., 1971
Fluorocarbon 11	0-26,500 ppm	Eaton, 1970
	NR	Williams and Johnson, 1968
	ND	Weathersby et al., 1987
Fluorocarbon 12	5-52 ppm	Williams and Johnson, 1968
	1-16 milliTor <sup>b</sup>	USS Michigan, 1986
	40-100 ppm	Smith et al., 1965
	8-50 ppm	Umstead et al., 1964
	0.5-12 ppm	Weathersby et al., 1987
	26 ppm and 30 ppm	USS Kamehameha, 1975
	1-8 ppm	Rossier, 1984
	NR	Kagarise and Saunders, 1962
	5-38 milliTor <sup>b</sup>	USS Daniel Webster, 1986
Fluorocarbon 113	0.2-2.4 ppm	Williams and Johnson, 1968
	<0.1-3 ppm	Weathersby et al., 1987
	4 ppm and 10 ppm	USS Daniel Webster, 1986
Fluorocarbon 114	1-11 milliTor <sup>b</sup>	USS Daniel Webster, 1986
	<0.1 to 14.2 ppm	Weathersby et al., 1987
	52 ppm and 60 ppm	USS Kamehameha, 1975
	1-19 milliTor <sup>b</sup>	Rossier, 1984
	0-21 milliTor <sup>b</sup>	USS Michigan, 1986
	NR	Kagarise and Saunders, 1962

TABLE A-1 (contd)

Substance	Concentration or Partial Pressure <sup>a</sup>	References
Fluorocarbon 114B2	<0.1 ppm	Williams and Johnson, 1968
Fluorocarbon 22	ND	Weathersby et al., 1987
Fluorodichloro-methane	NR	Saalfeld et al., 1971
Fluorotrichloro-methane	NR	Saalfeld et al., 1971
Furan	NR	Saalfeld et al., 1971
<i>n</i> -Heptane	NR	Kagarise and Saunders, 1962
<i>n</i> -Hexane	ND to 0.13 ppm	Weathersby et al., 1987
	NR	Saalfeld et al., 1971
Hydrazine	0.5 ppm	USS Cavalla, 1986
Hydrocarbons, total (excluding methane)	10-20 ppm	Wyatt, pers. comm., 1986
	15-49 ppm	Rossier, 1984
Hydrogen	0.01 - 0.03%	Rossier, 1984
	0.33% (battery room during charge)	Rossier, 1984
	0.35%	Johnson, 1963
	0.1-3.3 Torr <sup>b</sup>	USS Michigan, 1986
	0.1-1.0 Torr <sup>b</sup>	USS Daniel Webster, 1986
Hydrogen chloride	ND	USS Cavalla, 1986
Hydrogen cyanide	NR	Thompson, 1973
Hydrogen fluoride	0.3 ppm	Johnson, 1963
Indene	NR	Saalfeld et al., 1971
Isobutane	NR	Kagarise and Saunders, 1962
Isobutene	NR	Kagarise and Saunders, 1962
Isopentane	NR	Kagarise and Saunders, 1962
Isoprene	NR	Saalfeld et al., 1971
	NR	Kagarise and Saunders, 1962
Isopropyl alcohol	NR	Saalfeld et al., 1971
	NR	Kagarise and Saunders, 1962
Isopropylbenzene	NR	Johnson et al., 1964
	NR	Kagarise and Saunders, 1962
Mercury	ND	Rossier, 1984
Methane	10-30 ppm	Smith et al., 1965
	5-60 ppm	Umstead et al., 1964
	2-12 ppm	Weathersby et al., 1987
	NR	Kagarise and Saunders, 1962
	25 ppm	USS Kamehameha, 1975
Methoxy acetic acid	NR	Saalfeld et al., 1971
Methyl alcohol	NR	Saalfeld et al., 1971
	6 ppm	Johnson, 1963
	NR	Kagarise and Saunders, 1962

TABLE A-1 (contd)

<u>Substance</u>	<u>Concentration or Partial Pressure<sup>a</sup></u>	<u>References</u>
Methyl acetate	NR	Saalfeld et al., 1971
Methyl chloroform	0.9 ppm	Wyatt, pers. comm., 1986
	4-6 ppm	Williams and Johnson, 1968
	NR	Saalfeld et al., 1971
	ND	Weathersby et al., 1987
	6 ppm	Johnson, 1963
Methyl cyclohexane	0.05-0.2 ppm	Wyatt, pers. comm., 1986
Methyl cyclopentane	NR	Saalfeld et al., 1971
2-Methyl-3-heptanol	1 ppm	USS Kamehameha, 1975
Methyl ethyl benzene	NR	Johnson et al., 1964
Methyl ethyl ketone	NR	Saalfeld et al., 1971
	NR	Kagarise and Saunders, 1962
Methyl isobutyl ketone	NR	Saalfeld et al., 1971
	NR	Kagarise and Saunders, 1962
Monoethanolamine	<1 ppm	Johnson, 1963
Naphthalene	NR	Saunders and Saalfeld, 1965
Nitrogen dioxide	1.5 ppm	USS Cavalla, 1986
n-Nonane	NR	Kagarise and Saunders, 1962
	0.8 ppm	Wyatt, pers. comm., 1986
Octane	0.2 ppm	Wyatt, pers. comm., 1986
n-Octane	NR	Kagarise and Saunders, 1962
Oil smoke	NR	Thompson, 1973
Oxides of nitrogen	0.035 - 0.2 ppm	Bondi et al., 1983
Oxygen	20%	Johnson, 1963
	18.6-20.9%	USS Daniel Webster, 1986
Ozone	NR	Thompson, 1973
	Trace	USS Cavalla, 1986
	0.003-0.010 ppm	Rossier, 1984
	0.05 ppm	Johnson, 1963
Pentane	ND to 0.12 ppm	Weathersby et al., 1987
	NR	Saalfeld et al., 1971
n-Pentane	NR	Kagarise and Saunders, 1962
Pentylbenzene	NR	Saunders and Saalfeld, 1965
1-Pentene	NR	Saalfeld et al., 1971
Phenol	NR	Saunders and Saalfeld, 1965
Propane	ND to 0.06 ppm	Weathersby et al., 1987
	NR	Kagarise and Saunders, 1962
Propylbenzene	NR	Kagarise and Saunders, 1962
	0.2 ppm	Wyatt, pers. comm., 1986
Propyl nitrile	NR	Saalfeld et al., 1971
Propylene	NR	Saalfeld et al., 1971
sec-Butyl alcohol	NR	Saalfeld et al., 1971

TABLE A-1 (contd)

Substance	Concentration or Partial Pressure <sup>a</sup>	References
Silicone	0.5 ppm 1.1 ppm NR	Wyatt, pers. comm., 1986 Wyatt, pers. comm., 1986 Saalfeld et al., 1971
Sulfur dioxide	ND NR	USS Cavalla, 1986 Saalfeld et al., 1971
Stibene	0.01 ppm	Johnson, 1963
Tar-like aerosol	NR	Thompson, 1973
Tetrachloroethylene	NR 0.2-0.4 ppm	Saalfeld et al., 1971 Williams and Johnson, 1968
Tetramethylpentane	2 ppm	USS Kamehameha, 1975
Toluene	0.2-0.5 ppm ND ND 1.5 ppm and 10 ppm NR NR NR	Wyatt, pers. comm., 1986 USS Cavalla, 1986 Weathersby et al., 1987 USS Kamehameha, 1975 Saalfeld et al., 1971 Kagarise and Saunders, 1962 Johnson et al., 1964
Trichloroethylene	0.01-15.2 ppm 5 ppm and 8 ppm NR	Williams and Johnson, 1968 USS Kamehameha, 1975 Saalfeld et al., 1971
Trifluorotri-chloroethane	NR	Saalfeld et al., 1971
Trimethylbenzene	5 ppm	USS Kamehameha, 1975
2,2,3-Trimethylbutane	NR	Saalfeld et al., 1971
Trimethylfluoro-silane	NR <sup>f</sup>	Saalfeld et al., 1971
Trimethylheptanes	2 ppm	USS Kamehameha, 1975
Trimethylhexene	1 ppm	USS Kamehameha, 1975
Undecane	1.0 ppm NR	Wyatt, pers. comm., 1986 Saunders and Saalfeld, 1965
Vinylidene chloride	0.2-0.4 ppm NR 2 ppm	Williams and Johnson, 1968 Saalfeld et al., 1971 Johnson, 1963
Xylene	0.7 ppm 0.2-0.5 ppm NR ND 10 ppm NR NR	Wyatt, pers. comm., 1986 Wyatt, pers. comm., 1986 Johnson et al., 1964 Weathersby et al., 1987 USS Kamehameha, 1975 Saalfeld et al., 1971 Kagarise and Saunders, 1962

<sup>a</sup>NR, chemical cited in reference, but no concentration or pressure given.

ND, chemical not detectable.

<sup>b</sup>Aerosol concentration cannot be converted to ppm as the molecular weight is unknown; torr and millitorr values were not converted to ppm because variation can be due to fluctuations in total pressure.





# APPENDIX B

## BRITISH ROYAL NAVY DATA

TABLE B-1

Compounds Detected in British Royal Navy Submarines<sup>a</sup>

<u>Aromatic Compounds:</u>	<u>Boiling Point, °C</u>
2-Methylfuran (Sylvan)	63
Benzene	80
Thiophene	84
2-Ethylfuran	92-3
Toluene	110
Chlorobenzene	132
Ethylbenzene	136
<i>m</i> -, <i>p</i> -Xylene	138-9
Styrene	144
<i>o</i> -Xylene	146
Isopropylbenzene (cumene)	152
<i>n</i> -Propylbenzene	157
<i>m</i> -, <i>p</i> -Ethyltoluene	161-2
1,3,5-Trimethylbenzene (mesitylene)	164
<i>o</i> -Ethyltoluene	165
1,2,4-Trimethylbenzene (pseudocumene)	169
<i>tert</i> -Butylbenzene	169
Benzofuran	174
Isobutylbenzene	173
<i>p</i> -Dichlorobenzene	174
<i>sec</i> -Butylbenzene	173
1,2,3-Trimethylbenzene (hemimellitene)	176
<i>p</i> -Isopropyltoluene ( <i>p</i> -cumene)	177
2,3-Dihydroindene (indan)	178
Indene	183
Diethylbenzene (all 3 isomers)	181-4
<i>n</i> -Butylbenzene	183
Dimethylethylbenzene (5 of 6 isomers)	184-8
2-Phenyl-2-propanol	202
1,2,4,5-Tetramethylbenzene (durene)	197
1,2,3,5-Tetramethylbenzene (isodurene)	198
1,2,3,4-Tetramethylbenzene (prebnitene)	205
1,2,3,4-Tetrahydronaphthalene (tetralin)	208
Naphthalene	216
Methyltetralin (2 of 4 isomers)	220-2
Benzothiazole	231
2-Methylnaphthalene	241
1-Methylnaphthalene	245
2-Ethylnaphthalene	258
1-Ethylnaphthalene	259

TABLE B-1 (contd)

<u>Aromatic Compounds:</u>	<u>Boiling Point, °C</u>
Dimethylnaphthalene (5 of 10 isomers)	263-8
Phenanthrene	336
<u>Aliphatic Hydrocarbons:</u>	<u>Boiling Point, °C</u>
Methane	
Ethane	
2-Methylbutane (isopentane)	
<i>n</i> -Pentane	36
2-Methylpentane	60
3-Methylpentane	63
<i>n</i> -Hexane	69
Methylcyclopentane	72
Cyclohexane	80
2-Methylhexane	90
3-Methylhexane	92
2,2,4-Trimethylpentane	99
<i>n</i> -Heptane	100
Methylcyclohexane	101
Ethylcyclopentane	103-4
Dimethylcyclohexane (all 7 isomers)	119-130
2-Methylheptane	118
<i>n</i> -Octane	126
Ethylcyclohexane	130
4-Methyloctane	142
2-Methyloctane	143
3-methyloctane	143
<i>n</i> -Nonane	151
Isopropylcyclohexane	154-5
$\alpha$ -Pinene	156
<i>n</i> -Propylcyclohexane	157
Butylcyclopentane	
$\beta$ -Pinene	165
5-Methylnonane	165
4-Methylnonane	166
2-Methylnonane	167
3-Methylnonane	168
<i>n</i> -Decane	174
1-Methyl-4-isopropenylcyclohexene (limonene)	178
<i>n</i> -Butylcyclohexane	181
<i>trans</i> -Decahydronaphthalene ( <i>trans</i> -decalin)	187
5-Methyldecane	
4-Methyldecane	
2-Methyldecane	189
3-Methyldecane	188
<i>n</i> -Undecane	196
6-Methylundecane	
5-Methylundecane	

TABLE B-1 (contd)

<u>Aliphatic Hydrocarbons:</u>	<u>Boiling Point.°C</u>
4-Methylundecane	
2-Methylundecane	
3-Methylundecane	
<i>n</i> -Dodecane	218
6-Methyldodecane	
5-Methyldodecane	
4-Methyldodecane	
2-Methyldodecane	
3-Methyldodecane	
<i>n</i> -Tridecane	234
<i>n</i> -Tetradecane	254
<i>n</i> -Pentadecane	271
<i>n</i> -Hexadecane (cetane)	287
<i>n</i> -Heptadecane	
2,6,10,14-Tetramethylpentadecane (pristane)	
<i>n</i> -Octadecane	316
<sup>b</sup> 2,4-Dimethylhexane	110-11
<sup>b</sup> 2,3-Dimethylhexane	113
<sup>b</sup> 2,4-Dimethylheptane	133-4
<sup>b</sup> 2,5-Dimethylheptane	136
<sup>b</sup> 2,3-Dimethylheptane	140-1
<sup>b</sup> 2,6-Dimethyloctane	160-1
<sup>b</sup> 2-Methyl-3-ethylheptane	
<sup>b</sup> 2,3-Dimethyloctane	165
<sup>b</sup> 2,6-Dimethylnonane	
<sup>b</sup> 3,7-Dimethylnonane	
<sup>b</sup> 2-Methyl-6-ethyloctane	
<sup>b</sup> 2,6-Dimethyldecane	
<sup>b</sup> 2,6-Dimethylundecane	
<sup>b</sup> 2,2,6-Trimethyloctane	
<sup>b</sup> 2,2,6-Trimethyldecane	
<sup>b</sup> 2,6,11-Trimethyldodecane	
<sup>b</sup> 2,2,4,6,6-Pentamethylheptane	
<sup>b</sup> 2,2,6,6-Tetramethyl-4-ethylheptane	
<u>Compounds Containing Halogen:</u>	
1,1-Dichloroethylene (vinylidene chloride)	- 37
Dichlorodifluoromethane (Freon 12; Halon 12)	- 30
Fluorotrichloromethane (Freon 11; Halon 11)	24
Bromoethane (ethyl bromide)	38
1,1,2-Trichlorotrifluoroethane (Freon 113; Halon 113)	46
Dichloromethane (methylene chloride)	40
<i>trans</i> -1,2-Dichloroethylene	47-8
1,1-Dichloroethane	57
<i>cis</i> -1,2-Dichloroethylene	60
Chloroform	62
Bromochloromethane	68



TABLE B-1 (contd)

<u>Compounds Containing Halogen:</u>	<u>Boiling Point, °C</u>
1,1,1-Trichloroethane (methylchloroform)	72
1,2-Dichloroethane	83-4
Tetrachloromethane (carbon tetrachloride)	76
Trichloroethylene	87
1,2-Dibromoethane (ethylene dibromide)	131
Tetrachloroethylene (perchloroethylene)	121
Chlorobenzene	132
1,1,2,2-Tetrachloroethane	146
<i>p</i> -Dichlorobenzene	174
<u>Compounds Containing Oxygen:</u>	
Ethanol	78-9
Acetone	56
2-Methyl-2-propanol ( <i>tert</i> -butanol)	82
2-Methylfuran	63
2-Methyl-1-propanol ( <i>isobutanol</i> )	108
1-Butanol ( <i>n</i> -butanol)	117
Ethyl acetate	77
2-Ethylfuran	92-3
2-Ethoxyethanol	135
4-Methyl-2-pentanone ( <i>isobutylmethylketone</i> )	117
<i>Isobutyl</i> acetate	117
<i>n</i> -Butyl acetate	126
Furfural ( <i>furancarboxaldehyde</i> )	162
Cyclohexanol	161
2-Butanoxylethanol	
2-Ethoxyethylacetate	
Benzofuran	174
2-Phenyl-2-propanol	202
4,6,6-Trimethylbicyclo[3,1,1]hept-3-en-2-one	227-9
<u>Compounds Containing Other Elements:</u>	
Carbon disulfide	38
Thiophene	84
Dimethyldisulfide	110
Benzothiazole	231

<sup>a</sup>Data provided by British Royal Navy.<sup>b</sup>Mass spectral assignment only; not verified with standard compound.

TABLE B-2

Compounds for Which Maximal Permissible  
Concentrations in British Royal Navy Submarines Are Set<sup>a</sup>

Acetonitrile	Nitric acid vapor
Acetylene	Nitrogen dioxide
Ammonia	Otto fuel
Antimony	Oxygen
Beryllium	Ozone
Butanolamine	Phosgene
Beryllium	Sulfur dioxide
Cadmium	Tin
Carbon dioxide	Toluene
Carbon monoxide	Total aerosols
Chlorine	Total aliphatics
Chromium	Total aromatics
Cobalt	Total organics
Copper	Triaryl phosphate
Diethyltriamine (DETA)	Unsymmetrical dimethyl hydrazine
Ethylbenzene	Vanadium
Fluorocarbon-12	Vinyl chloride
Fluorocarbon-114	Xylenes
Fluorocarbon-1301	
Hydrazine	
Hydrogen	
Hydrogen cyanide	
Hydrogen fluoride	
Hydrogen sulfide	
Iron	
Lead	
Manganese	
Mercury	
Methane	
Methyl chloroform	
Molybdenum	
Monoethanolamine	
Nickel	

<sup>a</sup>Data from British Royal Navy.



# APPENDIX C

## AIR CONTAMINANT SOURCE DATA

TABLE C-1

General Physicochemical Characteristics of Cigarette Smoke<sup>a</sup>

<u>Characteristic</u>	<u>Mainstream Smoke</u>	<u>Sidestream Smoke</u>
Peak temperature, °C	900	600
pH	6.0-6.2	6.4-6.6
No. particles/ cigarette	$10.5 \times 10^{12}$	$3.5 \times 10^{12}$
Particle size, $\mu\text{m}$	0.1-1.0	0.01-0.8
Particle mean diameter, $\mu\text{m}$	0.4	0.32
Total particulate matter, $\mu\text{g}/\text{cigarette}$	100-40,000	130-76,000
Gas concentration vol. %		
CO	3-5	2-3
CO <sub>2</sub>	8-11	4-6
O <sub>2</sub>	12-16	1.5-2
H <sub>2</sub>	3-15	0.8-1.0

<sup>a</sup>Data from National Research Council, 1986a.

**TABLE C-2**  
**Chemicals in Nonfilter-Cigarette Undiluted Mainstream and Diluted Sidestream Smoke<sup>a</sup>**

<u>Substance</u>	<u>Concentration in Mainstream Smoke, <math>\mu\text{g}/\text{cigarette}</math></u>	<u>Sidestream-to-Mainstream Concentration Ratio</u>
<u>Vapor Phase:</u>		
Carbon monoxide	10,000-23,000	2.5-4.7:1
Carbon dioxide	20,000-40,000	8-11:1
Carbonyl sulfide	18-42	0.03-0.13:1
Benzene	12-48	5-10:1
Toluene	100-200	5.6-8.3:1
Formaldehyde	70-100	0.1-50:1
Acrolein	60-100	8-15:1
Acetone	100-250	2-5:1
Pyridine	16-40	6.5-20:1
3-Methylpyridine	12-36	3-13:1
3-Vinylpyridine	11-30	20-40:1
Hydrogen cyanide	400-500	0.1-0.25:1
Hydrazine	0.032	3:1
Ammonia	50-130	40-170:1
Methylamine	11.5-28.7	4.2-6.4:1
Dimethylamine	7.8-10	3.7-5.1:1
Nitrogen oxides	100-600	4-10:1
N-Nitrosodimethylamine	0.01-0.04	20-100:1
N-Nitrosodiethylamine	0-0.025	<40:1
N-Nitrosopyrrolidine	0.006-0.03	6-30:1
Formic acid	210-490	1.4-1.6:1
Acetic acid	330-810	1.9-3.6:1
Methyl chloride	150-600	1.7-3.3:1
<u>Particulate Phase:</u>		
Particulate matter	15,000-40,000	1.3-1.9:1
Nicotine	1,000-2,500	2.6-3.3:1
Anatabine	2-20	<0.1-0.5:1
Phenol	60-140	1.6-3.0:1
Catechol	100-360	0.6-0.9:1
Hydroquinone	110-300	0.7-0.9:1
Aniline	0.36	30:1



TABLE C-2 (contd)

<u>Substance</u>	<u>Concentration in Mainstream Smoke, µg/cigarette</u>	<u>Sidestream-to- Mainstream Con- centration Ratio</u>
2-Toluidine	0.16	19:1
2-Naphthylamine	0.0017	30:1
4-Aminobiphenyl	0.0046	31:1
Benz[ <i>a</i> ]anthracene	0.02-0.07	2-4:1
Benzo[ <i>a</i> ]pyrene	0.02-0.04	2.5-3.5:1
Cholesterol	22	0.9:1
γ-Butyrolactone	10-22	3.6-5.0:1
Quinoline	0.5-2	8-11:1
Harman <sup>b</sup>	1.7-3.1	0.7-1.7:1
N-Nitrosornicotine	0.2-3	0.5-3:1
NNK <sup>c</sup>	0.1-1	1-4:1
N-Nitrosodiethanolamine	0.02-0.07	1-2:1
Cadmium	0.1	7.2:1
Nickel	0.02-0.08	13-30:1
Zinc	0.06	6.7:1
Polonium-210	0.04-0.1 pCi	1-4:1
Benzoic acid	14-28	0.67-0.95:1
Lactic acid	63-174	0.5-0.7:1
Glycolic acid	37-126	0.6-0.95:1
Succinic acid	110-140	0.43-0.62:1

<sup>a</sup>From National Research Council (1986a).

<sup>b</sup>1-methyl 9H-pyrido [3,4-*b*]indole.

<sup>c</sup>4-(*N*-methyl-*N*-nitrosoamino)-1-(3-pyridal)-1-butanone.

TABLE C-3

Chemicals in Undiluted Mainstream Smoke from High-, Medium-, and Low-Tar Nonfilter Cigarettes<sup>a</sup>

Substance	Concentration, μg/cigarette	Substance	Concentration, μg/cigarette
Methyl butene	0.2-14	2,3-Dimethyl-1-butene	0.08
Acetaldehyde + isoprene	1.5-107	3,3-Dimethyl-1-butene	--
Cyclopentene	0.08-6	<i>cis</i> -2-Butene	29
Hexene	0.05-5	<i>trans</i> -2-Butene	41
Dimethylhexane	0.05-4	2-Methyl-2-butene	68
Cyclopentadiene	0.06-7	<i>trans</i> -2-Pentene	15
Methylpentene	0.01-1	<i>cis</i> -2-Pentene	10
Acetone	0.40-52	1-Hexene	0.4
Methylpentadiene	0.01-1	<i>trans</i> -2-Hexene	0.12
Acrolein	0.09-12	Acetylene	26
Methylacetate	0.02-14	Methylacetylene	7
Methylpentadiene	0.02-13	Ethylacetylene	--
Cyclohexane	0.02-24	Cyclopentane	1
Cyclohexadiene(s)	0.04-19	Methylcyclopentane	2
Methylfuran	0.07-86	Cyclohexene	0.01
Methyl cyclopentadiene	0.02-6	β-Pinene	3
Methyl ethyl ketone	0.03-131	4-Isopropyltoluene	7-14
Methyl vinyl ketone	0.02-44	1-Methyl styrene	1
Benzene	0.05-94	3-Methyl styrene	2
Methyl isopropyl ketone	0.03-52	Methyl alcohol	180
Butanedione	0.01-60	Acetonitrile	140
Dimethyl furan	0.02-34	<i>n</i> -Propanol	4
Isobutyronitrile	0.01-46	<i>n</i> -Butanol	5
Methyl propyl ketone	<0.01-26	Isobutanol	<6
Nonane	<0.01-5	<i>sec</i> -Butanol	<4
Toluene	0.10-126	Glyoxal	--
Methyl butyl ketone	<0.01-6	1-Penten-3-one	45
Ethyl benzene	<0.01-14	Isopropylformate	6
<i>p</i> -Xylene	<0.01-8	Formic acid	0.42
<i>m</i> -Xylene	<0.01-20	Acetic acid	117-322
<i>o</i> -Xylene	<0.005-10	Propionic acid	100-300
Styrene	<0.005-13	Hexanoic acid	500
Limonene	<0.005-34	Isohexanoic acid	700
Methane	~1,000	Furfuryl alcohol	--
Ethane	~500	Anisole	5
Propane	250	<i>o</i> -Methoxyphenol	15-25
Butane	70	<i>n</i> -Capronitrile	1
2-Methylpentane	6	Methacrylanitrile	3
3-Methylpentane	1	Methyl nitrite	19-91
Ethylene	240	Hydrogen sulfide	12
Propene	240	Carbonyl sulfide	--
Butene	6.2	3-Ethylpyridine	1.9

TABLE C-3 (contd)

<u>Substance</u>	<u>Concentration, μg/cigarette</u>	<u>Substance</u>	<u>Concentration, μg/cigarette</u>
2-Methyl-1-butene	24	3-Butenenitrile	4
3-Methyl-1-butene	1	Pyrrole	--
Methylisocyanate	0.55	Sulfur dioxide	~3
2,6-Dimethylpyridine	5	Vinyl pyridine	28
Propionaldehyde	40	Methyl formate	30
Propionitrile	30	Isovaleraldehyde	20
Crotonaldehyde	16	Isobutyraldehyde	12
Methacrolein	8	n-Valeraldehyde	8
Pivaldehyde	4	Methylacrylate	3
Ethyl alcohol	2	Thiophene	2
Tetrahydropyran	2	Isoprene	630

\*Data from: Elmenhorst and Schultz, 1968; Grob, 1966; Grob, 1963; Grob and Vollmin, 1969; Higgins et al., 1984; Higgins et al., 1983; Klus and Kubn, 1982.

TABLE C-4

Materials for Certification by Naval Sea Systems<sup>a,b</sup>

Adhesives  
Cleaning agents and detergents  
Coatings and sealants  
Deck coverings  
Duplicating products  
Dye penetrants  
Electric components  
Deck finishes and waxes  
Insulation materials  
Lubricants  
Office supplies  
Paints and varnishes  
Personal hygiene items  
Pesticides and insecticides  
Photographic supplies  
Polishes  
Preservatives/anticorrosion agents  
Solvents  
Miscellaneous items  
Solders, soldering fluxes, and cleaners  
Water treatment products  
Plastic/polymeric materials  
Packaging and packing materials

<sup>a</sup>Data from Demas and Greenberg (1986).<sup>b</sup>Substances are categorized according to restrictions on their use--permitted, limited, restricted, or prohibited.

TABLE C-5  
Coating Material Components<sup>a</sup>

<u>Chemical</u>	<u>Maximal Estimated Emission-- mg/m<sup>2</sup>/min (No. Materials Tested)</u>
1,1,1-Trichloroethane	12 (4)
1,1,2-Trichloro-1,2,2-trifluoroethane	41 (7)
1,4-Epoxy-1,3-butadiene	32 (12)
1-Butanol	1,000 (47)
1-Propanol	2,759 (9)
2,4-Hexadienal	6 (3)
2-Butanal	12 (3)
2-Butanol	1,325 (6)
2-Butanone	3,329 (170)
2-Butoxyethyl alcohol	120 (4)
2-Ethoxy-1-ethanol	620 (12)
2-Ethoxyethyl ethanoate	1,577 (54)
2-Hexanone	307 (3)
2-Methoxyethanol	960 (4)
2-Methyl-1-propanol	100 (19)
2-Propanol	1,590 (72)
2-Propanone	6,022 (115)
4-Methyl-2-pentanone	3,900 (60)
4-Methyl-3-penten-2-one	489 (16)
Acetaldehyde	460 (79)
Acrolein	19 (4)
Ammonia	120 (10)
n-Butanal	7,871 (26)
C <sub>10</sub> -C <sub>12</sub> saturated and unsaturated aliphatics	3,000 (26)
C <sub>5</sub> alcohols	1,325 (8)
C <sub>5</sub> aldehydes	310 (27)
C <sub>6</sub> aldehydes	120 (26)
C <sub>6</sub> ketones	30 (4)
C <sub>6</sub> saturated and unsaturated aliphatics	55 (12)
C <sub>7</sub> aldehydes	10 (4)
C <sub>7</sub> esters	97 (4)
C <sub>7</sub> ketones	6 (4)
C <sub>7</sub> saturated and unsaturated aliphatics	160 (22)
C <sub>8</sub> esters	2.5 (2)
C <sub>8</sub> saturated and unsaturated aliphatics	91 (16)
C <sub>9</sub> aromatics	145 (17)
C <sub>9</sub> saturated and unsaturated aliphatics	105 (13)
Cyclohexanone	2,800 (15)
Dichloromethane	21 (6)
Ethanol	590 (51)
Ethylacetate	85 (17)



TABLE C-5 (contd)

<u>Chemical</u>	<u>Maximal Estimated Emission-- mg/m<sup>2</sup>/min (No. Materials Tested)</u>
Ethylformate	200 (13)
Methanol	9,999 (56)
Methylacetate	20 (6)
Methylformate	31 (8)
Toluene	1,178 (78)
Propane	75 (12)
Propene	12 (8)
Siloxane tetramer	40 (2)
Siloxane trimer	9.6 (4)
Styrene	40 (6)
Trimethylbenzene	100 (2)
Xylenes	1,600 (92)
<i>n</i> -Butylacetate	5,000 (25)
<i>n</i> -Butylformate	3.9 (4)
<i>n</i> -Butyraldehyde	37 (2)
<i>n</i> -Propylacetate	2,400 (9)

<sup>a</sup>From NASA Materials Testing Data Base, 1986.

TABLE C-6

Vapor Emissions from Rubber Products<sup>a</sup>

<u>Chemical</u>	<u>Maximal Estimated Emission-- mg/m<sup>2</sup>/min (No. Materials Tested)</u>
1,1,1-Trichloroethane	41 (4)
1,1,2-Trichloro-1,2,2-trifluoroethane	23 (15)
1-Butanol	92 (3)
2-Butanone	160 (12)
2-Methyl-2-propanol	520 (13)
2-Propanol	770 (15)
2-Propanone	110 (18)
Acetaldehyde	5 (4)
Acetic acid	15 (3)
Carbon bisulfide	11 (19)
Carbon oxysulfide	14 (20)
Ethanol	330 (16)
Hexamethylcyclotrisiloxane	15 (3)
Methanol	1,200 (18)
Toluene	2,000 (16)
Octamethylcyclotetrasiloxane	12 (4)
Siloxane tetramer	50 (15)
Siloxane trimer	21 (10)
Xylenes	11 (4)

<sup>a</sup>From NASA Materials Testing Data Base, 1986.

TABLE C-7  
Vapor Emissions from Plastics and Insulation<sup>a</sup>

<u>Chemical</u>	<u>Maximal Estimated Emission-- mg/m<sup>2</sup>/min (No. Materials Tested)</u>
1,1,1-Trichloroethane	1.9 (2)
1,1,2-Trichloro-1,2,2-trifluoroethane	25 (5)
1-Butanol	1.4 (1)
2-Butanol	64 (16)
2-Butanone	632 (21)
2-Methyl-2-propanol	400 (18)
2-Propanol	38 (15)
2-Propanone	24 (9)
sec-Butyl acetate	58 (10)

<sup>a</sup>From NASA Materials Testing Data Base, 1986.

TABLE C-8  
Vapor Emissions from Wire, Cables<sup>a</sup>

<u>Chemical</u>	<u>Maximal Estimated Emission-- mg/m<sup>2</sup>/min (No. Materials Tested)</u>
1,1,1-Trichloroethane	1.8 (1)
FC-113	37 (2)
Xylenes	29 (3)
1-Pentanol	17 (1)
2-Methyl-2-propanol	14 (3)
2-Propanol	180 (2)
Hexamethylcyclotrisiloxane	115 (1)
Octamethylcyclotetrasiloxane	35 (3)

<sup>a</sup>From NASA Materials Testing Data Base, 1986.

TABLE C-9

Vapor Emissions from Personal Items<sup>a</sup>

<u>Chemical</u>	<u>Maximal Estimated Emission-- mg/m<sup>2</sup>/min (No. Materials Tested)</u>	<u>Examples</u>
2-Butanone	15 (3)	Creams
2-Methyl-2-propanol	51 (4)	Deodorants
2-Propanol	3,600 (12)	Wipes and leather
Acetaldehyde	67 (5)	Creams and deodorants
Ethanol	9,999 (4)	Creams and deodorants
Ethyl acetate	330 (2)	Creams
Methanol	12 (5)	Creams

<sup>a</sup>From NASA Materials Testing Data Base, 1986.



TABLE C-10  
Volatile Decomposition Products of  
Triglycerides During Simulated Deep-Fat Frying<sup>a</sup>

Compound	Relative Amount of Compound			
	Corn Oil	Hydrogenated Cottonseed Oil	Trilinolein	Triolein
<b>I. Acidic Products</b>				
<b>A. Saturated acids</b>				
Acetic	S	--	--	--
Propanoic	S	--	M	--
Butanoic	S	--	S	M
Pentanoic	L	S	M	L
Hexanoic	XL	S	XL	L
Heptanoic	L	S	L	M
Octanoic	L	S	M	XL
Nonanoic	L	S	M	XL
Decanoic	S	S	M	L
Undecanoic	S	XS	--	M
Dodecanoic	S	S	--	M
Tridecanoic	--	L	--	S
Tetradecanoic	--	M	--	S
Pentadecanoic	--	XS	--	--
Hexadecanoic	--	XL	--	--
Heptadecanoic	--	XS	--	--
Octadecanoic	--	L	--	--
<b>B. Unsaturated acids</b>				
<i>trans</i> -2-Butenoic	--	--	S	--
<i>trans</i> -2-Pentenoic	--	--	L	--
<i>trans</i> -2-Hexenoic	S	--	--	--
<i>trans</i> -2-Heptenoic	--	S	XL	--
<i>trans</i> -2-Octenoic	M	S	S	M
<i>trans</i> -2-Noneonic	M	XS	XL	M
<i>trans</i> -2-Decenoic	--	--	XL	M
<i>trans</i> -2-Undecenoic	S	--	--	L
<i>trans</i> -2-Dodecenoic	--	--	--	S
<i>trans</i> -2-Tridecenoic	--	--	--	S
<i>cis</i> -2-Heptenoic	--	--	S	--
<i>cis</i> -2-Nonenoic	--	--	L	--
<i>cis</i> -2-Decenoic	--	--	S	--
<i>trans</i> -3-Pentenoic	--	--	M	--
<i>trans</i> -3-Nonenoic	--	--	L	--
<i>trans</i> -3-Decenoic	S	S	--	XS
<i>cis</i> -3-Heptenoic	--	--	S	--
<i>cis</i> -3-Octenoic	--	--	S	M
<i>cis</i> -3-Nonenoic	--	--	S	S
<i>cis</i> -3-Decenoic	L	M	S	XS
<i>cis</i> -3-Undecenoic	--	--	S(tent.)	--

TABLE C-10 (contd)

Compound	Relative Amount of Compound			
	Corn Oil	Hydrogenated Cottonseed Oil	Trilinolein	Triolein
<i>cis</i> -3-Dodecenoic	--	--	--	M
<i>cis</i> -4-Nonenoic	--	--	S(tent.)	--
Hexenoic	--	--	S	L
6-Heptenoic	--	XS	L	L
7-Octenoic	--	S	S	L
10-Undecenoic	--	XS	--	--
Palmitoleic	--	XS	--	--
Elaidic	--	S	--	M
Oleic	--	XL	--	--
Linoleic	--	L	--	--
Linolenic	--	XS	--	--
<i>cis</i> -2- <i>trans</i> -4-Octadienoic	--	--	M	S(tent.)
<i>trans</i> -2- <i>cis</i> -4-Decadienoic	--	--	M	--
<i>trans</i> -2- <i>trans</i> -4-Decadienoic	--	--	M	--
C. Hydroxy acids				
3-Hydroxyhexanoic	S	--	S	--
2-Hydroxyheptanoic	S	--	M	--
2-Hydroxyoctanoic	--	--	S	--
3-Hydroxyoctanoic	--	--	S(tent.)	--
5-Hydroxyoctanoic	--	XS(tent.)	--	--
5-Hydroxydecanoic	--	XS(tent.)	--	--
10-Hydroxy- <i>cis</i> -8-hexadecenoic	--	--	--	XS(tent.)
D. Aldehydo acids				
Octanedioic acid semialdehyde	--	XS	--	S
Nonanedioic acid semialdehyde	--	XS	--	--
Decanedioic acid semialdehyde	--	XS	--	--
Undecanedioic acid semialdehyde	--	XS	--	--
Tetradecanedioic acid semialdehyde	--	XS	--	--
E. Keto acids				
4-Oxohexanoic	M(tent.)	--	--	--
4-Oxoheptanoic	S(tent.)	XS(tent.)	S(tent.)	--
4-Oxo-octanoic	S(tent.)	--	--	--
4-Oxononanoic	--	XS(tent.)	--	--
4-Oxo- <i>trans</i> -2-octenoic	--	--	--	L
4-Oxo- <i>trans</i> -2-nonenoic	--	--	--	M
4-Oxo- <i>trans</i> -2-undecenoic	--	--	--	S
4-Oxo- <i>cis</i> -2-decenoic	--	--	--	XS(tent.)

TABLE C-10 (contd)

Compound	Relative Amount of Compound			
	Corn Oil	Hydrogenated Cottonseed Oil	Trilinolein	Triolein
<b>F. Dibasic acids</b>				
Hexanedioic	S	--	S	--
Heptanedioic	S	XS	XS	--
Octanedioic	M	XS	S	S
Nonanedioic	L	XS	--	M
Decanedioic	--	XS	--	--
Undecanedioic	--	XS	--	--
4-Oxoheptanedioic	--	--	XS(tent.)	--
<b>II. Nonacidic Products</b>				
<b>A. Saturated hydrocarbons</b>				
Hexane	--	--	--	XS
Heptane	S	--	--	M
Octane	S	S	--	S
Nonane	M	--	S	XL
Decane	L	M	M	M
Undecane	M	M	--	S
Dodecane	S	S	--	L
Tridecane	S	XS	--	--
Tetradecane	S	S	S	--
Pentadecane	--	S	XS	--
Hexadecane	--	S	XS	--
Heptadecane	--	S	--	--
Octadecane	--	XS	--	--
<b>B. Unsaturated hydrocarbons</b>				
1-Octene	--	--	S	M
2-Nonene	--	--	S	M
1-Decene	--	--	--	S
1-Undecene	--	XS	--	--
<i>trans</i> -2-Octene	--	S	S	--
<i>cis</i> -2-Octene	--	--	S	--
<i>trans</i> -Undecene	--	--	S	--
<i>trans</i> -Dodecene	M	XS	S	--
<i>trans</i> -Tridecene	XS	S	--	--
<i>trans</i> -Tetradecene	S	XS	--	--
<i>trans</i> -Hexadecene	--	S	--	--
<i>trans</i> -Heptadecene	--	S(tent.)	--	--
<i>trans</i> -1,3-Octadiene	--	--	S(tent.)	--
<i>trans</i> -1,3-Nonadiene	--	--	S(tent.)	--
<i>trans,trans</i> -Tetradecadiene	--	--	S(tent.)	--
<i>trans,cis</i> -Tetradecadiene	--	--	S(tent.)	--

TABLE C-10 (contd)

Compound	Relative Amount of Compound			
	Corn Oil	Hydrogenated Cottonseed Oil	Trilinolein	Triolein
<b>C. Alcohols</b>				
Ethanol	--	--	M	--
1-Propanol	--	--	--	L
1-Butanol	S	M	L	M
1-Pentanol	XL	L	XL	--
1-Hexanol	S	M	S	L
1-Heptanol	--	L	S	L
1-Octanol	XL	M	L	L
1-Decanol	--	S	--	--
1-Undecanol	--	--	M	--
1-Dodecanol	--	--	S	--
2-Hexanol	--	XS(tent.)	--	--
2-Octanol	--	--	M	--
3-Octanol	XL	--	S	--
1-Penten-3-ol	L	--	--	--
1-Octen-3-ol	XL	L	XL	--
<b>D. Saturated aldehydes</b>				
Propanal	--	--	--	L
Butanal	--	--	S	M
Pentanal	XL	M	XL	--
Hexanal	XL	L	XL	M
Heptanal	XL	L	XL	L
Octanal	M	XL	M	XL
Nonanal	XL	XL	S	XL
Decanal	M	M	M	M
Undecanal	--	S	--	L
Dodecanal	--	XS	XS	M
Tridecanal	--	XS	--	--
Tetradecanal	--	XS	--	--
Pentadecanal	--	XS	--	--
3,4,5-Trimethylheptanal	L(tent.)	--	M(tent.)	--
4-Methoxy-3,3-dimethylbutanal	S(tent.)	--	S(tent.)	--
<b>E. Unsaturated aldehydes</b>				
<i>trans</i> -2-Hexenal	M	M	M	S
<i>trans</i> -2-Heptenal	XL	XL	XL	M
<i>trans</i> -2-Octenal	XL	XL	XL	M
<i>trans</i> -2-Nonenal	XL	XL	M	L

TABLE C-10 (contd)

Compound	Relative Amount of Compound			
	Corn Oil	Hydrogenated Cottonseed Oil	Trilinolein	Triolein
<i>trans</i> -2-Decenal	XL	XS	M	XL
<i>trans</i> -2-Undecenal	S	S	--	XL
<i>cis</i> -2-Heptenal	--	--	S	--
<i>cis</i> -2-Octenal	--	--	S	--
<i>cis</i> -2-Nonenal	--	--	XS	--
<i>cis</i> -3-Hexenal	--	--	M(tent.)	--
<i>trans</i> -4-Hexenal	S	--	S(tent.)	--
<i>trans</i> -3-Decenal	S	--	--	M
5-Hexenal	--	--	--	M
6-Heptenal	--	--	--	M
7-Octenal	--	--	--	L
5-Methyl-4-hexenal	S(tent.)	--	--	--
4-Oxo- <i>trans</i> -2-octenal	--	--	--	L(tent.)
<i>trans</i> -2- <i>cis</i> -4-Heptadienal	--	--	M	--
<i>trans</i> -2- <i>cis</i> -4-Nonadienal	S	L	M	M
<i>trans</i> -2- <i>trans</i> -4-Nonadienal	L	M	XL	--
<i>trans</i> -2- <i>trans</i> -6-Nonadienal	XL	--	--	--
<i>trans</i> -2- <i>cis</i> -4-Decadienal	S	L	XS	--
<i>trans</i> -2- <i>trans</i> -4-Decadienal	XL	L	XL	--

## F. Ketones

2-Heptanone	S	--	L	S
2-Octanone	S	--	M	--
2-Nonanone	--	XS	S	M
2-Decanone	S	S	--	L
2-Undecanone	--	--	M	--
2-Dodecanone	--	S	XS	--
3-Heptanone	--	--	S	S
3-Octanone	--	XS	S	S
3-Nonanone	--	--	S	S
3-Decanone	--	--	M	--
3-Dodecanone	--	--	XS(tent.)	--
4-Octanone	--	--	--	M
4-Undecanone	M	XS	--	--
4-Dodecanone	S	--	--	--
1-Octen-3-one	S(tent.)	--	--	--
2-Methyl-3-octen-5-one	S(tent.)	--	S(tent.)	--
<i>trans</i> -3-Nonen-2-one	XL	--	S(tent.)	--
<i>trans</i> -3-Undecen-2-one	--	--	S(tent.)	--
Nonenone	--	XS(tent.)	--	XS(tent.)
Dodecenone	--	--	--	XS(tent.)
1-Methoxy-3-hexanone	M(tent.)	--	L(tent.)	--



TABLE C-10 (contd)

Compound	Relative Amount of Compound			
	Corn Oil	Hydrogenated Cottonseed Oil	Trilinolein	Triolein
<b>G. Esters</b>				
Ethyl acetate	XL	XL	XL	XL
Butyl acetate	--	S	S	--
Hexyl formate	--	--	XS	L
Ethyl hexanoate	S	--	--	--
<b>H. Lactones</b>				
4-Hydroxypentanoic	S	--	M	--
4-Hydroxyhexanoic	L	--	S	--
4-Hydroxyheptanoic	S	XS	--	XS
4-Hydroxyoctanoic	L	--	M	S
4-Hydroxynonanoic	--	S	S	M
4-Hydroxydecanoic	--	S	S	S
5-Hydroxyhexanoic	--	--	S(tent.)	--
5-Hydroxydecanoic	--	--	S	--
6-Hydroxyhexanoic	--	--	S	--
4-Hydroxy-2-hexenoic	--	--	M	XS(tent)
4-Hydroxy-2-heptenoic	S	--	XS	--
4-Hydroxy-2-octenoic	--	--	XS	M
4-Hydroxy-2-nonenoic	L	--	XL	--
4-Hydroxy-2-decenoic	--	--	S	--
4-Hydroxy-3-octenoic	--	--	--	S(tent.)
4-Hydroxy-3-nonenoic	--	--	XL(tent.)	--
5-Hydroxy-2-nonenoic	--	--	M(tent.)	--
<b>I. Aromatic compounds</b>				
Toluene	S	--	--	--
Butylbenzene	--	--	S	--
Isobutylbenzene	M	--	--	--
Hexylbenzene	S	--	S	--
Phenol	L	--	--	--
Benzaldehyde	S	XS	M	--
Acetophenone	S(tent.)	--	--	--
4-Phenylbutanal	M(tent.)	--	XS	--
5-Phenylpentanal	S(tent.)	--	S	--
<b>J. Miscellaneous compounds</b>				
2-Pentylfuran	XL	L	XL	--
1,4-Dioxane	--	--	L	--

\*Data from Chang et al., 1978.

XS, extra small gas chromatographic peaks; S, small peaks; M, medium peaks; L, large peaks; XL, extra large peaks.

TABLE C-11  
Chemicals Identified in *d*-Glucose-Hydrogen  
Sulfide-Ammonia Model System<sup>a</sup>

Chemical	Area, %	Occurrence in Foods
Methanethiol	0.62	Onion, leek, garlic, beef
Dimethyl sulfide	7.45	Onion, garlic, beef
Diethyl sulfide	10.14	Cabbage
Thiophene	10.19	Coffee
Methyl isothio- cyanate (tentative)	3.56	Cabbage, sprouts, cauliflower
2,3-Pentanedione	0.45	Coffee, filberts
2-Methylthiophene	24.92	Chicken, beef
3-Methylthiophene	4.41	Beef
2,5-Dimethylthiophene	6.35	Beef, onion
2-Ethylthiophene	0.28	Pressure-cooked beef
2,4-Dimethylthiophene	0.51	Onion
2,3-Dimethylthiophene (tentative)	0.28	Beef
Thiazole	0.28	Peanuts, popcorn
2-Formylthiophene (tentative)	0.23	Coffee, filberts, beef
5-Methylthiazole	1.95	(Cysteine-pyruvaldehyde)
4-Methylthiazole	1.10	Peanuts
5-Methyl-2-formyl- thiophene (tentative)	0.23	Coffee, popcorn
2-Ethylthiazole	0.11	(Cysteine-pyruvaldehyde)
2-Ethyl-4,5- dihydrothiophene (tentative)	0.11	
4,5-Dimethyl- thiazole (tentative)	0.06	(Thiamine)
Furfural	10.67	Bread, chicory, popcorn
Methyl furfuryl sulfide	0.06	Coffee
2-Acetylfuran	11.18	Chicory, coffee, popcorn
(Furyl-2)-1- propanone-2	0.40	Coffee
Methyl 2-ethyl furyl sulfide	0.06	
Methyl thiofuroate	0.09	Coffee
5-Methylfurfural	0.52	Coffee, popcorn, filberts
Ethyl 2-furyl ketone	0.39	Coffee
2-Furylmethanethiol (tentative)	0.03	Coffee

<sup>a</sup>Modified from Shibamoto and Russell (1976).

TABLE C-12

Compounds Identified in Volatiles Formed in  
Roasting of *dl*- $\alpha$ -Alanine with *d*-Glucose<sup>a</sup>

2-Acetyl-1-ethylpyrrole  
2-Acetyl-5-methylfuran  
2-Acetylfuran  
2-Acetylpyrrole  
Acylpyrrole  
Alkylpyrazine  
Alkylpyrrole  
2,5-Dimethyl-1-ethylpyrrole  
2,5-Dimethyl-3-ethylpyrazine  
2,6-Diethyl-3-methylpyrazine  
Diethylmethylpyrazine  
3-Ethyl-5-methylpyrazine  
1-Ethyl-5-methylpyrrole-2-aldehyde  
Ethylmethylpyrrole  
1-Ethylpyrrole  
1-Ethylpyrrole-2-aldehyde  
2-Furaldehyde  
1-(5'-Methyl-2'-furfuryl)-pyrrole  
5-Methyl-2-furfuryl alcohol  
Methylpyrazine  
5-Methylpyrrole-2-aldehyde  
Oxazoline derivative  
Pyrazine derivative

<sup>a</sup>Data from Shigematsu et al. (1972).

**HEALTH EFFECTS IN DIVERS OF BREATHING  
SUBMARINE AIR UNDER  
HYPERBARIC CONDITIONS**

**REPORT OF THE PANEL ON HYPERBARICS AND MIXTURES**





# CHAPTER 1

## INTRODUCTION

This report assesses the health effects of breathing submarine air and especially the potential use of submarine air at increased pressure for submarine-based divers.

The pressure inside the submarine is generally 1 atmosphere absolute (1 ATA). Fluctuations can result from venting of pneumatic devices into the interior of the submarine, the periodic reduction of pressure by pumping of air into flasks, and snorkeling operations that, although infrequent, can cause fluctuations of as much as 150 torr. Temperature and humidity in the submarine are rigidly controlled to ensure crew comfort and reliability of electronic components.

The atmosphere of the nuclear-powered submarine is artificial. Oxygen generated from water is used to replenish oxygen consumed by the crew. Carbon dioxide, carbon monoxide, hydrogen, trace contaminants, and particles are partially removed from the atmosphere. From the early 1960s to the late 1970s, atmosphere control equipment on nuclear submarines was substantially improved. Ambient carbon monoxide during patrol was reduced from about 44 ppm in 1961 to 7-8 ppm by 1977, and ambient carbon dioxide was decreased from 1.2-1.5% to 0.85% (Tansey et al., 1979). Carbon dioxide is currently regulated not to exceed 0.8%.

Submarine personnel are generally semi-sedentary, and both work and recreation take place in warm well-lighted spaces. Divers operate in a very different environment. The ambient pressure for divers can vary from 1 ATA (sometimes less) to 30 ATA. The diving

environment is dark, generally cold, and relatively weightless. The physical activity of divers can be light, but is more commonly strenuous, sometimes maximal.

The biomedical problems confronting the submariner are principally toxicologic, nutritional, chronobiologic (circadian), and those related to a sedentary life style. The main biomedical concerns in diving are related to cold exposure, narcosis, carbon dioxide, toxic effects of oxygen, decompression sickness, and the effects of the diving environment on respiratory and central nervous system function.

Toxicologic problems are generally not important in diving, because such diving typically takes place at shallow depths and for short periods. As a consequence, purity standards for diver's air have been at best rudimentary extrapolations of existing standards for industrial and submarine atmospheres.

The submarine can serve as an ideal platform for diving operations. It is mobile and can launch divers underwater, where they cannot be observed. The advantages of submarines and other submersible vehicles for launching divers have been recognized for some years by the scientific, commercial, and military communities. Although a number of systems aboard these vessels lend themselves to the support of diving operations, the diver's breathing gas is usually stored in and supplied from sources separate from those used by the vehicles. Use of compressed air from submarine air banks as a breathing medium for divers was not intended by the original designers. For example, the

oxygen concentration in a nuclear submarine is 140-160 torr (18.4-21.1%) (U.S. Naval Sea Systems Command, 1979). U.S. Navy standard air decompression schedules have been developed for use with a constant oxygen content of 21% (U.S. Naval Sea Systems Command, 1985). Atmospheric concentrations of carbon dioxide in nuclear submarines are about 0.7-0.8%. Divers breathing such compressed air at 5 ATA would therefore be breathing the equivalent of

about 4% carbon dioxide, which is unacceptable. To circumvent this problem, before compressed air from submarine air banks is used for divers, carbon dioxide needs to be removed by passing the air through lithium hydroxide scrubbers. Submarine atmospheres have also been shown to contain hundreds of volatile organic compounds; it is reasonable to suspect that the trace contaminants of submarine air can become harmful at increased pressures.

## CHAPTER 2

# PHYSICS OF THE HYPERBARIC ENVIRONMENT

In an environment of compressed air, gas volumes, density, and partial pressures are drastically affected, and increased amounts of gases are dissolved in body fluids. Each of these consequences deserves careful consideration. Alterations in ambient pressure are the hallmark of the diving environment, so engineers, biomedical scientists, and operators associated with the operations need to become comfortable with the multiplicity of units for expressing pressure. The following equivalents illustrate the more common units of pressure (with commonly used approximations shown in parentheses):

- 1 ATA = 10.08 (10) m of seawater
- = 33.07 (33) ft of seawater
- = 33.90 (34) ft of fresh water
- = 760 mm Hg
- = 760 torr
- = 1.103 bars
- = 1.033 kg/cm<sup>2</sup>
- = 14.696 (14.7) lb/in<sup>2</sup>.

In the simplest conception, a gas is postulated to consist of a large number of very small, elastic particles in continuous motion in all directions. The pressure exerted by a gas is considered to result from the collisions of particles with the walls of the containing vessel. Anything that increases the number of impacts or the velocity of movement will increase the gas pressure. Several laws of gases (CRC, 1984) describe the relationships among the factors concerned with total and partial pressures of

gases and are pertinent to the hyperbaric environment.

### PRESSURE AND VOLUME

Boyle's law states that, as a contained gas is compressed at constant temperature, its volume varies inversely with the pressure exerted on it. That statement and its converse are of obvious importance during the changes in pressure that occur in the hyperbaric environment. The change from one pressure and volume to a second pressure and volume is expressed as follows, for an ideal gas under isothermal conditions:

$$P_1V_1 = P_2V_2.$$

Thus, 10 L of gas at sea level (1 ATA) will be compressed to 5 L at 2 ATA and to 2 L at 5 ATA. Volume changes are greatest near the surface. Going from the surface to 33 ft (2 ATA), the volume change is 5 L, and going to 165 ft (6 ATA), the volume is 1.7 L, a change of 3.3 L.

### TEMPERATURE AND VOLUME

Charles' law states that, if pressure is constant, the volume of a contained gas is proportional to the absolute temperature. (The absolute temperature is approximately 273° more

than the Celsius temperature). A useful expression of this law is the following:

$$V_1/T_1 = V_2/T_2.$$

Boyle's and Charles' laws may be used together if temperature and pressure both change. The combined laws can be expressed as the *universal gas equation*:

$$P_1V_1/T_1 = P_2V_2/T_2.$$

### PARTIAL PRESSURE OF GASES IN GAS MIXTURES

Dalton's law states that, in a gas mixture, the pressure exerted by each gas in a space is independent of the pressures of other gases in the mixture. Each gas behaves as though it were the only gas in a space and distributes itself uniformly, so total gas pressure is the sum of the partial pressures of each of the individual gases present. For example, in the pulmonary alveoli:

$$\text{total pressure} = P_{H_2O} + P_{CO_2} + P_{N_2} + P_{O_2}.$$

The partial pressure (P) of one gas in the mixture is therefore equal to the product of the percentage of the gas in the mixture and the total pressure of the gas mixture. Thus, oxygen partial pressure in a dry gas mixture containing 20.94% oxygen at a pressure of 1.0 atmosphere (760 torr) is:

$$(0.2094)(760) = 159.1 \text{ torr.}$$

In the calculation of partial pressure of a gas in a mixture, water vapor if present must be

considered as one of the gases. To determine the partial pressure of a gas in the lungs, where alveolar gas is saturated with water vapor, one must subtract the partial pressure of alveolar water vapor from the total ambient pressure to obtain the total pressure of dry gases. The saturation pressure of water vapor is a function of temperature and at normal body temperature is assumed to be 47 torr. For example, if the air is at 5.0 ATA and contains 0.8% carbon dioxide:

$$P_{CO_2} = (0.008)[(5 \times 760) - 47] \text{ torr} = 30 \text{ torr;}$$

$$P_{O_2} = (0.2094)[(5 \times 760) - 47] \text{ torr} = 786 \text{ torr.}$$

### PARTIAL PRESSURES OF GASES IN LIQUIDS

Henry's law states that the degree to which a gas enters into physical solution in a fluid is in direct proportion to the partial pressure of the gas to which the fluid is exposed. At equilibrium, the fluxes of gas passing into and out of solution are equal. At sea level (1 ATA), a diver's body fluids contain about 1 L of gaseous nitrogen in solution. If he dives to 99 ft and thus breathes air at 4 ATA, he eventually reaches equilibrium again and has 4 times as much nitrogen in solution in his body. The time taken to reach a new equilibrium depends on the solubility of the gas in a given tissue and the rate of gas delivery to each tissue.

When the total pressure is reduced, gas can pass out of solution. If a rapid and large drop in total pressure occurs, a tissue might contain more gas than it can hold in solution. In that situation, bubbles can form and cause decompression sickness.

## CHAPTER 3

# SUBMARINE AIR HANDLING SYSTEM

The following section provides a general overview of submarine atmosphere control and air quality as they might affect SCUBA (self-contained underwater breathing apparatus) divers who are based on submarines and who breathe compressed air from submarine air banks. Equipment and procedures vary with submarine size, type, age, and mission; therefore, details of this outline will not be universally applicable (it is based in part on information obtained by panel members on a visit to the USS Philadelphia, SSN 690). Most of what is presented here is well known among submariners, but the operating routines and descriptions of relevant equipment in part 1 of this report, *Monitoring the Air in Submarines*, should be helpful to readers of the report who are not submariners.

We outline here general features of submarine atmospheres and their management and then comment on the following separate systems: high-pressure air, burners, carbon filters, electrostatic filters, carbon dioxide scrubbers, oxygen generators, central air monitoring system, and diver's air. Table 11 summarizes various air handling devices on submarines. We have included comments on potential sampling sites throughout the air handling system because of the need for additional data on the components of submarine air, as outlined in part 1.

Submarines have "floodable volumes" of around 100,000 ft<sup>3</sup> and contain air near 1 ATA. Oxygen is removed and carbon dioxide is added by the crew's metabolism and by other processes of smaller magnitude. Contaminants have many

sources within the boat despite restriction of materials allowed on submarines.

The submarine atmosphere is periodically renewed by exchanging it with exterior air while the boat is at the surface or at periscopic depth. Two terms are used to describe this process (unfortunately, they are inconsistently defined). "Ventilating" refers to the use of pumps to draw air into and simultaneously eject it from the submarine. The boat's diesel engines might or might not be operating during ventilation. The "snorkeling" procedure (the exchange of interior submarine air via the gas intake called the snorkel), is generally used in connection with operation of the diesel engines, which draw large volumes of air from the boat's interior. Because of the possibility of taking in contaminants, the high-pressure air banks are not usually charged during operation of the diesel engines (or during or after a fire or when there have been battery or refrigerant leaks).

If the air intake becomes submerged during ventilating or snorkeling, it shuts, but air continues to be removed from the boat. Boat pressure can fall by as much as 150 torr within 1-5 min, and stay low for perhaps 1-15 min. Such pressure decrements might increase the risk of decompression sickness for divers recently returned to the boat. Even the routine variations in boat pressure ( $\pm 50$  torr) might be undesirable at such times. Such pressure variations can be largely avoided, if the crew is aware of the need to avoid them during diving operations.



TABLE 11  
Submarine Atmosphere Devices

<u>Device</u>	<u>Number</u>	<u>Location</u>	<u>Inlet</u>	<u>Outlet</u>	<u>Sampling Sites</u>
CAMS MK1	1	Variable	Fan room and other Sites	NA	Inlet filter paper
Main air banks	Several	Often outside pressure hull	Air tower	Many sites	Liquids via drain on each bank gases via high-pressure outlets
Compressors	2-3 high 1 low	Varies with sub-marine class	High-room location low-variable	High-air tower low-multiple	Inlet filters
Air tower Moisture separator CUNO filter Prefilter Dryer After filter	1	With compressor	High pressure air compressors	Main air banks	At each point in air tower sampling sites are available
Oxygen generator	1-2	Varies with class	Distilled water (from seawater)	Oxygen banks	--
Oxygen banks	Several	May be outside pressure hull	Oxygen generator	2 - O <sub>2</sub> bleed stations	O <sub>2</sub> bleed stations
CO <sub>2</sub> scrubbers	2	Varies with class	Room location	Fan room	Monoethanolamine before and after CO <sub>2</sub> absorption Silica-gel filters
Burners	1-2	Varies with class	Room location	CO <sub>2</sub> scrubber or fan room	Condensate collection jug and LiOH scrubber particles
Air-conditioners	Several	Fan room, and other compartments	Room location	Multiple	Multiple
Activated-carbon filters	Several	Fan room, galley, wash room, water closets, sanitary tanks	Room location system	Ventilation	Spent carbon
Electrostatic precipitators	Several	Within ventilation system	Room location	Ventilation system	Second-stage collector

The boat is sometimes isolated from exterior air for relatively long periods, so its atmosphere must be maintained artificially. Continuous circulation of air is usually maintained by blowers that distribute air through a system of ducts originating in a plenum chamber ("fan room") and leading throughout the boat; air is returned through ducts and through the spaces of the boat itself. The system allows choices of flow routing for different conditions (with variation among boat classes). Each compartment has local fan circulation through chillers and heaters. Such circulation minimizes local variations in air composition in the boat.

### HIGH-PRESSURE AIR

Compressed air has many uses in submarines. It powers a multitude of pneumatic devices, fewer of them in newer classes of submarine and few (if any) oil-lubricated; they exhaust into the submarine's interior. It is also used to displace seawater from ballast tanks to control buoyancy. Under some circumstances, large quantities of air at very high pressure are needed for surfacing. Less commonly, compressed air is used in operating the escape trunks, where it serves both for displacing water and as breathing air. Finally, compressed air is used for breathing in two other ways: first, an emergency air breathing (EAB) system with outlets throughout the boat provides compressed air to demand-valve masks for use (nominally at 1 ATA) if the submarine's interior air becomes unbreathable; second, SCUBA tanks are occasionally used and can be recharged from the boat's high-pressure system. Some boats are used for more extensive diving operations, and there the quality of diver's air (in SCUBA tanks, etc.) is of greater concern.

### Compressors

A submarine has two or three high-pressure compressors (up to about 4,500 psi) and one low-pressure compressor (150 psi). The low-pressure compressor can draw air from any compartment. High-pressure compressors draw air through only a coarse mesh filter from the compartments that house them. They are oil-lubricated, multistage, air-cooled devices that operate at or below about 350°F (177°C). They discharge air through an air cleaning system (air tower) and charge the high-pressure air banks.

During submergence, they are run periodically to keep the boat's interior pressure from exceeding the desired range (ordinarily near 1 ATA) because of the addition of exhaust gas into the boat from pneumatic devices and from the emergency air breathing system (which is used periodically for training).

### Air Tower

The air tower is a cluster of devices that process air from the high-pressure compressors. A submarine has one air tower. Compressed air first traverses a moisture separator (drier), an upright cylindrical chamber in which water and other substances condense; samples for analyses could easily be collected here. Next, it passes through a 5- $\mu$ m rigid polystyrene particle filter; the 3 x 12-in. cylindrical filter is replaced periodically and could easily be collected for analysis. The next steps include passage through a mesh-screen prefilter, a gas drier, and an after-filter; samples could also probably be collected from these items. From the air tower, air enters a high-pressure manifold that runs the length of the boat and connects with the air banks.

### Air Banks

A boat has about five high-pressure air banks, distributed, for example, two aft and three forward. Each bank is made up of some five steel air bottles about 2 ft in diameter and 10 ft long. Each bottle has a drain; the drains are manifolded to a petcock, one per air bank. The petcocks are opened at intervals ranging from daily on some classes of submarine, to as infrequently as monthly on others. On some boats little or no discharge (except air) is found; on others, tea-spoon quantities of water or other liquid effluent is found and could easily be sampled for analysis.

Once they are put into service, the air banks are not emptied--except during complete overhauls of the boat (up to 12 years apart), at which time they are carefully cleaned according to detailed specifications that include Freon rinsing and analysis of residual gases.

The use of air banks is based on the vital importance of compressed air for surfacing in emergency circumstances. A central tenet seems to be that the air banks will all be completely full (about 4,500 psi) at all times, except

for one (not always the same one) that is used for daily operations. In the daily-use air bank, the pressure may be allowed to cycle as low as 2,000 psi. During submerged operations, this bank receives much of its air from the submarine's interior after processing in the air tower; like the other air banks, it may also be charged with fresh air from the surface. Thus, the composition of the air in a bank depends on the composition of the air that it receives, on reactions within it, and on what is removed from it. The air in a particular bank can have a history that is long, undocumented, complex, and quite different from the histories of other banks.

The composition of air in individual banks can, of course, be measured with the central air monitoring system, but no routine sampling connections or procedures exist. The need for such an operation arises only when the air is to be used by divers.

### BURNERS

Burners are used to remove some oxidizable contaminants from the boat's atmosphere. Air from a compartment is drawn through a filter, then through a heat exchanger and heater, and then over a catalyst at 600°F (316°C), where hydrogen, carbon monoxide, hydrocarbons (including oil mists), and other substances are oxidized.

The products of oxidation are handled in three ways. Condensed water and other substances drain into a plastic jug for periodic disposal; samples could easily be collected from the jug. Acids (such as hydrofluoric acid and hydrochloric acid) are removed by a lithium carbonate scrubber operating at 140°F (60°C) or less; again, samples could easily be collected from the scrubber. Carbon dioxide is discharged into the submarine or directly to the CO<sub>2</sub> scrubber. Heavy metals (residue from burning oil mists) are deposited on the catalyst; samples could be collected. Complex reactions probably take place in the burners; effluent air from the burners has been sampled, but such sampling is not routine.

### CARBON FILTERS

Activated carbon is used to remove some organic contaminants and odors near their site of generation. The filters (cotton bats half-filled with activated carbon) are in the fan

room, galley, washroom, and water closets and above sanitary tanks. The carbon is changed on a schedule, and spent carbon has been collected and studied (in the 1960s), although apparently this is no longer done.

### ELECTROSTATIC FILTERS

Two-stage electrostatic precipitators at several sites in the ventilation system are used to collect particulate contaminants. The first stage charges the incoming particles, and they are collected by the second stage, which could be sampled. Examination of these particles showed that half (by mass) were generated by cigarettes; other sources of particles are cooking and machine lubrication oils.

### CARBON DIOXIDE SCRUBBERS

There are two high-capacity carbon dioxide (CO<sub>2</sub>) scrubbers on a boat. They provide for exchange of CO<sub>2</sub> between cocurrent flows of air and aqueous monoethanolamine (MEA) spray (which absorbs CO<sub>2</sub>), draining through and over Goodloe woven mesh (an arrangement that presents a large surface area). The MEA is then circulated to, and continuously regenerated in, a heater that evolves CO<sub>2</sub> to be pumped overboard. "Rich" and "poor" samples of the amine are easily collected. The air is drawn from a compartment, processed, chilled to condense MEA vapor, passed through a silica gel filter (the "bag," which is periodically replaced and easily sampled) to remove suspended MEA and discharged into the fan room, still containing MEA at 1-2 ppm. The scrubbers remove only about 70-80% of the CO<sub>2</sub> from the air presented to them. The cocurrent design probably contributes to the relative inefficiency of the scrubbers.

Backup CO<sub>2</sub> removal uses lithium hydroxide (LiOH) granules, which absorb and react with CO<sub>2</sub>, in canisters with circulating fans. In emergencies, the LiOH may be spread on surfaces open to the submarine's interior. The granules tend to pulverize during handling, and the dust is irritating if inhaled. A supply of LiOH adequate for at least 3 d (often twice as that) is carried on a submarine.

## OXYGEN GENERATORS

Electrolysis of distilled water provides  $O_2$ . The production rate is adjusted to maintain a pressure of about 2,100 psi in a line connected to one of several  $O_2$  storage banks.  $O_2$  from it is independently bled to the boat in two or more locations at a rate adjusted to maintain the desired  $O_2$  fraction in the boat's atmosphere. Other  $O_2$  tanks are kept closed and fully charged at about 3,000 psi. Total  $O_2$  storage is a nominal 5-d supply.

Hydrogen produced by the electrolysis is discharged overboard. Traces that enter the submarine's air are burned; permissible limits are determined on the basis of fire considerations, not biologic considerations. There appear to be no other airborne contaminants as byproducts of the electrolysis.

Backup  $O_2$  generation uses chlorate candles, which give off irritant smoke that contains chlorine and CO.

## CENTRAL ATMOSPHERE MONITORING SYSTEM

The Central Atmosphere Monitoring System (CAMS) is a mass spectrometer that draws gas samples through a selector valve from any of about eight sample lines, then through a pickup head with filter paper at its inlet (the filters could easily be collected). The system runs continuously, usually sampling from the fan room, except when another site (of about eight) is selected. The CAMS monitors concentrations of  $O_2$ ,  $N_2$ ,  $CO_2$ , CO (by infrared absorption),  $H_2$ , and three fluorocarbons--FC-11, FC-12,

and FC-114. Sampling sites could be added (e.g., air banks, diver's tanks, dry deck shelters, and inlet and outlet air of devices described above). Hourly readings are logged, and the system activates an alarm when a limit is exceeded. The next generation of equipment will provide continuous records.

Backup monitoring for additional substances is provided by sets of indicator tubes and by portable instruments for sampling  $O_2$ , FCs, and hydrocarbons.

## DIVER'S AIR

Most submarines carry only two or three divers. SCUBA tanks can be filled directly from a high-pressure line on board, but the line does not include a  $CO_2$  scrubber. SCUBA tanks are usually brought aboard filled and rarely used, and the on-board filling system is almost never used. It is not clear that divers know of the potential problems associated with breathing air with 0.5-0.7%  $CO_2$  (as would be expected in gas taken from a submarine's main air banks) at 5-6 ATA.

Some submarines are equipped for more extensive and specialized diving activities, for example, dry deck shelter (DDS) operations. In these submarines, diver's air from the banks is passed through  $CO_2$  scrubbers before (at least) some uses, reducing the  $CO_2$  to an acceptable fraction, around 0.1%. Again, it is not clear that all Navy divers know of the potential problems associated with breathing air with 0.5-0.7%  $CO_2$  at 5-6 ATA.





## CHAPTER 4

# EFFECTS OF BREATHING MAJOR GASES AT UP TO 6 ATMOSPHERES ABSOLUTE

This chapter considers the acute effects on submarine-based SCUBA divers of breathing clean air at pressures up to 6 atmospheres absolute (ATA) for up to 12 h, at rest and during bursts of violent activity.

There is wide experience with SCUBA diving from the surface using air that was compressed from the atmosphere. The literature is large and readily available (Bennett and Elliott, 1982; Edmonds et al., 1976; Flynn et al., 1981; Lanphier, 1964; Miller, 1979; Strauss, 1976; U.S. Naval Sea Systems Command, 1985). For readers unfamiliar with diving, this chapter introduces basic issues in diving and then discusses differences between surface-based and submarine-based diving.

### BASIC ISSUES IN DIVING

During a dive,  $N_2$  narcosis impairs higher brain functions, and increased gas density impedes breathing; during emergence, decompression sickness can occur. These phenomena are related to each other and to cold, immersion, dehydration, stress, and fatigue (Bennett and Elliott, 1982; Shilling et al., 1976). Other issues, not addressed here (for example, oxygen toxicity and exposure to hypoxic gas mixtures) are not related to the subjects of this report.

### Nitrogen Narcosis

Nitrogen has narcotic effects (Bennett, 1982) that increase with its partial pressure ( $PN_2$ ), calculated as the product of its fraction in the respired gas (about 0.79 in air) and the total pressure. Thus, during air breathing,  $PN_2$  increases in proportion to absolute pressure, 1 ATA at the surface (sea level) and 1 ATA more for each 33 ft of seawater. Narcosis does not occur when one breathes air at 1 ATA; at 6 ATA, there are appreciable decrements in judgment and problem-solving and measurable, although probably unimportant, effects on other nervous system functions. The associated sensations are similar to those of mild intoxication with alcohol or mild hypoxia. Individual responses vary, and some experienced people believe that they can compensate fairly well; but task performance and especially safety suffer enough for conservative practice to limit compressed-air diving to 5 ATA (132 ft of seawater).

Onset and remission of  $N_2$  narcosis depend on  $N_2$  delivery to and removal from the brain, an approximately exponential process with a time constant (time required to achieve 63% of the change from one state to another after a step-change in respired  $PN_2$ ) of about 2 min (Bennett, 1982); thus, for ordinary rates of change of depth, narcosis varies almost directly with depth (pressure). Hypercapnia (high  $CO_2$  concentration in blood) potentiates  $N_2$  narcosis (Hesser et al., 1971).

### Breathing of Dense Gases

The breathing of dense gases increases airway resistance and the work of breathing and decreases maximal expiratory flow rates; therefore, maximal achievable ventilation might be less than the ventilation required for heavy exercise (Lanphier and Camporesi, 1982). The added mechanical load also influences the control of breathing, so, for example, the ventilatory response to exercise is diminished. Effects on the gas-transport and gas-exchange functions of lung are negligible at pressures up to 6 ATA.

### Airway Resistance

Increased gas density (at pressures up to 6 ATA) adds only negligibly to the work of inspiration at rest, but becomes significant during exercise with three consequences. Added inspiratory resistance causes a reflex increase in ventilatory drive and breathing effort, with an associated increase in the sense of effort. The increase in effort is not enough to offset the increase in mechanical load (Pengelly et al., 1974), so the ventilatory response to exercise is diminished; the resulting hypoventilation allows  $\text{CO}_2$  to increase to above normal in the body. An increase in the work of breathing leads to early fatigue of the breathing muscles (Hesser et al., 1981; Roussos and Macklem, 1985), decreasing the capacity for sustained hyperpnea and introducing a limit to sustained aerobic exercise that is not usually present at 1 ATA. All three--increased sense of effort, hypercapnia, and inspiratory-muscle fatigue--are involved in the control of breathing and probably contribute to unpleasant breathing sensations that play a role in exercise intolerance at depth.

### Maximal Expiratory Flow Rates

The maximal expiratory flow rate that can be achieved is determined by an effort-independent mechanism that depends on elasticity of lung and airways, lung volume, tissue characteristics, and the density of gases breathed (Hyatt, 1986). This physical mechanism is independent of conscious and reflex mechanisms controlling breathing. The smaller the lung volume and the denser the gases, the lower the maximal flow rate. The decrease in maxi-

mal flow rate caused by breathing dense gases forces extreme hyperpnea to take place at high lung volumes--an effect that becomes more pronounced as gas density increases (Wood and Bryan, 1969; Hesser et al., 1981), particularly during hyperpnea induced by exercise. There are several adverse consequences: the elastic work of breathing increases markedly and that creates a load that falls on the inspiratory muscles; and the inspiratory muscles work with disadvantageous lengths and mechanical arrangements, which require increased effort and oxygen and contribute to early fatigue of inspiratory muscles, dyspnea, and exercise intolerance.

Reduced maximal expiratory flow rates combine with reduced inspiratory flow rates (due to increased inspiratory resistance) to reduce maximal voluntary ventilation (MVV), for example, from around 200 L/min at 1 ATA to 95 L/min at 6 ATA (Hesser et al., 1981). This pulmonary function test is a 15-s ventilatory "sprint" that cannot be sustained; yet at depth, even this briefly achievable maximum is well below the 150 L/min that is required for intense aerobic exercise. Under these circumstances, an unusual and little-studied phenomenon can occur: exertion of modest severity can quickly elicit an intense air hunger of a terrifying quality never before experienced and slow to recede. One can speculate that a high inspired fraction of  $\text{CO}_2$  would make it worse.

### Control of Breathing

The effects described above lead to decreased ventilation during submaximal exercise, with slightly higher than usual  $\text{CO}_2$  concentrations in blood and tissues, despite increased breathing effort. These higher concentrations might contribute to unpleasant sensations and decreased exercise tolerance.

### Gas Transport

Complex coupling of convective and diffusive mechanisms influences the transport of gases and thus the distribution of gases in the lung (Engel, 1983; Pedley et al., 1977). These phenomena, which depend in part on gas density, have not been well studied in hyperbaric states; but pressures up to 6 ATA do not appear to have biologically important effects on them.

### Gas Exchange

Gas exchange in the lung depends in part on uniform regional distributions (i.e., matching) of alveolar ventilation and capillary blood flow. No significant impairment in gas exchange is known to be caused by pressures up to 6 ATA.

### Decompression Sickness

During air diving, the  $PN_2$  in alveolar gas is higher than usual, so  $N_2$  passes into solution in blood and tissues. The amounts are substantial -- in a long dive, 1-1.5 L (measured at standard temperature and pressure) for each ATA. During ascent, the process is reversed, with an important limitation: if the total pressure (that is, depth) is reduced too fast, dissolved nitrogen forms bubbles and causes decompression sickness (the bends). To avoid that, diver's ascent is carefully regulated with decompression tables that take the depth and duration of the dive into account. Standard tables assume that the dive starts and ends at sea level, with the diver breathing air. If either assumption is violated, the risk of decompression sickness might be increased, so special tables are used.

Most of the clinical manifestations of decompression sickness are thought to result from mechanical effects of bubbles that distort tissues and obstruct vessels. Bubbles also constitute a foreign surface in body tissues and fluids. Deleterious effects result from the interaction of this foreign surface with blood constituents (Lee and Hairston, 1971).

Intravascular bubbles can cause serious alterations in the secondary and tertiary structure of globular plasma proteins (Philp et al., 1972). Effects on lipoproteins result in the release of free phospholipids, cholesterol, triglycerides, and free fatty acids. Coalescence of released lipids into globules can occur, and the globules can contribute to embolic vascular obstruction.

It is thought that bubbles formed during decompression can damage vascular endothelium and that the damage can promote platelet aggregation and adhesion and fibrin deposition. Increased number of circulating endothelial cells have been observed after decompression stress. Histologic studies of saccular endothelium after decompression have shown areas of endothelial cell loss (Philp et al. 1972). Experimental animals with decompression sickness have shown endothelial cells trapped in capillary beds. The damaged endothelium is the site

for platelet aggregation and adhesion, fibrin deposition, and eventually clot formation.

In addition to platelet aggregation, stimulation of the coagulation and fibrinolytic systems and activation of the complement and kinin systems can occur in decompression sickness (Hallenbeck and Andersen, 1982). The roles of all these phenomena have not been thoroughly delineated, but experimental work has shown that bubbles activate Hageman factor and accelerate clotting of both whole blood and cellfree plasma (Hallenbeck et al., 1973). Platelet aggregation, the initial event in arterial thrombosis and a component of venous clotting, promotes thrombin generation and fibrin formation and releases serotonin. Red blood cells clump because of coating with denatured plasma proteins. Such aggregation increases blood viscosity and stasis and increases the tendency for blood to clot.

The consequences of the phenomena noted above in decompression sickness might be as follows. Serotonin, bradykinin, and histamine provoke pain. Serotonin and histamine cause increased vascular permeability by forming interendothelial gaps of 1,000-8,000 Å. Kinins also increase capillary permeability, as do the complement anaphylatoxins C3a and C5a. Increased viscosity and sludging of venular blood cause both capillary stasis and a local transcapillary loss of plasma. This further increases stress forces of venular blood. The disturbance leads to fibrin deposition in areas of stasis, which reinforces and perpetuates a vascular obstruction that is initiated by bubbles, platelet aggregates, and red-cell aggregates. The resulting tissue ischemic damage results in the synthesis of various eicosanoids, some of which can cause vasoconstriction, increased capillary permeability, and further platelet aggregation. As a consequence of the tissue damage and the derangement of regional tissue perfusion, progressive impairment of microvascular perfusion develops and can extend the ischemic damage.

When ambient pressure decreases, gas in the lungs (and other cavities) expands. On rare occasions, the lungs become overdistended and rupture; gas can then enter the pleural spaces and the systemic arterial circulation. If those effects occur in decompression, they usually lead, respectively, to tension pneumothorax and cerebral air embolism, both of which are likely to be lethal unless treated immediately.



## Cold

Cold is pervasive in the diving environment. Even in warm water, however, heat loss from the body is rapid. Thermal protective suits and heating systems offer some protection, but commonly allow mild heat loss.

Body cooling, as occurs in diving with protective gear, leads to a number of effects. The first phase--and the only one germane here--is excitation (Reuler, 1978), which occurs at core temperatures between 34° and 37°C. During excitation, hypothalamic stimulation results in shivering and increased metabolic heat production. Shivering is maximal at a core temperature of 35°C. Intense peripheral vasoconstriction and adrenal release of cortisol and catecholamines lead to increases in heart rate, blood pressure, cardiac output, central blood volume, and respiratory minute ventilation. Diuresis and natriuresis secondary to atrial distention ensue and are mediated by decreases in plasma antidiuretic hormone and aldosterone and an increase in natriuretic factor. Diuresis ultimately leads to a decrease in plasma volume and to hemoconcentration. Hyperglycemia is common and results from a decrease in pancreatic insulin release, peripheral insulin blockade, and the combined influence of increases in plasma epinephrine and cortisol. Free fatty acids and glycerol increase, and mild ketosis is often present.

Decrements in diver performance due to distraction are common during the excitation phase (Webb et al., 1976) and are caused by the aggravating effects of the cold water. Reaction time, symbol processing, target detection, navigation problem-solving, and memory are impaired by exposure to cold before significant core cooling has occurred. At body temperatures of 35.5-36°C, recall is significantly affected. In 6-h simulated missions in 6°C water, well-trained divers omitted important procedural steps for mission requirements (Vaughn, 1975).

Horvath (1981) reviewed the literature on the ability of humans to exercise in a cold environment. Tolerance of cold-water exposure is limited by the extent to which loss of body heat exceeds heat production when core temperature cannot be maintained (and is decreasing at an increasing rate). Once core temperature reaches 35°C, heat production decreases, respiratory and circulatory irregularities appear, and death can follow. Exercise in cold water places a more severe thermal load on the body than exercise in air at the equivalent temperature. During exer-

cise in cold water, core temperature can be reduced enough (to 35°C) to result in interference with normal muscular activity, and maximal aerobic capacity is reduced under these conditions, so the cost of performing submaximal work will be increased. Shivering, an inefficient method of increasing heat production, diminishes the ability to perform tasks that require dexterity. The lowered skin temperature of the extremities has an influence on the ability to exert hand strength; it might be reduced by up to 50%. The increased metabolic costs of being in cold water, whether one is active or inactive, will result in reduction of the possible duration of the exposure, because available tank air will be used faster. It is quite evident that the placement of divers outside the submarine environment has consequences beyond those directly related to the quality of the air in their tanks.

The degree and duration of projected activity will influence performance. As mentioned, the diver must contend at least with the inconvenience of having to work with markedly reduced blood flow to his extremities. Schmidt and Vandervoort (1987) have stated that the only means of heating divers in the field is via a hot-water umbilical line from the surface. Combat swimmers and divers operating from SEAL (sea, air, and land) delivery vehicles have inadequate heating. Diver-suit insulation (passive insulation) has improved, but remains inadequate to provide the thermal protection necessary for optimal performance.

At first glance, it might appear that exercise during cold-water immersion would enable a diver to increase heat production enough to prevent a reduction in core temperature. However, Keatinge (1969) showed that, below a critical water temperature of 25°C, rectal temperature of swimmer decreased faster if subjects performed moderate exercise than if they remained at rest. A large amount of body fat has some protective value. Pugh and Edholm (1955) showed that, although a fat man was easily able to maintain his rectal temperature while swimming in 16°C water, his thin companion showed a larger decrease in rectal temperature during exercise than when immersed at rest. In general, the presence of body fat sufficient to provide a protective effect will reduce one's capability to perform as desired.

### Interactions

The effects of  $N_2$  narcosis are potentiated by many factors, such as alcoholic-beverage consumption (Jones et al., 1979; Fowler et al., 1986), fatigue and exertion (Adolfson, 1964, 1965), apprehension and anxiety (Davis et al., 1972), and increases in exogenous or endogenous carbon dioxide (Hesser et al., 1971, 1978). Exercise tolerance and ventilatory responses to exercise are presumably influenced by those factors and by dehydration, fear, and perhaps inanition. Conditions and responses are so variable, and the interactions so little studied, that it is not possible to provide guidelines for reliable predictions.

### DIFFERENCES BETWEEN SURFACE-BASED AND SUBMARINE-BASED DIVING

We consider here four factors that make diving from a submarine different from surface-based diving:

- Total pressure in the submarine can vary from 550 to 850 torr.
- The  $N_2$  fraction in the submarine can vary from 0.789 to 0.816.
- The  $O_2$  fraction in the submarine can vary from 0.184 to 0.211.
- The  $CO_2$  fraction in the submarine is always high, averaging 0.6%.

### Total Pressure

To the extent that total pressure in the submarine departs from 1 ATA, divers can be saturated with  $N_2$  at  $PN_2$  other than the usual value of 600 torr ( $0.79 \times 760$  torr) before dives and return to pressures other than 1 ATA after dives. The potential problems after a dive are of two kinds: if total pressure is low, the probability of bubble formation is increased; and if the  $PN_2$  is high, the rate at which  $N_2$  is washed out of the body can be decreased. The difficulties are similar to those of diving at altitude: the variable conditions make it hard to establish appropriate decompression schedules, increase the risk of decompression sickness, and complicate repetitive diving and decompression schedules. If the pressure swings are small (say,

1.5%\*), or do not occur within 24 h of a dive, they can probably be ignored.

### Nitrogen Fraction

In the submarine, the product of  $N_2$  fraction and total pressure determines the inspired  $PN_2$ . Variations in the  $N_2$  fraction influence pre-dive  $N_2$  saturation and post-dive  $N_2$  washout, as outlined above. They also determine the inspired  $PN_2$  during a dive. If the  $N_2$  fraction in the diver's tank is higher than 0.79, then both  $N_2$  narcosis and  $N_2$  uptake will be greater than expected at any depth. The latter will make decompression schedules more difficult and presumably increase the risk of the bends. The difficulties are similar to those of mixed-gas (e.g., 50%  $N_2$  and 50%  $O_2$ ) diving: divers will have to be aware of their equivalent air depth (EAD), and not just gauge depth. However, if the  $N_2$  fraction in submarines and their air banks is held within narrow limits, these issues can probably be ignored.

### Oxygen Fraction

Within the currently allowable range, variations in the  $O_2$  fraction in submarines and diver's tank will not lead to significant  $O_2$  toxicity when the air is breathed at 1-6 ATA for up to 12 h. Such variations can probably therefore be ignored.

### Carbon Dioxide Fraction

Carbon dioxide is a major issue for submarine-based SCUBA divers, so we discuss it here in detail.

The  $CO_2$  in inspired (atmospheric) air is ordinarily negligible, about 0.03% by volume. Multiplying the inspired fraction by the total

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\*Standard U.S. Navy dive tables are used without making allowances for changes in barometric pressure. Barometric pressure at sea level rarely varies by more than 3% (Yarkin, NOAA, personal communication), so pressure swings half as great should be safe for divers from submarines.



pressure gives the inspired partial pressure; at sea level,  $0.0003 \times 760$  gives an inspired  $\text{PCO}_2$  of about 0.2 torr.  $\text{CO}_2$  is produced by aerobic metabolism in amounts averaging about 80% of the volume of  $\text{O}_2$  consumed, ranging from 0.2 L/min in adult humans at rest to over 5 L/min in extreme exercise. A person consuming 3,000 kcal/d in his diet produces  $\text{CO}_2$  at about 500 L/d (0.35 L/min); it constitutes about 3% of his expired air (at 1 ATA, and if inspired air is free of  $\text{CO}_2$ ). The partial pressure of  $\text{CO}_2$  in alveolar gas (thus in the body as a whole) is ordinarily regulated by adjusting alveolar ventilation ( $\dot{V}_A$ ) to be about 20 times the  $\text{CO}_2$  production ( $\dot{V}\text{CO}_2$ ). Thus, the normal alveolar  $\text{CO}_2$  fraction is about 5.6%, and the alveolar  $\text{PCO}_2$  is about 40 torr. Departures can occur—for example, when  $\dot{V}_A/\dot{V}\text{CO}_2$  is low (hypoventilation). Some of the effects are outlined below.

The  $\text{CO}_2$  exhaled into a submarine's environment has to be removed by chemical scrubbers to prevent its accumulation. Assuming that the scrubbers remove all the  $\text{CO}_2$  from gas passing through them (100% efficiency), the steady fraction of  $\text{CO}_2$  in the boat's environment is, in principle, equal to the ratio of  $\text{CO}_2$  input (summed crew  $\dot{V}\text{CO}_2$ ) to scrubber flow. That is, the boat's air can be maintained as nearly free of  $\text{CO}_2$  as desired, at the cost of geometric increases in scrubber flow. The practical compromise between that cost and the undesirable effects of long exposure to high inspired  $\text{PCO}_2$  is now struck at a 90-d threshold limit value (TLV) of 0.8% (about 6 torr) (U.S. Naval Sea Systems Command, 1979). Current scrubbers are only about 70% efficient, so a continuous scrubber flow of about 60 L/min (2 cfm) for each man is implied. A  $\text{CO}_2$  concentration range of 0.7–1.0% during *Polaris* patrols was reported in 1979 (Schaefer, 1979); more recent averages are around 0.6% (Weathersby et al., 1987), implying a scrubber flow of around 3 cfm per man.

The inspired  $\text{PCO}_2$  for submarine crews is higher than usual, about 6 torr. That tends to raise alveolar and arterial  $\text{PCO}_2$  in submariners, with several consequences (Consolazio et al., 1947; Guillemin and Radziszewski, 1979; Schaefer, 1975, 1979). Breathing is stimulated, so resting ventilation increases by approximately 20% and the alveolar  $\text{PCO}_2$  rises by about 2 torr (Schaefer, 1979). This very mild chronic respiratory acidosis is partially offset by a normal renal compensatory response. Such compensation is incomplete, so there is a slight residual acidemia; that is, the blood is slightly less than

normally alkaline, with an arterial blood pH that is about 0.03 below its normal value of 7.40. But these are small changes, within the range of normal variation for humans, which are functionally insignificant or nearly so. They may be compared with larger abnormalities tolerated for months or years by diseased humans; for example, arterial  $\text{PCO}_2$  over 50 torr is not uncommon in advanced chronic obstructive pulmonary diseases (COPD). Inspired  $\text{CO}_2$  concentrations of 3% (21 torr) were "long regarded as suitable in the U.S. Navy" (Behnke and Lanphier, 1965) before the advent of nuclear submarines. Those were shorter exposures, however, and those with higher  $\text{CO}_2$  concentrations were associated with significant symptoms and impaired function.

There is more to the subject than the above simple summary indicates. First, a great deal is known about chronic  $\text{CO}_2$  exposures on submarines. Acid-base state varies with time over periods of days to weeks, and there are measurable effects in several organ systems (Schaefer, 1979). Second, a great deal is uncertain and unknown about such exposures. What happens to the ventilatory responses to exercise and to exercise tolerance of people acclimated to, and breathing, inspired  $\text{CO}_2$  at a partial pressure of 6 torr? What if they are acclimated to that  $\text{PCO}_2$ , but exercising with higher or lower  $\text{PCO}_2$ ?

When gas is compressed and used by divers at pressures greater than 1 ATA, the inspired  $\text{CO}_2$  fraction is unchanged, but its partial pressure increases with the absolute pressure at which the gas is breathed. At 6 ATA, surface air (0.03%  $\text{CO}_2$ ) has a  $\text{CO}_2$  partial pressure of  $0.0003 \times 760 \times 6$ , or 1.4 torr. If gas from a submarine containing 1%  $\text{CO}_2$  were breathed at 6 ATA, the inspired  $\text{PCO}_2$  would be  $0.01 \times 760 \times 6$ , or 46 torr—greater than the normal alveolar  $\text{PCO}_2$ . During acute exposures under those conditions, alveolar  $\text{PCO}_2$  might rise to 55 torr or more, and there would be distressing symptoms, including headache and breathlessness at rest, with marked impairment of exercise and other performance (Consolazio et al., 1947; Schaefer, 1975, 1979).

If 6 torr is an acceptable inspired  $\text{PCO}_2$  in acute hyperbaric states, as in chronic normobaric states, then at 6 ATA the compressed gas must be no more than 0.13%  $\text{CO}_2$ , i.e., one sixth of the value now accepted in submarine atmospheres. We found no satisfactory basis for specifying this or any other inspired  $\text{PCO}_2$  greater than zero as acceptable during violent

exertion at pressures up to 6 ATA, but it is clear that submarine air must be further scrubbed of  $\text{CO}_2$  if it is to be used by divers (Weathersby et al., 1987). That should be done by passing divers' air through a lithium hydroxide scrubber as their tanks are filled from the boat's air banks (U.S. Naval Sea Systems Command, 1986), reducing the  $\text{CO}_2$  fraction to around 0.1%.

Divers will presumably be acclimated to the submarine atmosphere and thus display the respiratory, acid-base, and other effects of chronic mild hypercapnia. We do not know the effect, if any, of that background on the performance of divers; we think it is worth study.

Ideally, all  $\text{CO}_2$  should be removed from the gas to be breathed by SCUBA divers. Variations of up to about 1.5% in  $\text{PN}_2$  (around 600 torr) and in total pressure (around 1 ATA) in submarines are probably insignificant for submarine-based SCUBA divers. \*Larger variations might increase the risk of decompression sickness. Research is needed to see whether chronic adaptation to mild hypercapnia affects the performance of SCUBA divers while they are breathing gas free of  $\text{CO}_2$  or containing some  $\text{CO}_2$ .

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\*Standard U.S. Navy dive tables are used without making allowances for changes in barometric pressure. Barometric pressure at sea level rarely varies by more than 3% (Yarkin, NOAA, personal communication), so pressure swings half as great should be safe for divers from submarines.



# CHAPTER 5

## EFFECTS OF BREATHING SUBMARINE AIR CONTAMINANTS AT UP TO 6 ATA

Submarine air contains not only major gases ( $O_2$  and  $N_2$ ), but also contaminants that result from emission from human activities, from structural materials, and from equipment required to operate the submarine and complete its military missions. This chapter discusses the potential health effects of two major submarine air contaminants--carbon monoxide and cigarette smoke--and of trace contaminants, with reference to the use of the submarine air for divers operating at up to 6 ATA.

### CARBON MONOXIDE

Carbon monoxide (CO) on submarines has various sources, including incomplete combustion of cooking, smoking, and engine operations. The 90-d continuous exposure guidance level recommended by the National Research Council Committee on Toxicology for CO is set at 20 ppm or 15.2 millitorr (National Research Council, 1984a). CO in submarines undergoing sea trials has been reported at 1-5 millitorr (up to 6.6 ppm) (Rossier, 1984). Smokers would, of course, be exposed to higher concentrations (see the next section on tobacco smoke).

CO in inhaled air binds to hemoglobin (Hb) and forms carboxyhemoglobin (COHb) after passing through the alveolar membrane. The ratio of Hb affinity for CO to its affinity for  $O_2$  is approximately 235:1. The principal mechanism by which CO exerts its toxic effect in

mammals is commonly accepted to be by the reduction in blood  $O_2$ -carrying capacity (Coburn, 1979). Although research on environmentally relevant CO exposure remains to be done, it is also possible that CO itself is cytotoxic (Piantadosi et al., 1985, 1987).

### Pharmacokinetics

The formation of COHb has been described by Coburn et al. (1965) with a differential equation. On the basis of that equation, Figure 4 has been constructed to depict the formation of COHb (in percent saturation) for various CO concentrations as a function of time.

The Coburn et al. equation was also used to predict COHb formation and elimination at 1 and 5 ATA with exposure at 25 ppm. The 5-ATA results are appropriate to the case in which normobaric air containing CO at 25 ppm is compressed to 5 ATA. The results for COHb formation are shown in Figures 5 and 6 and for elimination in Figures 7 and 8. The figures must be interpreted with caution, because they are predictions based on a model that has not been tested in this context. The provisional conclusion that can be drawn from the figures is that increased atmospheric pressure increases the rate of COHb formation, but does not change the asymptotic concentration (Figures 5 and 6) and increases the rate of elimination (Figures 7 and 8). That holds true only if the





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CO in inhaled air and forms carboxyhemoglobin (COHb) by displacing oxygen from hemoglobin (Hb) in the blood. The rate of COHb formation is proportional to the partial pressure of CO in the inhaled air and to the duration of exposure. The rate of COHb elimination is proportional to the partial pressure of CO in the exhaled air and to the duration of exposure. The rate of COHb formation is proportional to the partial pressure of CO in the inhaled air and to the duration of exposure. The rate of COHb elimination is proportional to the partial pressure of CO in the exhaled air and to the duration of exposure.

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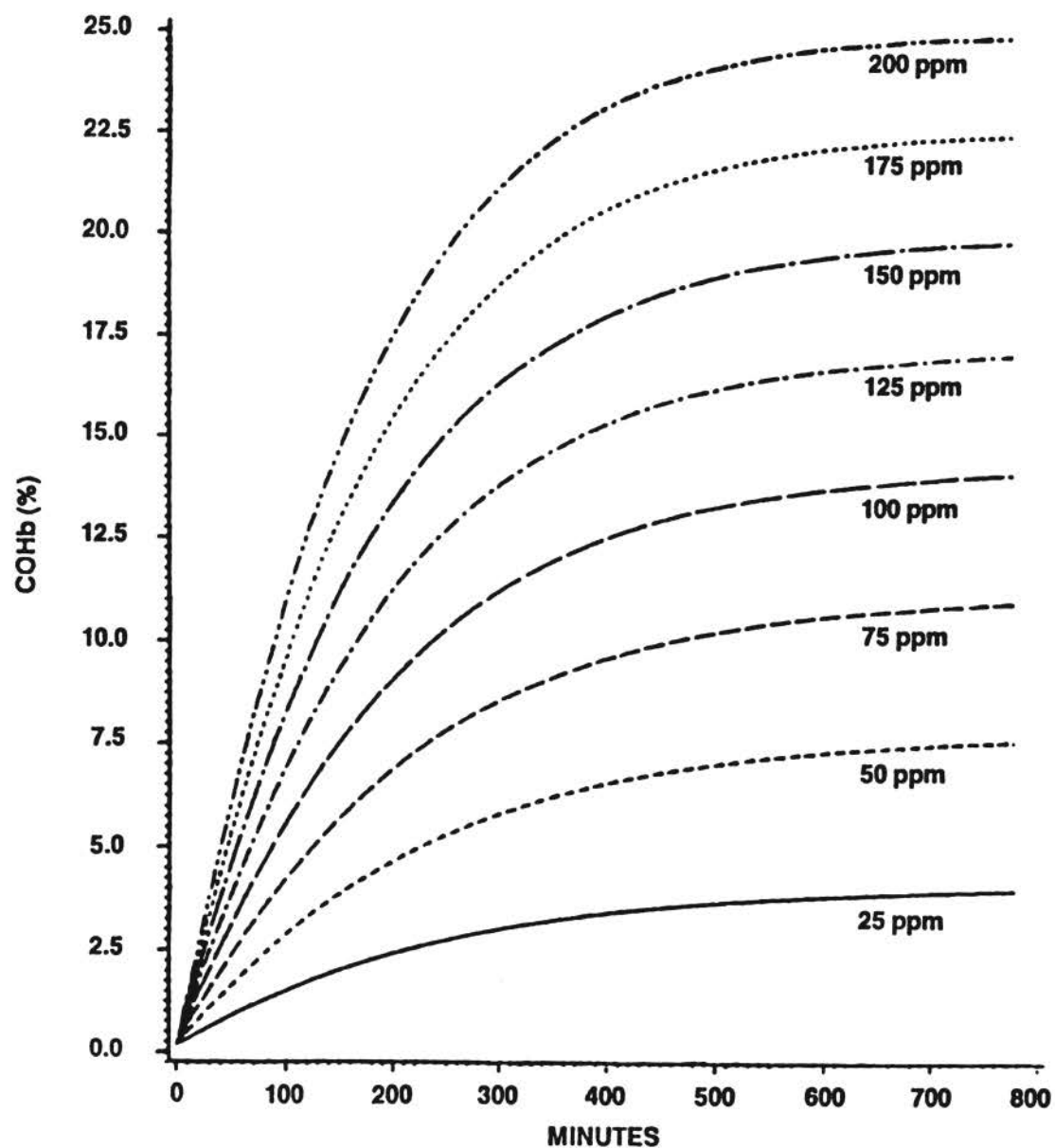


FIGURE 4 Projected COHb formation as function of time for CO exposures. Projections generated by use of Coburn et al. (1965) equation. For alveolar ventilation of 10 L/min at 1 ATA.

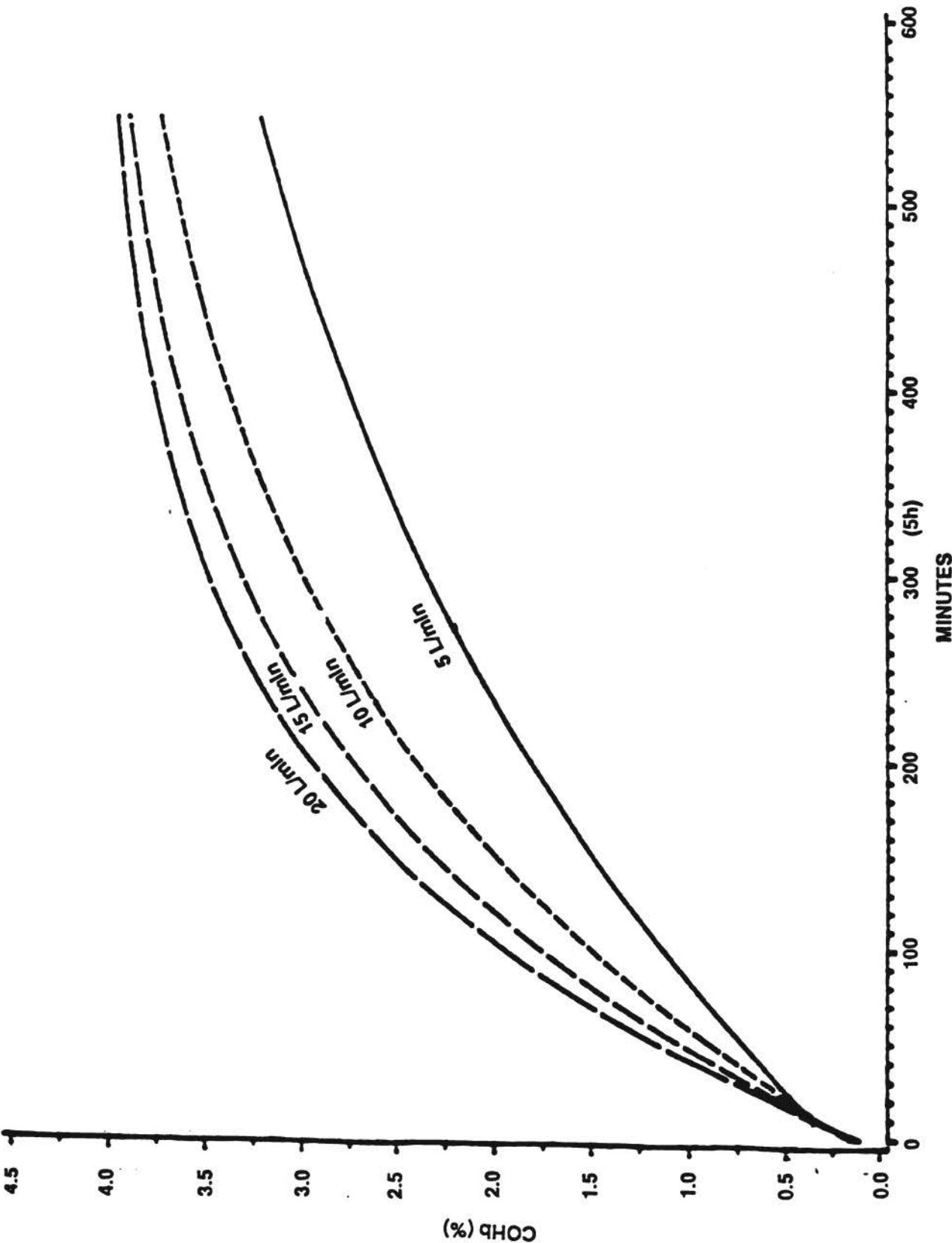


FIGURE 5 Projected COHb formation as function of time for CO at 25 ppm in normobaric air, at alveolar ventilation rates of 5-20 L/min.

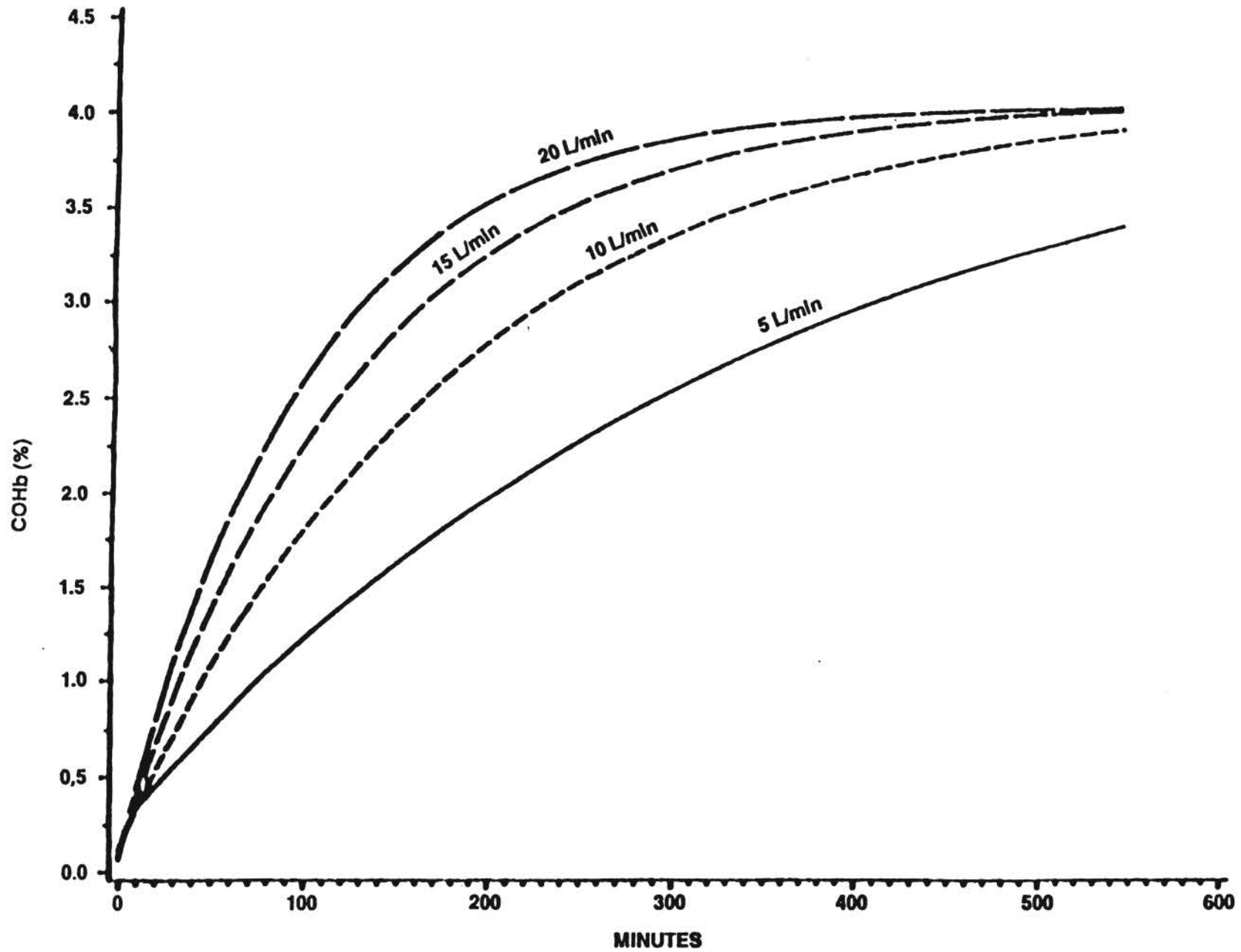


FIGURE 6 Projected COHb formation as function of time for CO at 25 ppm in air, compressed to 5 ATA at alveolar ventilation rates of 5-20 L/min.

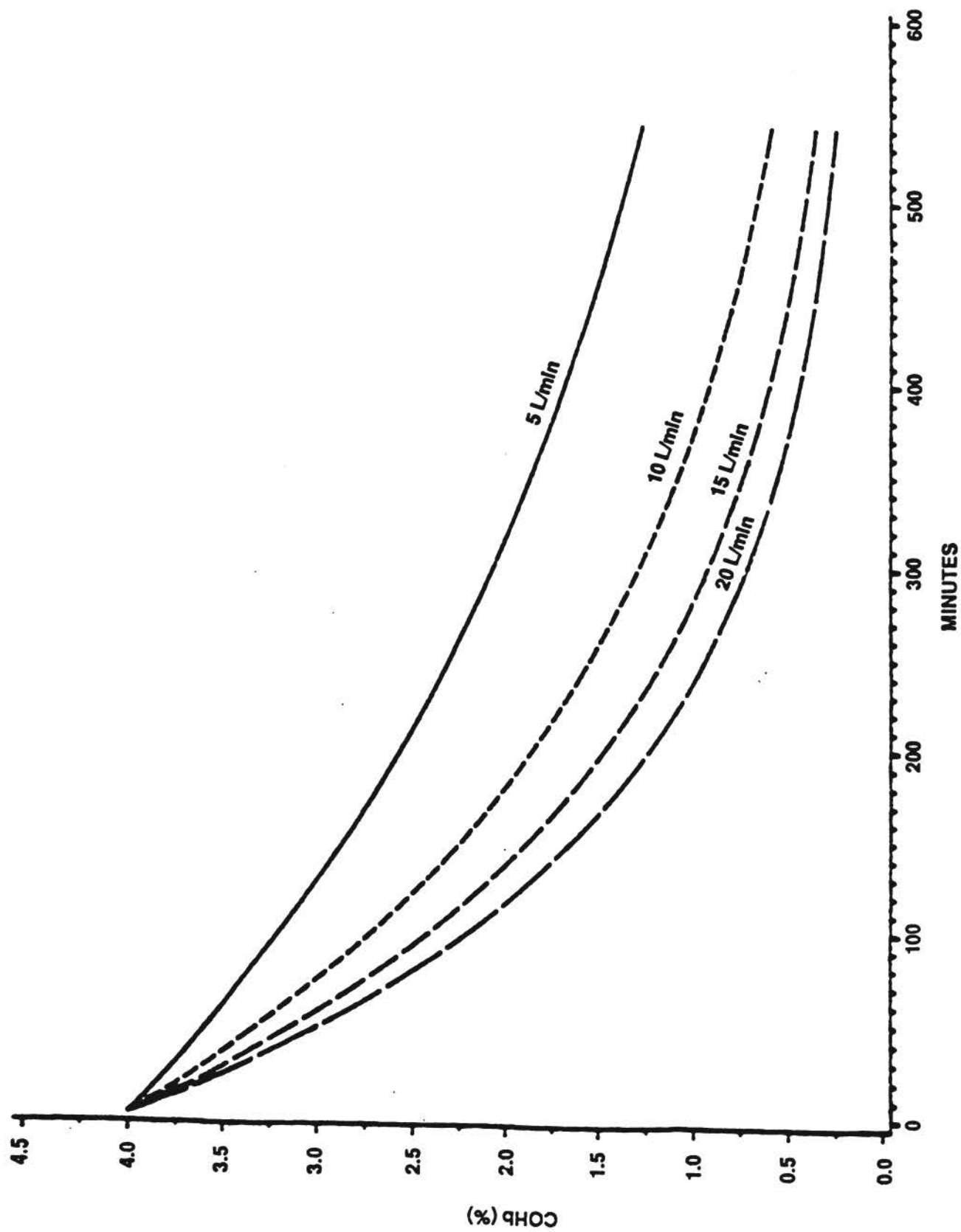


FIGURE 7 Projected COHb elimination in normobaric air for alveolar ventilation rates of 5-20 L/min.



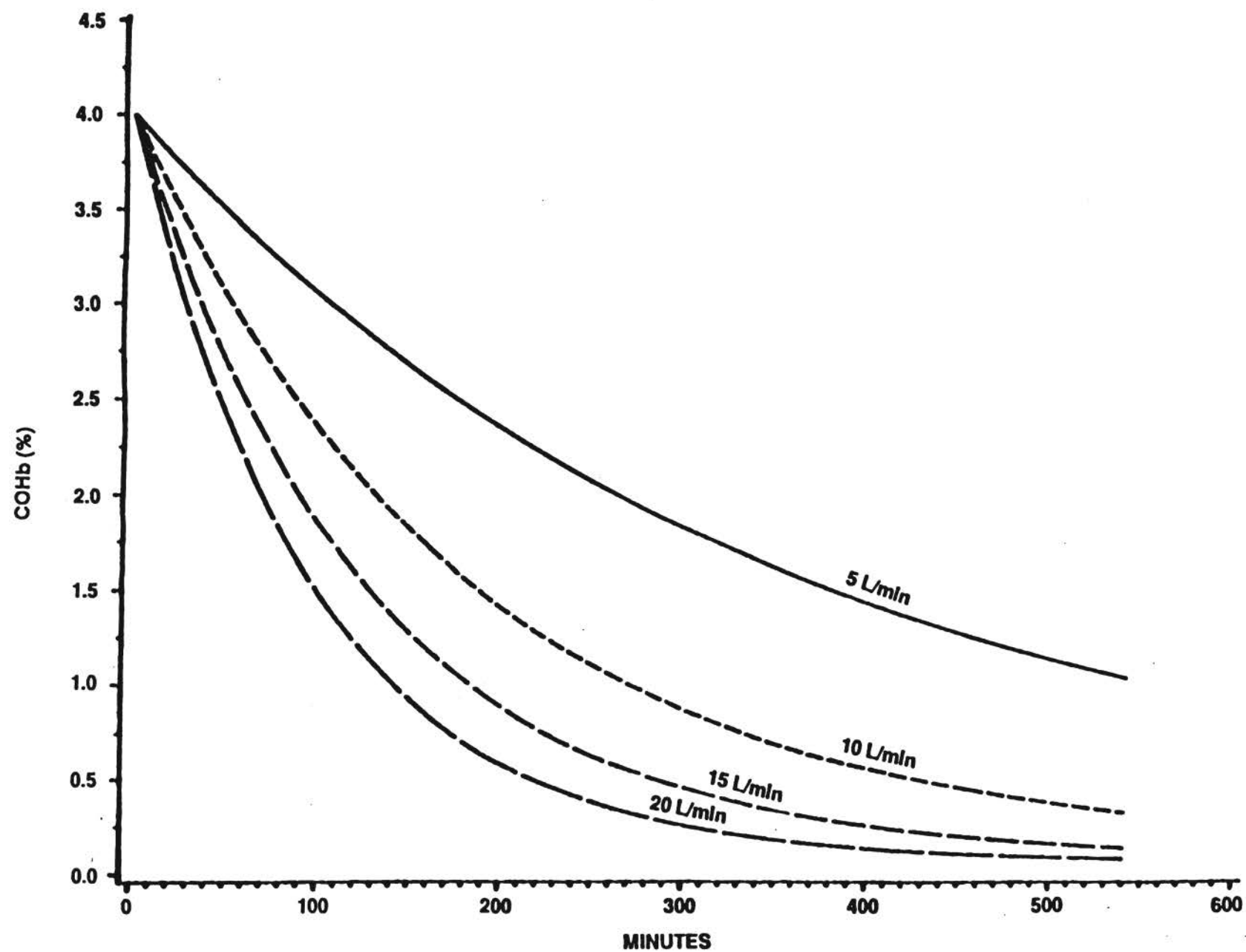


FIGURE 8 Projected COHb elimination at 5 ATA pressure for alveolar ventilation rates of 5-20 L/min.

PCO-to-PO<sub>2</sub> ratio remains constant. Data published by Rose et al. (1970) support the prediction that asymptotic COHb concentrations are not changed by increased pressure, but no data on COHb formation rate are available.

If those predictions regarding COHb formation under pressure are verified, then, at least for purposes of studying COHb pharmacokinetics, the asymptotic COHb concentration is not a function of PCO, but of the ratio, PCO/PO<sub>2</sub>. This is because CO competes with O<sub>2</sub> for binding sites on hemoglobin. It remains true, however, that, for exposure periods that are shorter than one time constant (time to reach 63% of equilibrium value) for COHb formation, more COHb would be formed under high pressure than would be formed with the same CO concentration at normal pressure; the reason is the predicted pressure-associated increase in the rate of COHb formation.

Other mechanisms have been postulated whereby CO could reduce O<sub>2</sub> transport. Carbon monoxide can bind to intracellular hemoproteins, such as myoglobin and cytochrome oxidase and binding depends on the relationship of O<sub>2</sub> tension (PO<sub>2</sub>) and CO tension (PCO) to CO binding constants (Coburn, 1979). The affinity of cytochrome oxidase for CO is similar to that for O<sub>2</sub>. This is in marked contrast to the much higher affinity for CO over O<sub>2</sub> exhibited by myoglobin (30-50x) and hemoglobin (235x). Thus, cytochrome oxidase is less likely to be responsible for impairing diffusion of O<sub>2</sub> to the mitochondria than are proteins with high CO/O<sub>2</sub> affinity ratios. However, if steep O<sub>2</sub> tension gradients exist between the extracellular and intracellular environments, then the PO<sub>2</sub> surrounding the mitochondrial terminal oxidase would be low enough for increased binding with CO. That hypothesis was tested by Coburn (1979) in studies on isolated vascular smooth muscle. He concluded that significant CO binding to cytochrome oxidase was unlikely to be an *in vivo* mechanism of CO toxicity in that tissue. Myoglobin binding was also unlikely, because it is absent or present in only low concentrations. Carbon monoxide might bind to hemoproteins other than hemoglobin, to myoglobin, or to cytochrome oxidase. Cytochrome P-450, tryptophan deoxygenase, and tryptophan catalase all have high enough binding affinities for CO in specific tissues to be considered as possible candidates (Coburn, 1979).

The binding of CO to myoglobin in heart and skeletal muscle might be high enough to reduce intracellular oxygen transport in those tissues

(Coburn, 1979; Agostoni et al., 1980). Using a computer simulation of a three-compartment model (arterial blood, venous capillary blood, and tissue myoglobin), Agostoni et al. (1980) predicted that conditions would be favorable for formation of carboxymyoglobin at COHb concentrations of 5-10%, particularly where the PO<sub>2</sub> was low in normal physiologic conditions (e.g., in subendocardium) and when hypoxia, ischemia, or increased metabolic demand was present. This model for formation of carboxymyoglobin could provide theoretical support for experimental evidence of myocardial ischemia, such as electrocardiographic irregularities and decrements in work capacity (discussed later). However, it is not known whether binding of CO to myoglobin could cause health effects (e.g., decreases in maximal oxygen consumption during exercise) at COHb concentrations as low as about 4-5%. Additional research is needed for this possibility to be more definitively evaluated.

## Neurobehavioral Effects

### Brain Energetics

Blood O<sub>2</sub>-carrying capacity is reduced in proportion to the hemoglobin available for O<sub>2</sub> binding, but the presence of COHb in the blood or the reduction in O<sub>2</sub> supply triggers a compensatory increase in cerebral blood flow (CBF) (Häggendal et al., 1966; Paulson, 1977; Traystman and Fitzgerald, 1977; Doblar et al., 1977; Traystman, 1978). The adequacy of compensatory CBF responses can be judged by the tissue partial pressure of O<sub>2</sub> (PtO<sub>2</sub>) or, as a surrogate, the venous partial pressure of O<sub>2</sub> (PVO<sub>2</sub>). From such measurements and calculations (Paulson, 1973; Zorn, 1972; Miller and Wood, 1974; Forster, 1970; Permutt and Farhi, 1969), it appears that PtO<sub>2</sub> falls by about half the amount that would be expected if no compensatory action were occurring. Apparently, the compensatory increase in CBF is not adequate to prevent the fall of PtO<sub>2</sub> due to increased COHb. However, the amount of O<sub>2</sub> consumption in the brain, as measured by Traystman and Fitzgerald (1977) and Traystman (1978) as a function of COHb in anesthetized dogs, did not change significantly until concentrations exceeded 30%. The latter findings could be used to argue that the compensatory mechanisms of increased CBF were adequate.

The issue of adequacy of compensatory mechanisms remains to be resolved.

### *Central Nervous System Functional Effects*

The literature on the motor, sensory, and vigilance effects of increased COHb is large and internally inconsistent. No neurobehavioral data were reported on CO effects at increased pressures. Despite the lack of consistency, it appears that COHb as low as 5% at normal pressures will sometimes deleteriously affect some aspect of motor coordination, visual sensitivity in dim light, and possibly alertness. Many references are available to document that conclusion, as follows.

**Motor Effects.** Accuracy in various target tracking tasks appears to be decreased by COHb of 5% (Putz et al., 1976; Putz, 1979; Benignus et al., 1987; Wright et al., 1973; Rummo and Sarlanis, 1974), although other tracking tasks were not affected (O'Donnell et al., 1971a; Forbes et al., 1937; Weir and Rockwell, 1973; McFarland, 1973). Task complexity seems to increase the effects of CO (Bender et al., 1971, 1972). Other kinds of motor behavior seem not to be affected (Stewart et al., 1970, 1975; Wright et al., 1973; Fodor and Winneke, 1972; O'Donnell et al., 1971a).

**Sensory Effects.** Small but reliable concentration-related decreases in visual sensitivity were reported by McFarland et al. (1944) and Halperin et al. (1959) when COHb was increased to values ranging from 4.5 to 19.7%. Critical flicker fusion was decreased at similar concentrations (Seppanen et al., 1977). Many other sensory abilities seem to be unaffected by COHb up to 26% (Stewart et al., 1970; Wright et al., 1973; Ramsey, 1972, 1973; Fodor and Winneke, 1972; Guest et al., 1970; Lilienthal and Fugitt, 1946; O'Donnell et al., 1971b; Vollmer et al., 1946; Von Post-Lingen, 1964). Beard and Wertheim (1967) reported that time-duration judgments were affected by COHb, but others have been unable to confirm that (O'Donnell et al., 1971b; Stewart, 1975; Stewart et al., 1973; Otto et al., 1979; Mikulka et al., 1970).

**Vigilance Effects.** Impairment of vigilance might be among the effects of COHb up to 6% (Horvath et al., 1971; Fodor and Winneke, 1972;

Beard and Grandstaff, 1970), but some have failed to show such impairment (Christensen et al., 1977; Winneke, 1974; Roche et al., 1981; Benignus et al., 1977).

### *Pulmonary Function and Exercise*

#### *Maximal Work*

The work of Chiodi et al. (1941) and Roughton and Darling (1944) indicated that work capacity is reduced to zero when COHb approaches 50%. Goldsmith (1970) reported that competitive swimmers' performance is impaired when events are conducted in atmospheres containing CO at 30 ppm.

#### *Oxygen Uptake and Heart Rate*

The presence of COHb does not appear to affect  $O_2$  uptake during submaximal work (Brinkhouse, 1977; Chevalier et al., 1966; Ekblom and Huot, 1972; Ekblom et al., 1975; Gliner et al., 1975; Nielsen, 1971; Pirnay et al., 1971; Vogel and Gleser, 1972); Chevalier et al. (1966) and Klein et al. (1977) studied men with a light workload and reported that, although  $O_2$  uptake was not affected by COHb of 4%, there was a significant increase in  $O_2$  debt in relation to total  $O_2$  uptake. Klausen et al. (1968) found no differences in energy expenditure related to CO. Vogel and Gleser (1972), Pirnay et al. (1971), and Gliner et al. (1975) reported higher heart rates at submaximal workloads and increased ventilation per unit of  $O_2$  uptake with COHb of 15-20%.

#### *Aerobic Capacity*

In short-term maximal exercise of several minutes, in which capacity for effort depends mainly on aerobic metabolism, it is reasonable to predict that maximal aerobic capacity would be diminished approximately in proportion to the concentration of COHb. Such diminution in  $\dot{V}O_{2max}$  when COHb is 7-33% has been observed by Seppanen (1977) and Ekblom et al. (1975). There is a linear decline in  $\dot{V}O_{2max}$  as COHb ranges from 4 to 33% (Horvath, 1981).

### Cardiovascular System

People in constant contact with CO are reported to develop ECG evidence of left ventricular hypertrophy and conduction system abnormalities (Zenkevic, 1973; Ejam-Berdyev, 1973; Komatsu, 1959). Davies and Smith (1980) studied subjects living continuously in a closed-environment chamber for 18 d. During the middle 8 d, they were continuously exposed at CO concentrations of 50 ppm, 15 ppm, or 0 ppm (control). P-wave changes were observed in 6 of 15 subjects at 50 ppm and 13 of 15 subjects at 15 ppm, but in none of 14 subjects at 0 ppm. COHb concentrations were 0.4, 2.4, and 7.0% for exposure concentrations at 0, 15, and 50 ppm, respectively. At higher ambient CO concentrations (75 ppm), 7 of 10 subjects had significant ECG changes.

### Effect of High Pressure

Other than the pharmacokinetic considerations mentioned earlier, no data on human CO effects under hyperbaric conditions are available. If the pharmacokinetic predictions prove correct, however, the effects of CO exposure at high atmospheric pressure should be the same as at normal pressure, except that the onset should be earlier because COHb is formed more rapidly. Rose et al. (1970) reported that the lethality of CO exposure was not increased by high atmospheric pressure, as long as the PCO:PO<sub>2</sub> ratio remained constant. The latter finding supports the prediction that the effect of COHb would not increase at high pressure, although lethality is not a sensitive measure of adverse effects. More research is required to discover the interaction of COHb and hyperbaric conditions, in that the predictions were based on the idea that CO effects are due to hypoxia resulting from COHb formation. No account was taken of the possibility of cytotoxicity of CO in either normobaric or hyperbaric conditions.

### Summary

The principal effect of CO appears to be hypoxia due to COHb formation, although CO cytotoxicity itself is also possible. COHb formation and elimination are predicted to be more rapid as atmospheric pressure increases, but the asymptotic concentration of COHb appears to

be independent of pressure as long as the PCO/PO<sub>2</sub> remains constant.

Such neurobehavioral variables as motor coordination, visual sensitivity, and vigilance appear to be decreased when COHb is greater than 5%. The effects seem to depend heavily on the circumstances in which measurements are made.

When COHb is as high as 5%, aerobic capacity is reduced in proportion to COHb. Oxygen uptake at COHb up to 20% is not affected during short exposures. Chronic CO poisoning may cause a myocarditis and in some cases myocardial infarction. Severity of these disorders increases with increasing CO blood levels (Graziani and Rossi, 1959).

### TOBACCO SMOKE

Tobacco-smoking, which is permitted on U.S. Navy submarines, produces effects both in smokers and, via air pollution, in others (National Research Council, 1986a,b). The extent of tobacco-related pollution in submarine air is not known, and estimates are difficult to make, because tobacco smoke has so many components and their longevity is not known. Furthermore, the components might be removed, to an unknown extent, either by active "scrubbing" or as a side effect of compression of air in the air banks.

Rossier (1984), in a report on the atmospheric control in a Trident submarine during a sea trial, noted an aerosol generation rate from cigarettes of 2.5 g/h in the submarine. The cigarette-smoke generation rates were calculated on the basis of crew distribution in the submarine and 42.9 mg of aerosol produced per cigarette. A medical survey indicated that 40% of the 177 crew members were smokers, and an average of 77 packs of cigarettes were smoked per day (Rossier, 1984). This information indicates that cigarette smoke was a major source of aerosols in the submarine, but the report did not include analyses of other tobacco-smoke components.

Despite the lack of estimates of tobacco-smoke components in submarine air, effects on smokers themselves are known. Cigarette-smoking induces a significant rise in the incidence of carcinoma of the lung and of coronary arterial disease (U.S. Surgeon General, 1964, 1982; Astrup and Kjeldsen, 1974; Kjeldsen, 1975). A recent National Research Council (1986a) report on environmental tobacco smoke



suggested that, although cigarette-smoking increases the risk of lung cancer in smokers by over 1,000%, the risk in nonsmokers frequently exposed to environmental cigarette smoke may increase as much as 30%. These diseases are long-term effects of smoking and would not be of immediate concern in connection with the shorter exposures expected in submarine duty, even in prolonged underwater patrols of 6-8 months. However, cigarette-smoking can be documented to have immediate effects that can alter performance, and these should be considered in relation to the environment of the submarine.

### Irritation

Nonsmokers experience irritation of the nose, eyes, and throat when subjected to a smoky environment, and conventional air-cleaning systems often do not filter the irritating substances (National Research Council, 1986a,b), such as phenols, aldehydes, acids, and oxides of nitrogen. In industrial settings, high ventilation rates--perhaps over 50 ft<sup>3</sup>/min per occupant--are necessary to make room air acceptable to most nonsmoking adults when people are smoking cigarettes in the environment (National Research Council, 1986a). Some of the symptoms of irritation might be allergic reactions to constituents of the smoke, tearing of eyes, and complaints of noxious odors.

### Cardiovascular Effects

#### *Physiologic and Clinical Studies*

It has been noted for a number of years that cigarette-smoking increases the risk of coronary arterial disease (U.S. Surgeon General, 1983; U.S. Centers for Disease Control, 1986; Astrup and Kjeldsen, 1974; Kjeldsen, 1975). The mechanism of the increased risk is not clear, but it has been documented in a large national trial, the Coronary Artery Surgery Study (Kennedy et al., 1982). In that study, the risk of coronary arterial disease was significantly higher in males and females who smoked cigarettes than in nonsmokers. Cigarette-smoking can also produce a more acute effect on blood vessels than the development of disease in the coronary arteries. A recent article demonstrated that the risk of stroke was 2-3 times higher in male

cigarette-smokers than in nonsmokers (Abbott et al., 1986).

#### *Effects on Coronary and Other Arteries*

Studies on the effects of cigarette smoke on blood vessels can be divided into those based on isolated arteries or the intact heart and those based on clinical observations. Cox and co-workers (1984) used isolated segments of carotid and femoral arteries from dogs subjected to the smoking of 12 cigarettes/d for 2 years. They compared their data with data from unexposed controls and demonstrated a small increase in passive artery stiffness in the smoking animals. Active force generation in arterial smooth muscle was reduced in the smoking animals' arteries, and their arteries were less sensitive to the constricting effects of potassium.

That study in isolated blood vessels demonstrated a direct effect of chronic cigarette-smoking on the blood vessels of smoking dogs. The model, in which carotid and femoral arteries were studied, suggested that arteries throughout the body can be affected by chronic cigarette-smoking. Studies of skin circulation in humans have demonstrated reduced blood flow in the presence of cigarette-smoking (Waeber et al., 1984)--evidence of an acute vasoconstrictor effect. Recent human studies that examined myocardial perfusion suggested that smoking causes coronary vasoconstriction (Winniford et al., 1986, 1987; Maouad et al., 1984; Deanfield et al., 1986). In studies by Winniford and co-workers (Winniford et al., 1986, 1987; Deanfield et al., 1986), cigarette-smoking induced coronary vasoconstriction and a change in myocardial perfusion in patients with coronary arterial disease. Other studies have demonstrated a rise in blood pressure associated with cigarette-smoking (Richards et al., 1986; Martin et al., 1984).

#### *Additional Smoking Studies in Animals*

Human studies involving vasoreactivity and effects of cigarette-smoking on blood vessels are based on the results of numerous animal studies that have shown alterations in vasoreactivity and myocardial function during or after cigarette-smoking. A study by Piascik and co-workers (Piascik et al., 1985) showed that 23 weeks of exposure to cigarette smoke in rats caused an increase in coronary vasoreactivity

responses to angiotensin-induced vasoconstriction.

As in human studies, Gillespie and co-workers (Gillespie et al., 1985) found that nicotine exaggerated release of norepinephrine from hearts of atherosclerotic rabbits. That result supported several clinical observations and suggested that smoking affects coronary and other vessels through the sympathetic nervous system. Studies of nicotine alone, which has actions like those of acetylcholine, have demonstrated changes in the heart directly related to its action. Fenton and Dobson (1985) demonstrated that nicotine augments cardiac contractility and oxygen consumption independently of sympathetic influences and increases the release of adenosine in the coronary circulation. In a study of chronically smoking dogs, cigarette-smoking led to an increase in myocardial-infarct size (Sridharan et al., 1985). The combination of nicotine and alcohol reduced cardiac contractility in dogs given both cigarettes and alcohol for 18 months (Ahmed et al., 1985).

Some of the cardiovascular effects of smoking might be related to high CO in cigarette smoke. However, the contribution of CO has not been isolated from the contributions of other smoke constituents. CO effects on the cardiorespiratory system have been reviewed (Turino, 1981; Ahmed et al., 1980). In a study by Lough (1978), guinea pigs were exposed to the smoke of eight cigarettes/d, 5 d/week for 12-15 weeks. The heart rate of the smoking animals was found to be significantly increased. Toxic changes associated with edema, increased lipids, and increased lysosomal activity were noted in the myocardial mitochondria. The investigator suggested that the cardiomyopathy probably caused by CO from cigarette smoke resembles the changes of chronic intermittent hypoxia. Wanstrup and co-workers (1969) demonstrated that the endothelial surface of arteries can be damaged by prolonged exposure to CO. Endothelial cells play a major role in maintaining normal coronary vasoregulatory tone (Brum et al., 1984), and regulatory mechanisms can be damaged by inhalation of CO in cigarette smoke. Results of studies by Astrup and co-workers (Astrup et al., 1967) indicated that chronic CO exposure of cholesterol-fed rabbits augmented the development of atherosclerosis. Castro de Souza and co-workers (1977) showed that nicotine causes release of vasopressin, a potent vasoconstrictor. Studies that attempted to separate the effects of nicotine from those of other constituents of cigarette

smoke in dogs demonstrated a slight reduction in left ventricular performance and an increase in blood pressure, but no myocardial hypertrophy or ultrastructural abnormalities (Ahmed et al., 1976). Interstitial fibrosis was evident in animals given both cigarette smoke and nicotine and led the authors to conclude that the cardiovascular abnormalities depended on the nicotine in cigarettes.

Reece and Ball (1972) examined the effects of cigarette smoke on treadmill exercise in dogs; they found a rapid reduction in exercise capacity when animals were exposed to cigarette smoke while exercising. Summers and co-workers (1971) noted that cigarette-smoking increased the excretion of lactate by the heart in patients with severe coronary atherosclerosis. Other data show that cigarette-smoking can damage blood vessels in the heart. Auerbach and co-workers (1971) demonstrated that myocardial arterioles increased in thickness in dogs exposed chronically to cigarette smoke and in smokers who died from unrelated causes.

In summary, reports of animal studies of the effects of cigarette smoke or nicotine on the cardiovascular system confirm that cigarette smoke causes vasoconstriction of blood vessels. Apparently, cigarette smoke can directly augment the reactivity of blood vessels in the presence of such vasoconstrictors as vasopressin and angiotensin. Carbon monoxide in cigarette smoke alters endothelial function in animals, and both CO and cigarette smoke accelerate atherosclerosis in experimental models.

Cigarette smoke appears to affect the myocardium directly (Klein et al., 1983). That is a long-term effect; it is manifested by reductions in cardiac contractile performance and apparent structural anatomic changes, such as fibrosis in large animals and damage to mitochondria in small animals. In addition, cigarette-smoking can increase myocardial-infarct size in experimental animals, can lower the threshold of fibrillation in response to ventricular tachycardia in acute myocardial infarction in animals and accelerate atherosclerosis, and can result in acute vasoconstriction of coronary and other blood vessels. Those characteristics suggest that the effects of cigarette-smoking in the submarine environment deserve more attention; long-term effects, such as carcinoma of the lung and increased incidence of atherosclerosis, are clearly not the only major health factors associated with cigarette-smoking in this enclosed environment. The fact that cigarette-smoking alters exercise performance, can produce



ischemia in patients with coronary arterial disease, and is known to affect pulmonary function indicates that smokers are likely to perform suboptimally, especially when strenuous physical activity is required.

### Neurobehavioral Effects

A short-term decrement in performance of a critical task by a person exposed to tobacco smoke can have immediate effects on many other persons. Such immediate effects could produce consequences as important as chronic health effects. Effects of environmental tobacco smoke on neural and behavioral variables have not been studied, except for sensory measures, such as odor and irritation. An important body of literature does, however, exist on neurobehavioral effects of smoking in smokers themselves (Thornton, 1978; Emley and Hutchinson, 1984; Wesnes and Warburton, 1983b; Henningfield, 1984). Effects of tobacco-smoking on military task performance were recently reviewed extensively by Dyer (1986). Others have also reviewed the neurobehavioral effects of tobacco-smoking. This section reviews the effects of mainstream smoke and attempts to generalize them to the effects of environmental tobacco smoke at up to 6 ATA.

### Mainstream Smoke

Of the approximately 3,800 compounds identified in tobacco smoke (National Research Council, 1986a), few are present in sufficient quantities to rank as important contributors to acute neurobehavioral effects. The two outstanding exceptions are CO and nicotine.

Motor tremor appears to increase with increased tobacco-smoking. Hull (1924) reported increased tremor, heart rate, and blood pressure after pipe-smoking. Habitual smokers showed greater effects than nonsmokers. Similar results were reported by others (Edwards, 1948; Frankenhaeser and Myrsten, 1968; Frankenhaeser et al., 1970; Smith et al., 1977; Lippold et al., 1980; Shiffman et al., 1983; Heimstra et al., 1967).

Simple reaction time is reportedly decreased by smoking in persons habituated to cigarette-smoking (Heimstra et al., 1967; Smith et al., 1977; Wesnes and Warburton, 1983a, 1984). Comparison of habituated smokers with nonsmokers (Heimstra et al., 1967) indicated that

smokers had the shortest reaction time while smoking, nonsmoking habituated smokers the longest reaction time, and nonsmokers reaction time between them. Cotten et al. (1971) studied habituated smokers and reported that the decrease in reaction time after smoking was only temporary and was followed by a "rebound" during which reaction-times were longer than normal. Thus, the improved performance in reaction-time tasks after smoking in habituated smokers is temporary and comes at the price of a later decrement when there is no smoking, as during diving.

In persons habituated to cigarette-smoking, smoking appears to improve performance of tasks that involve vigilance (Hull, 1924; Tarriere and Hartemann, 1964; Heimstra et al., 1967; Frankenhaeser et al., 1971; Myrsten et al., 1972; Wesnes and Warburton, 1983b; Wesnes et al., 1983; Tong et al., 1980; Williams, 1980). In general, the vigilance performance of habituated smokers while smoking declined least as a function of time, that of habituated smokers not permitted to smoke declined most, and that of nonsmokers (when included) declined to a degree between those. Again, it is noteworthy that the nonsmoking habituated smoker is worse in vigilance performance than the nonsmoker in the same circumstances. Thus, for habituated smokers, the improvement in vigilance and reaction time is temporary and comes at a cost in performance during times when smoking is not going on.

### Combined Effects of Mainstream Smoke and Other Substances

The combined effects of smoking and exposure to other substances on neurobehavioral variables are only rarely reported. Smith et al. (1977) studied effects of smoking and caffeine administration in habitual smokers. Effects of smoking and ethanol administration on vigilance in habitual smokers were studied by Tong et al. (1980). They studied the effects of smoking and ethanol on two-flash discrimination. In most instances, the results indicated additive effects in the directions expected from the drugs used. For example, the effects of a stimulant and a depressant usually nullified each other, and the effects of two stimulants were additive.

### *Neurobehavioral Effects of Environmental Tobacco Smoke from Systemic Uptake*

Limited studies are available on the neurobehavioral effects of environmental tobacco smoke, such as those related to odor or irritation. However, some informed speculation can be made about such effects from knowledge of effects of environmental tobacco smoke and observations of body burdens of some smoking products in nonsmokers. Such findings may be compared with those in active smokers, and the effects of mainstream smoke may be extended (with caution) to possible (or likely) effects of exposure to environmental tobacco smoke.

Exposure to environmental tobacco smoke has been reported to produce no increase in COHb in nonsmokers (Foliant et al., 1983). It has also been reported to produce an increase comparable with that in a smoker who has just consumed one cigarette (Jarvis et al., 1983). Unless specific conditions are known or in situ measurements of COHb are made, the neurobehavioral importance of environmental tobacco smoke is difficult to estimate.

In most studies of the concentrations of nicotine and cotinine (a metabolite of nicotine) in the blood of nonsmokers exposed to environmental tobacco smoke, the values were only a few percent of those of smokers (National Research Council, 1986a). In the worst reported case (Hoffmann et al., 1984), blood nicotine contents of exposed nonsmokers were no more than 6% of those of smokers. Thus, at these concentrations, nicotine appears not to be neurobehaviorally important in nonsmokers exposed to environmental tobacco smoke.

It can be conjectured that, when environmental tobacco smoke becomes neurobehaviorally important, it is COHb that is the variable of concern for nonsmokers. This conjecture implies that some of the neurobehavioral effects of environmental tobacco smoke exposure in nonsmokers should be similar to those of CO exposure (as discussed earlier in this chapter). Also, cigarette smoke can be a potent source of irritants, such as phenols, acids, and oxides of nitrogen.

### **Summary**

An important source of particulate and volatile organic contaminants in submarine air is cigarette smoke. Cigarette-smoking adversely affects pulmonary function and exercise per-

formance; increases the risk of lung cancer, heart disease, and several other diseases; and increases motor tremor. Recent reports and extrapolations indicate potential adverse effects of cigarette smoke on nonsmokers in the same enclosed space. In nonsmokers, environmental tobacco smoke can be acutely irritating to eyes and upper airways. It also produces noxious odors. The nonsmoking habituated smoker is less vigilant and has slower reactions than a nonsmoker in the same circumstances. Obviously, a diver cannot smoke while diving.

### **TRACE CONTAMINANTS**

In addition to consideration of the effects of high pressure on breathing O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and CO, one must consider the potential toxic effect of the many trace contaminants found in submarine atmospheres. The objectives of this consideration are as follows:

- To determine which contaminants normally found on submarines might pose the greatest hazards if such atmospheres were used as breathing gases for divers at 1-6 ATA for missions lasting up to 12 h.
- To determine exposure criteria for trace contaminants at these pressures and for these durations of exposure.
- To determine whether exposure to multiple trace contaminants at high pressure might have additive or synergistic effects.

The first two objectives are addressed in this chapter; the third is the subject of Chapter 6.

### **Toxicity of Contaminants**

Careful perusal of the data on concentrations of trace contaminants (Table A-1, pp. 60-65) found in submarine atmospheres and on emergency and continuous exposure guidance levels for atmospheric contaminants (National Research Council, 1984a,b,c, 1985a,b, 1986c, 1987a) and exposure limits recommended by other agencies (Table 12) reveals that the contaminants of greatest concern are in four toxicologically functional categories: those which produce central nervous system depression; those which affect the cardiovascular system; those which produce irritation of eye, nose, throat, and respiratory system; and those which are known or suspected human

TABLE 12

Exposure Limits for Airborne Contaminants  
(Limits are in ppm Unless Otherwise Noted)

Compound	OSHA <sup>a</sup> 8-h TWA	ACGIH <sup>b</sup> 8-h TLV-TWA	Navy <sup>c</sup> 90-d Limit	DDS <sup>d</sup> TWA	NRC <sup>e</sup> 90-d CEGL	NRC <sup>f</sup> EEGLs	
						24-h	1-h
Acetaldehyde	200	100	0.01	50	--	--	--
Acetonitrile	40	40	--	10	--	--	--
Acrolein	0.1	0.1	0.1	0.025	0.01	0.01	0.05
Ammonia	50	25	25	12.5	50	100	100
Arsine	0.05	0.05	0.01	0.0125	--	0.1	1.0
Benzene <sup>g</sup>	10	10	1	0.25	--	2	50
Bromine	0.1	0.1	--	0.025	--	--	--
Butyl cellosolve	50	25	--	12.5	--	--	--
Carbon dioxide	5,000	5,000	8,000	1,250	--	--	--
Carbon disulfide	20	10	--	0.25	--	--	50
Carbon monoxide	50	50	15	12.5	20	50	400
Carbon tetrachloride	10	5	--	2.5	--	--	--
Chlorine	1(C)	1	0.1	0.25	0.1	0.5	3
Chlorobenzene	75	75	--	19	--	--	--
Chlorodiphenyl (PCB) 1 <sup>h</sup>	1 <sup>h</sup>	1 <sup>h</sup>	--	0.25 <sup>h</sup>	--	--	--
(42% chlorine)							
Chlorodiphenyl (PCB) 0.5 <sup>h</sup>	0.5 <sup>h</sup>	0.5 <sup>h</sup>	--	0.125 <sup>h</sup>	--	--	--
(54% chlorine)							
Chloroethane	1,000	1,000	--	250	--	--	--
Chloroform <sup>g</sup>	50(C)	10	--	12.5	1	30	100
Cumene	50	50	--	12.5	--	--	--
Cyclohexane	300	300	--	75	--	--	--
1,2-Dichloroethylene	200	200	--	50	--	--	--
Dimethyl formamide	10	10	--	2.5	--	--	--
Dioxane	100	25	--	25	--	--	--
Di-sec-octyl phthalate	5 <sup>h</sup>	5 <sup>h</sup>	--	1.25 <sup>h</sup>	--	--	--
Ethyl acetate	400	400	--	100	--	--	--
Ethyl benzene	100	100	--	25	--	--	--
Ethylene dichloride	50	10	--	12.5	--	--	--
Ethylene glycol	--	50(C)	--	12.5	4	20	40
FC 11	1,000	1,000(C)	5	250	100	500	1,500
FC 12	1,000	1,000	200	250	100	1,000	10,000
FC 113	1,000	1,000	--	250	100	500	1,500
FC 114	1,000	1,000	200	250	100	1,000	10,000
Formaldehyde <sup>g</sup>	3	1	0.5	0.75	--	--	--
Heptane	500	400	--	125	--	--	--
Hexane	500	50	--	125	--	--	--
Hydrazine <sup>g</sup>	1	0.1	0.25	0.25	--	0.005 <sup>i</sup>	0.12 <sup>i</sup>
Hydrogen chloride	5(C)	5(C)	1	1.25	0.5	20	20
Hydrogen fluoride	3	3(C)	0.1	0.75	--	--	--
Isopropanol	400	400	50	100	1	200	400

TABLE 12 (contd)

Compound	OSHA <sup>a</sup> 8-h TWA	ACGIH <sup>b</sup> 8-h TLV-TWA	Navy <sup>c</sup> 90-d Limit	DDS <sup>d</sup> TWA	NRC <sup>e</sup> 90-d CEGL	NRC <sup>f</sup> EEGLs	
						24-h	1-h
Methanol	200	200	10	50	--	10	200
Methyl acetate	200	200	--	50	--	--	--
Methyl bromide	20(C)	5	--	5	--	--	--
Methyl cellosolve	25	5	--	6.2	--	--	--
Methyl chloride	100	50	--	25	--	--	--
Methyl chloroform	350	350	2.5	88	--	--	--
Methylene chloride <sup>g</sup>	500	50	--	125	--	--	--
Methyl ethyl ketone	200	200	--	50	--	--	--
Methyl isobutyl ketone	100	50	--	25	--	--	--
Naphthalene	10	10	--	2.5	--	--	--
Nitrogen dioxide	5(C) <sup>j</sup>	3	0.5	0.25 <sup>j</sup>	--	0.04 <sup>i</sup>	1 <sup>i</sup>
Nonane	--	200	--	50	--	--	--
Octane	500	300	--	125	--	--	--
Ozone	0.1	0.1	0.02	0.025	0.02	0.1	1.0
Perchloroethylene	--	50	--	12.5	--	--	--
Phenol	5	5	1.25	1.25	--	--	--
Phosgene	0.1	0.1	--	0.025	0.01	0.02	0.2
Styrene	100	50	--	25	--	--	--
Sulfur dioxide	5	2	1	1.25	1	5	10
Toluene	200	100	50	50	20	100	200
1,1,2-Trichloro- ethane	10	10	--	2.5	--	--	--
Trichloroethylene	100	50	25	25	--	--	--
Trimethyl benzene	--	25	--	6.25	--	--	--
Vinyl chloride <sup>g</sup>	5	5	1	1.25	--	--	--
Vinylidene chloride	10	5	2	2.5	0.15	10	--
Xylene	100	100	50	25	50	100	200

<sup>a</sup>Occupational Safety and Health Administration (OSHA) 8-h TWA. C = ceiling. Many of the TWAs were proposed in 1968 and have not been revised.

<sup>b</sup>American Conference of Governmental Industrial Hygienists (ACGIH) (1986) recommended Threshold Limit Values-Time Weighted Average (TLV-TWA) for 8-h workday. C = ceiling.

<sup>c</sup>Navy 90-d limits (U.S. Naval Sea System Command 1979).

<sup>d</sup>Dry Deck Shelter recommendations (U.S. Naval Sea Systems Command, 1986) for exposure limits for diver's air based on dividing OSHA TWA by 4.

<sup>e</sup>National Research Council's recommended 90-d continuous exposure guidance levels (CEGLs) (National Research Council, 1984a,b,c, 1985a,b, 1986c, 1987a).

<sup>f</sup>National Research Council's recommendations for 1-h and 24-h emergency exposure guidance levels (EEGLs) (National Research Council, 1984a,b,c, 1985a,b, 1986c, 1987a).

<sup>g</sup>Carcinogen or suspected carcinogen.

<sup>h</sup>Concentrations in mg/m<sup>3</sup>.

<sup>i</sup>Short-Term Public Emergency Guidance Levels (SPEGLs) (National Research Council, 1985a,b).

<sup>j</sup>NIOSH has a 1 ppm ceiling (15 min) for nitrogen dioxide. This is the limit listed in the U.S. Navy Interim Air Purity Guidelines for Dry Deck Shelter (DDS) Operations and is the basis for the 0.25 ppm limit for the DDS (U.S. Naval Sea Systems Command, 1986).



carcinogens. CNS depressant activity can result from overexposure to alcohols, straight-chain hydrocarbons, aromatic hydrocarbons, and halogenated hydrocarbons. Cardiovascular effects are due primarily to the halocarbons, nicotine, and CO. Irritants in submarine air include ammonia, ethanolamine, aldehydes, acrolein from cooking, and the acid gases, such as HCl, HF, HBr, the nascent halogens, and NO<sub>2</sub> from catalytic burners. The carcinogens or suspected carcinogens that have been detected in submarine air are benzene, chloroform, hydrazine, and vinyl chloride.

### Central Nervous System Effects

Of the various CNS depressants found in operational submarines under normal conditions--i.e., without spills--the halogenated hydrocarbons appear to reach the highest airborne concentrations. Those compounds are used primarily as refrigerants and solvents or are contaminants released from paints and coatings. Pharmacologically important exposure of humans to the compounds, whether by design or by accident, is usually by inhalation, inasmuch as most have relatively high vapor pressures. The halogenated hydrocarbons, especially the haloalkanes, readily diffuse through cell membranes, because of their lipid solubility. Availability to the alveolar membrane, coupled with lipid solubility, results in the potential for substantial pulmonary absorption. In general, the haloalkanes are not pulmonary irritants, and acute exposure to relatively low concentrations is not an unpleasant experience, nor does prolonged exposure result in pathologic changes in the respiratory tract or lungs (Back and Van Stee, 1977). Acute exposure to the compounds is not considered to be very toxic, in that the LC<sub>50</sub>s are calculated in percent concentrations and not in parts per million (Back and Van Stee, 1977). For instance, rats, guinea pigs, dogs, and cats can be exposed to 60% trifluorobromomethane for 70 h without observable effects, and the reported LC<sub>50</sub> for chlorobromomethane is about 2.9% (29,000 ppm) in mice (Back and Van Stee, 1977).

The pharmacodynamic effects of those compounds are in part associated with their lipid solubility. Their solvent power ranges from poor (the highly fluorinated compounds) to fairly good (those containing less fluorine). Halogenated hydrocarbons are typical nonpolar liquids and, as such, are good solvents for other

nonpolar materials and poor solvents for highly polar materials. Generally, the better solvents are also the more lipid-soluble.

The most important toxic effects of the haloalkanes are on the CNS and the cardiovascular system (Van Stee, 1974). The neurologic effects are manifested as alterations of perception, increased reaction time, and impaired ability to concentrate on complex intellectual tasks. At greater exposures, more obvious end points might be drowsiness, drunkenness, and anesthesia, depending on the compound. As with most compounds producing CNS effects closely allied to anesthesia, lipid solubility is important. The relative solubilities of three halogenated hydrocarbons have been studied with respect to accumulation in brain tissue of animal models and extent of CNS depression. The relative lipid solubilities of the compounds are  $\text{CBrF}_3 < \text{CBrClF}_2 < \text{CH}_2\text{ClBr}$ , and their relative biologic activities are 30:6:1. That is, the concentration of  $\text{CBrF}_3$  that can be tolerated is about 5 times that of  $\text{CBrClF}_2$ , the concentration of  $\text{CBrClF}_2$  that can be tolerated is about 6 times that of  $\text{CH}_2\text{ClBr}$ , and the concentration of  $\text{CBrF}_3$  that can be tolerated is about 30 times that of  $\text{CH}_2\text{ClBr}$  (Van Stee, 1974).

Clinically important CNS effects almost always appear in response to smaller exposures than clinically important cardiovascular effects. That relationship to dose has been found in both animals and humans for a number of the haloalkanes. For instance, men exposed to  $\text{CBrF}_3$  at 5% for 25 min showed no performance decrement, whereas those exposed at 7-12% evinced drowsiness, decreases in judgment, disturbances in equilibrium, and failure to perform neuromuscular skills without cardiovascular effects. Electrocardiographic changes--such as flattening of the T wave, premature ventricular beats, and tachycardia--with decreased blood pressure were elicited at concentrations of 15% (Hine et al., 1968).

Many volatile organic compounds, especially solvents, can depress the central nervous system and decrease performance. These substances might interact with cold and N<sub>2</sub> narcosis to decrease performance.

### Cardiovascular Effects

The cardiovascular effects of halogenated hydrocarbons are manifested as changes in cardiovascular dynamics and electric activity of the heart. Typically, these can include a decrease



in blood pressure via reductions in total peripheral resistance as a consequence of autonomic ganglionic blockade, and cardiac arrhythmias with concurrent negative inotropism (Back and Van Stee, 1977).

In the mid-1970s, a body of literature suggested that sudden death could be related to fluorocarbon-containing aerosols (Frank, 1975; Aviado, 1975; Aviado and Belej, 1975). Studies on the effects of fluorocarbons on the cardiac conduction system (Grabowski and Payne, 1983) suggested that those agents might have direct effects on cardiac conduction tissue. Cardiotoxic effects of  $\text{CBrF}_3$  (FC-1301) have recently been reviewed (National Research Council, 1984c), and some deaths after shipboard exposure to halocarbons have been reported (Clark et al., 1985). Lessard and Paulet (1985) described alterations in cardiac membrane activity in the presence of  $\text{CF}_2\text{Cl}_2$  (FC-12). These reports support the clinical observations of a decade earlier that  $\text{CF}_2\text{Cl}_2$  and other fluorocarbons can stimulate cardiac arrhythmias. Halocarbons have been shown to increase the frequency of cardiac arrhythmias in the presence of excess catecholamines (Fogel, 1976; Carlson and White, 1983; Steadman et al., 1984). Although studies in this field are controversial, it is generally accepted that the combination of adrenergic stimulation of the myocardium and halocarbon exposure increases the incidence of cardiac arrhythmias. Adrenergic stimulation is not required, however, for the production of cardiac arrhythmias. Indeed, blood pressure, blood pH, and carotid sinus reflexes can influence arrhythmogenic activity (Back and Van Stee, 1977). Carlson and White (1983) demonstrated that aromatic hydrocarbons also can be arrhythmogenic. Steadman et al. (1984) reported deaths of several adolescents who inhaled fluorocarbons from fire extinguishers.

Halogenated alkanes, such as fluorocarbons, have been shown to sensitize the heart to the arrhythmogenic effect of endogenous epinephrine. During cold stress, a generalized increase in sympathetic tone results from epinephrine release. Moreover, moderate to heavy exercise causes large increases in catecholamine release. Thus, a heavily working, mildly hypothermic diver might be especially susceptible to the cardiac effects of fluorocarbons in his breathing medium.

## Irritation

The submarine atmosphere can contain irritants that affect the mucous membranes of the eye, nose, mouth, and respiratory tract. Possible irritants include ammonia, ethanalamine, acrolein, carbon disulfide, hydrazines, ozone, phosgene,  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{HCl}$ ,  $\text{HF}$ , and  $\text{HBr}$ .

For the most part, irritant gases--such as acrolein, formaldehyde,  $\text{HF}$ ,  $\text{HBr}$ ,  $\text{HCl}$ ,  $\text{NO}_2$ , and ammonia--have not been found in submarines, in greater than trace amounts. Ozone has been found at 3-50 ppb, and hydrazine at 0.5 ppm (Table A-1, pp. 60-65). The acute effects of irritants depend in part on the dose delivered to various parts of the respiratory tract. Reactive gases with high water solubility--such as  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HF}$ , and formaldehyde--are largely absorbed as soon as they enter the respiratory tract, mainly in the nose. Reactive gases of lower water solubility, such as  $\text{NO}_2$  and ozone, penetrate deeper into the respiratory tract and, at high concentrations, cause pulmonary edema. Some gases--such as  $\text{SO}_2$ , ammonia, and formaldehyde--are known sensory irritants and cause an intense burning sensation in the nose and upper airways that leads to a reduction in respiration rate. Sulfur dioxide and ammonia also cause bronchoconstriction. Some pulmonary irritants, such as  $\text{NO}_2$  and ozone, result in a sensation of dyspnea or breathlessness, rather than pain, and cause an increase in respiration rate.

Lowry and Schuman (1956) and Grayson (1956) reported that  $\text{NO}_2$ -induced pneumonia in silage workers resulted from inhalation of silage gas, which contains a high concentration of  $\text{NO}_2$ . Bronchiolitis fibrosa obliterations was a sequelae. The exposure concentrations that caused this condition were much higher than the contaminant concentrations that might occur on a submarine. More relevant to low concentrations of  $\text{NO}_2$  and ozone is the finding that these gases can reduce resistance to infection. Lowering of mouse resistance to bacteria has been observed at exposure to  $\text{NO}_2$  as low as 0.5 ppm for 6 months for 6 h/d (Ehrlich and Henry, 1968) and to ozone at as low as 0.08 ppm for 3 h (Miller et al., 1978). Speizer et al. (1980) reported a greater incidence of respiratory illness before age 2 in children in homes with gas stoves (and peak concentration of  $\text{NO}_2$  of 0.5 ppm) than in children in homes with electric stoves (and lower  $\text{NO}_2$  concentration). Frampton et al. (1987) and Kulle et al. (1987) reported reduced resistance to viral infections in humans exposed

to  $\text{NO}_2$  at 0.6 ppm for 3.5 h (Frampton et al., 1987) or at 1-2 ppm for 2 h/d for 3 d (Kulle et al., 1987).

### Carcinogenesis

Some compounds that are known or suspected human carcinogens have been detected in submarine air. They include benzene, chloroform, vinyl chloride, and hydrazine. The National Research Council Committee on Toxicology does not recommend 90-d exposure guidance levels for carcinogens, and such compounds should be removed from submarine air to the greatest extent possible with charcoal filters or the best technique available. Removal is necessary for both divers and personnel on the submarine.

### Effects of Particles

Two types of aerosols make up the majority of the particles found in submarine air: oil mist or smoke from the engines and particulate material from smoking tobacco (Rossier, 1984). In the early 1960s, aerosol concentrations were often as high as  $500 \mu\text{g}/\text{m}^3$ . Since then, the addition of more electrostatic precipitators has lowered shipboard aerosols to  $150\text{--}200 \mu\text{g}/\text{m}^3$  (General Dynamics 1972). Approximately half the aerosol particles have been reported to have aerodynamic diameters less than  $0.4 \mu\text{m}$  in the engine room and approximately 70% of the particles less than  $0.4 \mu\text{m}$  in the forward compartment. In a recent sea trial of a Trident nuclear submarine, aerosol concentrations were approximately  $100\text{--}200 \mu\text{g}/\text{m}^3$ , except for spaces where electronic equipment was kept, where concentrations of  $20\text{--}40 \mu\text{g}/\text{m}^3$  were maintained with high-efficiency particle-absorbing (HEPA) filters (Rossier, 1984).

The presence of particles in submarine air that is to be compressed for use by divers poses several potential problems. Particles in the air would be concentrated under hyperbaric conditions to the same extent as gases, because the volume in which the particles are suspended would be decreased in proportion to the increase in pressure. At the high pressures used to compress submarine air for storage, physicochemical interactions of particles with vapors and gases might result in the association of slowly desorbed toxicants with the particles. Information on the extent to which that occurs

is not available. The effect of dense gases on the deposition of inhaled particles is also unknown. Increased pressure would change submicrometer particle behavior through the corresponding decrease in the mobility of these particles. The lower mobility might decrease respiratory tract deposition that is due to Brownian diffusion mechanisms. Changes in breathing patterns due to breathing of dense gases could also alter the pattern of deposition. The solution to any anticipated problems with particle-contaminated air is to filter the air before use. It would be best to filter particles out of the air breathed by divers, both for health reasons and to prevent fouling of breathing equipment.

### EFFECT OF HIGH PRESSURE ON TOXICITY OF CONTAMINANTS

Given the same absolute concentration, will the toxic or pharmacologic effects of a contaminant be the same at 6 ATA as at 1 ATA?

It is important to distinguish between relative or fractional units, parts per million and percent, and absolute units, such as partial pressures and milligrams per cubic meter. Values expressed as parts per million or percent are relative to the total number of moles of gas in a given volume and are independent of pressure. A value given as partial pressure or milligrams per cubic meter indicates the absolute amount of a gas in a given volume and is directly proportional to the total pressure of the system. For toxicity concerns, the absolute units (i.e., the partial pressures of the volatile organic compounds or the concentrations of particles) are of interest. On the basis of the physical laws governing the characteristics of ideal gases, one would expect an increase in the toxicity of a compound proportional to an increase in its partial pressure. At pressures up to 6 ATA, one would not expect deviations from the ideal-gas laws (Smith, 1959). An increase in pressure will cause an equivalent increase in the partial pressure of each gas in the atmosphere (in accordance with Dalton's law) and, within limits, one would expect the dose-response relationship to vary linearly with partial pressures. The question is whether a compound at a given absolute concentration (partial pressure) would be more toxic at a higher pressure than it is at 1 ATA, especially if an exposed person is working under stressful conditions of low temperature and increased exercise.

Very little research has been done on the effect of high environmental pressure on the uptake, disposition, and toxic effects of inhaled gases. Rose et al. (1970) reported that the  $LC_{50}$ s of CO in guinea pigs, rats, and mice were not changed by high pressures (25, 50, 75, and 100 psig), as long as  $PO_2$  remained normal; i.e., CO exposures were at 2.7, 4.4, 6.1, and 7.8 ATA, and  $PO_2$  was held at about 158 mm Hg.

Carter et al. (1970) studied the effects of  $CBrF_3$  on operant behavior of monkeys at normal pressure. Monkeys exposed to  $CBrF_3$  at 20–25% had significant decrements in operant behavior with no visible signs of CNS depression. Higher concentrations produced complete loss of function with catatonic states. In addition, Van Stee and Back (1969) recorded spontaneous cardiac arrhythmias when dogs and monkeys were exposed to  $CBrF_3$  at concentrations of 40% or more at 14.7 psia.

Greenbaum et al. (1972) exposed cats to 5%  $CBrF_3$  at a simulated depth of 165 ft (6 ATA) and showed the same cardiovascular effects, namely, hypotension and altered cardiac rhythmicity. At 6 ATA, 5%  $CBrF_3$  has a partial pressure of 228 mm Hg or 30%, which is 5% more than that used by Carter et al. (1970) to show performance decrement.

The results are compatible and lend credence to the idea that the partial pressure of the gas, rather than the overall environmental pressure, is the important characteristic to relate to untoward effects.

Some studies have been conducted at low pressures. McNerney and MacEwen (1965) reported similar toxic effects of exposure to carbon tetrachloride at the same absolute concentration inhaled at ambient pressure or reduced pressure (258 mm Hg). The study was done in mice, rats, dogs, and monkeys, and serum enzymes were used to monitor liver damage. Similar studies in the same species exposed to ozone or  $NO_2$  at ambient or reduced pressure (but with the toxic gases at constant absolute concentration) produced no evidence of an effect of pressure on the toxicity of the gases (MacEwen et al., 1967; MacEwen and Geckler, 1968). Rats exposed to  $CBrF_3$  at constant absolute concentration at reduced pressures indicated no effect of the pressure changes on the toxicity of the compound (Call, 1972, 1973). Reduction in pressure was not found to alter the toxicity of methylisobutylketone (MacKenzie, 1971). Similarly, ozone,  $NO_2$ , and methylisobutylketone have shown the same degree of toxicity at low pressure, as long as the

partial pressure of the compound remained equivalent (Small and Friess, 1975).

As long as the  $PO_2$  does not exceed 380 mm Hg, there is little chance of marked pathologic effect that has been shown many times at low, normal, and high pressures.

Research on the effect of high and low pressures on the action of pharmaceuticals is of interest, because it can provide information on potential interactive effects of pressure and exogenous chemicals. Such studies were included in the review by Small and Friess (1975), who concluded that, although there were some inconsistent reports, pressure seemed to have little effect on the action of the drugs examined. The small amount of information on the action of gases in hyperbaric environments suggests that toxicity of gases is not changed by increases in ambient pressure. The data indicate that the partial pressure of the gas, rather than the total environmental pressure, is the important characteristic in determining effects.

Additional research is needed to determine the effect of high pressure on the toxicity of inhaled organic compounds. Not all compounds can be studied under all conditions. Recent advances in physiologic modeling allow extrapolations between compounds and between species to elucidate the disposition and fate of inhaled gases (Fiserova-Bergerova et al., 1980, 1984; Andersen, 1981; Fiserova-Bergerova, 1983, 1985; Clewell and Andersen, 1987). A model developed for one compound in one species can be adjusted for the physiologic characteristics appropriate for another compound in another species. Such quantities as body weight, alveolar ventilation, blood flow rates, tissue volumes, blood-air partition coefficients, tissue-blood partition coefficients, maximal reaction rate ( $V_{max}$ ), and the Michaelis constant (substrate concentration at half the maximal reaction rate) can be used to scale from one compound or species to another (Ramsey and Andersen, 1984). That approach should be useful in the research required to estimate the effect of high pressure on the toxicity of inhaled volatile submarine air contaminants.

## SETTING LIMITS OF EXPOSURE

The manual *Interim Air Purity Guidelines for Dry Deck Shelter Operations* (U.S. Naval Sea Systems Command, 1986) bases acceptable limits for gaseous contaminants in submarine air compressed for use as diver's breathing air on



the 8-h time-weighted average (TWA) established by the Occupational Safety and Health Administration (OSHA). At greater than 1 ATA, the applicable limit for a contaminant is the OSHA limit divided by the pressure in atmospheres absolute. That is based on the idea that the toxicity of the compound increases in direct proportion to its partial pressure. It remains to be determined whether that approach is valid.

There is little information on the effect of high pressure on the toxicity of airborne gases and aerosols. Results of the research that has been done indicate no effect of pressure up to 6 ATA on the toxic properties of gases. There is no information on the effect of breathing dense gases on the deposition and potential toxicity of aerosols inhaled as contaminants. Therefore, the conceptual approach described in *Interim Air Purity Guidelines for Dry Deck Shelter Operations* appears to be acceptable for pressures of 1-6 ATA. An additional question is what guideline should be used for the air pollutants at 1 ATA.

Several sets of guidelines are available on permissible concentrations of air pollutants (Table 12). One is the OSHA set of legal standards or limits, which are 8-h TWAs designed to regulate atmospheres in occupational settings where the workday is 8 h. The Navy is using these standards divided by 4 (on the basis of the assumed pressure of 4 ATA for divers) to set the limits for the Dry Deck Shelter (U. S. Naval Sea Systems Command, 1986). Most of the OSHA TWAs have not been reviewed for many years. Another set of guidelines is published by the American Conference of Governmental

Industrial Hygienists (ACGIH) (1987) and consists of voluntary guidelines, including 8-h TWAs similar to those of OSHA. The ACGIH values are reviewed more often than the OSHA rules. A third set of guidelines consists of the emergency and continuous exposure guidance levels (EEGLs and CEGs) recommended by the Committee on Toxicology of the National Research Council (1984a,b,c, 1985a,b, 1986c, 1987a). The CEGs are designed for situations in which personnel will be continuously exposed to an atmosphere for 90 d. The EEGLs are for situations in which personnel will be exposed rarely and for only a short period (1 h up to 24 h) and must be able to continue their work during the exposure. EEGLs and CEGs have been developed for only a relatively few compounds.

The 8-h TWA values designed for occupational settings appear to be the most appropriate for divers because divers work for several hours at a time and do so repeatedly. Where OSHA or ACGIH standards have not been reviewed within the past 15 years, they should be carefully evaluated before their incorporation. The most recent (usually more conservative) value of the OSHA and ACGIH guidelines should be used as the basis for calculations for the DDS air, from which diver's air will come.

Although the use of TWAs is appropriate, it should be noted that submarine air is already regulated by the Navy 90-d limits (Table 12). That should further reduce problems of toxicity to divers breathing the air at 6 ATA, in that the 90-d limits are no more than one-fourth the TWA limits set by OSHA and recommended by ACGIH.

## CHAPTER 6

# INTERACTIONS OF SUBMARINE AIR CONTAMINANTS AT UP TO 6 ATA

Concepts of interactions are central to the understanding of toxicology. A toxic response is usually considered to be the result of an interaction between a target and an exogenous chemical or toxic agent. This interaction presumably results in an alteration (or toxic effect) in the target and often is accompanied by an alteration in the toxic chemical itself. Such a toxic effect is assumed to be related to the dose at the site of action. The biologically effective dose usually is not known, but is assumed to be related to the amount to which the organism is exposed (National Research Council, 1987b,c, 1988). Exposure commonly can be measured, or at least approximated; the dose at the site of action is commonly not known. The more knowledge that is available on absorption, solubility, transport mechanisms, etc., the more accurate and reliable are the estimates of dose at the site of action.

### TYPES OF INTERACTIONS

Two circumstances are required for a toxic episode to occur: there must be an exposure, and the exposure must elicit some effect. An exposure that results in a dose that does not elicit an effect is considered to be below the threshold for the effect in question, and an effect in the absence of an exposure might not be a toxic response at all. Toxicologic interactions can occur in two forms: the quantity of an active form of a chemical available for interac-

tion at the target can be altered by the presence (or past presence) of another chemical, or the reactivity of the target with the toxicant can be altered.

Exposures to submarine atmospheres, either normobaric or hyperbaric, are actually exposures to mixtures of chemicals. Problems and uncertainties associated with exposures to mixtures are not new (Fairchild, 1983; Murphy, 1980, 1983; National Research Council, 1980, 1988; WHO, 1981). A toxicologic interaction is usually considered to be a condition in which exposure to two or more chemicals results in a biologic response qualitatively or quantitatively different from what would be predicted for exposure to a single chemical (Murphy, 1980). For the purposes of predicting the potential sequelae of exposing divers to compressed air from a nuclear submarine's air banks, it is necessary to expand any definition of potential sources of interaction to include consideration of the stress of physical activity and physiologic adaptation, as well as the effects of exposure to an abnormal environment. The potential for interactions involving pressure, the total gaseous environment, and a toxic agent has been recognized (Doull, 1980).

### CHEMICAL INTERACTIONS

Interactions among chemicals can occur in the exposure environment itself. Interactions can also occur between the airborne materials



and the container through which they are circulated and in which they are compressed. The environment of a nuclear submarine is dynamic, and the identity and concentrations of contaminants are changing constantly. Contaminants can interact with components of and contaminants in atmosphere purification systems that are not working at optimal efficiency, thereby creating new and different contaminants. For example, 1,1-dichloroethylene (vinylidene chloride) can be generated from methyl chloroform that was originally leached from adhesives; fluorocarbon refrigerants can decompose to hydrogen chloride and hydrogen fluoride (Davies, 1975); and the degreasing agent trichloroethylene can generate dichloroacetylene (Saunders, 1967; Siegel et al., 1971).

### INTERACTIONS WITH THE ORGANISM

Various pathologic and physiologic states can affect the metabolism (and therefore the effect) of drugs and other exogenous chemicals (Kato, 1977). If several contaminants are present at the same time and the effect of each is determined by the amount (dose) that reaches the target, the usual concepts of toxic-chemical interaction--such as synergism, antagonism, and potentiation--can be assumed to apply. Such interactions can occur at sites of absorption, sites of elimination, sites of biotransformation, and sites of storage, as well as at sites of action, or targets (National Research Council, 1980). The interpretations of those interactions usually imply some knowledge of the mechanisms of the effects of the toxicants and an ability to measure the effects.

### INTERACTIONS WITH THE ENVIRONMENT

The effects of the environment itself on an organism exposed to a toxic chemical must be considered. Divers work in environments that are usually not addressed in the science of toxicology. In an ordinary occupational or community setting, the environment in which an exposure occurs is usually considered to be constant. In the case of diving, an abnormal or nonconstant environment and the effects of that environment on the persons exposed cannot be overlooked, because it is known that the environment can exert substantial effects on biologic responses to toxic chemicals (Doull, 1972;

Fouts, 1976; Hayes, 1975; Sanvordeker and Lambert, 1974).

Many environment-induced effects are mediated through the microsomal enzyme system (Vesell et al., 1976; National Research Council, 1980), although changes in absorption, diffusion, quantity and rate of tissue distribution (Fuller et al., 1972; Setnikar and Temelcou, 1962), and effect on endogenous catecholamines (Muller and Vernikos-Danellis, 1970) can be important independently, as well as for their effects on metabolism. Thus, alterations in the dose delivered to a site of action and in the sensitivity (or threshold) of the target can come about as a result of interactions between environmental stressors and an organism exposed to those stressors in combination with toxic chemicals.

Most experimental knowledge of the effects (and mechanisms of effects) of chemicals has been gathered from organisms exposed in a "normal" physical environment. In fact, in most animal experimentation, the investigator goes to a great deal of trouble to keep the temperature, lighting cycle, humidity, and many other physical characteristics constant (Lang and Vesell, 1976; Vesell et al., 1976), so that they will not complicate the experiment being done. Because many observable toxic effects are either biochemical or physiologic, environmental stressors that also affect those biochemical or physiologic processes must be considered for their contribution to interactions between chemicals and organism.

### MIXED STRESSES

Divers breathing an air mixture might be exposed to several stresses at the same time. For example, the exposure will be under hyperbaric conditions. There is some information on the effects of exposure of experimental animals to inhaled toxicants, such as CO (Rose et al., 1970), and drugs (Small and Friess, 1975) at increased atmospheric pressure. The results suggest that there is some continuity in the case of exposure to a gas when the gas is considered in terms of its partial pressure. The toxic effects must be interpreted in the light of the physiologic state of the animal when it is at a pressure of several atmospheres.

The physical environmental factors that are most likely to result in interactions that should be considered for divers are temperature (Burn, 1961; Cremer and Bligh, 1969; Fuller et al.,

1972; Keplinger et al., 1959; Muller and Vernikos-Danellis, 1970; Nomiya et al., 1980; Setnikar and Temelcou, 1962; Weihe, 1973) and pressure (Rose et al., 1970; Small and Friess, 1975). More information is available on the effect of temperature on toxic response than on the effect of pressure. There is virtually no information on the effect of combination of temperature and pressure on toxicity, the combination that divers are most likely to be exposed to.

The diving environment also exposes subjects to cold and the attendant alterations in physiologic status. Thus, the potential for interactions between toxic chemicals and targets must be interpreted in the light of the knowledge of adaptation to cold under pressure. It is unlikely that divers will be exposed for the entire duration of their submersion in a constant state of physical activity. For example, there will probably be periods of inactivity interspersed with periods of extreme activity. Adaptation to cold induces two major physiologic protective mechanisms--increased metabolism and marked peripheral vasoconstriction (Horvath, 1981), both of those can affect the vascular transport and hepatic metabolism of exogenous chemicals.

Exposure to cold has an effect on the secretion of endogenous catecholamines (WHO, 1981). Some of the low-molecular-weight chlorinated hydrocarbons affect the myocardium and can result in fatal arrhythmia (Aviado, 1978; Balazs et al., 1986; Cornish, 1980). Some have been implicated in reducing heart rate, contractility, and conduction and are thought to act by sensitizing the heart to the arrhythmogenic effect of endogenous epinephrine (Balazs et al., 1986). The combination of excess catecholamines and some halocarbons probably increases the incidence of cardiac arrhythmia, so the potential for interaction between the toxic-chemical stress and the cold stress should be looked into. Furthermore, because bursts of physiologic and physical activity are likely, it is important to know whether the adaptations to cold and physiologic effects of chemicals will interact so as to affect cardiac function. Such interactions could shift the threshold at which toxic effects of chlorinated hydrocarbons occur or change the slope of the expected dose-response curve. Any such interactions must be anticipated and interpreted in the context of the maximal physical activity that the heart must respond to. The potential for interactions with the physiologic sequelae of psychologic stress must also be considered.

The use of mathematical models is increasingly popular in toxicology. In general, models are often useful for extending experimental observations, particularly in species-to-species extrapolation needed for risk assessment. They also have utility in addressing some of the unknowns for estimating the potential for toxic interactions associated with exposure to multiple chemicals (Jenkins et al., 1977; National Research Council, 1980, 1988).

Few data are available on the descriptive toxicology or mechanisms of toxicity of many (or most) of the contaminants of submarine air banks. Derivation of experimental data from laboratory animals on the myriad responses to a mixed-stress environment is extremely difficult, expensive, and time-consuming, because of the complexity of experimental equipment and protocols. Many approaches, however, are available through the use of mathematical models of both the physiologic adaptations to the environment and the kinetic distribution of toxicants introduced into the body.

Much of the early work in deriving physiologically based toxicokinetic models of the interaction between the body and toxic chemicals was developed as part of the Navy's nuclear submarine habitability program (Andersen et al., 1980). One of the original goals of the program was the development of concepts and information that would enable realistic permissible exposure limits to be set while eliminating or minimizing the use of safety factors that are necessary when serious data gaps exist. Many physiologic models of the hyperbaric environment have been developed in the Navy's hyperbaric medicine and physiology programs. Conceptually, those models could be combined and provide much better definitions of the physiologically based criteria that must be considered as integral parts of any exposure-effect predictions.

Pharmacokinetic models accept physical constants related to the solubility of a given chemical in an aqueous medium. Because perfusion is a major parameter, the combination of solubility of an inhaled toxicant in blood with such physiologic information as organ and tissue blood flow and perfusion during adaptation to a physiologic stress can provide information on delivered dose. Models can then be manipulated to combine physiologic and toxicologic parameters and aid in predicting toxicity (National Research Council, 1987b).

Vinylidene chloride is a known contaminant of both nuclear submarines and spacecraft. The

induction of microsomal metabolism in rat liver increased the hepatic toxicity of vinylidene chloride delivered orally or intraperitoneally. That was not the case, however, when the animal was exposed to vinylidene chloride by inhalation. The use of a physiologically based toxicokinetic model indicated that the increase in hepatotoxicity depended on both microsomal induction and the delivery of sufficient vinylidene chloride to the liver. The model showed that, in the case of inhalation, delivery of vinylidene chloride to the liver by the systemic circulation was a rate-limiting step, because of the solubility of vinylidene chloride; metabolism was therefore "saturable" (Andersen et al., 1979a,b).

Models based on hyperbaric, thermal, and exercise (work) physiology, which consider organ blood flow and perfusion, could be combined with the toxicokinetic models to estimate the probability of altered organ perfusion in response to delivery of toxic substances to a particular organ. That sort of operation, coupled with the derivation of some descriptive and dose-response data in the toxicology research laboratory, could improve the prediction of the effects of exposures to toxic chemi-

cals under the mixed-stress conditions to be encountered when divers breathe air from submarine's air banks.

### STANDARD-SETTING

One of the more demanding (and useful) things that modern toxicology is being asked to assist in is quantitative risk assessment. The utility of using physiologically based pharmacokinetic models in this endeavor has been shown (Andersen et al., 1987). Much of the effort expended to date has been in attempting to quantify the risks of exposure to carcinogens, but models can be adapted and modified to address the quantitative risk of almost any untoward event. Improvement in the physiologically based kinetic models, with addition of parameters related to the physiologic adaptation to the hostile environment in which exposures are likely to take place, should be important in setting realistic standards for exposure. Standards thus set can serve the double purpose of protecting the health of service members and assisting in ensuring the reliability of military missions.

# CHAPTER 7

## CONCLUSIONS AND RECOMMENDATIONS

### TOXICITY OF AIR CONTAMINANTS AT HIGH PRESSURE

In hyperbaric as in normobaric states, the effects of air contaminants depend on their absolute concentration; i.e., under hyperbaric conditions, the toxicity of a substance increases in direct proportion to its partial pressure.

1. **Recommendation:** The proposed approach of the U.S. Navy to setting limits for contaminants in diver's air by dividing current Occupational Safety and Health Administration (OSHA) 8-h TWAs by the pressure (in atmospheres) at which the air will be breathed is reasonable. The OSHA or American Conference of Governmental Industrial Hygienists (ACGIH) exposure limits are based on moderate activity; commanders must use judgment in adjusting the exposure limits downward for increased air intake during strenuous activity (except in the case of CO--see below). The most recent limits proposed by ACGIH and OSHA should be used for the calculations.

2. **Recommendation:** Additional research is needed to determine the potential for formation of toxic products during compression of the air and the behavior of particles in dense gases, in terms of deposition in the respiratory tract and interactions with compressed gases.

3. **Recommendation:** Additional research is required to determine whether hyperbaric conditions have any unexpected effects on toxicity

of inhaled contaminants in gaseous atmospheres.

### PHYSIOLOGIC GASES

A CO<sub>2</sub> fraction (e.g., 0.8%) that is acceptable at 1 ATA may be unacceptable at 6 ATA, because the partial pressure of CO<sub>2</sub> increases with absolute pressure. CO<sub>2</sub> fractions in diver's air should be zero, but fractions up to about 0.1% are considered acceptable.

4. **Recommendation:** Air in high-pressure submarine air banks should be checked for CO<sub>2</sub> content, to ensure acceptably low values before use by divers, and if the CO<sub>2</sub> concentration is higher than 0.1%, it should be passed through an effective CO<sub>2</sub> scrubber before being used. The gas that has passed through the scrubber should be checked with a real-time monitor for CO<sub>2</sub>.

Divers based on submarines will presumably be adapted to inspired CO<sub>2</sub> at up to 0.8%. The effects of such acclimation on diving performance are not known.

5. **Recommendation:** Exercise tolerance and other aspects of diving performance should be studied at increased FICO<sub>2</sub> (fraction of CO<sub>2</sub> in inspired air). These studies should be conducted at atmospheric conditions that might reasonably be encountered in submarines and at pressures up to 6 ATA in humans already



acclimated to inspired  $\text{CO}_2$  at up to 0.8% at 1 ATA.

Human responses to higher than normal inspired  $\text{CO}_2$  fractions vary with time and are incompletely known. Thus, the physiologic states of divers acclimated to submarine atmosphere are not well known and might vary in unknown ways during the course of a cruise.

**6. Recommendation:** Responses of experimental animals and possibly humans to chronic  $\text{CO}_2$  exposure needs to be experimentally determined with inspired  $\text{CO}_2$  at up to 2% for up to 3 months.

Marked variations in total pressure and therefore partial pressure of  $\text{N}_2$  in the submarine atmosphere pose risks for divers based in submarines. Some variations on submarines occur during routine submarine operations and in accidents.

**7. Recommendation:** During diving operations, whenever possible, the pressure in the submarine should be maintained at 1 ATA, to reduce risk to divers.

### CARBON MONOXIDE

The mechanism by which CO exerts its principal toxic effects is reduction of the oxygen-carrying capacity of the blood. Because CO competes with  $\text{O}_2$  for binding sites on hemoglobin, the toxicity of CO depends on the ratio  $\text{PCO}:\text{PO}_2$  in the blood and is independent of the absolute pressure. Carbon monoxide might have a cytotoxic effect as well. Any direct cytotoxicity that is not related to the competitive binding of CO to hemoglobin can be expected to depend on PCO.

Mathematical modeling of the binding of CO to hemoglobin at different absolute pressures predicts that increased absolute pressure will increase the rate of carboxyhemoglobin (COHb) formation and elimination. For periods shorter than one time constant for COHb formation (less than approximately 8 h), the model predicts that more COHb will be formed under high pressure than at the same CO concentration under normal pressure. The maximal COHb concentration (in such models) is, however, not affected by pressure.

**8. Recommendation:** The proposed approach of the U.S. Navy to setting limits for CO in diver's air by dividing the OSHA limits by the pressure (in atmospheres) at which the air will be breathed is a reasonable and conservative approach and should be more than adequate to prevent CO toxicity.

**9. Recommendation:** Research on the rates of COHb formation and elimination under hyperbaric conditions should be performed, to test the prediction of current mathematical models that these rates will be increased by high pressures.

**10. Recommendation:** Research should be conducted on the effects of hyperbaric conditions on the relative binding of CO to hemoglobin and myoglobin at sites in the body where PCO remains high while  $\text{PO}_2$  falls (peripheral tissues, tissue capillary blood, venous blood and arterial blood, when there is venous admixture).

### CARCINOGENS

Trace amounts of substances that are known human carcinogens (such as vinyl chloride and benzene) or suspected human carcinogens (such as chloroform and hydrazine) or that are highly toxic (such as vinylidene fluoride) have been detected in submarine air. For carcinogens, there are no recommended 90-d NRC guidance levels or the recommended guidance levels are below the detection limit of the monitoring system. Therefore, carcinogenic compounds, obviously of concern for their long-term health effects, are not of immediate concern in the submarine environment, excepting where associated with other acute short-term effects.

**11. Recommendation:** The above type of compounds should be removed from submarine air to the greatest extent possible using available techniques. Potential sources of these compounds should be restricted from submarines when possible.

### SMOKING

An important source of particles and volatile organic contaminants is cigarette smoke. Residues from cigarette smoke contaminate electronic equipment and foul surfaces throughout the submarine. Cigarette-smoking adversely



affects pulmonary function and exercise performance. Environmental tobacco smoke produces irritation of eyes and upper airways; it also produces noxious odors. There is evidence that the habituated smoker who is unable to smoke is less vigilant and has slower reactions than a nonsmoker in the same circumstances. A diver who is a habituated smoker is unable to do so when diving and his performance may be impeded.

The long-term effects of cigarette smoking include increased risk of lung cancer and cardiovascular disease. Recent reports indicate adverse effects on nonsmokers exposed to environmental tobacco smoke. Although the long-term effects are not of immediate concern in the submarine environment, they cannot be ignored when considering the overall health of those who serve on submarines.

**12. Recommendation:** Cigarette-smoking is an important source of air contaminants in submarine air. The Navy should eliminate or curtail smoking on submarines.

## INTERACTIONS

In addition to hyperbaric conditions, divers are exposed to other stress factors, such as cold, darkness, and extreme exercise. Those factors might induce physiologic changes that influence the disposition and fate of inhaled contaminants.

**13. Recommendation:** Physiologic research is required to provide information on the interaction of breathing compressed gases (nitrogen, oxygen, and endogenous and exogenous carbon dioxide) in air at up to 6 ATA, cold, and extreme exercise. Such research would provide data for use in physiologically based toxicokinetic and hyperbaric models for predicting interactions between the hostile environment and toxic effects of breathing compressed submarine air.



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