INDOOR AIR QUALITY IN SUBMARINES

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ABSTRACT
The next generation of conventional submarines will be submerged for several weeks, creating a need for regenerative air purification methods and new air monitoring instruments. Submarine air is a complex mixture of compounds, where the most obvious contaminant is metabolically produced carbon dioxide. Normal eight-hour occupational exposure limits are not applicable on a submarine, instead special longtime exposure limits must be set. A number of air purification methods for submarines are either available or under development, e.g. cryogenic plants, biological plants and solid amine plants. For air monitoring compact GC/MS is an interesting option, already in use onboard nuclear submarines.

INDEX TERMS
Submarine, air purification, air monitoring, confined space

INTRODUCTION
Until recently conventional (non-nuclear) submarines operated with battery power when submerged. Every other day, the batteries had to be recharged at the surface, using diesel engines and oxygen from the air. Development of Air Independent Propulsion (AIP), using liquid oxygen in Stirling engines or fuel cells, have made it possible for conventional submarines to stay submerged for several weeks. The transition from diesel-electric propulsion to AIP has been made without thorough investigations of how the indoor air quality onboard is influenced. Onboard air is still purified with non-regenerative methods, e.g. by removing carbon dioxide with soda lime and VOCs with activated carbon filters. One drawback with non-regenerative air purification methods is the necessity to store the purification agent for the entire mission onboard, occupying valuable storage volume. To save space and make better use of available internal resources, there is a need for regenerative techniques.

Prolonged submerged periods, without proper venting, make it likely for air pollutants to accumulate over time. Therefore it is necessary to monitor compounds that were earlier unlikely to be found in volatile concentrations. Nuclear submarines have faced this problem for a long time, and it is likely that the solutions developed there can be adapted to AIP submarines.

METHOD
The purpose of the paper is to review the air monitoring solutions and regenerative air purification methods that are available or that are likely to become available in the future. This paper is based on a literature search on air quality in submarines, spacecrafts and other confined spaces. Since nuclear submarines have almost unlimited energy resources and

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conventional submarines have not, it is important to distinguish between air purification methods suitable for nuclear submarines and methods suitable for conventional submarines. We also discuss the possible impact the most recent findings in the indoor air quality field can have on submarine air quality.

AIR CONTAMINANTS IN SUBMARINE AIR

In the literature we have mainly found measurements of inorganic gases and VOCs. Measurements of aerosols, semi-volatile organic compounds, matter of microbial origin etc have not been found in the same extent, however, Morris and Fallon (1973) studied the microbial flora in the air of submarines.

The main contaminant of submarine air is CO_2. In ordinary buildings 1000 ppm is usually considered as a maximum concentration. This value is not based on health effects but on the rate of ventilation. In submarines, higher CO_2 concentrations are permitted, usually 5000-7000 ppm.

A submarine atmosphere consists of a large number of contaminants, e.g. ozone, which can be formed in electrical devices and hydrogen, which is formed when the batteries are charged (Bremer 2001). Measurements onboard submarines and space shuttles show that a submarine atmosphere is even more complex than a space shuttle atmosphere (Saalfeld and Saunders 1979). To ensure the health of the crew on short and long term, it is important to specify the permitted composition of the submarine atmosphere. Table 1 shows a submarine air specification for a conventional submarine (Loncar 1997).

Table 1. Typical submarine air specification for a conventional submarine (Loncar 1997) maximum levels

Compound	Limit	Compound	Limit
NO_2	5 ppm	NH_3	25 ppm
CO_2	5000 ppm	O_3	0.1 ppm
CO	35 ppm	H_2	2 %
SO_2	2 ppm	Cl_2	1 ppm
Formaldehyde	2 ppm	H_2O_2	1 ppm
Akrolein	0.1 ppm		

Since the crew is continuously exposed to the submarine air for several weeks, normal eight-hour occupational exposure levels are not applicable and special exposure limits must be determined. The Institute of Naval Medicine, U.K. has set Maximum Permissible Concentrations (MPC) for a number of compounds likely to be found in a submarine (Raffaelli 1988). The MPCs are set for an exposure time of 90 days. They have also set emergency MPCs for 24 h and 60 min. An important question is how MPCs should be set to take into consideration the influence of the prolonged exposure time on the crew, on a short and long basis.

AIR PURIFICATION IN SUBMARINES

In diesel-electric submarines carbon dioxide is usually purified with either soda lime or lithium hydroxide. As air is fed through a soda lime/lithium hydroxide canister, the carbon dioxide is chemically attached to the purification agent. This process is not easily reversed, making it necessary to store a full mission load onboard, occupying valuable space. Even though soda lime/lithium hydroxide is not the optimum solution for an AIP submarine, it is, because of its simplicity, still the best choice for air purification in an emergency situation. Therefore, AIP submarines will likely always be equipped with an emergency supply of soda lime/lithium hydroxide. However, for prolonged submerged periods, regenerative air purification is needed. Most desirable is a purification technique that can take care of the majority of the air pollutants in one process. A number of possible methods that are available or under development are presented below.

In a monoethanolamine (MEA) plant, CO_2 rich air is passed through a porous plate covered with liquid MEA. This creates a foam providing conditions for intimate contact between the CO_2 and the MEA. At room temperature CO_2 is chemically absorbed to the MEA, and thus removed from the air. The CO_2-rich MEA is then drawn off and regenerated. The regeneration is performed in a boiler, in which the MEA is heated under pressure, releasing the CO_2, which can be discharged overboard. MEA is currently used onboard nuclear submarines and on some diesel-electric submarines. One risk with this solution for submarine air purification is that MEA vapor may leak into the submarine atmosphere, possibly harming the crew. Heating the MEA is also a rather energy consuming process (Mazurek 1998) (Dams, Leppard and Martin 1991).

A solid amine plant operates in the same way as a MEA plant, but with solid benzyl amine attached to a polymer instead of liquid MEA. Each unit consists of two beds one operating in adsorption mode and one being regenerated at about 110°C. The heating is preferably performed with waste heat from the AIP system. At times when the AIP system is not operating, the heat can be generated with electricity from the batteries. With a solid amine plant, the risk for amine vapor in the submarine atmosphere is greatly reduced compared to a MEA plant. A solid amine plant has recently been tested on one of the Swedish Navy's AIP submarines with promising results (Östberg and Schauer 2000). Successful experiments have also been carried out at the Defence and Civil Institute of Environmental Medicine, Toronto, Canada (Eaton 2000).

A molecular sieve (grade 5A) is an industrially produced zeolite material with an extremely large internal surface. Each pore is of uniform size and is slightly larger than a CO_2 molecule. As CO_2 contaminated air is passed through the zeolite bed the CO_2 molecules are adsorbed to the bead pores. When the majority of the pores are occupied, the airflow is switched to a parallel bed, and the first bed is heated, releasing the CO_2, which can be discharged overboard. A drawback with molecular sieves is that they are energy intense in the regeneration phase. Larger contaminant molecules, e.g. freons, can also be removed by mixing a quantity of 10A grade sieve with the 5A grade (Dams, Leppard and Martin 1991).

Cryogenic air purification is a new promising method to purify air in AIP submarines carrying liquid oxygen (LOX) at approximately –180°C for their propulsion system. Here the heat sink in the LOX is utilized to cool the contaminated air to approximately -150°C, thus separating pollutants from the air stream by condensing or freezing them. Cryogenic air purification is efficient for a large number of air pollutants, e.g. CO_2, VOCs (except methane), particles, ozone, etc. It is therefore a highly attractive technique to develop further. The use of energy that is otherwise wasted is another feature making cryogenic air purification to a suitable method for the future. A European patent for a cryogenic air purification plant has been issued in France (Kussener 1994).

Biological air purification, mainly with green plants, has been used and tested in ordinary buildings (Darlington, Chan, Malloch et al 2000). However, biological air purification for use on submarines is still on an experimental stage. Biological purification uses either photosynthesis or enzymes to purify the submarine air. The photosynthesis approach, a photobioreactor, is based on marine green algae that are kept onboard the submarine (Roe 1992). The algae are fed with CO_2-rich air and a nutrient while being exposed to fluorescent light, thus converting the CO_2 to O_2 in a natural way. A possible problem with this method is to keep the algae alive. The Defence Science and Technology Organization (DSTO) in Australia has performed studies on this air purification method. It is not known if this system can also remove other air contaminants than CO_2. EnviroBio Inc and Defence R&D in Canada have developed air purification based on the enzyme carbonic anhydrase. The enzyme is working as a catalyst, catalyzing the following reaction:

$$CO_2 + H_2O \xrightarrow[\text{anhydrase}]{\text{carbonic}} HCO_3^- + H^+ \quad (1)$$

Results from laboratory tests show that the technique is promising for the future (Bernier, Fradette and Johnson 2000).

AIR MONITORING IN SUBMARINES

Continuous air monitoring in conventional submarines has historically been limited to oxygen, hydrogen and carbon dioxide. Other air contaminants have been retrospectively monitored, e.g. using adsorption tubes. The results from this kind of measurements are normally not analyzed until the submarine is back at its base. This is not acceptable for a submarine with continuous submerged operation for several weeks. In such a submarine, the crew must be able take actions against high levels of air pollutants that may impair their ability to fulfill their mission. For this purpose, compact GC/MS is a suitable technique that has been implemented on nuclear submarines (Almén and Olofsson 1999).

The U.S. Navy has developed central atmosphere monitoring systems (CAMS), for monitoring of preselected air compounds in the air. CAMS allow the crew to analyze the air throughout the entire submarine in a few minutes. CAMS also incorporate an alarm system if out-of-tolerance limits are exceeded for any of the monitored compounds. A system like this is a necessity on the next generation of conventional AIP submarines (Wyatt, Callahan and Daley 1995).

DISCUSSION

It has recently been shown that increased ventilation in a building increases productivity (Wargocki, Wyon, Sundell et al 2000) and reduces sick leave. One can speculate in that submarine air quality influence crew alertness and that low levels of pollutants is an advantage for mission fulfillment.

It has also recently been experimentally proved that gas reactions between ozone and unsaturated VOCs form strong airway irritants (Wolkoff, Clausen, Wilkins et al 2000). This calls for an expansion of the VOC window (Wolkoff and Nielsen 2000) to include and focus not only on the normally measured VOC, which may be rather harmless at low concentrations, but also on other organic compounds. In submarines it may be even more important to specifically monitor compounds that are known to react to produce irritants, e.g. ozone and unsaturated hydrocarbons.

For submarines it is inevitable that condensation forms on the inside of the uninsulated hull, especially when operating in cold waters. Consequently there will be locations of high humidity, where mold and other microorganisms may grow. It is known that substances of microbiological origin like endotoxins, glucans and mycotoxins (Thorne and Heederik 1999) can cause health problems. This may be a minor problem in cold waters, where the low submarine air temperature reduces microbiological growth. However, during operations in warmer seas, this might become a threat to mission efficiency.

Today there are a number of tools developed to help building manufacturers select low emitting materials. There are also a number of studies describing emissions from different types of materials, e.g. Saarela's (Saarela 1999) review on emissions from floor coverings. A submarine contains both common emission sources, e.g. floor coverings, paints, furniture and fittings, and materials that are not normally used in buildings, e.g. diesel oil, hydraulic oil and electrical motors. At least for common building materials one can probably decrease irritating emissions substantially by choosing materials according to the Danish Indoor Climate Labeling System (DSIC 2000) or some other similar system. However, in a submarine, other demands on the materials might interfere with the desire to select low emitting materials. As an example, a fire onboard a submarine may quickly become fatal to the entire crew and only fireproof materials are allowed.

To ensure the health of the crew in the short and long term, it is necessary to control the submarine atmosphere, but it is not a trivial problem to decide what to control and to what levels. Increased knowledge of low-dose toxicology of air borne contaminants is of fundamental importance here. When setting MPCs and deciding on submarine air specifications, it is important that the specified concentrations are possible to monitor onboard.

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