KEY DEVELOPMENTS IN SUBMARINE AIR MONITORING AND AIR PURIFICATION DURING THE PAST 20 YEARS

W. Mazurek

During the 1960s and 70s, a massive research program into submarine air monitoring and air purification (SAMAP) was undertaken by the US Navy in order to provide a habitable atmosphere in nuclear-powered submarines. That technology has endured, fundamentally unchanged for 25 years. The attained technology and air quality standards established a benchmark for both nuclear- and diesel-powered submarines. However, due to the space and power limitations much of the air purification technology was unsuitable for diesel-powered submarines which maintained WWII SAMAP technologies. To a large extent, these problems have been overcome since the first SAMAP conference in 1994. During this period, a number of innovative air monitoring and air purification technologies have been developed for both nuclear- and diesel-powered submarines. This review examines the merits and limitations of existing and emerging SAMAP technologies with respect to deployment in submarines

Occupational health requirements have spawned a plethora of dedicated electrochemical air monitors which have been deployed in submarines with various degrees of success due to long-term stability (>6 months) problems and interference from hydrogen (>0.5%). The application of infrared monitors, using tuneable laser (Quantum Cascade and Tuneable Diode Lasers) sources, have successfully overcome the monitoring of carbon monoxide in the presence of hydrogen: a problem unique to submarines and spacecraft. Other infrared instruments developed by Los Gatos Research (CA, USA) and Kayser-Threde GmbH (ANITA, Analysing Interferometer for Ambient Air) are able to measure a number of gases simultaneously at ambient air concentrations. Multiple air contaminants have also been measured in real-time using miniature gas chromatograph equipped with Ion Mobility Spectrometer (Smiths) and Differential Mobility Spectrometer (Sionex Microanalyzer).

GC-MS retrospective analysis of whole air samples is the method of choice for a comprehensive analysis of submarine air contaminants, but air analysis provides a guide for inhalation exposure while ignoring the contribution of dermal exposure. Biomonitoring of body fluids provides an indication of the total body burden and is therefore a much more important metric although rarely used. Exhaled breath and saliva analysis are two non-invasive techniques which may be used for biomonitoring.

The two most important gases requiring control are oxygen and carbon dioxide. In diesel-powered submarines oxygen is commonly generated by oxygen (perchlorate) candles or in the case of Air-Independent Propulsion, liquid is available. Carbon dioxide is generally removed by irreversible adsorption onto soda lime or lithium hydroxide. Recently, better packing of soda lime granules has led to an improvement in absorption capacity by volume and the development of self-contained relocatable units (CASPA, Molecular Products Plc) that has provided additional flexibility for carbon dioxide removal. Similarly, incorporation of lithium hydroxide particles into a porous polymer sheet has reduced the hazard of lithium hydroxide and has allowed deployment of these sheets in disabled submarine scenario without the need for mechanical ventilation.

Regenerative carbon dioxide removal is uncommon in diesel-powered submarines, including those with air-independent propulsion. However, extended dive capability (> 10 days) is best served by this technology. Monoethanolamine scrubbers have been deployed in most nuclear-powered submarines and two classes of conventional submarines. A solid mine scrubber, based on an amine resin bed, is also available and one based on porous silica bed containing a sorbed amine is being developed. Membranes have also been

developed for carbon dioxide removal in submarines. Cryogenic systems, although complex, offer the potential for the removal of carbon dioxide as well as organic contaminants from the submarine atmosphere.

Volatile organic compounds are generally removed from the submarine atmosphere through the use of activated charcoal filters. A regenerative system has been investigated as well as catalytic reactors but have not been trialled in submarines. However, the Koala system consisting of a charcoal filter and an electrostatic precipitator has been successfully deployed in Italian submarines.

Integration of new technologies into submarines is a slow process as submarine builders are very conservative. An existing system will only be replaced if it is highly unreliable, labour intensive or requires far more energy than an alternate system. Some of these new technologies have already been successfully integrated into submarines. Others have been demonstrated to be effective and practical but have not yet be deployed. Some are still in the experimental phase and will require further evaluation and modification to reach maturity.

OPERATIONAL USE OF THE AIR QUALITY MONITOR ON ISS AND POTENTIAL FOR REAL-TIME VOC MEASUREMENTS ABOARD SUBMARINES

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Abstract

The air quality monitor (AQM) began operations on the International Space Station (ISS) in March 2013 and was validated for operational use in January 2014. The AQM is a gas chromatograph-differential mobility spectrometer that currently monitors 22 target volatile organic compounds (VOC) in the ISS atmosphere. Data are collected twice per week, although data collection can be more frequent in contingency situations.

In its second year, the AQM has provided data to decision-makers on several ISS contaminant-related issues in both air and water. AQM has been used in strictly air incidents, such as a potential ammonia leak, and to investigate air contaminants affecting water recycling equipment (excess ethanol). In the latter case data from water monitors and AQM were compared to understand an issue with the water processor. Additionally, the AQM has been moved to different ISS modules to determine whether air is sufficiently mixed between modules so that a central LAB module location is representative of the entire ISS atmosphere. Historical data, from archival samples (ground lab analysis), on the ISS atmosphere in different modules suggest that the atmosphere is usually quite homogenous.

This presentation will briefly describe the technical aspects of the AQM operations and summarize the validation results. The main focus of the presentation will be to discuss the results from the AQM survey of the ISS modules and to show how the AQM data have contributed to an understanding of environmental issues that have arisen on ISS. Presentation of a potential ammonia leak (indicated by a pressure/quantity sensor alarm) incident in 2015 will illustrate the use and value of the AQM in such situations.

RESULTS OF A LONG-TERM DEMONSTRATION OF AN OPTICAL MULTI-GAS MONITOR ON ISS

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Previously at SAMAP we reported on the development of tunable diode laser spectroscopy (TDLS) based instruments for measuring small gas molecules in real time. TDLS technology has matured rapidly over the last 5 years as a result of advances in low power diode lasers as well as better detection schemes. In collaboration with two small businesses Vista Photonics, Inc. and Nanoracks LLC, NASA developed a 4 gas TDLS based monitor for an experimental demonstration of the technology on the International Space Station (ISS). Vista invented and constructed the core TDLS sensor. Nanoracks designed and built the enclosure, and certified the integrated monitor as a payload. The device, which measures oxygen, carbon dioxide, ammonia and water vapor, is called the Multi-Gas Monitor (MGM). MGM measures the 4 gases every few seconds and records a 30 second moving average of the concentrations. The relatively small unit draws only 2.5W. MGM was calibrated at NASA-Johnson Space Center in July 2013 and launched to ISS on a Soyuz vehicle in November 2013. Installation and activation of MGM occurred in February 2014, and the unit has been operating nearly continuously ever since in the Japanese Experiment Module. Data is downlinked from ISS about once per week. Oxygen and carbon dioxide data are compared with that from the central Major Constituents Analyzer. Water vapor data are compared with dew point measurements made by sensors in the Columbus module. The ammonia channel was tested by the crew using a commercial ammonia inhalant. MGM is remarkably stable to date. Results of 18 months of operation are presented and future applications including combustion product monitoring are discussed.

Real Time Monitoring of Volatile Organic Compounds in Submarine Air by Chemical Ionization Mass Spectrometry

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Volatile Organic Compounds (VOCs) have become a health concern since some of these compounds are classified as CMR (carcinogenic, mutagen and toxic for reproduction). Therefore, air quality and in particular indoor air quality in public areas (schools, nurseries, etc) or in the workplace is really challenging in today's society.

In the specific case of a submarine, indoor air quality is even more critical due to confined areas and the difficulty in replacing polluted indoor air by fresh air while the submarine is in operation. Consequently, any VOCs emissions from materials (paints, chemical products…), even at low concentration, could be a future health risk.

To date, in French submarines, indoor air is sampled with Tenax tubes and analyzed by conventional laboratory techniques (TD-GC/MS) according to the standard "Iso 16000-Part 6". One limitation of this protocol is that analysis can only be done at the end of the submarine mission when samples can be send to a laboratory. With this protocol, information about indoor air quality is not accessible in real-time. Therefore, if a problem occurs in the air purification process unit -when the submarine is in operation- no corrective action can be implemented.

As a result, there is an increasing need for field instruments to make comprehensive real-time measurements of VOCs on-site: mass spectrometry can play a key role in this area. Hence a precise mass measurement combined with a soft ionization technique provides identification and quantification of the compounds.

The solution developed by AlyXan combines Chemical Ionization (CI) with a new compact FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometer: BTrap.

The use of FTICR provides specific and significant advantages for mass detection: (i) mass measurement precision of 0.01u for identification of chemical formulas, (ii) mass resolution enabling isobaric separation, (iii) broad band detection for multicomponent monitoring.

The gas sample is directly introduced into the analyzer without any prior preparation. As the ions are trapped into the ICR cell, this technique is also very convenient for the implementation of chemical ionization. These methods are: (i) more sensitive; no reaction with the matrix, (ii) with less fragmentation enabling a better identification, (iii) quantitative without any calibration; absolute quantification. Ion-molecule reactions enable the use of a wide variety of reactant ions for the detection of numerous compounds: positive ions; Xe^+, O_2^+, NO^+, CF_3^+ or negative ions; O^-, OH^-.

Among these methods, Proton Transfer Reaction Mass Spectrometry (PTRMS), which has a proven efficiency, is widely used for VOCs analysis. For instance, Proton transfer reactions from H_3O^+ are quite fast and efficient for the detection of many organic compounds.

In BTrap devices, a direct-pulsed injection of air in the trap allows the compounds to be detected in real time (within a few seconds) from several % to ppb level with a linear response. The technique is robust and the instrument can carry out measurements over long periods: weeks or months.

AlyXan adapted a BTrap to specific submarine environment needs at the request of DGA TN: the SMHR instrument. It enables air monitoring, and specifically VOCs and CFC detection. Besides, the efficiency of the air purification process unit can be measured at various points by using a multiplexing inlet system.

REVIEW AND RATIONALISATION OF POST-FIRE MONITORING FOR ATMOSPHERE CONTROL IN SUBMARINES

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In the event of a fire in the enclosed space of a submarine a set routine for post-fire monitoring and air purification is detailed in Royal Navy (RN) documents. Currently there is a set of chemical species required to be monitored throughout all compartments of the submarine. During the fire and post-fire clean-up the crew have to remain on a secondary breathing system to sustain life, a period which may last several hours, which is uncomfortable, restricts an individual's movement and is ultimately time limited. Because of the time involved, the consequence to operations and the discomfort to the crew a full review of the process is being undertaken. This is being carried out to evaluate the likelihood of the chemicals being produced in a fire and their toxicological effects, which may indicate marker gases, to prevent the need to monitor all gases currently listed and determine if post-fire routines may be revised.

As with all high energy/hazard engineering environment the potential for a fire breaking out on a submarine is omnipresent but managed and mitigated appropriately by the MoD through existing safety management arrangements to ensure that the hazards present are reduced to a level as low as reasonably practicable (ALARP). Very few fires on submarines have been reported. The majority of fires occurring in ships and submarines have been small and have been extinguished promptly with only very minor damage.

The purpose of this paper is to analyse the toxic gases produced from fires on RN submarines and to underline the acute and chronic effects those gases have on the human body. The fire characteristics of materials used in the construction, operation and maintenance of submarines, obtained by the fire testing on materials, will be summarised. Additionally, information has been extracted from records of actual instances of fire on board submarines. The data on the amount of fire effluent (narcotic gases, irritant gases, and smoke), and the toxic effects have been summarized, including the sub lethal effects, which are important because they may reduce the effectiveness of crew performing critical tasks. From this review recommendations for the measurements of marker gases for post fire monitoring have been recommended.

Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Diesel Engine Exhausts: A Review

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous air contaminants known to be present in diesel exhaust emissions (Hoffman et al., 1963). The prevalence of diesel powered engines within the Royal Australian Navy (RAN) coupled with the well-established carcinogenicity of certain PAHs, makes it imperative to have a thorough knowledge of the PAHs present as well as parameters that can alter their concentrations.

A review was undertaken to characterise PAHs present in diesel exhaust emissions. PAHs originating from diesel engine sources typically contain elevated concentrations of methylated naphthalene and phenanthrene with enrichment of benzo[a]anthracene and benzo[a]pyrene (Claxton 2015). The ability to provide a definitive profile of PAH emissions using the available literature is difficult for one of two reasons:

1. Both the number and types of PAHs investigated often differs making accurate comparisons and conclusions difficult. There are over 100 different PAH compounds possible, with over 50 identified in diesel exhaust emissions (Zielinska et al., 1998; Xu et al., 1982).
2. A large number of parameters such as engine size, operating conditions, engine technology, maintenance status and fuel composition have all been shown to influence the number and types of PAHs present, thus complicating comparisons between various studies (Bachmann and Gong 2002; Jones et al., 2004; Maricq 2007; Nelson et al., 2008).

Changes to diesel fuel composition over the years has had a significant effect on PAH emissions and is clearly one of the main reasons why PAH exhaust emissions have reduced over the last 30 years (Martins et al., 2012). Lowering both the sulphur and aromatic content of diesel fuels have resulted in significant reductions in PAHs (Lim et al., 2005; Nelson et al., 2008). As changes in the sulphur content were often introduced at the same time as were other fuel specifications, it is often difficult to separate the effect of these reductions on engine emissions. In those cases where the parameters have been studied individually, results are often contradictory because of changes in one or more of the parameters listed above (Claxton, 2015). The use of biofuels, or biofuel blends has gained much interest in recent years, resulting in a large volume of work in this area. Unfortunately many of the results using biodiesel are often contradictory. Research using biodiesels has identified on occasions a reduction in PAH emissions while in other instances an enhancement of PAH emissions has been reported (Karavalakis et al., 2009; Ratcliff et al., 2010). The benefit if any of using biodiesel appears highly dependent upon both the amount and type of biodiesel used. In those instances where the use of biodiesel does yield benefits, this benefit may simply be due to the dilution of the sulphur and aromatic content (Karavalakis et al., 2009).

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Importance of Structural Properties in Diesel Particulate Characterisation

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Agglomerates in fine diesel particulate matter (DPM) are known to cause adverse health effects (IARC 2012). However, the greater toxicity of smaller particles has raised significant concern (Kittelson 1998). Ultrafine (< 100 nm) and nanoparticles (<50 nm) from vehicular sources, with DPM as the most important component, may be directly translocated to the central nervous system (Costa et al 2014). Findings were recently reported for decreased cognitive function in healthy children, Alzheimers disease-like pathology in autopsied young adults and canines, and ultrafine metal deposition in the brains of young canines caused by air pollutant exposures in Mexico City (Calderon-Garciduefas et al 2012). In addition, cognitive deficits (intelligence, memory) were found in children exposed to black carbon in Boston (Chiu et al 2013). Further, pre-natal exposure to polycyclic aromatic hydrocarbons was associated with detrimental brain development, decreased cognition and behaviour in later childhood (Peterson 2015). The geometrical complexity of the DPM and the link with health effects has not been well established. Further studies to examine this association between the size, morphology and composition of the DPM (Park et al 2004) and their exposure implications are warranted.

Determination of the ultrafine particle characteristics was achieved by measurements of mobility size and aerodynamic-sized mass enabling the determination of structural properties, including effective density, fractal dimension and the relationship between mobility and aerodynamic size (Park et al 2003). In previous studies of two Euro 0 turbo charged engines using low sulphur (30 ppm) F76 fuel, DPM was characterised under constant load conditions for the V18 Hedemora engine, and under variable load and idling conditions for the L6 Mercedes Benz (MB). It was found under these conditions that DPM masses of both turbo-charged engines were localised in particles of < 250 nm (Gan et al 2011a, Gan et al-2011b).The mobility size range of slightly diluted MB engine exhaust under idling conditions was 15 – 214 nm, with a peak at 51 nm. Due to non-steady state exhaust sampling conditions, mobility measurements were difficult to obtain for the Hedemora engine. Instead, the MB engine DPM mobility size was used as a surrogate. Justification was provided by mobility measurements of 9 light and heavy duty vehicles and engines, which showed a single peak in the particle size range of 16 nm to 270 nm (EC 2001).

Further, diluted exhaust from a Scania DC1102 turbo charged L6 engine operating on marine fuel with sulphur content of 500 ppm (Euro 2), showed a unimodal count median diameter of 55-65 nm at maximum engine speed, 76 nm at medium and high loads, and a bimodal distribution at 15 nm and 82 nm at low load (Ushakov et al 2013). Mobility and mass measurements of the 4-cylinder John Deere 4045 EPA Tier 2 engine using high sulphur (360 ppm) fuel and at 50% load, showed a single peak at ~110 nm in the size range 11 nm – 7000 nm (7µm), with 80% mass < 500 nm (0.5 µm). These extreme operating conditions and lognormal size distributions suggest the mobility peak for the Hedemora engine as 50 - 76 nm for efficient combustion, as high sulphur fuel increases the number concentration of nanoparticles (Abdul Khalek et al 1999).

On the basis that the Hedemora emission particle size distribution was similar to that of the MB engine, a fractal dimension of 2.66 for the Hedemora DPM indicates non-spherical but compact particles over the size range 16 nm – 214 nm, compared with 3 for a sphere. This is in agreement with 2.35 for the turbo-charged John Deere engine (Park et al 2003). The compact Hedemora DPM finding is consistent with the fuel-filled particles observed in the SEM image of DPM of 100 – 140 nm (Mazurek et al 2003) and high organic carbon (OC) content of 55 % of total carbon or TC (Gan et al 2010). Using size-dependent effective densities of DPM measured for the John Deere 4045, Yamaha EDA 3000 and Audi A4 TDI engines (Park et al 2003), peaks with closely similar mobility-adjusted masses and effective densities were used to derive dynamic shape factors for the Hedemora DPM. Resulting values of 1.2 and 1.9 for 68 nm and 191 nm particles, respectively, may be compared with the shape factor of 1 for a sphere. Thus, non-spherical 68 nm particles are very compact and fractal 191 nm particles although compact, were relatively irregular shaped agglomerates, in agreement with the shape factors of 1.3 for 50 nm and 2.0 for 220 nm DPM determined by Park et al (2004) for the John Deere engine. The Hedemora DPM shape factor differences were also consistent with the high OC content of 59 % TC in 68 nm particles and 52% TC in 191 nm agglomerates measured under idling conditions (Gan et al 2011b).

These size, shape and composition characteristics of ultrafine DPM support associations of cytotoxin and neurotoxin exposures with detrimental brain effects in humans and canines (Calderon-Garciduenas et al 2012, Calderon-Garciduenas 2014, Chiu et al 2013, Levesque et al 2011, Calderon-Garciduenas et al 2008, Peterson et al 2015). Exposure to particles of 2.5 µm for periods of greater than 9 months and that meet the US environmental standards, were found to alter brain inflammatory phenotype and promote progression of Alzheimers-like pathology in mice (Bhatt et al 2015).

Thus, as DPM exposure standards are mass based, smaller particles are more toxic, as the dose by number and surface area and efficiency of lung and brain deposition will increase as size decreases (Kittelson 1998, Oberdoster 2004). But, for the same size, more compact shaped particles (higher fractal dimension and smaller shape factors) with larger surface area and volume imply a proportionally higher dose by mass (Park et al 2004).

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Glossary

DPM : Diesel particulate matter
EPA : Environment Protection Agency
Euro 0 : European Union diesel engine emission standard for heavy duty engines tested before 1992.
MB : Mercedes Benz
OC : Organic carbon
RAN : Royal Australian Navy
SEM : Scanning Electron Microscope

BREATH computer modelling of submarine atmosphere purge regimes

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Abstract

The running of diesel generators on-board submerged submarines has always been a potentially hazardous operation. With the exhaust from an average diesel engine containing between 200 to 600 ppm of carbon monoxide (CO) any leak has the potential to increase the CO concentration in the diesel generator compartment to hazardous levels within a very short space of time. The potential hazard is not just confined to leaks from the exhaust trunking. Re-ingestion of the exhaust plume, via the Snort Induction Mast, while the diesel generators are running is a phenomenon that is known to occur under certain conditions. The severity of the problem is mainly dependent upon meteorological conditions and the heading of the submarine in relation to the prevailing wind direction. Although submarines are instructed to maintain a heading that will take the exhaust plume away from the Snort Induction Mast when running the diesels, this may not always be possible, particularly if the wind direction is variable. QinetiQ has undertaken an investigation into the effect of exhaust leaks and re-ingestion on the atmosphere of Royal Navy (RN) submarines. Using their proprietary BREATH ventilation modelling software, specifically designed for the simulation of submarine enclosed atmospheres, QinetiQ have simulated a number of submarine ventilation states and the effect on the dispersion of CO resulting from exhaust leaks and re-ingestion. With an exhaust CO concentration of 600 ppm, an exhaust leakage rate of just 2 % would result in the atmosphere in the diesel generator compartment breaching the RN 90 day maximum permissible concentration (MPC_{90}) of 12 ppm within 3 min. An increased leakage of 10 % would breach the 24 hour maximum permissible concentration (MPC_{24}) of 60 ppm in 3 min. If a leakage of 30 % or greater was present the 60 min maximum permissible concentration (MPC_{60}) of 175 ppm would be breached within 3 min. Re-ingestion of the diesel exhaust can result in an equally rapid rise in CO concentrations throughout the whole boat. A re-ingestion of between 2 – 10 % can breach the MPC_{90} within 1 min for the diesel generator compartment and 54 min for the ‘whole boat’. Due to the acute toxicity of CO there is a need for a real-time CO monitor in the diesel generator compartment. This would provide an early warning system which could initiate a rapid response to an increasing CO concentration. Changes to the design of the submarine ventilation system are proposed that could reduce the atmosphere contamination from exhaust gas re-ingestion.

Introduction

Since the end of World War 2 Royal Navy (RN) submarines have been fitted with Snort Induction Masts (SIM) to allow them to remain submerged while they charge their batteries using diesel generators. Even after the introduction of nuclear power RN submarines are still routinely ‘snorting’ to charge their batteries. It is during the operation of the diesel generators that large amounts of carbon monoxide (CO) are produced, which in normal operation is exhausted outboard. However, there are scenarios whereby CO can feasibly be returned to the submarine’s atmosphere, either through a direct leak of the diesel generator exhaust system, or through re-ingestion of the diesel exhaust plume. Whilst there are facilities on-board the submarines to remove low levels of CO contamination, the speed and volume of the contamination due to exhaust leaks or re-ingestion, could temporarily overwhelm the removal capacity and prove hazardous to the crew.

Utilising the BREATH modelling software various leakage and re-ingestion scenarios have been simulated to determine their impact on the atmosphere of the submarine.

BREATH modelling software

The BREATH modelling software was developed jointly by QinetiQ and the Buildings Research Establishment (BRE) at Watford, United Kingdom, specifically to simulate submarine ventilation systems and, following acquisition of the intellectual property rights (IPR), is now proprietary to QinetiQ. The software has been subject to a programme of continuous improvement and the version used in this study was BREATH 3.3-0. The underlying mathematical function that drives BREATH is a fourth order Runge-Kutta method. The model has been validated in the laboratory [1] using sealed plastic crates connected by plastic pipes and arranged in various configurations to replicate different ventilation flow paths. Carbon dioxide (CO_2) was used as the tracer gas and an air purification capability was replicated by introducing soda lime absorption beds in some of the crates. Excellent agreement was obtained between the experimentally monitored CO_2 concentrations and the values predicted by the corresponding BREATH simulation.

The framework of the submarine atmosphere purge model (and all BREATH models) was built around three primary information sets:

- Breathable volumes of compartments
- Ventilation system architecture (*i.e.* the ventilation pathways between compartments)
- Ventilation flow rates

Building on the framework, the model was refined by entering the following details into individual compartments, depending on the scenario to be simulated:

- Initial contaminant concentration
- Contaminant production rate
- Contaminant removal rate (*i.e.* an air purification capability)

Submarine model

For the purposes of this work a BREATH model of a RN VANGUARD-class submarine was created (Figure 1). In common with all submarines, the VANGUARD-class has a number of different ventilation states corresponding to different ventilation and purge regimes.

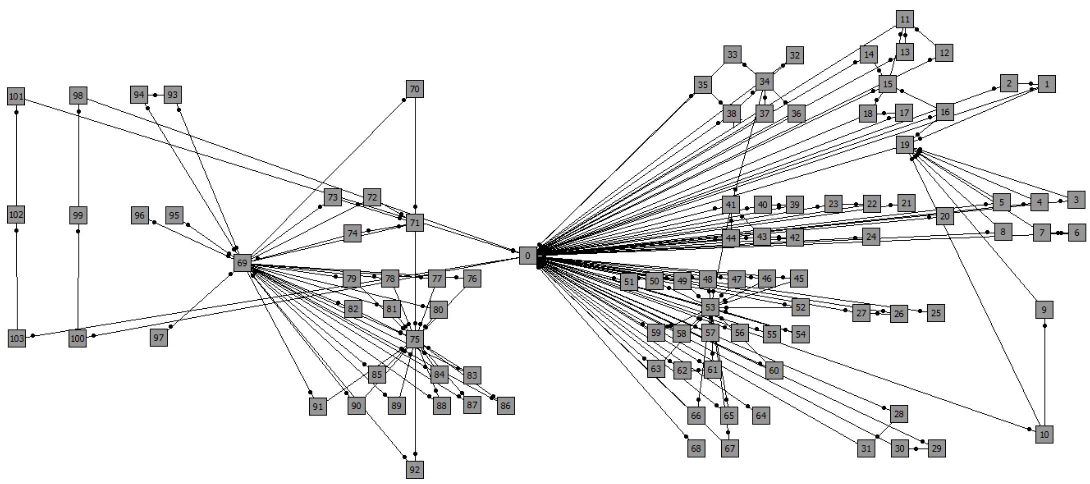

Figure 1: BREATH model of VANGUARD-class

When the diesel generators are running the ventilation system is operated in vent state BLUE. A simplified schematic diagram of the vent state BLUE arrangements is shown below in Figure 2. The diesel generators take their air supply (168 $m^3.min^{-1}$ [2]) from the Diesel Generator (DG) compartment and the exhaust is discharged outboard *via* the Diesel Exhaust Mast. Replacement fresh air is drawn into the submarine *via* the SIM. The majority of this air goes to the DG compartment but a smaller proportion is drawn into the Forward (Fwd) Fan Room where it combines with the air being recirculated around the submarine. The additional air needed to make up the diesel induction air flow is drawn from 3-Deck Passage, via the Battery Compartment. This air flushes the Battery Compartment during this vent state.

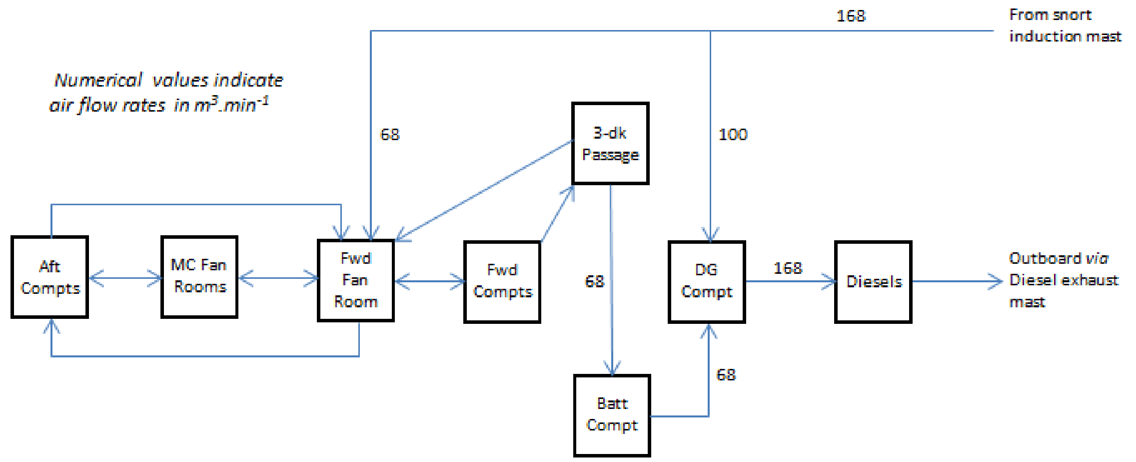

Figure 2: Simplified schematic of vent state BLUE

Proposed changes, to the ventilation system shown in Figure 2, would direct the 68 $m^3.min^{-1}$ air flow to the Battery Compartment, rather than pass it to the Fwd Fan Room. This would create an isolated loop of air that would prevent CO contamination due to exhaust re-ingestion from reaching the bulk of the submarine's atmosphere.

Impact of diesel exhaust leaks

It has been reported that an average submarine diesel engine produces between 200 to 600 ppm of CO in their exhaust [3]. For the purposes of this study a 'worst case' scenario was assumed, *i.e.* that the exhaust from the engines installed on the submarines contain 600 ppm of CO. Since the total diesel exhaust flow is 168 $m^3.min^{-1}$ it can be calculated that the CO production rate is approximately 100 $l.min^{-1}$. Thus a diesel exhaust leak has the potential to increase the CO concentration in the DG Compartment to hazardous levels within a very short space of time. As there is no exchange of air between the DG Compartment and the Fwd Fan Room (and hence the rest of the submarine) during vent state BLUE no other compartments are affected.

In order to investigate the impact of a diesel exhaust leak a series of BREATH simulations were carried out to determine how rapidly the CO concentration would increase, and the equilibrium concentration that would be attained for different leakage rates. Table 1 shows the CO leakage rates for different percentage exhaust leakage rates. Figure 3 shows how rapidly the CO concentration increases and the equilibrium concentration that was attained for each of these leakage rates. Leakage rates greater than 40 % were not modelled as they were considered by QinetiQ to be highly unlikely scenarios.

Exhaust leakage rate (%)	Volumetric exhaust leakage rate ($m^3 \cdot min^{-1}$)	Volumetric Carbon Monoxide Leakage Rate ($l.min^{-1}$)

2	3.4	2
5	8.4	5
10	6.8	10
20	33.6	20
30	50.4	30
40	67.2	40

Table 1: Diesel exhaust and CO leakage rates

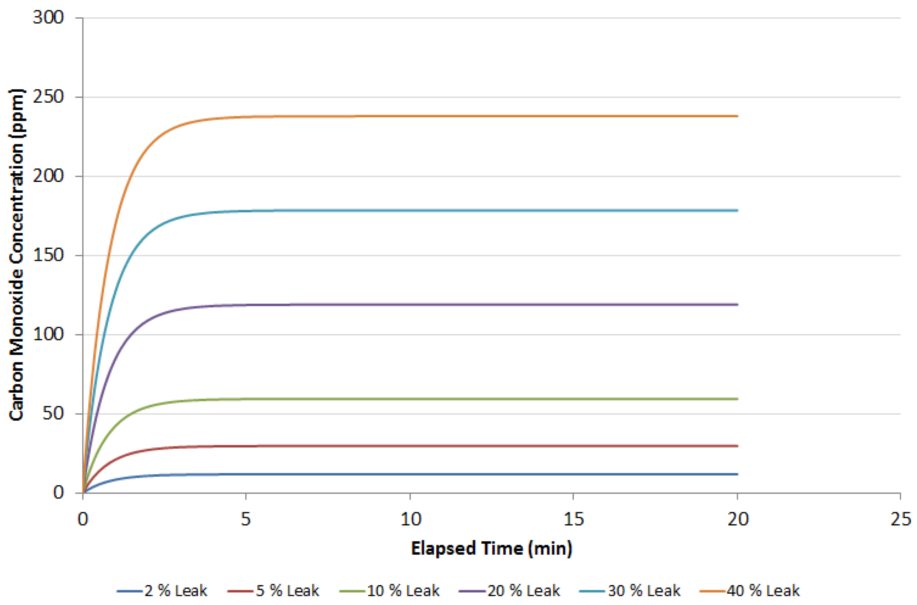

Figure 3: Modelled effect of Diesel exhaust leakage on DG Compartment CO concentrations

Figure 3 demonstrates that the RN's 90-day maximum permissible concentration (MPC_{90}) of 12 ppm will be breached if the Diesel exhaust leakage rate is greater than 2 %, the MPC_{24} of 60 ppm will be breached if the leakage rate is greater than 10 %, and the MPC_{60} of 175 ppm will be exceeded if the leakage rate is greater than 30 %.

Table 2 compares the times taken to breach the three CO MPC values at each of the leakage rates. It can be seen in Table 2 that for leakage rates that result in a MPC being exceeded the breach will occur after an extremely short period of time. The distance between the DG compartment and the central atmosphere monitoring system (CAMS) also poses a problem. The response time of the CAMS is adequate, but the distance the sample must travel means that in the time it takes for the initial sample to travel to the CAMS and be analysed, and an alarm raised, the atmosphere in the DG compartment could already be hazardous. Therefore it is recommended that a CO detector be installed in the DG compartment that would warn the crew in the event of a breach.

Leakage rate (%)	**Time taken to breach MPC value (min)**		
	MPC90	**MPC24**	**MPC60**
2	3	-	-

5	<1	-	-
10	<1	3	-
20	<1	<1	-

Table 2: Times taken to breach CO MPC values

Impact of exhaust re-ingestion

Re-ingestion of the diesel exhaust plume, *via* the SIM, can occur under certain conditions [4, 5]. The severity of the problem is mainly dependent upon meteorological conditions and the heading of the submarine in relation to the prevailing wind direction. Although submarines are instructed to maintain a heading that will take the exhaust plume away from the SIM when running the diesels this may not always be possible, particularly if the wind direction is variable.

BREATH cannot model the dispersion of the exhaust plume, but it can be used to assess the impact of different degrees of plume re-ingestion. As already noted during vent state BLUE the majority of the induced air goes to the DG Compartment, but a proportion also goes to the fwd Fan Room from where it is distributed around the submarine. Thus the re-ingested exhaust plume will affect a large proportion of the submarine. In order to assess this, a series of BREATH simulations were carried out in which the induced air flow contained various concentrations of CO depending upon the amount by which the exhaust plume has been diluted before being re-ingested. Since the assumption has already been made that the diesel exhaust contains 600 ppm CO, the 'worst case' scenario will be that the induced air also contains 600 ppm CO (*i.e.* 100 % plume re-ingestion). Figure 4 shows the relationship used in the model between the degree of plume re-ingestion and the concentration of CO in the induced air flow.

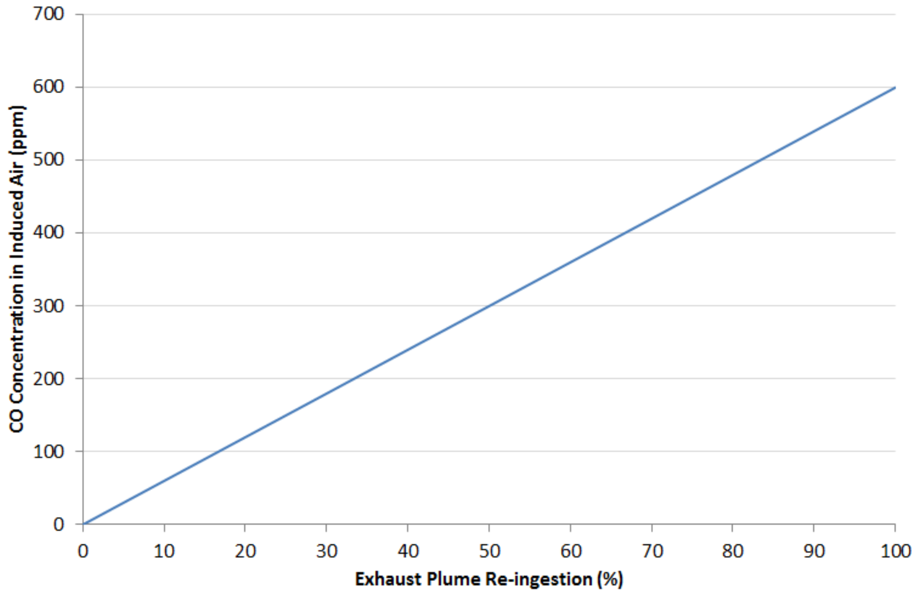

Figure 4: Relationship between degree of plume re-ingestion and the concentration of CO in the induced air flow

Figure 5 shows how the CO concentration in the DG Compartment increases with different degrees of exhaust plume re-ingestion.

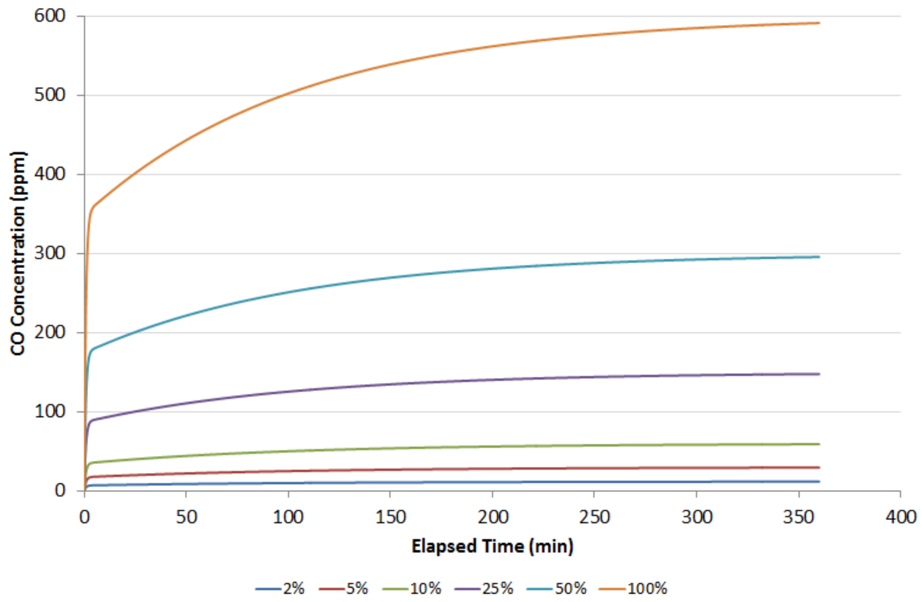

Figure 5: Increase in DG Compartment CO concentration for different degrees of exhaust plume re-ingestion

In each case there is a rapid increase in the CO concentration until it reaches approximately 60 % of the concentration in the induced air flow. This initial rapid rise is due to the direct air flow from the SIM. The following gradual increase is due to the diluent air flow, received from the front of the boat, becoming increasingly more contaminated as the re-ingestion affects the entire boat atmosphere. The very rapid rise in CO concentration, even at low percentage re-ingestion values, further reinforces the requirement for a CO monitor to be fitted in the DG Compartment.

Figure 6 presents the equivalent data for the remaining volume of the submarine which has been treated as a single, homogeneous entity in BREATH. It can be seen that the rate at which the CO concentration increases is much slower than in the DG Compartment, due to the greater breathable volume. Nevertheless the concentration will eventually reach that of the induced air flow and, consequently, there is potential for MPC values to be breached. The MPC_{90} would be breached if re-ingestion is greater than 2 %, the MPC_{24} would be breached if re-ingestion is greater than 10 %, and the MPC_{60} would be exceeded if re-ingestion is greater than 30 %.

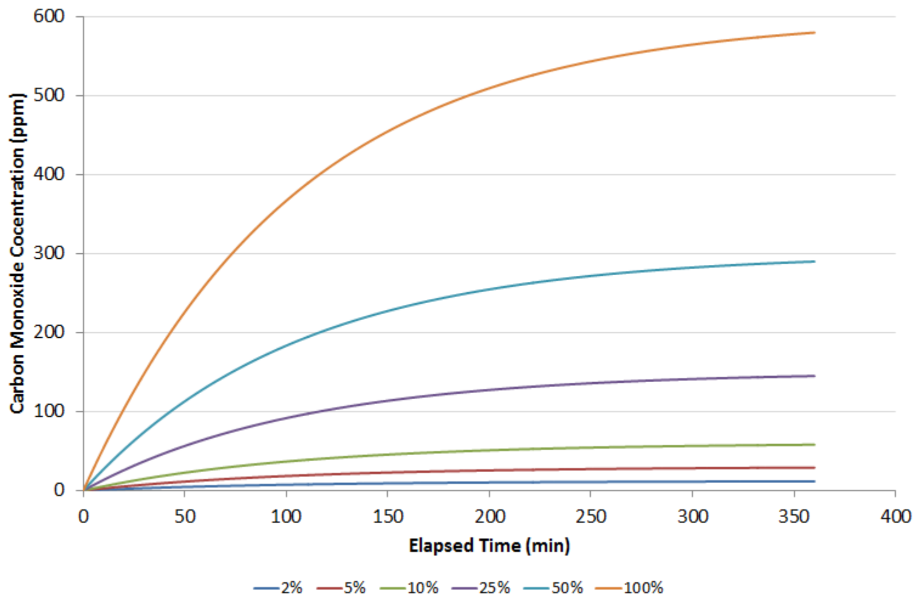

Figure 6: Increase in 'whole boat' CO concentration for different degrees of exhaust plume re-ingestion

Table 3 details the 'whole boat' times taken to breach the three CO MPC values for different degrees of exhaust plume re-ingestion. These times are considerably longer than for the DG Compartment and consequently adequate warning of a rising trend in CO concentration would be provided by the submarine's Central Atmosphere Monitoring System.

Re-ingestion (%)	**Induced CO concentration (ppm)**	**Time taken to breach MPC value (min)**		
		MPC90	**MPC24**	**MPC60**
2	12	-	-	-
5	30	54	-	-
10	60	24	-	-
25	150	9	54	-
50	300	4	24	93
100	600	2	12	37

Table 3: 'Whole boat' times taken to breach CO MPC values

Conclusion

In the event of diesel exhaust gases either leaking from the discharge pipework, or from exhaust re-ingestion, the CO concentration in the submarine atmosphere can breach safety levels within minutes. The pre-existing CAMS cannot respond in sufficient time to warn of the production of a dangerous atmosphere. Due to this and it is recommended that a real time CO monitor be fitted into the diesel generator compartment.

Proposals were made for modifications to the arrangement of the vent state BLUE purge regime that, if implemented, would reduce the hazards from CO exposure.

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Complexities of CO_2 Exposure Limit Derivations for RAN Submarines

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The 90-d and 60-m Royal Australian Navy (RAN) MPC for carbon dioxide (CO_2) exceed the SWA 8-h and 15-m occupational limits requiring exemptions. Thus the aim of this study was to review the 90-d, 24-h and 60-m MPC for CO_2 for appropriate and compliant levels in the RAN ABR 6105 submarine atmosphere manual.

CO2 is a toxicant and asphyxiant (ACGIH 2014). Acidosis appears reversible at ≤ 2% CO_2 for 1-3 days (Sliwka cited in James 2008) but prolonged exposure required 3-4 weeks cessation for restoration of electrolyte balance (Schaefer 1959 cited in ACGIH 2014). No study meets current standards or provides guidance for standards, indicating derived exposure limits as only defensible (James 2008).

As visual impairments for motion detection and depth perception are also unacceptable in RAN submarines, the LOAEL of 2.5% CO_2 for 1-h (NRC 2007 cited in James 2008) was adjusted by a UF of 5 rather than 3 to yield a RAN 90-d MPC of 0.5% as the NOAEL. This was supported by the RN 90-d MPC of 0.5% (Bollan 2013), based on studies of prenatal development effects in rats (HLS 2010) and the NOAEL of 0.7% for mental impairment over 26-d exposure (Manzey 1998 cited in James 2008).

Adjustment of the NOAEL for CNS depression at 3% CO_2 exposure for 5-d (Glatte 1967 cited in James 2008) using a UF of 3, instead of the NASA 'small n' UF (James 2008) suggests 1% as more appropriate for the RAN 24-h MPC. This limit was supported by the LOAEL of 1.2% for cognitive deficits over 26-d (Manzey 1998 cited in James 2008). Further, reanalysis of foetal effects in the USN rat study (NAMRU-D 2013) using the NASA adjustment method (James 2008) for extrapolation to humans resulted in a foetal safety upper limit of 1%.

Persistence of mild acidosis until removal of exogeneous CO_2 (Schaefer 1980) during a 1-h exposure to 2% CO_2 (Sinclair 1969 cited in James 2008) suggests adverse effects on foetal health (NAMRU-D 2013), thus is unsuitable as a 1-h exposure limit for pregnant submariners. However, other discomforts of mild headache and hyperventilation at 2% (Radziewski 1988, Sinclair 1969 cited in James 2008) indicate suitability as routine for the RAN 1-h MPC. This limit is supported by the ***new*** NASA 1-h exposure limit of 2% (James 2008).

Hence it is recommended that the RAN 90-d, 24-h and 60-m exposure limits be reduced from 1%, 2% and 3% respectively, to 0.5%, 1% and 1%, for ***pregnancy intending*** submariners and routine limits of 0.5%, 1% and 2% in compliance with SWA occupational limits.

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Glossary

CNS : Central Nervous System
LOAEL : Lowest Observable Adverse Effect Level
NAMRU-D : Naval Medical Research Unit Dayton, OH
NASA : National Aeronautics and Space Administartion
NOAEL : No Observable Adverse Effect Level
SWA : Safe Work Australia

Integrated Atmosphere Management

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Peter Row - Atmosphere Control International, UK

Abstract

Royal Navy submarine atmosphere control currently relies upon manual operation of the atmosphere control equipment using the data obtained from the Atmosphere Monitoring System based upon the know-how of the well trained crew. The three main parts of this overall system (atmosphere monitoring, oxygen generation and carbon dioxide removal) are totally autonomous and independent upon each other, whereas the submarines atmosphere is totally dependent upon the operation of all three. In addition the atmosphere control equipment requires regular watch keeping duties.

Introducing smart communications between the Atmosphere Monitoring System and the Atmosphere Control equipment, together with an increased level of automation could lead to a more stable submarine atmosphere whilst simultaneously reducing the necessary manpower. As with any automation, safety is of paramount importance especially where life support is involved therefore there will be a fall-back case to manual operation.

Holistic Atmosphere Management System

This paper looks to set out the next generation of development of Air Purification and Management in Royal Navy submarines. A joint enterprise involving the MoD and Industry is starting to research and develop a concept that will see a significant step in automation and control that will pave the way for an end goal of a safe, fully automated, Holistic Atmosphere Management System (HAMS).

Currently the management of atmosphere within the Submarine involves well established careful management by trained personnel of a number of bespoke pieces of equipment. These include equipment sets, that allow for Oxygen Generation, CO2 removal and other supporting machinery as well as a dedicated Atmosphere Monitoring system, again with a series of supporting pieces of equipment. The management of the internal, life supporting atmosphere requires constant vigilance in an environment that can change, quite dramatically, at very short notice.

Crew watch changeovers, practice drills as well as the obvious routines that a modern nuclear submarine can and may undertake, illustrate how maintaining a steady atmosphere can be, a difficult and currently manpower intensive job. Ensuring that the internal environment will continue to support the crew as well as the additional need to remain covert and therefore manage the waste products from the equipment requires a dedicated team on board. This team comprises an Environmental Control Officer with a small team of Engineering Technicians and medics who are trained to monitor, operate and maintain the equipment for the length of a patrol/deployment. It should be pointed out that this team carry out this function on top of their own dedicated section work and watch keeping requirement on board.

With the current view to reducing crew numbers in future classes of submarine and the restructuring of the engineering cadre within the submarine flotilla, a need to look at ways to reduce the management burden for embarked personnel is needed. For atmosphere management the technology to automate the equipment exists but has never previously been fully considered. Allowing a machine to dictate what you breathe can be a difficult concept to accept.

A staged process of development is the obvious way to go forward, with UK industry now reviewing the 'art of the possible', and combining this with existing and future equipment and technology.

On UK submarines, the following are manual autonomous individual pieces of equipment:-

- carbon dioxide scrubbing system
- electrolyser
- atmosphere monitoring equipment

The scrubbers require routine watch keeping during the day to ensure correct running, as does the electrolyser. The atmosphere monitoring system is a stand-alone unit, displaying readings depending on the sampling points selected. The oxygen level in the atmosphere is maintained by manual intervention and planning which could be automated. The carbon dioxide level balances itself depending on the number of scrubber units in operation and the carbon dioxide production rate. Manual titration ensures the correct solution in the scrubber, which could be automated.

This automation would save time. Electronically linking the equipment together would provide a further time saving and maintain a more stable atmosphere. Currently crew variations can result in different equipment reliability figures so automation and linking could achieve an increased and more predictable availability.

In order to maintain stealth, the atmosphere purification system has to be subtly managed to keep the equipment and atmosphere controlled, and in balance. The existing method of manual management can result in excursions from the optimum set points, which degrades equipment life and ultimately increases the through life cost of the equipment. Consequently, there is a desire for a Holistic Atmosphere Management System freeing up personnel to conduct other activities or requiring a smaller crew to run the submarine.

By drawing on their collective experience of designing automatic, safety critical, control systems for commercial and military diving customers and atmosphere management systems, Analox Military Systems and Atmosphere Control International believe that they can safely automate the management of the atmosphere on a submarine. Together they plan to demonstrate that the atmosphere management equipment can be controlled and optimised in order to reduce the work load on the crew, maximise equipment life, maintain stealth and most importantly deliver a safe atmosphere to the crew.

As with any automated system there are safety implications, so the existing manual system would be maintained as a selectable option. A complete and thorough safety assessment will flag up the requirement for additional sensors and warnings

CO2 Absorbtion on board Walrus class Submarines.
Jos Bogaert

Present situation :

- At the moment CO2 absorbtion is done by 2 sodalime scrubbers with each 6 cannisters .
- The design was made for 48 people.
- Complement of Walrus class is now 62 people.
- This results in high CO2 levels on board.
- Snorting is now mostly done to refresh the air then instead of charging the battery

Research

- From 2004 onwards reseach has been done by the RNLN and TNO in membrame gas absorbtion.
- This resulted in a working laboratorium model.
- Because the membrame needed a lot of water for cleaning this project was cancelled.

Tender

- In 2006 a tender was placed on the markety for a regenerative CO2 absorbtion system.
- Two bids were received.
- Bid one was from Wellman defence.
- This was based on a liquid MEA scrubber.
- Bid two was from EADS this was based on a solid MEA scrubber
- Both bids were rejected
- Bid one was considered to dangerous .
- Bid two used too much water for regenerating the solid MEA

Further research

- Micropore indicated that they were interrested in such a project but that they could not deliver a regenarative system.
- They would try to increase the performance of the existing cannisters by use of sodalime or LIOH
- Micropore has rerun there granular baseline and will set the granular bench mark at 500 to 540 liters of CO2 over 5 to 5.5 hours for a single can (operating at 1% CO2 and room temperature and pressure).
- ExtendAir® Power Cube has 27% more absorbent than the 8-12 mesh (1-2.5 mm) square can, stores in same volume, and offers consistent flow, pressure drop and duration even after subjecting to shock and vibration.

- This replacement absorbent enables the submariner to free up 21% stowage space, or increase crew compliment by 27%, or extend mission time b

CO2 Trial on board Zr Ms Dolfijn

Toon Marien / Jos Bogaert.

In third quarter of 2014 the Royal Netherlands Navy conducted on board testing of Micropore's PowerCube® adsorbent that replaces granular cans. The test was designed to compare performance of solid adsorbent cubes with granule cans. The test was conducted on the Royal Netherlands Submarine Zr. Ms. Dolfijn. The submarine was pier side and hatches were sealed. All three compartments in the submarine were open; ventilation and air conditioning was aligned for submerged operation. Prior to operating the scrubbers, the CO2 concentration in the submarine was increased to 0.75% by injecting 18 kg of CO2. Carbon dioxide concentration was monitored at 7 fixed locations throughout the submarine using NDIR analyzers manufactured by Analox. This test replicated scrubber operation after diving the submarine. Two scrubbers (12 adsorbent containers total) were energized and testing begun. CO2 was injected at a rate to replicate a crew of 62 people (1.3 kg CO2 every 30 minutes to represent 56 sailors plus 6 people on board (62 equivalent people total injected CO2)). For the first batch of adsorbent, two scrubbers were operated; each scrubber with six cubes or cans. As the carbon dioxide concentration increased to 1.0%, fresh adsorbent was installed and a third scrubber was operated. This paper reports test results for granules and calcium hydroxide PowerCubes®.

Recent Experience With Non-Powered Oxygen Generators in the UK Submarine Service

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Unpowered Oxygen Generators are carried by Royal Navy submarines primarily for emergency use (escape) purposes and as a back up to the normal powered oxygen generation equipment (i.e. electrolysers). Until 2007, a single design of Oxygen Generator, the Self-Contained Oxygen Generator 26 (SCOG 26, or simply "SCOG") was used for both purposes. Each oxygen generator was a single-use-only unit and the design based around well understood chemistry; namely the thermal decomposition of sodium chlorate to produce oxygen. Following a fatal accident the Royal Navy introduced a new design of generator, a previous SAMAP presentation (presented at SAMAP 2013) discussed the development process that resulted in the successful introduction of a new non-powered oxygen generator. This paper will now discuss the recent anomalies found in UK use of the new generator.

Introduction and Background

On 20th March 2007, onboard HMS TIRELESS, a SCOG exploded upon initiation resulting in the death of two crew members, injury to a third and damage to the submarine. After extensive investigations by the Royal Navy Special Investigations Branch (RNSIB), the Board Of Inquiry (BOI)[1], the UK Defence Science and Technology Laboratory (DSTL) and the US National Aeronautics and Space Administration (NASA)[2], the accident was attributed to liquid hydrocarbon contamination of the sodium chlorate "briquette" within the SCOG.

[1] Report of the Board of Inquiry into the circumstances surrounding the deaths on Her Majesty's Ship Tireless on 20 Mar 07.
[2] Investigation, Analysis and Testing of Self-contained Oxygen Generators – NASA Document No. WSTF-IR-1129-001-08, Dec 08.

Figure 1: HMS Tireless emergent through ice, post incident

As a consequence of the HMS Tireless accident, the Equipment Authority (EA) responsible for Submarine Air Purification undertook further investigation and implemented an immediate replacement to maintain the capability. Looking ahead, it also commissioned an independent review to ensure that a robust and safe final design product could be developed, addressing all the concerns and actions raised by the formal investigations. The outcome of this process was the procurement and introduction of the Multi Purpose Oxygen Generator (MILSPEC MPOG) which came in to service in all royal Navy submarines in 2011. The new MILSPEC MPOG has a sealed outer over-pack metal canister. This outer canister protects the Oxygen Generator inside from external contamination. Each MILSPEC MPOG has a unique serial number for location traceability. Each MILSPEC MPOG is carefully inspected to ensure there is no damage present and that the outer surface is contamination free. The serial number of the item must be checked against the documentation held locally. It is opened using the supplied key to wind-off the tear strip around the top and, once the top has been removed, the Oxygen Generator can be safely removed. The Oxygen Generator has an additional safety feature; a moisture indicator disc located on the T-bar handle that will have changed colour from white to orange/brown if moisture, and potentially hydrocarbons, has penetrated the outer canister. The igniter port is then accessed by lifting the T-bar, breaking the welded seal, then pulling back to remove the remainder of the welded circular seal. This forms the second seal to prevent contamination ingress. This exposes the igniter point and the oxygen exhaust ports. Having proceeded to this stage, the Generator must be used right away. It is activated by inserting the red phosphorous tipped threaded brass igniter, and screwing gently down until a puff of smoke is observed. This indicates the Generator has been ignited. The MILSPEC MPOG is designed to burn for approximately 70-90mins and produce a standard known volume of pure oxygen; 2,600 litres. At any stage in the activation process, should there be any doubt as to the integrity of the Generator, whether damage or contamination is visible, if the moisture indicator has changed colour, or if the Generator fails to ignite, the unit is considered to be compromised and is declared as ‘quarantined’. It is then suitably marked and stored in a dedicated quarantine storage locker to await removal and eventual disposal. Generators that successfully ignite and burn are allowed to cool (the external metal surface temperature can reach 500°C), before being sealed and repackaged. Both the MILSPEC MPOG and its Igniter have a stowage shelf life of 10 years from the date of manufacture.

Figs 2-3 The Multi Purpose Oxygen Generator showing opening of Outer (middle) and Inner (right) canister seals.

Fig 4. The Phosphorous tipped match for igniting the MILSPEC MPOG

The MILSPEC MPOG design provides robust capability due to the improved canister design and standard of liquid hydrocarbon contamination protection. The design improvements resulted in a two-layer physical seal which, together with documented and detailed handling and movement protocols reduces the assessed risk of hydrocarbon contamination or damge to ALARP. Specially designed contamination-proofed lockers provide a high level of secure onboard stowage. Unique, individual MILSPEC MPOG serial identification provides full item traceability from manufacturer through to eventual use and subsequent disposal. This allows a database to be maintained which will enable the known location of any MILSPEC MPOG to be identified should product recall be requested by the manufacturer. MILSPEC MPOGs are issued under the supervision of the Equipment Authority, who also provide training and guidance in handling and operation.

Recent Developments

In late April of 2014 a report was received by the Equipment Authority, via Naval stores, that a MILSPEC MPOG has been returned by an alongside platform due to swelling. This was the first reported incident, of any type, with the new design and initially believed to be a one off anomaly. The Authority and the OEM; Molecular Products Ltd (MPL) visited Faslane to look at the store and decide what action should be taken. The can was visually inspected and showed no signs of external damage but the thinner outer can was slightly swollen across all surfaces. The decision was made to return the MPOG to the manufacturer and open the store, under laboratory conditions, to ascertain what had caused the outer can to swell.

After arranging for the store to be returned to the manufacturer it was examined in the laboratory with a report being received by the Equipment team in July. The examination had identified a release of pressure upon opening the outer can that had been analysed and shown to be oxygen rich when compared to normal atmosphere. This was information enough for further urgent investigation and with a member of the Equipment team already onsite at the Naval Base, the decision was made to remove a number of MPOGs from the same platform as the original anomaly for laboratory investigation. At this point it was still believed to be a single anomaly however this very quickly proved to not be the case.

Upon starting to remove the MPOGs for testing it became obvious that further cases of swelling, from the same locker location as the original, were present. These were removed along with three non swollen ‘test’ stores for analysis. A full 100% audit was carried out by both Ships Staff and the EA straight away and in total 5 MILSPEC MPOGs were identified as being swollen and removed from the platform.

The issue now no longer being an isolated incident, the platform raised a safety alert with the UK MoD Design Authority for Ships Systems (DASS) sending out an instruction for all platforms to carry out a 100% audit to look for further swollen stores. A plan was put in place to try and identify what hazard, if any, existed and therefore what further action was needed. In addition to the identified swollen MILSPEC MPOGs from the first platform a further fifteen MILSPEC MPOGs were found in other platforms. A week later, with the EA in attendance, MPL carried out further analysis[3]. This consisted of swollen and non swollen MILSPEC MPOGs and some further 'test' MILSPEC MPOGs that had been in MOD stores but had not been in a submarine environment. At the same time further MILSPEC MPOGs were opened at Qinetiq in Haslar[4]. The aim of the testing was to positively identify what was present in the gas escaping from the cans and therefore if any hazard was present.

Figs.5-7 Swollen MILSPEC MPOG(right) in Faslane Stores next to standard MILSPEC MPOG and comparison next to straight edge in the laboratory.

The testing regime, at both locations comprised a controlled opening of each MILSPEC MPOG (outer and then inner cans), assessment of any gases emitted, initiation iaw Standard Operating Procedures, analysis of quality of the burn during operation and destructive examination of a couple of samples.

[3] Molecular Products Ltd Quality Report, P. Hutchinson (dated 24 July 14).
[4] Analysis of the Gas contained in oxygen generators, S. Woods, A. Chapman, G. Toft (dated 24 July 14).

Fig. 8 Qinetiq Laboratory Analysis
Fig. 9 Gas detection equipment during opening of outer canister

The results of these investigations showed that ALL the MILSPEC MPOGs (including those that had not been in the submarine environment) contained a slight overpressure of oxygen rich gas (100ml samples showed 30-55% oxygen by volume) in the inner cans, and that, in a number of cases, an overpressure was to be observed in the interspace between the inner and outer cans as well. In the case of the swollen stores, once the outer can had been opened the cans returned to their original shape. None of the inner cans exhibited any evidence of distortion and crucially the burn process was unaffected by the overpressure. No other foreign gases were identified, either in the pressure release or during the burn and the generators performed within design specifications. As an aside it was also noted that the swollen MILSPEC MPOGs had all been located in particularly hot areas of the submarines (eg Aft Escape Compartment), indicating that temperature possibly has an impact on the amount of oxygen production.

Following this analysis a Submarine Operating Instruction[5] has been released giving guidance and direction on this issue with the following key points:

1. THE FREQUENCY OF ROUTINE LOCKER INSPECTIONS IS TO BE INCREASED TO THREE MONTHLY TO ENABLE EARLY DETECTION OF MILSPEC MPOG SWELLING.
2. IF FURTHER SWELLING IS IDENTIFIED DETAILS OF THE NUMBERS, LOCATION AND EXTENT OF SWELLING ARE TO BE NOTIFIED TO THE EQUIPMENT AUTHORITY.
3. ANY UNIT IDENTIFIED AS SWOLLEN IS TO BE PRIORITISED THE NEXT TIME MILSPEC MPOGS ARE INITIATED, WHETHER IT IS FOR NORMAL READY USE OR TRAINING PURPOSES. ANY AFFECTED MILSPEC MPOG WHICH HAS NOT BEEN BURNED SHOULD BE RETURNED THROUGH NAVAL STORES UPON RETURN ALONGSIDE TO BASE PORT.
4. OPERATION OF MILSPEC MPOGS IN ACCORDANCE WITH RESPECTIVE CLASS SOPS IS UNAFFECTED.

Identifying The Root Cause

With the reason for the swelling now having been identified; build up of oxygen rich gas, the mechanism behind the production was still unknown. Content that no immediate hazard was present and that the use of MILSPEC MPOGs should continue, the next step was to investigate the reason behind the production of the oxygen. Having discussed the issue within the Ministry, the EA were advised to contact the US Navy about the issue as they were another user of similar technology. This was done with the permission of Molecular Products Ltd (MPL) and under the Memorandum of Understanding agreement held between UK Naval Authority Group and the US Naval Sea Systems Command (NAVSEA). This discussion proved highly beneficial and allowed for a re-introduction to NASA personnel based in Houston and to NESC (NASA Engineering Safety Committee) based in New Mexico who had assisted with the TIRELESS investigation in 2007.

What next

[5] Royal Navy Fleet directive Submarine Operating Instruction F/G/060 (dated 05 Aug 2014)

At this time a testing plan is being finalised that will allow a joint investigation involving UK MoD, USN (NAVSEA) and NASA (NESC) to take place. The aim of this this is to look at various sodium chlorate candle make ups and ascertain what mechanism is causing the slow release of oxygen over time, what acerbates it and what modifications or safeguards are required if any. The testing regieme is to be finalised and is complicated by the nature of what is to be researched; that being the very slow release of minute volumes of gas.

Acknowledgements

The author would like to acknowledge the permission granted by Molecular Products Ltd UK for the use of product images, the co-operation and involvement of NASA, MoD DE&S colleagues for assistance with this paper, and lastly, the UK Royal Navy.

The Naval Submarine Code - Update

C C Clark

Naval Authority Group

UK MoD

At SAMAP 2013 in New Orleans the then current draft of the atmosphere control chapter of the Naval Submarine Code was presented. This presentation will provide delegates with the current status of the Naval Submarine Code and an overview of the developments in the since SAMAP2013 using the atmosphere control chapter as the example. The next steps leading to its eventual publication as an Allied Naval Engineering Publication, ANEP, will be discussed.

SAMAP 2015

MICROPORE CARBON DIOXIDE ADSORBANT FOR HIGH PRESSURE APPLICATIONS

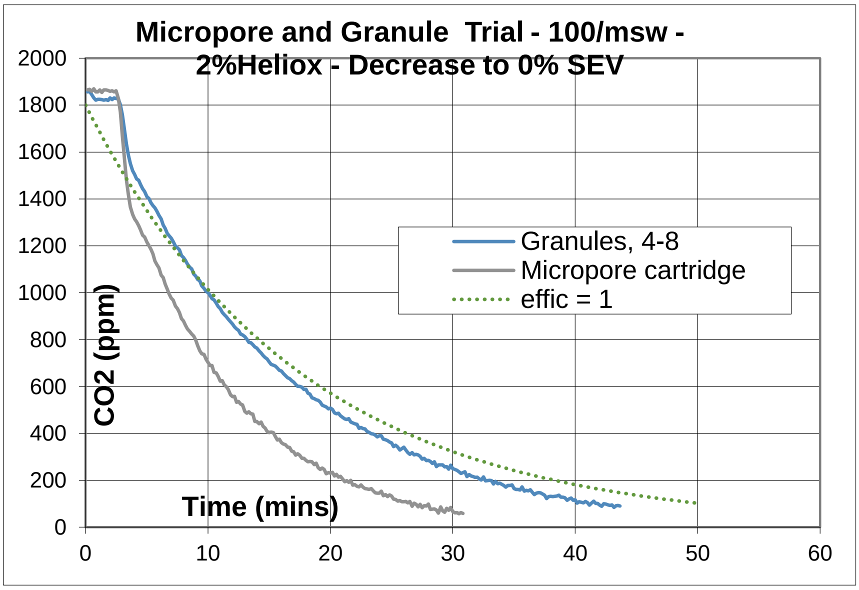
Tom Daley
Micropore Inc.

Scott Waddell
JFD Global

ABRSTRACT
In normal submarine applications carbon dioxide (CO_2) is removed from breathable air at pressures very close to 1 Atmosphere. In the case of disabled submarine awaiting rescue CO_2 removal may occur at pressures up to 5 atmospheres absolute (5 ATA). There are some scrubber applications that operate at much higher pressures. Hyperbaric scrubbers operate down to 350 meters of sea water (350 msw, 35 ATA). Submarine applications include scrubbing high pressure air banks at pressures in excess of 3,000 psig (204 ATA). Micropore is expanding its ExtendAir® adsorbent technology to perform in high pressure applications.

Micropore is teaming with JFD Global for high pressure applications; JFD Global resulted from the 2014 merge of James Fisher Defence and Divex. This new company has extensive experience in both the submarine and diving industries. In 2015 JFD Global acquired the National Hyperbaric Center (NHC), Aberdeen Scotland. This facility operates multiple test and hyperbaric chambers, both unmanned and man rated, at pressures up to 800 ATA. The testing reported in this paper was conducted at NHC.

Using an 11 cubic meter chamber (entry lock #2), testing was conducted at pressures of 10 and 30 ATA. This pressure represents diving operations in support of off shore applications. This paper will report test parameters and results for multiple high pressure operations. A sample results is shown in the figure below.



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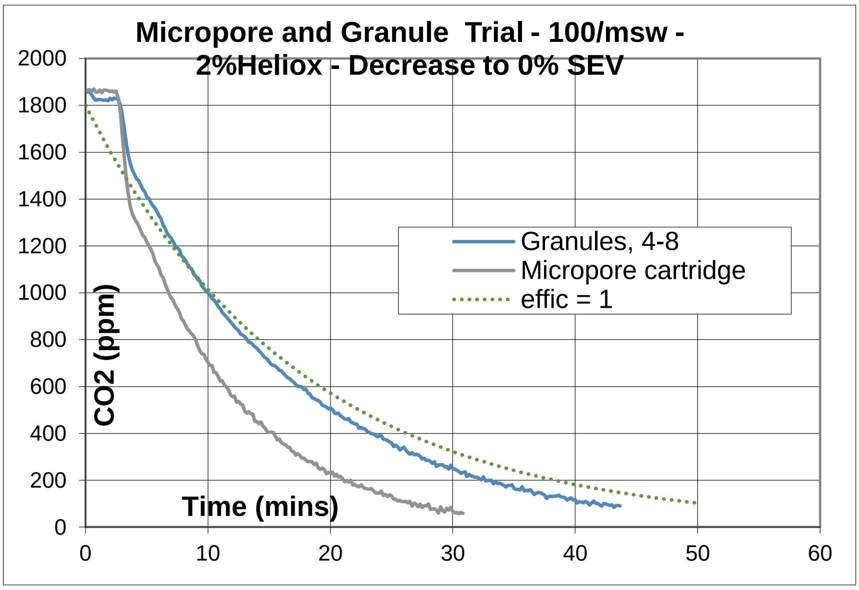

Canadian Air Quality Manual

- The Royal Canadian Navy's 'Air Quality Manual' defines mandatory requirements for the management of Air Quality in Victoria Class Submarines.
- Retrospective Monitoring for a list of 44 potential atmospheric contaminants is required:

  - Semi-annually (not further defined)

  - Post extended docking work period (EDWP)

  - Whenever contamination is suspected (not further defined)

- Two sets of samples are required; one during dived operations, and the other while snorting with diesels running.
- Collecting these samples has proven to be both technically and financially challenging.
- The RCN would like to know:
-

1) Do other Navies perform retrospective monitoring in circumstances similar to those listed above?

2) Does such monitoring include a similar list of potentialcontaminants?

3) Is there a link between nationally legislated OHS standards and submarine monitoring requirements?

4) What evidentiary base was used to establish the list of monitored contaminants?

5) Who performs the sampling procedures and laboratory analysis?

6) What is the approximate cost of performing such sampling?

The referenced contaminants are listed on the next slide:

Acetylene	**Lead**
Acetonitrile	**Manganese**
Ammonia	**Methane**
Aerosols	**Methanol**
Antimony	**Mercury**
Benzene	**Molybdenum**
Beryllium	**Nickel**
1.3-Butadiene	**Ozone**
Butanolamine	**Phosphine**
Cadmium	**Refrigerant 134a**
Chromium	**Refrigerant 426a**
Cobalt	**Sulphur dioxide**
Copper	**Tin**
Ethylbenzene	**Titanium**
Ethyltoluenes	**Toluene**
Halon 1301	**Total Aerosols**
Hydrogen Bromide	**Total Organics**
Hydrogen Chloride	**Triaryl Phosphate**
Hydrogen Cyanide	**Trimethylbenzenes**
Hydrogen Fluoride	**Vanadium**
Hydrogen Sulphide	**Vinyl Chloride**
Iron	**Xylenes**

New Air Monitoring System (AMS) Walrus Class

Isaac Barendregt

History

New build submarines (RDM), commissioned 1990-1994
Perkin Elmer-Hamilton Sund-strand Pomona Ca. 1965-?
Maintainability, more defects, obsolescence, downtime in years, costly mods, no service.
Costs to high, 2012 shut down.
Maintenance budget used for temporarily solution.
Replacement part of midlife upkeep program (IPW).

Temporarily Solution

Hand held/portable instruments.
Per submarine:
5 Analox SUB Aspida's CO_2 en O_2
2 Dräger X-AM 5600
CO (compensated for H_2)
CO_2 and O_2
Always on board for Escape/emergency:
2 Analox SUB MKIIp

Program Of Requirements with Main technical requirements:

O_2, CO_2, H_2, R134A, CO. Ranges and accuracy.
No preference for central suction or "local" sensors.

General requirements (shock, voltage, EMC, noise, etc).
Built in Redundancy.
Continued measurement at complete closure of bulkheads (suction lines closed).
No cross sensitivity for H_2.
Dynamic and static pressure variations. (750 mbar – 1300 mbar/ RoC of pressure variations 10 mbar/s)
Central (CCU) and Local control units (LCU) in a network(screens, information, alarms, control)
Logging
Min. 6 weeks continues working without calibration.
Not for submarine in distress.
6 hours UPS time.
Ambient Temperature (0 ºC - 60ºC)

Selection of Supplier

6 parties invited for an offer (SICK, Dräger, Analox, Imtech/Bionics, DCNS (Simtronics), Hamilton Sundstrand.
3 out of 5 offers were ranked
(HS did not offer, Bionics offer was not competitive and withdrew themselves from competition, DCNS above budget (nuclear price)
Analox, Sick, Dräger remained.

Sick was selected

PROs
Great redundancy
Great track record of more than 50 submarine systems (all submarines from HDW)
(Italian navy (U212, HDW) satisfied customer)
Price competitive and within budget.
All sensors commercial available and large numbers supplied.
All sensors shock tested and reports available

Cons
Largest power consumption (accommodated in delta IPW-program)
Largest volume/weight (could be accommodated on board and weight balance)
Not a system integrator

Progress and Planning

FAT February 2014
HAT 7/8 sept 2015 Zr.Ms. Zeeleeuw.
Some minor issues (software, defects)
HAT 2; October/November 2015
SAT spring 2016 Zr.Ms. Zeeleeuw.
Succes HAT 2 triggers construction system 2, 3 and 4.
System 2 on Zr.Ms. Dolfijn 2016/2017
Standalone CCU of System 3 and 4 on operational boats Zr.Ms. Bruinvis and Zr.Ms. Walrus 2016/2018.
2017-2021 completion of systems 3 and 4.
2015→ service contract with Sick for repairs and calibration.