



**Submarine Air Monitoring & Air Purification –
International Symposium**

SAMAP 2015

PROCEEDINGS

5 – 8 October
Hotel Den Helder
Den Helder
The Netherlands

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FORWARD

SAMAP 2015 was held in the Netherlands at the invitation of Martin Jansen, representing the Directorate Materiel RNLN. Subsequently, Martin moved to another position within NL MoD and Jos Bogaert took over the principal organising role for the conference with the assistance Sam Hopkins of Sonistics Ltd, UK.

Both Martin and Jos had been long-standing participants of SAMAP and both were involved in the organisation of the 2007 SAMAP conference in Amsterdam.

The conference was well attended and the presentations were a mixture of scientific and technical subjects to cater for various levels of interest.

The proceedings of this conference have taken on a slightly different format in that the slide presentations were distributed on memory sticks to the attendees at the conclusion of the conference and only the written papers are included in the proceedings.

On behalf of the SAMAP Organising Committee, I wish to thank the conference participants for attending and participating in the conference and Analox Plc as the prime sponsor and Dräger, Micropore, Molecular Products, OC Lugo and Sonistics as supporting sponsors.

I also wish to thank Jos Bogaert and Sam Hopkins for their splendid effort in organising the conference logistics and the NL MoD for their support.

Wally Mazurek,

Convenor,

wal.mazurek@gmail.com

PROGRAM

Tuesday 6 October 2015

08.00 Coffee and registration

09.00 Welcome by Captain Amerlaan, head of submarine flotilla

09.15 Opening by Wally Mazurek and introduction of delegates

09.30 Key Developments in SAMAP over the past 20 years –
W Mazurek

10.30-11.00 *Coffee break*

Air Quality Session – Chair Hilary Bollan/Tom Limero

11.00 Operational use of the air quality monitor –
Tom Limero, Paul Mudgett

11.30 Results of a Long-Term Demonstration of an Optical Multi-Gas
Monitor on ISS – *Paul Mudgett, Jeffery Pilgrim*

12.00 *Lunch*

13.00 Real-Time Monitoring of Volatile Organic Compounds in
Submarine Air by Chemical Ionization Mass Spectrometry- *Julien
Leprovoist, Elsa Bauchard, Joël Lemaire, Michel Henninger,
Fabrice Arzac, Corninne Grégoire*

13.30 Parameters that are known to influence the PAH Emission
Profile from Diesel Engines – *Michael Leist*

14.00 Post Fire Monitoring – *Hilary Bollan*

14.30 Importance of Structural Properties in Diesel Particulate
Characterisation – *William Gan*

15.00 *Tea Break*

15.30 Diesel ventilation - *Gareth Toft*

16.00 Wrap up for the day

Wednesday 7 October 2015

09.15- 0930 Opening by Wally Mazurek

Air Purification Session 1 Chair: Lucio Ricciardi/Jos Bogaert

09.30 Integrated Atmosphere Management – *Peter Row*

10.00 Coffee break.

10.30 Air purification on Walrus Class - *Jos Bogaert*

11.00 CO2 Trials on Walrus Class Submarine – *Toon Marien*

11.30 CFD Modelling on Walrus CO2 scrubber – *Barend van der Giesen*

12.00 - Lunch

Thursday 8 October 2015

Air Purification Session 2 Chair: Tom Daley/Chris Clark

09.15- 09.30 CFD Modelling on Walrus CO2 scrubber – *Lela Baku*

09.30 Non-Powered Oxygen Generators - *A Goodall, M Leadbeater*

10.00 Coffee break.

10.30 Naval Submarine Code on Air Purification – *C Clark*

11.00 CO2 Adsorbent for High Pressure Applications – *Tom Daley*

11.30 Oil removal in industrial applications through catalysis –
Thomas Lettman

12.00 Lunch

13.00 Monitoring for contaminants - Canada

13.30 New Atmospheric Monitoring System Walrus Class – *Isaac Barendregt*

14.00 SAAB Kockums A26 *Lena Marie Hoglund*

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

W. Mazurek

Introduction

SAMAP Conferences

The Australian Department of Defence first took serious interest in submarine atmospheres with the building of the Collins class submarines which were the largest conventional submarines in the world. As part of that initiative, in 1991 I was posted to the UK, at DERA, Holton Heath, to work in Paula Dibben's group on submarine atmospheres. During that attachment I found that the UK had a good co-operative arrangement with the US Navy (USN) and the French Navy but there was little interaction with other navies. However, very little was known of the activities of other navies in submarine air purification and air monitoring.

At the time the Royal Navy (RN) was retiring its newly built Upholder class diesel-electric submarines and concentrating exclusively on its nuclear-powered submarines. As a result UK interest in diesel-electric submarines and air-independent propulsion (AIP), was lost. However, plans for retrofitting AIP in the Collins class submarines were not withdrawn. Although still in its infancy, AIP had the potential to provide an underwater endurance somewhere between that of a diesel- and a nuclear-powered submarine. To facilitate habitability in an AIP submarine, air purification technology from the nuclear-powered were adapted during the initial construction of the Collins class submarines in addition to applying air quality standards from RN and USN nuclear-powered submarines. Hence, submarine air purification and air monitoring (SAMAP) technologies from both diesel- and nuclear-powered submarines became relevant to the Collins program. As it turned out, the AIP modification was never implemented but the air purification equipment and air quality standards became an integral part of the Collins class submarines.

In order to provide a forum for sharing information on SAMAP issues without relying on formal agreements, I organized the first international SAMAP conference in Adelaide, Australia in 1994. Subsequent conferences were held in Portsmouth, UK (1997); Toronto, Canada (2000); Emden, Germany (2003); Uncasville, CT., USA (2005); Amsterdam, Netherlands (2007); San Diego, USA (2009); Taranto, Italy (2011); New Orleans, USA (2013) and now in Den Helder, Netherlands.

Post-WWII Submarines

In order to appreciate advances in SAMAP technologies over the past 20 years, it is important to be aware of the state of these technologies, from the end of WWII to the first SAMAP conference meeting (1994). For most of that period, conventional diesel-powered submarines were essentially up-dated versions of WWII boats. The UK Oberon class submarines (1957-1978) were such an example. They were highly regarded and operated by many countries including UK, Australia, Brazil, Canada and Chile. Air monitoring was by colorimetric tubes, soda lime was used to remove carbon dioxide and oxygen candles provide a source of oxygen replenishment. Due to the ever present hydrogen hazard from charging of the lead acid batteries and carbon monoxide from diesel engine exhaust leaks, Pd/Al₂O₃ oxidation catalysts, were distributed throughout the submarines and were used to convert these gases to water and carbon dioxide respectively. Like the WWII predecessors, deep dive times were commonly less than 24 h and consequently air revitalization was by snorting or surface ventilation.

The greatest advance in SAMAP technology came with the deployment of nuclear-powered submarines. The requirement for extended deep dive times of several weeks or even months necessitated the introduction sophisticated technology for SAMAP. The use of consumable soda lime was no longer adequate for carbon dioxide removal and a regenerative carbon dioxide system was introduced. Similarly, consumable oxygen candles were replaced with electrolyzers which generated oxygen from the electrolysis of water. Carbon monoxide and hydrogen were oxidized with high temperature Hopcalite (CuO/MnO₂) catalysts. For the first time organic vapours were recognized as a hazard and were removed with activated charcoal filters. Aerosol pollution was also recognized and electrostatic precipitators were installed. These technologies were adopted from industry and their use was made possible by the availability of an abundance of power provide by the nuclear reactors (Mazurek, 2005).

The need for continuous air quality monitoring was recognized beyond oxygen, carbon dioxide and carbon monoxide to include refrigerant gases, hydrocarbons (Nui et al., 2009). This was achieved by a Central Atmosphere Monitoring System (CAMS) consisting of a central analyser (mass spectrometer) connected air sampling lines leading to various locations in the submarine.

Recent Advances

Since the first SAMAP meeting the air purification system in submarines has undergone some changes. In nuclear-powered submarines high pressure electrolyzers have been replaced by more efficient low pressure units. A new Advanced Carbon Dioxide Removal Unit (ACRU) is being developed and the CAMS is being upgraded with current technology. However, in new conventional and AIP submarines, in most cases the air purification system remains unchanged. For example only the Collins class (non-AIP) and the Japanese Sōryū class (AIP) submarines have regenerative carbon dioxide scrubbers. Likewise, the Collins class submarine is the only conventional submarine with continuous air monitoring. Nevertheless, new technologies have been explored in air purification and air monitoring over this period and some of the more notable advance are described in this review and have come to light through the SAMAP conference series.

Air Purification

Regenerative Liquid Amine Carbon Dioxide Removal

Reactions of Carbon Dioxide with Amines

Regenerative carbon dioxide removal is a key requirement for extended submarine deep dive deployment. With the exception of molecular sieve technology, regenerative carbon dioxide removal is based on a reaction of carbon dioxide with amines. Carbon dioxide “absorption” occurs at ambient temperatures while “desorption” is facilitated by elevated temperatures. To the design engineer “absorption” and “desorption” is simply a mass transfer process, but familiarity with the chemical reactions can assist in the choice of amines and an appreciation of the reasons and conditions for troublesome precipitate formation. It was for this reason that a study of the reactions was undertaken by Robert Hook (1997) at the Defence Science and Technology Organisation in Australia. Hook examined 8 low molecular weight amines including monoethanolamine (MEA), which was already used in submarine carbon dioxide scrubbers (RN, USN and RAN) and Alkazid M, a solid amino-acid salt which had been trialled by Wellman Defence, plc (Cassidy, 1995) as a non-volatile substitute for MEA (Fig. 1). The use of MEA in a confined space can be problematic due to its low permitted continuous exposure levels of 0.5 ppm (Aitchinson, 2005) and the corrosive effects on copper printed electronic circuit boards (Cassidy, 1995). It turned out that the main limitation of Alkazid was precipitate formation in the scrubber (Cassidy, 1995) the chemistry of which was unknown.

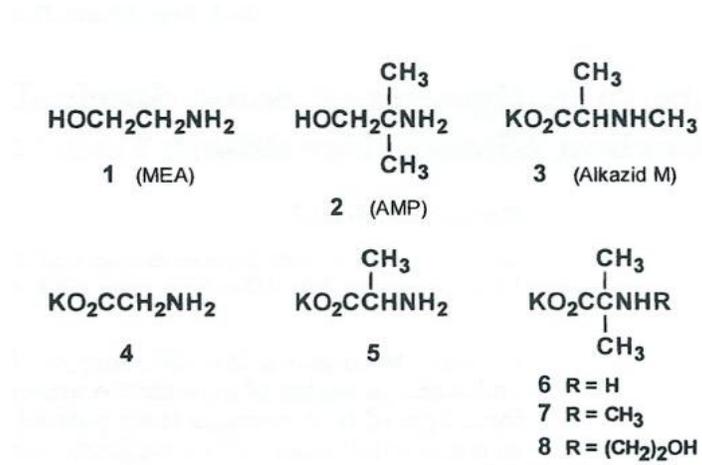


Figure 1. Amines studied for submarine carbon dioxide scrubbing (Hook, 1997).

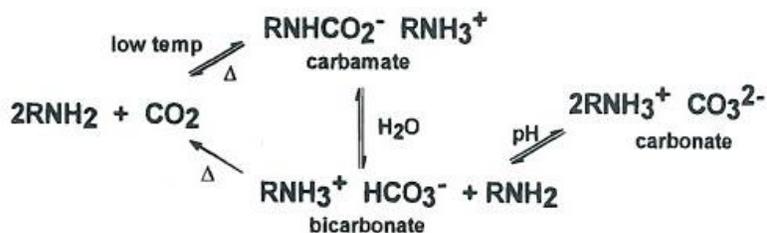


Figure 2. Proposed mechanism for the reaction of carbon dioxide with amines.

At ambient temperatures, the absorption of carbon dioxide in aqueous amine solution proceeds via the formation of the carbamate salt in equilibrium with the bicarbonate (Fig. 2). At elevated temperatures (> 100 °C) the bicarbonate decomposes to liberate the carbon dioxide and amine. Using NMR, Hook (1997) identified the precipitate as the carbonate salt of the amine. The precipitation was measured as a function of carbon dioxide loading (CO_2/amine) using 100% CO_2 and 2.5 M amine solution. It was found that Alkazid M precipitated at (1.0 mole/mole), **5** (0.94), **7** (0.9) **8** (0.5) and **6** (0.32). No precipitate formation was observed for MEA, AMP and **4** under the conditions of the study which required higher amine concentrations for precipitation. In addition to avoiding precipitation a rapid CO_2 absorption rate is an essential characteristic of the amine. It has been suggested that hindered amines (**2, 3, 5-8**) absorb CO_2 more rapidly than their unhindered counterparts (**1** and **4**) and exhibit a more complete CO_2 desorption (Hook, 1997).

This CO_2 scrubbing technology was adopted from industry where CO_2 levels were high. For CO_2 concentrations in the range 0.5%-1.0% expected in a submarine, the CO_2 absorption rate of MEA was found to be significantly higher compared with the other amines. For all the amines studied, the absorption rate was found to decrease significantly with decreasing CO_2 concentrations. Considering the rates of absorption and desorption, Alkazid M appeared to be a better substitute for MEA than the other amines. Despite the problem of precipitation, when using Alkazid M, it is conceivable that operating parameters could be adjusted in order to avoid carbonate precipitation.

MEA Air Monitoring

Because of the low continuous exposure limit of the MEA in air (0.5 ppm) and potential for spillage and leakage from the CO_2 scrubber, monitoring of MEA concentrations is an important aspect of submarine air quality (Bollan et al., 2000). This is usually achieved by bubbling a known quantity of submarine air through an acid solution, followed by laboratory analysis with base titration. Real-time measurements can be carried out through the use of colorimetric tubes such as Draeger, 0.25a Ammonia (Aitchenson, 2005). However, neither method is specific to MEA.

Using an Ion Mobility Spectrometer (IMS) in the form of a hand-held Chemical Agent Monitor (CAM, Fig. 3) it was found that could MEA and its principal decomposition product, ammonia could be measured if 4-heptanone was substituted for water as the reagent gas in the instrument (Gan and Corino, 2000). An additional benefit was the sensitivity of the instrument to refrigerant gas R22 (Fig. 4). The response to MEA was found to be linear over the range 0.005 – 0.7 ppm. This method

had the advantage of requiring only a minor modification to an existing ruggedized military instrument.

A prototype dedicated MEA monitor was subsequently developed by Graseby Dynamics (now known as Smith Instruments) through RN funding (Bollan et al., 2000). In addition to changing the reagent gas, the membrane was replaced with a capillary inlet which reduced the response and recovery times. During RN sea trials the instrument was found to provide stable readings for a period exceeding 8 months with a dynamic range of 0.05 to 3 ppm. The trial revealed MEA concentrations in the range 0.5 – 2.5 ppm in the vicinity of the scrubber (Bollan et al., 2000). These were encouraging results since long-term stability at the desired sensitivity is an essential requirement for submarine deployment. Despite the successful trial results a usable production model was never produced.



Figure 3. Portable Chemical Agent Monitor

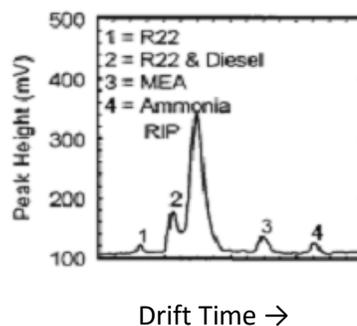


Figure 4. Separation MEA , ammonia R22 and diesel vapour by IMS (RIP=reactant ion peak).

Reduction of MEA Scrubber Emissions

A number of strategies have been developed for the reduction of fugitive emissions of MEA from the scrubber. The major sources include spillage and leakage from pump seals. Spillage can be reduced by improving the liquid transfer procedures and the problem of leaky pump seals has been addressed by deploying magnetically coupled pumps and emersion pumps. In addition to this problem, there are both amine and ammonia vapours are entrained with the scrubbed air (Aitchison, 2005). These emissions are minimized through the use of resin filter bags in the air outlet from the scrubber.

In a review of the materials used was reported by QuinetiQ (Aitchison, 2005), activated carbon filters, natural zeolite and a macroporous ion exchange resin were tested against the presently used resin, for efficacy and longevity. The experiments were carried out in a laboratory set-up and 0.25a Draeger, Ammonia colorimetric tubes were used measure emissions. The tubes did not discriminate between MEA and ammonia.

It was found that the zeolite was less effective than the activated charcoal filters and the macroporous ion exchange resin provided a significantly better improvement over the other materials in reducing the emissions.

Regenerative Solid Amine Carbon Dioxide Removal.

Solid amines address the problem of spillage and reduce fugitive amine emissions. Solid polymer ion exchange resin with primary amine groups attached were initially developed for the space program but later applied to submarine use by Airbus Defence and Space (formerly Dornier Aerospace) Germany (Schauer et al., 1994; Raatchen et al., 2003). A similar system has been developed by UTAS (formerly Hamilton Sundstrand) for space applications but never marketed for submarines. More recently Veneman et al. (2014) reported a CO₂ absorption study using a polystyrene ion exchange resin (Lewatit VP OC 1065) with benzyl amine groups attached for industrial applications for carbon capture. The authors claimed that the resin system required less energy for CO₂ removal than the liquid amine system. However, the use of such resins comes at a significant cost penalty compared to simple amines.

The Airbus scrubber which is due for deployment on a French submarine, has been designed to operate at $\geq 0.5\%$ CO₂ which is a considerable achievement for any CO₂ removal system. As with the MEA carbon dioxide scrubber carbon dioxide absorption occurs at ambient temperatures and desorption at elevated temperatures (steam). The system can be configured into a 2- or 3-bed unit where one or two beds are in the absorption mode while the other bed is in the desorption mode. A typical cycle involves 1 h carbon dioxide absorption and 0.5 h desorption (Fig. 5).

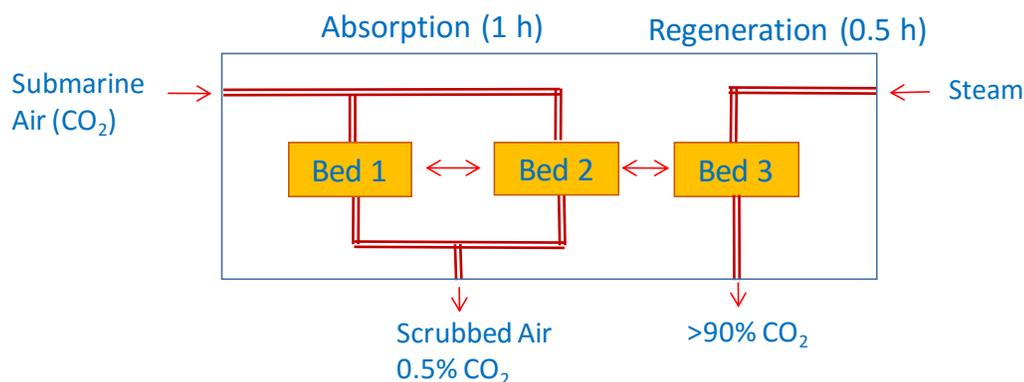


Figure 5. Carbon dioxide absorption and desorption configuration cycles for a polymer resin amine scrubber.

Although there are many advantages of this system in terms of amine containment, a fundamental problem is the lower heat transfer efficiency in the solid resin bed compared with a liquid amine bed. However this may be offset by a lower heat capacity of the resin compared with an amine solution. In order to reduce the energy requirements, the system can be configured for supplementation with waste heat from an AIP engine (Raatchen et al., 2003).

Membrane Carbon Dioxide Absorption

Another approach to the reduction in amine emissions from an amine based carbon dioxide scrubber is the separation of the amine from the air stream through the use of a membrane (Jansen and Feron, 2003). The system involves passing carbon dioxide laden air over hollow fibre membranes through which amine solution is circulated (Fig. 6). The role of the membrane is to allow the permeation of CO₂ but not of the amine. The carbon dioxide is provided by the amine. As in the conventional liquid amine carbon dioxide scrubber, the carbon dioxide is liberated from the amine in a boiler then cooled in a heat exchanger and recirculated through the membrane.

The scaled model was based on a carbon dioxide removal rate of 2.9 kg/h with gas flow rates of 328 m³/h (0.5% CO₂) and 110 m³/h (1.5% CO₂) at a thermal power of 4 kW. The system showed a high degree of selectivity with only trace losses of nitrogen and oxygen in the carbon dioxide discharge. A problem encountered with the system was precipitate formation which was addressed by flushing the membrane with demineralized water. The problem was attributed to hydrocarbon contamination (Bogaert, 2015) but it is the view of this author that the precipitate may have been due to amine carbonate formation.

In July 2002, the Royal Netherlands Navy (RNLN) tasked TNO to develop a full scale demonstrator for sea trials with a 2.82 kg/h CO₂ removal capacity suitable for 62 persons. Completion was scheduled for 2004 but unfortunately the project was abandoned.

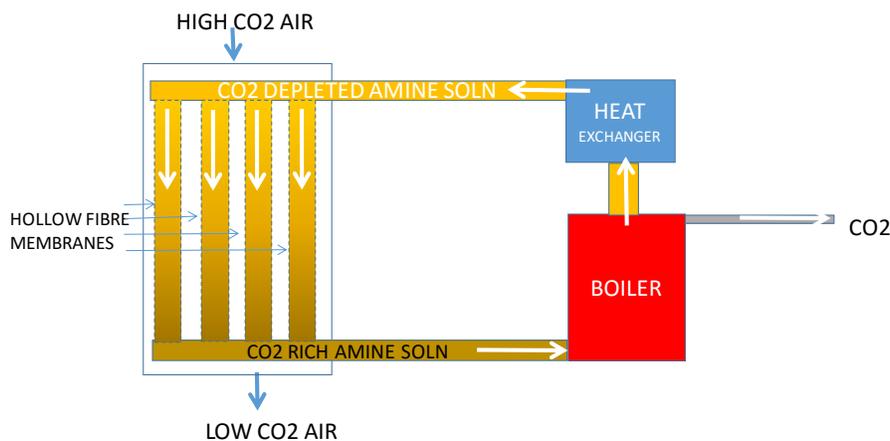


Figure 6. Schematic diagram of RNLN membrane carbon dioxide scrubber.

Hollow Fibre Membrane Amine-Facilitated Transport

A variation of the above method was developed by the Defence Evaluation and Research Agency (DERA, now QinetiQ), UK and based on the studies carried out during the 1990s on hollow fibre membranes (Headley, 1992). The process involved facilitated transport of CO₂ through supported liquid membranes containing an amine carrier solution to confer the desired selectivity for CO₂ and was further evaluated by QinetiQ (Toft et al., 2001).

A Koch Membrane System was impregnated with carrier solution under pressure and the excess solution drained and evacuated. The system was tested by passing humidified 1 % CO₂/air mixture

through the hollow membrane fibres while a reduced pressure was applied to outer side of the fibres (Fig.7). A CO₂ flow rate of 0.5 l/min was achieved with the following effluent gas composition: CO₂:O₂:N₂ = 1:1:1.

Although the results of this technology demonstrator were encouraging, the permeation rates and gas selectivity appeared to be inadequate and required further development.

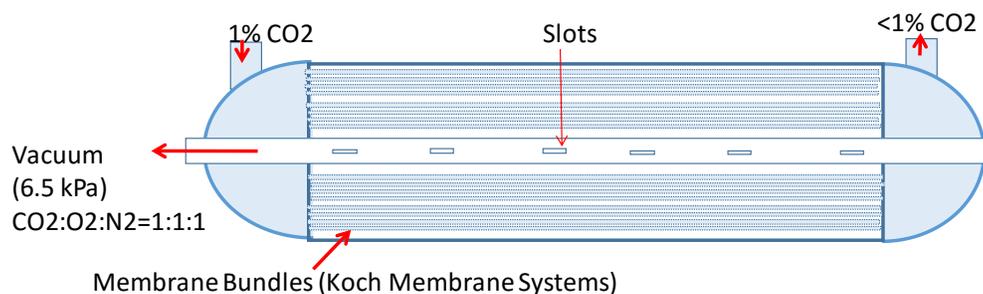


Figure 7. Fibre membrane module set-up for carbon dioxide removal (QinetiQ, UK)

Solid Amine Scrubber USN ([Advanced Carbon dioxide Removal Unit](#))

Another approach to immobilizing the amine in a carbon dioxide scrubber is by sorption onto a solid substrate such as mesoporous silica.

This process falls into 3 classes :

1. Physical Impregnation
2. Covalent tethering (amino silanes through siloxane bonding to the substrate)
3. Direct covalent tethering (where the amino group reacts directly with the substrate (eg polyethyleneimine, PEI))

The USN ACRU system is based on this approach but it is not clear if the immobilization belongs to class 1 or 3. Many related studies have been published in the scientific literature, with a vast range of amines and support substrates (Bacsik et al., 2010; Yu et al., 2010; Zhang et al., 2014). The principal mode of CO₂ uptake is by chemisorption in the form of carbamates (Bacsik et al., 2010) as observed in amine aqueous reactions (Hook, 1997). As expected, desorption occurs at elevated temperature and steam may be the preferred method (Li et al, 2010) as the use of electrical heating elements may result in a large temperature gradient with the potential for thermal decomposition of the amine.

The ACRU program is at an advanced stage with a full-scale prototype currently being tested. Qualification is expected in 2016 and production in 2018/29 (Swartley, 2015). It is expected that deployment of ACRU will reduce the operating costs, weight and volume compared with existing system. However, the cost of the PEI impregnated mesoporous silica could be significantly higher than MEA.

Absorption Media Tube (AMT) Technology

An elegant variation on the USN ACRU system has been developed by Nano-porous Solutions and evaluated by QinetiQ (Toft, 2013), consists of polysulfone tubes lined with zeolite 5Å molecular sieve as the CO₂ adsorbent being used as a proof of principle. The study was to be a prelude to the development of a polyethyleneimine impregnated mesoporous silica (MCN41/PEI) in place of the molecular sieve (Fig. 8). The containment of the MCN/PEI within the tubes overcomes the handling difficulties of the fine powder and the conductive carbon-coated outer wall of the tube provides an elegant means of resistive heating for thermal desorption of the CO₂.

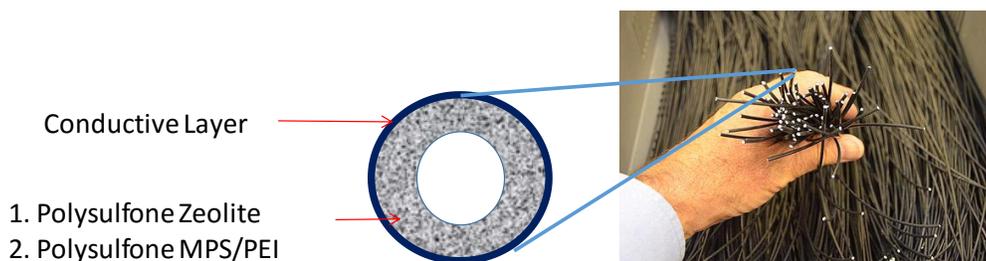


Figure 8. Carbon-coated hollow tubes formed from adsorbent/polysulfone mixture with a diagram of the cross-sectional of a tube.

In laboratory scaled experiments, CO₂ concentrations in the range 0.15-3.0% were used for the evaluation, bearing in mind that the RN continuous exposure levels are set at < 0.7%. Desorption was achieved by heating 100 – 150 °C and the application of a vacuum (0.03 mbar) and the CO₂ absorption appeared to be reversible. However, the desorption temperatures may be a little excessive for the MCN41/PEI and hot spots may be difficult to avoid. Thus there is a potential for thermal decomposition. It remains to be seen how the absorption and desorption characteristics of the zeolite compare with the MCN41/PEI.

Cryogenics

Liquid oxygen (LOX) is an integral part of AIP systems and conversion of the liquid into the gas requires a heat-exchanger as part of the MESMA (Module d'Énergie Sous-Marine Autonome) system for a Rankine cycle steam turbine. Using the heat-exchanger, submarine air can be cooled to -150 °C through the LOX heat-exchanger. At this temperature, 0.7% CO₂ (continuous exposure level) will solidify. In this process, the air first needs to be pre-cooled in order to remove the moisture to avoid producing a dry atmosphere and the accumulation of ice in the cryogenic cooler. The system has an additional advantage whereby volatile organic compounds (VOCs) and refrigerant gases are also removed along with the CO₂ (Bry-Peel et al., 1994).

These low temperatures can also be generated through the use of a pulse tube refrigerator in the case of nuclear-powered submarines where LOX is unavailable and energy supply is plentiful (Jouandon, et al., 2013).

The major advantages of the cryogenic systems is the absence of consumables and low maintenance compared with molecular sieve (for CO₂ removal) replacement every two patrols (and charcoal filter (removal of VOCs) replacement, twice during a patrol in nuclear-powered submarines (Jouandon et al., 2013). In the case of the MESMA AIP system where the hotel loads are critical, the energy is provided by the liquid oxygen evaporation and additional electrical energy is only required to drive a fan.

Non-Regenerative CO₂ Removal

Soda Lime

Soda lime has been the mainstay of CO₂ removal in submarines for a century. It is inexpensive effective and relatively non-hazardous. Lithium hydroxide has also been favoured by some navies (USN, Germany) over soda lime but it is more corrosive and a much greater health hazard than soda lime. However, it has a weight advantage and less susceptible to pressure and temperature effects than soda lime.

Carbon dioxide absorption units (CDAU) generally use soda lime packaged in 4 L canisters and connected to a manifold through which submarine air is circulated with the aid of a dedicated fan. Several canisters are deployed in parallel depending on the crew numbers and the size of the canisters. In the case of the Swedish navy, soda lime granules are used loose form within the CDAU. The unit is emptied and manually filled from 20 L commercial containers.

German submarines use a Draeger CDAU where the lithium hydroxide is deployed in trays within a metal cabinet through which the submarine air is passed. The trays are stacked as in an oven or refrigerator. In the case of the USN nuclear-powered submarines lithium hydroxide is reserved for emergency use and until recently it was supplied in 4 L sealed metal cans. As such, the granules were to be spread over bunks and floor of the accommodation areas for CO₂ removal. The procedure was a hazard in itself as the lithium hydroxide dust is a severe respiratory irritant.

The CDAU technology remained unchanged for a century since the development of soda lime (Mazurek, 2005). However, about 10 years ago there were two developments in the packaging of soda lime and lithium hydroxide which affect the way these materials are used. Molecular Products plc (UK) were able to increase the density of packing in their soda lime canisters by snowstorm filling in a self-contained CDAU for DISSUB (disabled submarine scenario) use. Powered by an internal battery driven fan, the soda lime (7.8 kg) reaches near capacity in approximately 4 h at 20 °C for an influent CO₂ concentration of 2 % and a flow rate of 19 m³ h⁻¹ (Fig. 9; Clarke et al., 2005). In addition to the DISSUB application the unit has potential to supplement the existing CO₂ removal systems in areas of poor ventilation and high personnel concentration such as the control room.



Figure 9. CASPA Self-Contained CDAU.



Figure 10. DSTO Relocatable CDAU.

It was for this purpose that a relocatable CDAU was developed by DSTO. Due to presence of additional personnel in the control room, CO₂ levels were at times, elevated. The relocatable CDAU simply consisted of an MP Sofnalime canister fitted with a commercial cooling fan designed to be connected to the 110 V supply in the submarine (Fig. 10; Hanhela et al., 2011). It represented a simple and inexpensive solution to an important problem and gained immediate acceptance by the fleet.

Encapsulated Lithium Hydroxide

By encapsulating lithium hydroxide into a polymer binder to form a sheet, Micropore ExtendAir were able to eliminate the hazard of handling lithium hydroxide while retaining the benefit provided by the sorbent (McKenna and Oddo, 2003). Initially produced in roll form, with channels to facilitate air flow (Fig. 11) the soda lime version was designed as a drop-in replacement for rebreathers used by scuba divers.

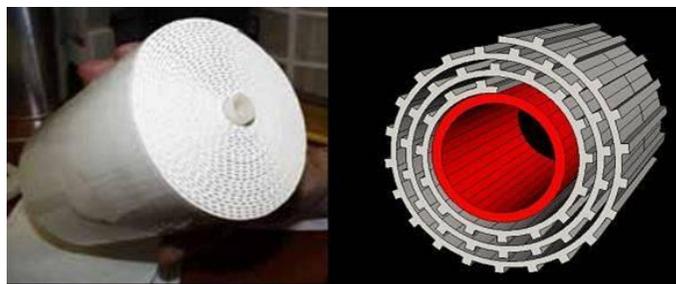


Figure 11. Micropore ExtendAir cartridge.

By unravelling the roll and allowing the sheet to hang in a CO₂ rich atmosphere, the lithium hydroxide impregnated material was found to be a superior and less hazardous alternative to established method of spreading lithium hydroxide granules on the floor and bunks of the submarine (McKenna and Oddo, 2003).

Since the introduction of the ExtendAir at SAMAP in 2003 the product has gained acceptance for passive CO₂ removal in the form of sheets for DISSUB applications.

Hydrogen and Carbon Monoxide Removal

The extensive use of lead-acid batteries in both nuclear- and diesel-powered submarines may give rise to an explosive hazard as a result of the generation of hydrogen gas during battery charging. Nuclear-powered submarines also generate hydrogen as a by-product of oxygen production from the electrolysis of water. The hydrogen is generally vented to the sea water. In the case of the diesel-powered submarines most of the hydrogen is removed by ventilation during snorting or surface running.

Carbon monoxide is a toxic product of incomplete combustion commonly arising from a fire or engine exhaust. It is a particular hazard in diesel-powered submarines where there is a potential for engine exhaust leaks.

Both hydrogen and carbon monoxide can be removed from the submarine atmosphere by catalytic oxidation. The hazard and its removal was recognised in WWII submarines, many of which were fitted with “catalytic burners” using an electrically heated (60 – 120 °C) palladium/alumina catalyst granules contained in nickel mesh envelopes (Fig. 12). The post-war Oberon class submarines were fitted with many such small units throughout the boat and relied on the air circulation system for exposure to the catalysts (Mazurek, 2005).



Figure 12. Hydrogen/carbon monoxide catalytic burner used in Oberon class submarines.

The more recent generation of Collins and Upholder (Victoria) class submarines used a more active catalyst (Pt/Pd/SnO₂) for CO/H₂ removal which was active at ambient temperatures. The Collins class submarine is fitted with one such “burner” in the engine room (Mazurek, 2005). In a system built by Atmosphere Control International, Corac Plc (formerly Wellman, CJB Engineering) air is driven by an electrical fan, through a charcoal filter to remove VOCs, before passing over the catalyst (Fig. 13).

Although hydrogen and carbon monoxide oxidation is uncomplicated there are many other air contaminants that can react with the catalyst to produce toxic products. For example, ethanol undergoes partial oxidation to produce an irritant (acetaldehyde), on both Pt/Al₂O₃ and Pt/Pd/SnO₂ catalysts and trichloroethane solvent vapour forms the more toxic product, vinylidene chloride on contact with Pt/Pd/SnO₂ (DeNola et al., 2007). However the fluorinated refrigerants R22 and R134a appeared to be unaffected under the conditions studied

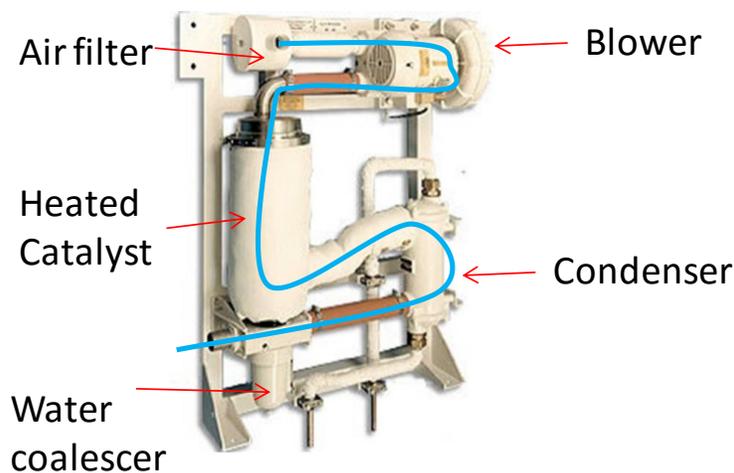


Figure 13. Low temperature CO/H₂ burner, Atmosphere Control International, Corac Plc (formerly Wellman, CJB) www.naval-technology.com.

VOC Removal

In newly built submarines the major source of VOC air contaminants is off-gassing of materials with paint being a principal source. The most common means of VOC removal from the submarine atmosphere is by activated charcoal filters. However, as mentioned above, some VOCs are unintentionally, but beneficially affected by the CO/H₂ catalysts (eg. toluene, hexane and acetone). Oxidation catalysts formed from gold nanoclusters are intended for oxidation of carbon monoxide, hydrogen and VOCs (Santiago et al., 2013) at room temperature, fulfilling the function of both the charcoal filter and the CO/H₂ burner. As previously indicated, the danger with catalytic oxidation of VOCs is the potential for the formation of toxic by-products. Although the gold catalyst has the potential to be an effective broad spectrum catalyst, to date, only one common VOC, formaldehyde, has been studied on the gold catalyst.

In contrast to the use of catalysts the appeal of the cryogenic removal of CO₂ with the added benefit of VOC removal (Jouandon et al., 2013) has the advantage of a physical process without the potential hazard producing toxic compounds.

Air Quality Monitoring

Submarine Escape Monitor

Arguably the most critical period for submarine atmosphere monitoring is in a DISSUB situation when a number of toxic air contaminants could be present. However, the concentrations of oxygen and carbon dioxide are of fundamental importance for survival. In 1994 the RAN sought to replace the existing procedure of using colorimetric tube (eg Draeger) for monitoring oxygen and carbon

dioxide in a DISSUB situation with continuous gas sensor monitoring (DeNola et al., 2007; Hook and Hanhela, 2010). The specifications for such an instrument were:

1. capacity for continuous measurement of O₂ and CO₂ at pressure of up to 7 bar;
2. battery powered using readily available dry cells with an endurance of 7 days;
3. portable;
4. waterproof case;
5. shock resistant (drop test 1m).

A survey of commercial O₂ and CO₂ monitors revealed only one instrument which fulfilled most of these requirements, the Environmental (Geotechnical) Instruments, Anagas hyperbaric O₂ and CO₂ monitor (Environmental Instruments, 1995) (Fig. 14). However, the instrument case appeared to be insufficiently robust and the operating procedure was far too complex for the intended use. As a result, it was decided that an O₂ /CO₂ monitor meeting all of the above requirements, should be developed in conjunction with a reputable instrument company experienced in hyperbaric air monitoring. To this end, funding was provided to Analox (formerly Scottish Anglo) plc, UK to produce a prototype instrument to the required specifications. In order to conserve battery life, air sample introduction was by diffusion membranes rather air sampling pumps and an electrochemical oxygen sensor was used instead of a paramagnetic sensor, initially selected for its longevity. A small pressure vessel was built at DSTO specifically for the evaluation of the prototype variants under hyperbaric conditions. Successive modifications to the instrument were tested under pressure to ensure proper pressure corection. An earlier version of the instrument is shown in Fig. 14. After many years of marketing and minor modifications by Analox, the Submarine Escape Monitor is now deployed by most submarine fleets (Fig. 15).



Figure 14. Analox (left) and Anagas hyperbaric O₂ and CO₂ monitors.



Figure 15. Analox Submarine Escape O₂/CO₂ monitor, current model.

Portable CO Monitors

Tuneable Diode Laser

Because of its high toxicity and ubiquitous presence, carbon monoxide is a target gas for submarine air monitoring. Due to the wide range of exposure limits, 200 ppm and 10 ppm for short-term and continuous exposure, respectively (Dibben and Nicholson, 2000), a large dynamic linear instrument response range is required. Most industrial CO monitors utilise electrochemical sensors which are subject to interference from hydrogen. This is generally acceptable as there is insufficient hydrogen in most industrial environments to affect the measurements and some monitors are able to compensate for up to 500 ppm hydrogen. However, in the case of diesel-electric submarines which use lead acid batteries, it is not unusual for hydrogen concentrations to exceed these levels. To overcome this problem infrared optical sensors have been deployed in submarines. Such instruments with a CO detection limit of <30 ppm are bench-top or rack-mounted whereas a small portable instrument is best suited for submarines where there may be localised high CO concentrations as a result of a fire or engine exhaust leaks.

Inexpensive tuneable diode lasers, used in telecommunications, offer low power consumption, high intensity infra-red light source operating in the near IR and hence are ideally suited as a portable battery-powered CO monitor. A prototype instrument based on this technology was developed by Southwest Sciences, Santa-Fe, NM, USA and funded by DSTO (Fig. 16). The instrument had a linear response from 0 – 300 ppm and a sensitivity of ± 1 ppm when used in conjunction with a multiple pass optical cell with a path length of 9 m. In a 15 day sea trial aboard a Collins class submarine, CO readings from the instrument were consistent with the results obtained from a Hartmann & Braun Uras 10e laboratory benchtop non-dispersive infra-red instrument (Fig. 17; Hanhela et al., 2011).

The development of a pre-production version of the instrument was planned for shock testing and acceptance trials, however the project has languished for lack of resources.

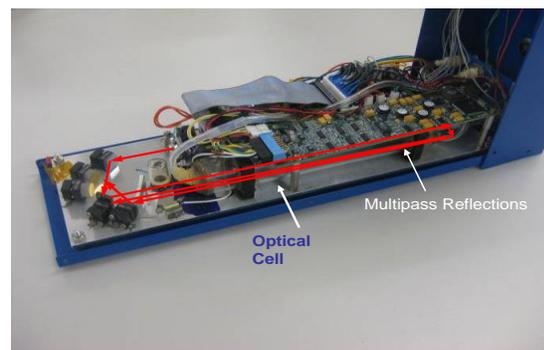
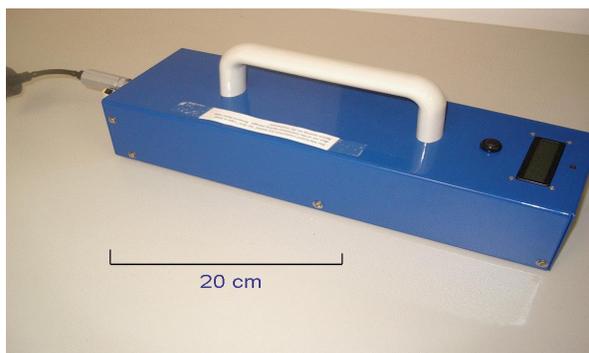


Figure 16. Southwest Sciences, prototype, portable CO monitor.

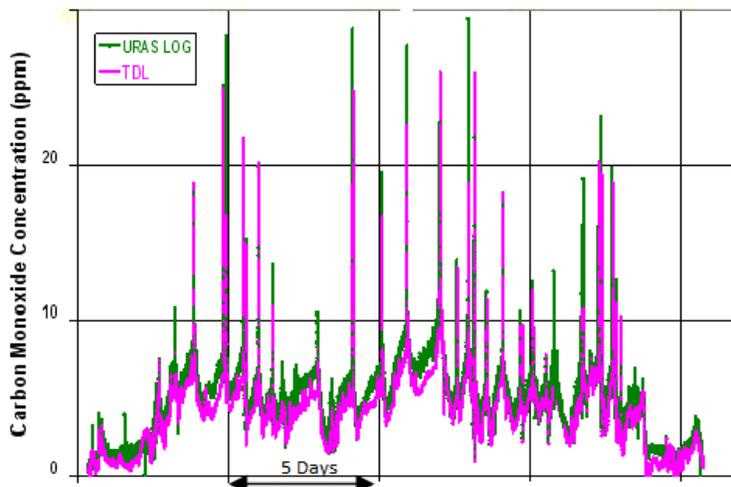


Figure 17. Comparison of CO measurements from the prototype TDL CO monitor (purple trace) and the Hartmann & Braun Uras 10e laboratory benchtop Non-Dispersive Infra-Red instrument (green trace).

Tuneable Quantum Cascade Laser (QCL)

The development of a tuneable quantum cascade laser (QCL) based CO monitor was reported at SAMAP 2009 as a result of a collaborative project between Analox Plc and TDL Sensors, UK (Brown and Holdsworth, 2009; Lewis et al., 2013). The prototype instrument was designed as a bench-top unit due to the size of the optical, single pass, sample cell (Fig. 18). Unfortunately the lack of portability restricts the use of the instrument for submarine atmosphere.

The main advantage of the QCL is the mid-infrared operational wavelength where there is a strong fundamental vibration absorption band at approximately 2180 cm^{-1} ($4.6\text{ }\mu\text{m}$) compared with the near-IR for the TDL (4228 cm^{-1} or $2.365\text{ }\mu\text{m}$) which is a much less intense absorption band (Fig. 19). This results in a high sensitivity, linear response (10 – 200 ppm) and low signal-to-noise ratios ($\pm 0.25\text{ ppm}$) without resorting to long sample path lengths to enhance instrument sensitivity. The major disadvantage lies in the expense of the QCL, representing about half the cost of the instrument. However, the cost of QCLs are expected to decrease in the future which should make technique commercially viable.

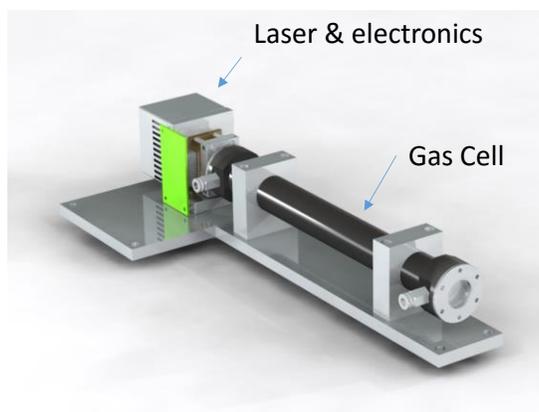


Figure 18. QCL and cell used in the Analox prototype CO monitor (Brown and Holdsworth, 2009).

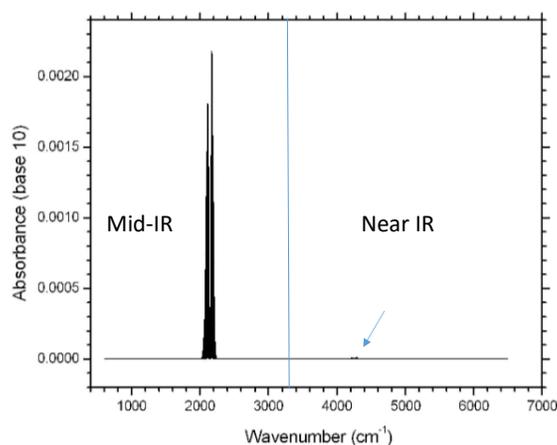


Figure 19. IR absorption bands of CO in the mid-IR and near-IR spectral region (Brown and Holdsworth, 2009)

Los Gatos Research IR Spectrometer

The Los Gatos Research (LGR) off-axis Integrated Cavity Output Spectroscopy (ICOS), cavity-enhanced absorption technique offers an IR tuneable diode laser instrument operating in the near-IR region of $6700 - 6000 \text{ cm}^{-1}$ ($1.5\text{-}1.65 \text{ }\mu\text{m}$). The ICOS LGR multiple pass cell provides an effective path length $> 2500 \text{ m}$ with environmental CO sensitivity of 36 ppb (Baer et al., 2002; Niu et al., 2009). An unexpected requirement of this system is the operation at reduced pressures (75 mm Hg) in the cell which requires the use of a vacuum pump, creating a source of unwelcome noise in a submarine.

A degraded version using a TDL and a multi pass cell with a detection limit <1 ppm has been evaluated alongside the ICOS instrument and found to satisfy the detection, dynamic range (1 – 130 ppm) and stability requirements (7 days without calibration) for submarine use (Niu et al., 2009). The instrument is intended as a replacement for the existing and obsolete IR monitor used in conjunction with the CAMS in USN submarines.



Figure 20. Los Gatos carbon monoxide analyser.

Analysing Interferometer for Ambient Air (ANITA)

A Fourier transform infra-red spectrometer operating between 600 and 3600 cm^{-1} has been developed for the International Space Station with a capability of analysing 32 trace gases with ppm or sub-ppm detection limits including low boiling alcohols, aldehydes, ketones, aromatic hydrocarbons, refrigerants, siloxanes, ammonia, carbon dioxide, carbon monoxide and methane. (Stuffer, et al., 2007). The ANITA I spectrometer consists of two modules with one containing the gas cell and the FTIR system while the electronics and gas flushing system is located in the other module. The combined weight of the modules is 50 kg with a volume of 100 L and a power consumption of ~ 200 W (Fig. 21). A laptop computer is also required to interface with the equipment.

A more recent version (ANITA II) consisted of a single module with a weight of 30 kg, a volume of 50 L and a power consumption of 150 W with the computer and monitor included in the module. The technological advance of this system is not only in the robust hardware but also in the algorithms used to identify and quantify the mixture of compounds from a myriad of overlapping spectra.



Figure 21. ANITA FTIR analyser.

Sionex Micro Gas Chromatograph

Gas chromatography (GC) is well established as a separation and quantification technique for complex mixtures of volatile compounds. The technology has been previously used as a central atmosphere monitor aboard US and RN submarines (Mazurek, 2005). Most GCs require a source of inert carrier gas (eg. nitrogen or helium) and in the case of the commonly used flame ionization detector, hydrogen and high purity air are also required.

The Sionex GC-DMS (Microanalyzer) combines a pre-concentrator, a rapid and a standard selective GC column (eg. 10 m RTX-200 Restek) that operates at high temperatures, an air carrier gas recirculation and filtration loop and a differential mobility spectrometer (DMS) and an optional ion mobility spectrometer (IMS) ion filtration and detection system (Fig. 22). The instrument is operated through a standard laptop computer. Unlike most other GCs the Sionex does not require consumable gases (Limero and Cheng, 2007).

The relatively low sensitivity of DMS (and IMS) to low molecular weight saturated hydrocarbons (Luong et al., 2006) has both advantages and disadvantages in diesel submarine air monitoring. The advantages lie in the monitoring of low molecular weight air contaminants such as formaldehyde, acetaldehyde, benzene, toluene, xylene, chlorinated hydrocarbons and refrigerant gases while reducing the interference from hydrocarbons (Limero and Cheng, 2007). The disadvantage is that hydrocarbons such as the butane isomers used as propellants (DeNola et al., 2011) and associated with illicit spray can products, would be difficult to detect.

The instrument is designed to operate in both a survey (Fig. 23) and quantification (single ion) mode providing a flexibility of routine quantification of selected air contaminants as well as scanning for other contaminants. It has been successfully used in spacecraft since 2002 and it has been trialled aboard RN nuclear-powered submarines. However, the ubiquitous presence of diesel fuel vapour in conventionally powered submarines may require some changes to the pre-concentrator and operating conditions in order to avoid retention of high boiling hydrocarbons on the column.

Seemingly, the Sionex Microanalyser has all the necessary attributes for submarine air monitoring:

1. stable (> 1 year between calibrations),
2. small,
3. low power requirement,
4. no consumables and
5. relatively inexpensive.



Figure 22. Sionex Microanalyser

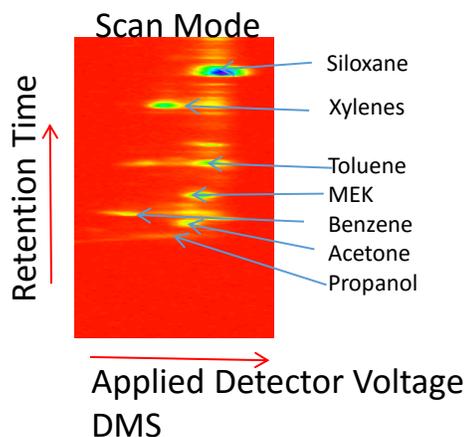


Figure 23. Identification of contaminants in scan mode (Limero and Cheng, 2007).

Femto Scan GC-IMS

Developed under contract to the US Army, the Femto Scan Environmental Vapor Monitor is a GC-IMS, based on the Smiths Detection (Graseby Dynamics), Chemical Agent Monitor (Fig. 24) and in principle is similar to the Sionex Microanalyser. It is fully portable with a built-in battery and a small LCD display for response indication. When coupled to a notebook computer operating parameters can be set and chromatograms displayed.

The automated vapor sampling system uses pneumatically controlled carrier gas and analyte gas flows for sample introduction while separation is via a 5m fast, micro-machined column. Like the Sionex instrument, the Femto Scan can be used in a survey mode or selective ion mode for quantification.

The Femto Scan has never been trialled in a diesel electric submarine but using a test mixture of aromatic and aliphatic hydrocarbons to simulate diesel fuel vapour, both benzene and toluene were identified in the survey mode (Gan, 2000). However, high boiling hydrocarbons present in commercial diesel fuel vapour were difficult to purge from the column. Thus for submarine use some modification would need to be incorporated into the air sampling system in order to avoid chromatographing these compounds.

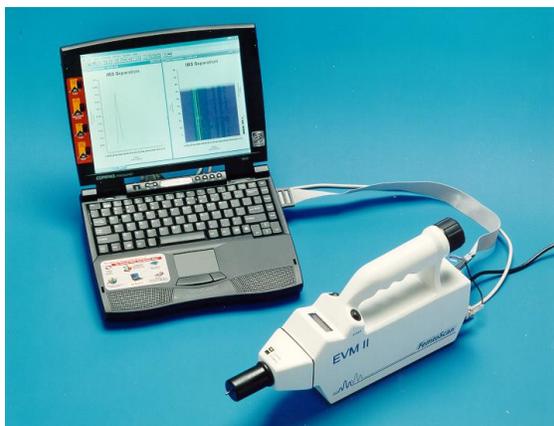


Figure 24. FemtoScan EVMII GC-IMS



Figure 25. Smiths Detection, UK (Graseby Dynamics) Chemical Agent Monitor.

Central Atmosphere Monitoring System (CAMS)

A reliable real-time central atmosphere monitoring system (CAMS) came of age during the 1970s with the installation of a magnetic sector based mass spectrometer in US nuclear-powered submarines. Developed by Perkin-Elmer Corp. It was the culmination of a long process of trialling six generations of analytical instruments for submarine atmosphere monitoring during the 1960s (Wyatt, 2000, 2001). Initially, infra-red (NDIR) was used to monitor carbon monoxide, hydrocarbons and refrigerant gases. In order to achieve the necessary detection limits, long path length (120 cm) cells were used, followed by high pressure (7 atm) cells. Due to poor reliability and insufficient sensitivity, the IR instruments were replaced with an automated gas chromatograph which could analyse a wide range of air contaminants. Again, the system was plagued with reliability problems and finally, in desperation, a relatively new type of instrument at the time, a mass spectrometer, was successfully evaluated in sea trials and prototype analysers were installed aboard two submarines.

The CAMS I was a single-focusing magnetic sector mass spectrometer, with a mass range of 2 -135 amu was hard-wired for the detection of 8 gases including life gases and refrigerants with a detection limit of 10 ppm. Carbon monoxide was measured by infra-red. Because of its limited resolution and hardware, it was unable to measure some trace hydrocarbons of interest and could not be easily retuned for other species. Consequently, a more sophisticated double focusing mass spectrometer (CAMS II) was developed with a scanning capability. Designed to analyse 25 gases it had a mass range of 2 -300 amu with a detection limit of 1 ppm. However, the improved capability and complexity came with an increased price and higher maintenance cost (Nui et al., 2007).

As a result of the successful development of the CAMS, a smaller and slightly less capable version of the CAMS-II instrument was developed for use in diesel-electric submarines and presented at the SAMAP conference held in Adelaide in 1994 (Koslin and Carson, 1994; Shadle et al., 1994). The Mini-CAMS weighed 160 kg and stood 1 m high (Fig. 26). Consisting of a magnetically scanning single focus mass spectrometer. It was designed to analyse 25 gases over a mass range of 1 -160 amu with a detection limit of 1 ppm, an accuracy of 5% and a precision of 3%. It was a highly stable

instrument requiring calibration and overhauls with 2 year intervals. Despite these advantages the Mini-CAMS was not a commercial success mainly due to the high cost.

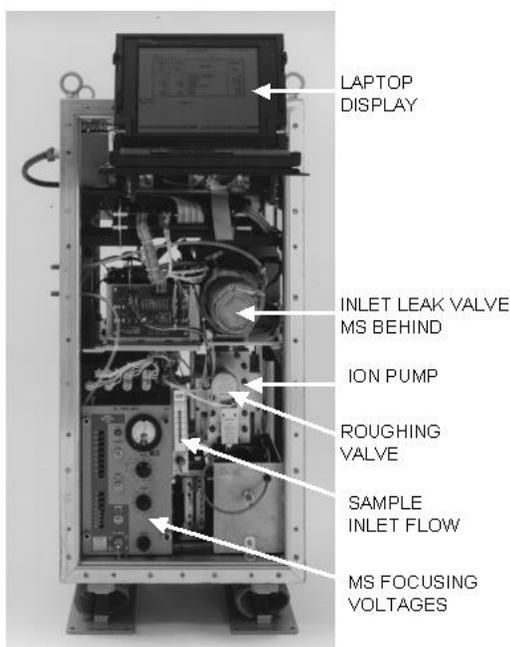


Figure 26. Mini-CAMS central atmosphere monitor for diesel-electric submarines.

As a cost-cutting measure the new version of the CAMS (CAMS IIA) was developed in 2012 which was a compromise between the CAMS I and II. The instrument has a single-focusing magnetic sector analyzer which is simpler and cheaper to manufacture and to maintain than the CAMS II, while still capable of analysing 25 gases (Nui et al., 2007).

Bio-Monitoring

Submarine atmosphere monitoring is a good indicator acute exposure to air contaminants in the case of equipment malfunction or fire. Multiple point real-time monitoring also serves to identify the likely source of air contamination for remedial action. This is one of the reasons why atmosphere monitoring is favoured over personnel exposure monitoring used in industry. However, low dose, chronic exposure, in addition to inhalation, is likely to involve dermal exposure as well as contributions from diet. For example, exposure to diesel fuel is likely to originate from both inhalation of diesel vapour and dermal exposure to the liquid fuel (Hanhela et al., 2007; DeNola et al., 2009). Exposure to polycyclic aromatic hydrocarbons (PAHs) may arise from inhalation exposure to tobacco smoking, diesel fuel vapour and diesel exhaust as well as dermal exposure to fuel and oil. There is also a potential for dietary contribution bearing in mind that

barbequed meat, sausages and smoked fish contain PAHs (Bradley et al., 2013). The limitations of inhalation exposure have been recognized by the European Commission (Bolta and Thier, 2006) and in 2000, 25 substances were listed for skin absorption.

Biological exposure limits were first introduced in Germany in 1981 by the Deutsche Forschungsgemeinschaft (DFG) as Biologischer Arbeitsstoff-Toleranz-Wert (BAT) and by the American Conference of Government and Industrial Hygienists (ACGIH) in the USA as Biological Exposure Indices (BEI) in 1984 (Bolta and Thier, 2006; Drexler et al., 2008). As of 2015, 71 compounds have been assigned BATs, the peak ceiling values due to the acute toxicity of the compounds (Deutsche Forschungsgemeinschaft, 2015). BEIs however, represent average concentrations corresponding to exposure at the Threshold Limit Value (TLV) air concentrations (Jakubowski and Trzcinka-Ochocka, 2005).

The media of choice for monitoring the target substance or its metabolites are usually blood, urine and exhaled breath (Bolta and Their, 2006). In the pharmaceutical industry, saliva has been extensively used for the biomonitoring of drugs and their metabolites (Haeckel and Hänecke, 1996) but for some reason it has found little favour in occupational and environmental biomonitoring (Smolders et al., 2009). Like exhaled breath, saliva offers a non-invasive means of biomonitoring which is essential to subject acceptance and participation. Results from both techniques can be related to blood/serum concentrations which is the gold standard for biomonitoring (Haeckel and Hänecke, 1996; Béliveau and Krishnan, 2000).

Exhaled Breath Monitoring

The first reported investigation of exhaled breath (EB) measurement for volatile compounds was published by 1971 (Pauling et al.). Samples consisting of 10 -15 breaths were collected in a stainless steel tube, cooled in dry ice bath and analysed by flame ionisation gas chromatography. The aim of the study was to illustrate the number of VOCs present in EB. However, the first human exposure measurements from EB was carried out on USN submariners in 1984 (Knight et al.) in order to prioritise submarine air contaminants for toxicological effects. Breath samples were collected in sorbent tubes and analysed by GC-MS. An average of 468 VOCs were found to be present in each sample. At the time smoking was commonly practiced aboard submarines and all but one subject were smokers. As the samples were taken aboard the submarine there was a possibility of contamination from submarine air. This is a significant problem of EB sampling in an enclosed and contaminated atmosphere.

The EB sampling procedure is simplified in ambient air. Such a study was conducted on jet fuel exposure of ground crew at USAF bases (Lemasters et al., 1997). Sampling was carried after three consecutive working days, one hour after the last 8h shift. The subjects breathed zero grade air while exhaling for 20 min into a sample collection apparatus containing a Tenax sorbent tube. In a similar study evacuated 1 L canisters were used for EB sampling (Pleil et al., 2000) with the subject expelling the tracheal dead volume prior to sampling. The mean solvent and fuel VOC concentrations in the EB were found to be very low (< 25 ppb) as were the air concentrations (< 6 ppm) unlike the submarine scenario.

Applying a similar methodology to RAN submariners (DeNola et al., 2007; 2009) EB samples from RAN submariners were taken dock-side as soon as the submarine tied up. This corresponded to approximately 1 h between exposures to the submarine atmosphere and sampling during which the subjects were breathing ambient air. Breath samples were collected in 1 l canisters as reported by Pleil et al. (2000) using a filter in the mouthpiece to reduce contamination by saliva (Fig. 27). Sampling was self-administered under supervision of the investigators and the samples were analysed retrospectively by GC-MS at DSTO.



Figure 27. Self-administered exhaled breath sampling using an evacuated canister.

Comparisons between the reconstructed chromatograms of submarine air and EB samples (non-smoker) showed an overwhelming presence of diesel hydrocarbons in the EB samples (Fig. 28). Hydrocarbons in submarine air tend to be biased towards the higher boiling components due to the evaporation and ventilation of the volatile components and the contribution of lubricating oils. Hence the differences between the diesel fuel head-space composition and the submarine atmosphere sample (Fig. 28). The other abundant compound in the EB sample is refrigerant gas R-22 which is present in the submarine atmosphere at relatively high concentrations due to leakage from refrigeration units (DeNola et al., 2007, 2009). Acetone and isoprene in the EB sample are the products of human respiration while ethanol dimethyl sulfide (DMS) and limonene are associated with foods and flavours (Pleil et al., 2000). Methyl chloride was also present being a common volatile halocarbon present in the environment from numerous sources (Yokouchi et al., 2000).

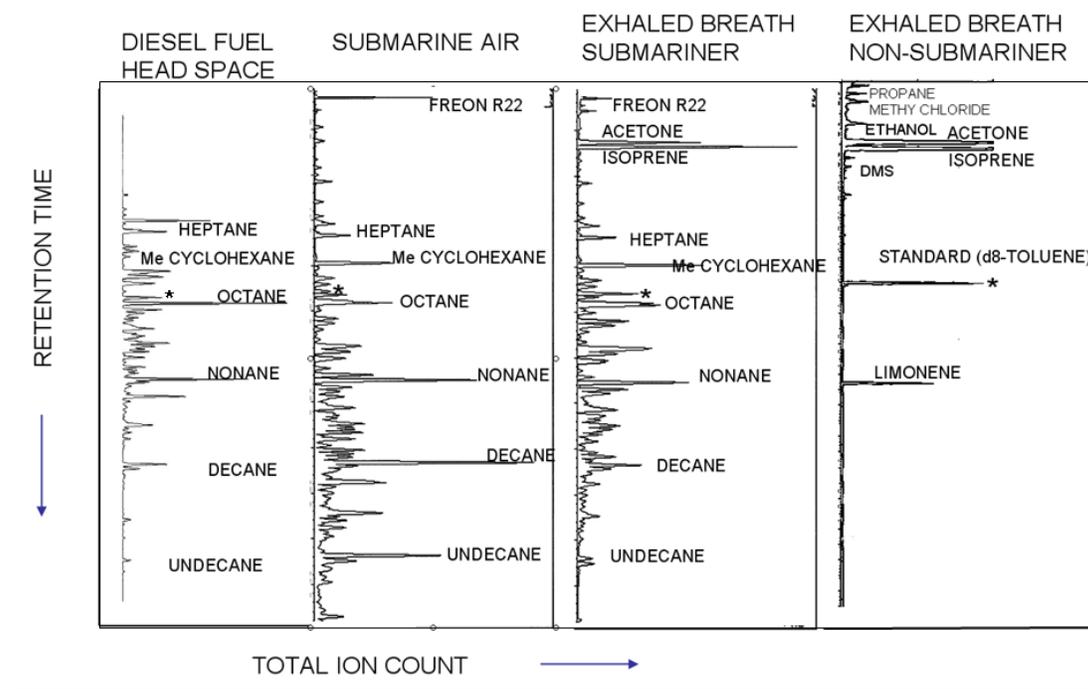


Figure 28. Comparison of chromatograms from a sample of an submarine diesel fuel head-space, OBERON submarine air and an EB sample from a submariner after submarine exposure and an EB sample from a non-smoker submarine before exposure to a submarine environment (note: acetone and isoprene are products of human respiration, while ethanol, dimethyl sulfide (DMS) limonene is commonly associated with foods and flavours). *d8-toluene was used as internal standard.

A major benefit of EB is the ability to differentiate individual exposures and the effects of elimination of air contaminants from the body during the time spent in cleaner areas of the submarine. For example, the after compartment of the COLLINS class submarine contains the engine and the propulsion system and hence there is a major contribution from diesel fuel vapour and lubricant oil vapour to air quality compared to the forward compartment. This was manifested in the in C₉ – C₁₂ hydrocarbon air concentrations (DeNola et al., 2009). These differences were reflected in the EB samples from submariners serving in those compartments (DeNola et al., 2009). By contrast, a higher level of diesel and lubricant hydrocarbon air contamination occurred throughout the older OBERON class submarines as indicated by the air and EB sample analyses (DeNola et al., 2009).

EB data is generally semi-quantitative because elimination of the air contaminants from the body occurs rapidly (initially) and in practice it is difficult to determine the interval between exposure and breath sampling. However, the rate of elimination is logarithmic and depending on the partition coefficients of the contaminants between air and blood, muscle tissue, fatty tissue and other organs (Wallace et al., 1993; Béliveau and Krishnan, 2000) the decay in EB concentrations of some VOCs can be measured over a period of days. For example, EB samples from one OBERON

submariner, showed detectable levels of heptane, decane and undecane for a period of up to 38 h after 62 h of continuous exposure to the submarine atmosphere (Fig. 29; DeNola et al., 2009). This was consistent with anecdotal evidence from Oberon submariners that the submarine body odour persisted for many days after submarine deployment.

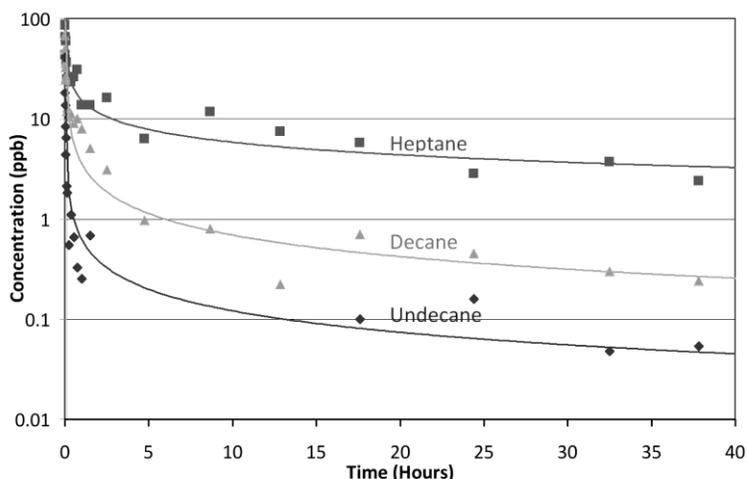


Figure 29. Exhaled breath decay in heptane, decane and undecane from a subject exposed to a submarine atmosphere for 62 h at 13.5 ppm total VOCs excluding refrigerant gas.

Saliva Biomonitoring

Polycyclic aromatic compounds (PAHs) are a ubiquitous group of compounds associated with combustion but are also present in hydrocarbon fuels and lubricants. Some have been classified as probable and possible carcinogens (Scherer, 2005). The engine rooms of diesel-electric submarines are commonly contaminated with PAHs from diesel exhaust, fuel and lubricating oils which are present in the atmosphere and on surfaces (Hanhela et al., 2007). Although exposure to diesel particulate matter (DPM) is monitored in RAN submarines, dermal exposure is ignored. However, dermal exposure to PAHs has been taken into consideration in some occupations such as the aluminum smelting industry where baked carbon anodes, formed from coal-tar pitch/petroleum coke are in the electrolysis of molten cryolite (Vanrooij et al., 1992; Di Corleto, 2010), coke oven workers (Vanrooij et al., 1993), shale oil processing workers and asphalt roof and asphalt road workers (Väänänen et al., 2005; McClean et al., 2007; Fustinoni et al., 2010). In these cases dermal absorption was considered to be an important pathway for PAH exposures. Biomonitoring focused on the urine metabolite biomarker, 1-hydroxypyrene.

Saliva provides an alternative means to blood and urine for biomonitoring of PAHs. It has the advantage of being non-invasive and like breath sampling for blood alcohol it is widely used for the detection of illicit drugs by law enforcement agencies. Therefore this technique is most likely to be accepted by submariners. With the aim of demonstrating proof-of-concept saliva samples (approx. 2 ml) were taken from a small cohort of smokers and non-smokers and analysed by HPLC for common PAHs (US EPA, 1993). The results showed that the method was sensitive to background

levels of PAHs in saliva and significant differences in PAH concentrations were found between the two cohorts (Fig. 30; Bradley et al., 2013).

The technique is yet to be applied to submariners to determine if submariners assigned to mechanical maintenance duties show a difference in the body burden of PAHs compared with a control group.

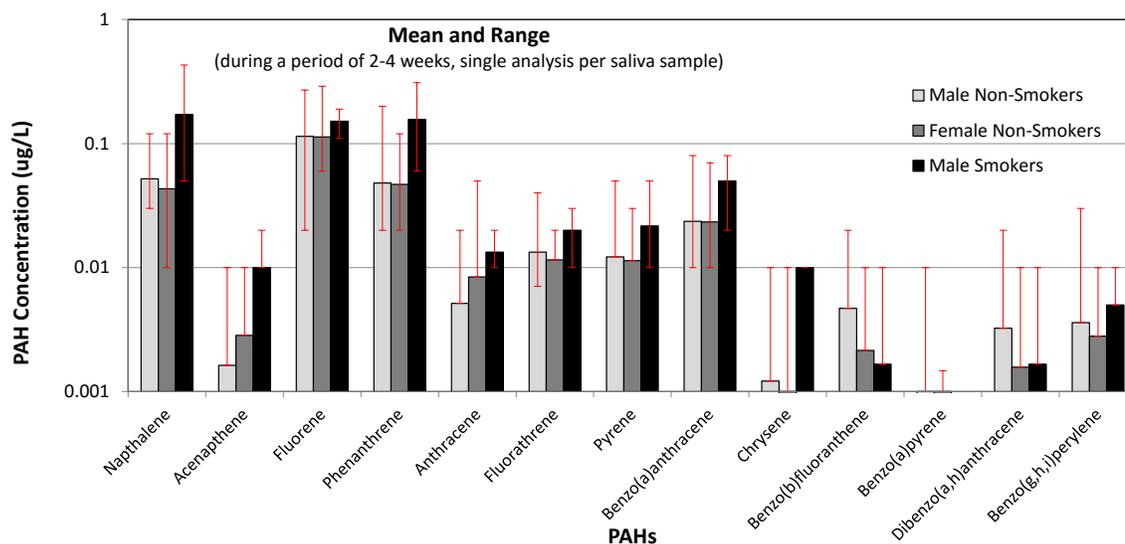


Figure 30. PAH concentrations in saliva samples from smokers and non-smokers as determined by HPLC using a fluorescence detector.

Regulations

Exposure to Diesel Particulate Matter (DPM)

Diesel exhaust is probably the most studied pollutant in the urban environment consisting of a complex mixture of 100 organic compounds, including n-alkanes, n-alkanoic acids, benzoic acids, benzaldehydes, PAH, oxy-PAH, steranes, pentacyclic triterpanes and azanaphthalenes. (Rogge et al., 1993).

In 2003 DSTO recommended to the RAN that continuous exposure limits to diesel particulate matter (DPM) should not exceed 200 mg/m³ (Gan and Mazurek, 2003) this was based on existing and impending international regulations although at that stage there were no regulatory exposure limits for DPM in Australia. The recommendations were adopted by the RAN in 2004 on the insistence of the squadron medical officer. Thus the RAN became the first navy to specifically regulate DMP exposures aboard submarines.

In Germany, maximum exposure limits for general occupational exposures had been enforced at 200 mg/m³ DPM since 1993 (Dahman and Bauer, 1997). While the US Mine Safety and Health Administration (MSHA) metal/non-metal mine rule established an interim DPM limit of 400 µg/m³

to be observed from July 2002, with the final limit of 200 $\mu\text{g}/\text{m}^3$ DPM or 160 $\mu\text{g}/\text{m}^3$ total carbon (assuming 80% total carbon in DPM), by January 2006, to be phased in over 5 years.

In 2012 the International Agency for Research on Cancer (IARC) classified diesel exhaust as “carcinogenic to humans” based on evidence for increased risk to lung cancer (IARC, 2012). While in Australia the government of New South Wales adopted the MSHA rules in 2013 for mines (NSW Government, 2013).

Exposure to Diesel Fuel Vapour

Continuous exposure to “Total Organics” adopted by the RAN from the RN submarine exposure levels were established at 7.5 ppm (Dibben and Nicholson, 2000; Gan and Mazurek, 2005). In diesel submarines the main constituent of organic vapours is diesel fuel. In 2002 the American Conference of Government and Industrial Hygienists (ACGIH) reduced the 8h time-weighted average exposure to diesel vapour from 100 ppm to 15 ppm (ACIGH, 2002). The once seemingly very low exposure limit set by the RN was now in close agreement with the ACGIH values for working day exposures.

Smoking

Despite being banned in the workplace, anachronistically cigarette smoking is still tolerated in submarines of many countries. The RN and Canadian Navy were amongst the first navies to ban smoking aboard submarines in 2007 (Pestell, 2007) respectively then followed by the USN and the RN (2011). The RAN has permitted smoking at the commanding officer’s discretion and only in the engine room while the engines are operating. No doubt, with time, the practice will be phased out by all navies.

Carbon dioxide

There is a trend towards establishing 0.5% carbon dioxide for continuous exposure in submarines and the French (Jouandon et al., 2013) and UK navies are committed to this change. The US Navy already operates close to 0.5% (Bishop Jr., 2009). Initially, this requirement arose from the European Union regulations for the ventilation of inhabited buildings. As the efficacy of carbon dioxide absorption decreases with concentration, existing scrubbing capability will be stretched to the limit and soda lime absorbers may need to be replaced with lithium hydroxide thus representing a new challenge for air purification in submarines.

However, it has been suggested that fluctuations in the concentrations of carbon dioxide maybe more important in affecting cognitive functions than absolute concentrations in the region of 0 – 2% (James, 2013). This postulation requires further study.

Conclusions

Research into submarine air quality issues over the past 20 years has resulted in the development of new and innovative technologies in air purification and air monitoring. Some are at a mature stage of development and may be deployed in a new class of submarines while others require further development. Navies tend to be relatively conservative and generally submarine habitability is not a high priority area and so it remains to be seen which of these technologies will be adopted in future.

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POLYCYCLIC AROMATIC HYDROCARBONS EMISSIONS FROM DIESEL EXHAUSTS: A REVIEW

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Air quality aboard the vessels of the Royal Australian Navy (RAN) including the diesel electric submarines of the Collins Class can be degraded by the ingress of engine exhaust emissions, potentially exposing crew to chemicals such as Polycyclic Aromatic Hydrocarbons (PAHs). An important step in mitigating the risk of PAH exposure is to have a thorough understanding of parameters that can influence both the numbers and concentrations of PAHs. Many parameters can influence the PAHs present in diesel exhaust as will be shown in this review.

Diesel fuel has changed significantly since the early 1970's when investigations into the PAH composition of diesel exhaust emissions first began. Changes to both the aromatic and sulphur contents of diesel fuel are known to effect PAH concentrations (Lim 2005; Nelson 2008), making comparisons between studies spanning multiple years difficult. The impact of fuel changes will continue as the use of biofuels increase. Generalisations with regards to the PAH emissions from biodiesels can be difficult due to the numerous biodiesel feedstocks available and the differing percentages that they are added to conventional diesel fuels (Karavalakis 2010).

The numbers and types of PAHs investigated in diesel exhaust emissions also differ making accurate comparisons and conclusions difficult. There are over 100 different PAH compounds possible, with over 50 identified in diesel exhaust emissions (Zielinska 1998; Xu 1982), however often only a small subset are measured due to differences in measurement methodologies and regulatory requirements.

A large number of parameters such as engine size, operating conditions, engine technology are known to influence the number and types of PAHs present, also complicating comparisons between various studies (Bachmann 2002; Jones 2004; Maricq 2007; Nelson 2008).

Additionally, the amount of research focused on maritime engine emissions is limited. It is therefore often necessary to examine vehicle PAH emissions to gain a further understanding of factors that can influence PAH emissions.

1.0 Background

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic chemicals, which include carbon and hydrogen with a fused ring structure containing at least two benzene rings. Many PAHs are known or suspected to be carcinogens and mutagens, however many characteristics are known to vary with molecular weight (Ancelet, Davy et al., 2011). The lower molecular weight PAHs (e.g., 2 to 3 ring group of PAHs such as naphthalenes, fluorenes, phenanthrenes, and anthracenes) have significant acute toxicity to aquatic organisms, whereas the high molecular weight PAHs, 4 to 7 ring (from chrysenes to coronenes) do not. However several

types of the high molecular weight PAHs are considered to be carcinogenic. Benzo[a]pyrene (BaP) is considered to be one of the most toxic of the PAHs (EPA 2002).

PAHs can enter the atmosphere from a number of sources such as waste incineration, domestic heating emissions and natural emissions such as forest fires (Pandey, Kim et al. 2011). PAHs can also be generated as a component of diesel exhaust emissions, an area of concern for the Australian Defence Force given the use of diesel engines in land vehicles and aboard both the surface and sub-surface fleets of the Royal Australian Navy.

An important step in characterising the potential risk is reviewing the current literature to ascertain the types of PAHs typically present in diesel exhaust. The following paper will outline a review undertaken to characterise the emission of PAHs from diesel engines.

2.0 PAH emissions from diesel engines

Polycyclic Aromatic Hydrocarbons (PAHs) can be emitted into the atmosphere from multiple combustion sources, resulting in the PAH profile differing both in terms of the concentrations and types of PAHs present dependant on the source (Claxton 2015). The variations in the PAH emission profiles between sources are so significant that it can be used as a source fingerprint (chemical signature) (Khalili 1995, Tobiszewskiet 2012). It is generally assumed that PAHs originating from diesel engine sources contain elevated concentrations of methylated naphthalenes and methylated phenanthrene isomers. Enrichment of benzo[a]anthracene and benzo[a]pyrene has also been observed under some conditions for diesel engines (EPA 2002).

Efforts to provide a more definitive description of the PAHs expected in the diesel engine exhaust can be complicated by differences in the numbers of PAHs investigated. Upwards of 50 PAHs have been detected in vehicle diesel exhaust emissions (Zielinska 1998, Xu 1982). However only a small subset of these PAHs are routinely monitored due in part to differences in the sampling and analysis techniques required for some PAHs. Differences in defining what PAHs are significant and warrant monitoring (from a health perspective) can also differ. This will affect which PAHs are monitored. For example, French authorities list seven PAHs (not including naphthalene) while the American EPA list includes 16 species including naphthalene (European Commission 2001). The International Standards Organisation choose not to list specific PAH species but merely define PAH as “compounds that contain two or more fused aromatic rings made up only of carbon atoms” (International Organisation of Standardisation 2000).

2.1 Maritime PAH emissions

Efforts into the characterisation of PAH emissions from diesel engines have focused largely on vehicle diesel engine emissions presumably because of the availability and the comparative ease of which vehicle emissions can be evaluated. Of the research focusing specifically on maritime engine emissions, it is suggested that the PAH emissions are dominated by five naphthalenes (Naphthalene, 2-Methyl-naphthalene, 1-Methyl-naphthalene, 2,6-Dimethyl-naphthalene and 2,3,5-Trimethyl-naphthalene) and two phenanthrenes (Phenanthrene and 1-Methyl-phenanthrene) with these typically accounting between 63% and 92% of the total PAH present

(Cooper et al 1996, Cooper 2001, Lloyds Register Engineering Services 1995, Khalili et al 1995).

Little is known about the PAH emissions from submarines, whether from conventional powered or from the emergency diesel engine of nuclear submarines. When investigating emissions from the emergency diesel generator of the Los Angeles, Ohio and the Sturgeon Class Submarines, the US EPA based the emissions on those of large stationary diesel engines of > 600 horse power (hp). The larger molecular weight PAHs were determined to be in the minority and the lower molecular weight PAHs Naphthalene, Fluorene and Phenanthrene being the most abundant PAHs in the engine exhaust (EPA 1999).

Some work has been undertaken to characterise the PAHs present within the main engine room of the conventional powered Collins Class Submarines of the RAN. The studies have involved both the analysis of surface swab samples and filters (Hanhela 2011). The largest contribution to the total PAHs from the swab samples was seen from Acenaphthene, which is in contrast to the dominance of Naphthalene typically expected in maritime emissions (Cooper et al 1996, Cooper 2001, Lloyds Register Engineering Services 1995, Khalili et al 1995). The absence of Naphthalene from the surface samples however is not unexpected given the volatility of Naphthalene, which could have resulted in its evaporation and subsequent loss from the internal submarine surfaces. Naphthalene is known to sublime at normal room temperatures.

In further studies on the Collins Class Submarines, Naphthalene could be detected in airborne samples (Leist 2013), though acenaphthylene was routinely identified as the most prolific airborne PAH. The volatility of Naphthalene can result in lower than expected concentrations during sample preparation and analysis (Falquet 2012; Leist 2013). Benzo[a]pyrene, known for its toxicity was detected, though at much lower concentrations than the more abundant lower molecular weight PAHs. Differences were found in the PAH emission profile in the samples taken from two different Collins Class Submarines. Some differences in the PAH emission profile is not unexpected given the large number of parameters including the operating conditions and engine maintenance conditions that are known to effect PAH emissions (IPCS 1996; Bachmann and Gong 2002; Jones, Chughtai et al. 2004; Maricq 2007; Nelson, Tibbett et al. 2008; de Abrantes, Assuncao et al. 2009).

Factors including the both the size and power of the engine, as well as the fuel type have also been shown to influence PAH emissions from maritime engines (Diesch et al 2013, Cooper 2003). A variety of fuels can be used to power maritime engines including Residual Oil (RO) which is derived from the residue of the crude oil refining process. The residue is highly viscous and is composed of very large molecules of high aromaticity and has a sulphur content typically in the range of 2.0 to 3.5% (IMO 2011). Marine Distillate (MD), less dense and viscous than RO and has a sulphur content between 0.1% and 1.5% can also be used as well as Ultra Low Sulphur Diesel (ULSD) with a sulphur content of 0.001%. The Standard diesel fuel purchased by the Royal Australian Navy (RAN) for its surface and sub-surface fleets meets DEF(AUST)5213A standard which allows the use of fuel with up to 1% sulphur. Fuels that are lower in aromatic and sulphur contents have been shown to result in reduced PAH emissions (Wingfors 2001).

2.2 Diesel vehicle emissions

The PAH emissions from other diesel vehicles are not expected to mirror those from maritime engines, with difference in both the magnitude of the emissions and the prevalence of certain PAHs expected (Diesch 2013; Claxton 2015). Some of these differences are attributable to differences in both the sizes and efficiencies of the engines. The larger the engine, generally the lower the PAH emissions (Diesch 2013; Zielinska 1998; Xu 1982).

Despite the differences known to exist between maritime and vehicle PAH emissions, the examination of vehicle emissions can still prove useful given the lack of maritime specific literature. Many factors such as fuel type and engine conditions have similar effects, regardless of the application of the diesel engine (Lim, Ayoko et al. 2005 (IPCS 1996; Bachmann and Gong 2002; Jones, Chughtai et al. 2004; Maricq 2007; Nelson, Tibbett et al. 2008; de Abrantes, Assuncao et al. 2009). Reviewing literature focused on vehicle PAH emissions can therefore provide useful clues as to the possible impact on maritime platform applications.

2.2.1 Nitro PAHs

Nitrated polycyclic aromatic hydrocarbons (Nitro-PAHs) are an important category of derivations of PAHs and are of special interest because they include potential mutagens and carcinogens. They have been recognized as direct-acting mutagens and carcinogens to mammalian systems and are, thus, considered to have far greater toxicity than unsubstituted PAHs (Byeong-Kyu 2010). Nitro-PAHs are formed mainly from incomplete combustion processes or by the reaction of PAH with atmospheric oxidants, such as dinitrogen pentoxide, nitrogen trioxide, and oxygen radicals in the presence of nitrogen oxides (Byeong-Kyu 2010). A number of nitro-PAHs have also been identified in vehicle diesel exhaust emissions and include 1-nitropyrene; 2-methyl-1-nitronaphthalene; 4-nitrobiphenyl; 2-nitrofluorene; 9-nitroanthracene; 9-methyl-10-nitroanthracene; 2-nitroanthracene; 2-nitrophenanthrene; 1-methyl-9-nitroanthracene; 1-methyl-3-nitropyrene; 1-methyl-6-nitropyrene; 1-methyl-8-nitropyrene; 1,3-, 1,6-, and 1,8-dinitropyrene; and 6nitrobenzo[a]pyrene (EPA 2002). Forty-five additional nitro-PAHs were tentatively identified in diesel particulate extract (Paputa-Peck 1983). Usually 1-nitropyrene is the predominant component, and concentrations ranging from 7 to 165 $\mu\text{g/g}$ of particles have been reported (Levson, 1988). The emissions of nitro-PAH compounds from diesel engines are typically at least an order of magnitude lower than PAH emissions (EPA 2002).

2.2.2 Engine after treatment systems

As a consequence of changes in the emission standards for Nitrogen Oxides (NO_x) and Particulate Matter (PM) modern vehicle engine systems are typically equipped diesel particulate filters (DPFs). Given the variety of filters and catalysts that are in existence, this complicates the characterisation of PAH emissions. It is generally acknowledged that engines not fitted with after treatment technology produce higher concentrations of PAHs (Hesterberg, Lapin et al. 2008). Modern diesel engines equipped with catalysed emission control systems are capable of producing PAH emissions that are 3-4 orders of magnitude lower than legacy engines (Laroo, Schenk et al. 2011).

Intense research and development on DPFs have produced a great variety of systems with different materials, filtration and regeneration mechanisms. In regard to PAH emissions, DPFs can reduce the total PAH emissions (Heeb, Schmid et al. 2008; Heeb, Schmid et al. 2010). DPFs that are regenerated at high temperature in an oxidative atmosphere are akin to other catalytic exhaust gas treatment systems. That is they can act as chemical reactors which may also induce the formation of new pollutants (Heeb, Zennegg et al. 2007). Since considerable amounts of PAHs may reside on the soot particles, the filter structure may act as a reaction chamber for the nitration chemistry that can result in the post-combustion formation of Nitro-PAHs (Carrara, Wolf et al. 2010). It has been reported that pyrene and benzo(a)pyrene can become nitrated under conditions encountered in DPFs (Carrara, Wolf et al. 2010). Low engine load conditions have also been identified as the most favourable conditions for PAH nitration (Carrara 2011)). Since nitro-PAH are both more mutagenic and toxic than their parent PAH, the conversion of PAH into nitro-PAH within a DPF can result in an increase in diesel exhaust toxicity, offsetting the gains made by the net reduction in PAHs when using DPFs.

2.2.3 Biodiesel

Biodiesel is made through a chemical process which converts oils and fats into fatty acid methyl esters (FAMES). The chemical difference between biodiesel and conventional diesel is the length of the carbon chains and the presence of oxygen in the former. These differences can result in property differences such as freeze point, energy density, specific energy density and thermal stability. Common biodiesel feedstocks include: canola oil, palm oil, coconut oil, animal fats, waste products and algae.

While the RAN has currently not set any targets with regards to the use of biodiesel, the United States Navy's have a goal to generate 50% of its energy from alternative sources including biofuels by the year 2020 (EIA 2014). To meet fuel specifications it is expected that Navy biofuels be mixed in a 50-50 blend with conventional petroleum fuel (Siuru 2010).

To date the effect on biodiesel on PAH emissions is heavily reliant on studies investigating vehicle emissions given once again the lack of maritime specific research. From these studies it is apparent that using biodiesel can decrease PAH emissions, although a dependence on engine operation conditions is usually acknowledged (Bagley, Gratz et al. 1998; Corrêa and Arbilla 2006; Yang, Chien et al. 2007; Kalam, Saifullah et al. 2008; Karavalakis, Stournas et al. 2009; Lin, Hsu et al. 2011). The PAH emissions detectable when using biodiesel have shown to be highly dependent on the oil (palm, soy, sunflower, rapeseed) and alcohol (methanol, ethanol) used in the transesterification (Baldassarri, Battistelli et al. 2004). In instances where a decrease in PAH emissions has been noted, it can on occasions be attributed merely to the initial PAH content in the biodiesel being lower.

The PAH emissions from an agricultural tractor fuelled with ULSD blended with soybean oil or beef tallow biodiesel was shown to reduce emissions, (Magara- Gomez, Olson et al. 2012) with reductions >80% achievable for both biodiesel blends (Magara- Gomez, Olson et al. 2012). The results were in agreement with (Lin, Lee et al. 2006), with the use of waste cooking oil (Lin, Hsu et al. 2011) and soybean oil based biodiesel (Tsai, Chen et al. 2010). The work however conducted by (Tsai, Chen et al. 2010) did show that the percentage reduction of PAHs decreased as the percentage of biodiesel was increased which is in contrast to other results. It was postulated by the authors the higher ratios of soybean biodiesel were less effective because of

the incomplete fuel combustion in the combustion chamber, due to changes in viscosity and the lower cetane number.

Karavalakis et al. (2009) investigated the effect of diesel fuel and palm based biodiesel blends at proportions of 5%, 20% and 40% (v/v) with a Euro 3 compliant light duty, diesel powered truck. The authors concluded the majority of PAHs and nitro-PAH emissions decreased with the addition of biodiesel. Other authors have also reported that the addition of biodiesel can reduce PAH and nitro-PAH emissions (Abbas, Andrews et al. 1990; Cardone, Prati et al. 2002; Yang, Chien et al. 2007; Kalam, Saifullah et al. 2008; Ratcliff, Dane et al. 2010) and oxy-PAH emissions (Kooter, van Vugt et al. 2011). (Ratcliff, Dane et al. 2010) investigated the differences in PAH and nitro-PAH emissions from a heavy duty (HD) diesel truck using ULSD, soy biodiesel (B100) and a 20% blend thereof and noted that biodiesel resulted in a significant decrease in nitro-PAH, most notably 1-nitropyrene which reduced by 78% when using B100. There were exceptions however, most notably benzo[a]pyrene which exhibited an increasing trend across several studies. Other PAHs namely fluoranthene and pyrene emissions were higher for the 40% blend (Karavalakis, Alvanou et al. 2009). Ten out of the 16 PAHs were found to increase (30-72% higher) when using a 15% volume palm oil biodiesel blend (Rojas, Andres Milquez et al. 2011), whilst the effects of biodiesel and rapeseed oil were varied with reduced emissions of the lighter PAHs (less toxic), however little difference in the emissions of the more toxic PAHs (Vojtisek-Lom 2012; Zou 2003).

Karavalakis et al. (2010) investigated five different types of methyl esters at proportions between 10 and 90% on diesel emissions from a Euro 3 diesel passenger car. A total of 12 PAHs, 4-nitro-PAHs and 6 oxy-PAHs were analysed. Differences in PAH and nitro-PAH emissions were particularly noticeable between the various biodiesel blends in contrast with the oxygenated PAHs (oxy-PAHs) where the differences between the fuel blends were negligible. Oxygenated PAHs are mainly emitted from combustion processes. They can also originate from heterogeneous reactions between PAHs and ozone. Oxy-PAHs are semi-volatile compounds with higher molecular weights and lower vapour pressure than their parent PAHs (María Del Rosario Sienra 2006; Tsapakis and Stephanou 2007). In contrast with their parent PAHs most of the oxy-PAHs are directly toxic and mutagenic (Schuetzle 1983). Low molecular weight PAHs phenanthrene and anthracene increased while higher molecular weight PAHs exhibited some increases with the addition of biodiesel. Nitro-PAHs were found to reduce with biodiesel whereas oxy-PAH emissions increased. The authors found that as the degree of unsaturation increases, PAH formation is especially favoured.

Conclusion

Maritime diesel engine emissions are dominated by lower molecular weight PAHs, rather than the more toxic PAHs such as Benzo[a]pyrene. Many parameters are known to influence the PAH emission profile. To enhance the knowledge in the maritime domain of PAH emission profiles, vehicle PAH are called upon given the significant volume of work that has been undertaken in this area. Some trends in PAH emissions are identical regardless of the engine type, for example the benefits from reducing the sulphur and aromatic contents of diesel fuel. Advances in after-treatment technologies such as particle traps have reduced, but not eliminated PAH emissions from diesel engines.

Studies examining the effect of biodiesel on PAH emissions have yielded inconclusive results. In some instances a reduction in the levels of all PAHs were reported, while other studies have

reported reductions for some lower weight PAHs while other PAHs such as Benzo[a]pyrene have increased. The lack of clarity with respect to the use of biodiesels can be due to differences between the biodiesel feedstocks as well as changes in fuel chemistry that can occur as the percentages of biodiesel increase.

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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 (MPC₉₀) of 12 ppm within 3 min. An increased leakage of 10 % would breach the 24 hour maximum permissible concentration (MPC₂₄) of 60 ppm in 3 min. If a leakage of 30 % or greater was present the 60 min maximum permissible concentration (MPC₆₀) 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 MPC₉₀ 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 (CO₂) 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 CO₂ 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.

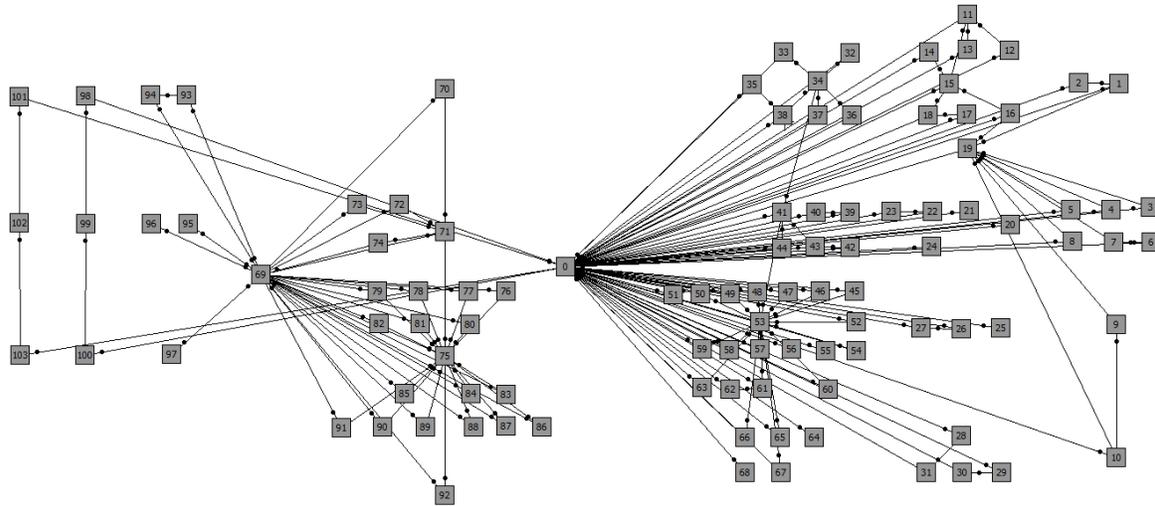


Figure 1: BREATH model of VANGUARD-class

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 ($168 \text{ m}^3 \cdot \text{min}^{-1}$ [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.

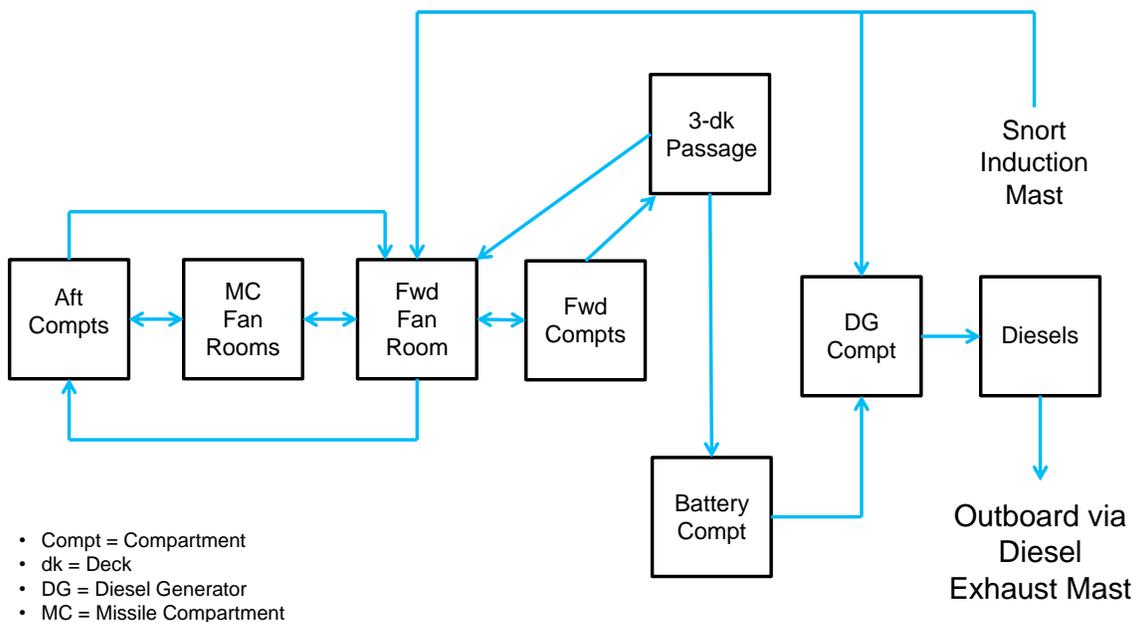


Figure 2: Simplified schematic of vent state BLUE

Proposed changes, to the ventilation system shown in Figure 2, would direct the 68 m³.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 exhaustre-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 m³.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 (l.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

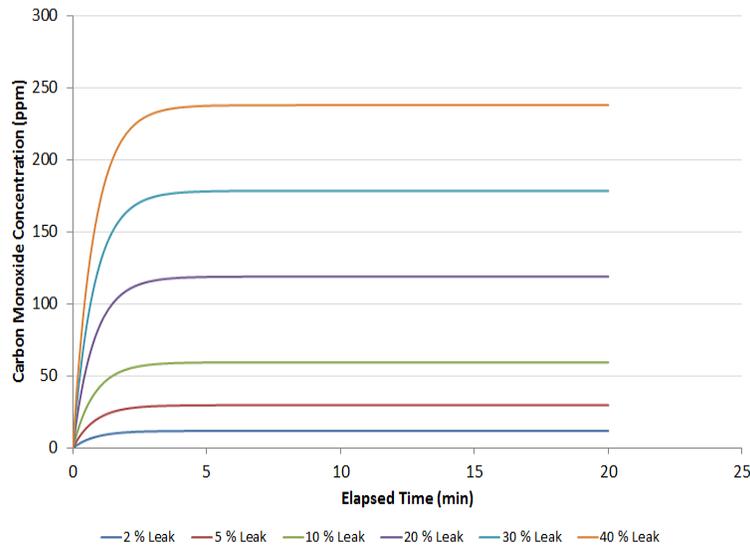


Figure 3: Modelled effect of Diesel exhaust leakage on DG Compartment CO concentrations

Figure 3 demonstrates that the RN's 90-day maximum permissible concentration (MPC₉₀) of 12 ppm will be breached if the Diesel exhaust leakage rate is greater than 2 %, the MPC₂₄ of 60 ppm will be breached if the leakage rate is greater than 10 %, and the MPC₆₀ 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) | | |
|------------------|--------------------------------------|-------------------|-------------------|
| | MPC ₉₀ | MPC ₂₄ | MPC ₆₀ |
| 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.

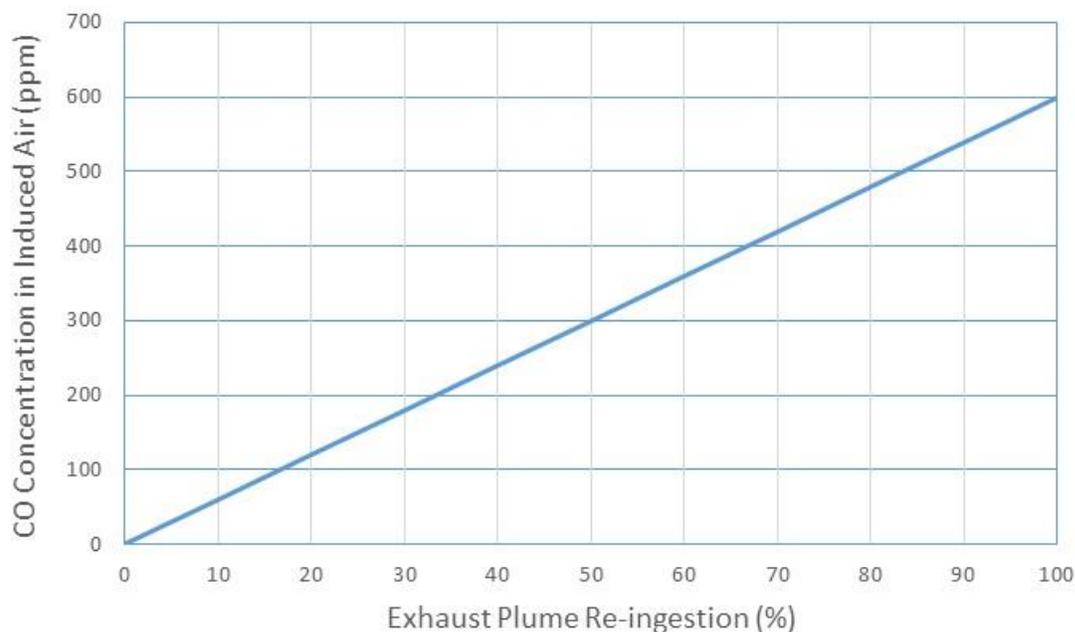


Figure 4: Relationship between degree of plume re-ingestion and the concentration of CO in the induced air flow

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

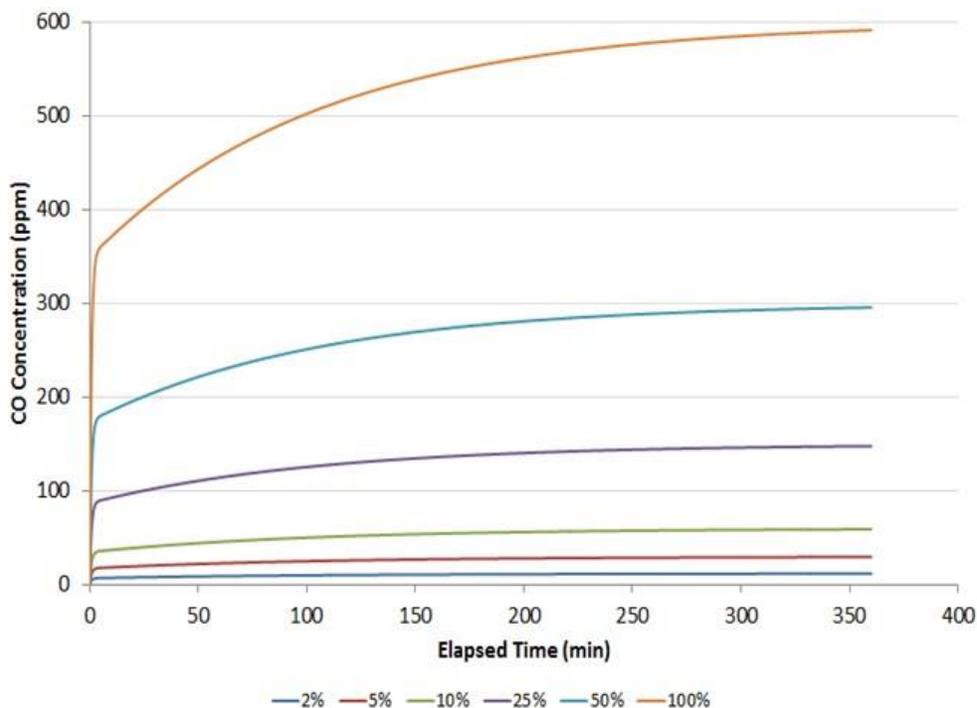


Figure 5: Increase in DG Compartment CO concentration for different degrees of exhaust plume re-ingestion

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 MPC₉₀ would be breached if re-ingestion is greater than 2 %, the MPC₂₄ would be breached if re-ingestion is greater than 10 %, and the MPC₆₀ would be exceeded if re-ingestion is greater than 30 %.

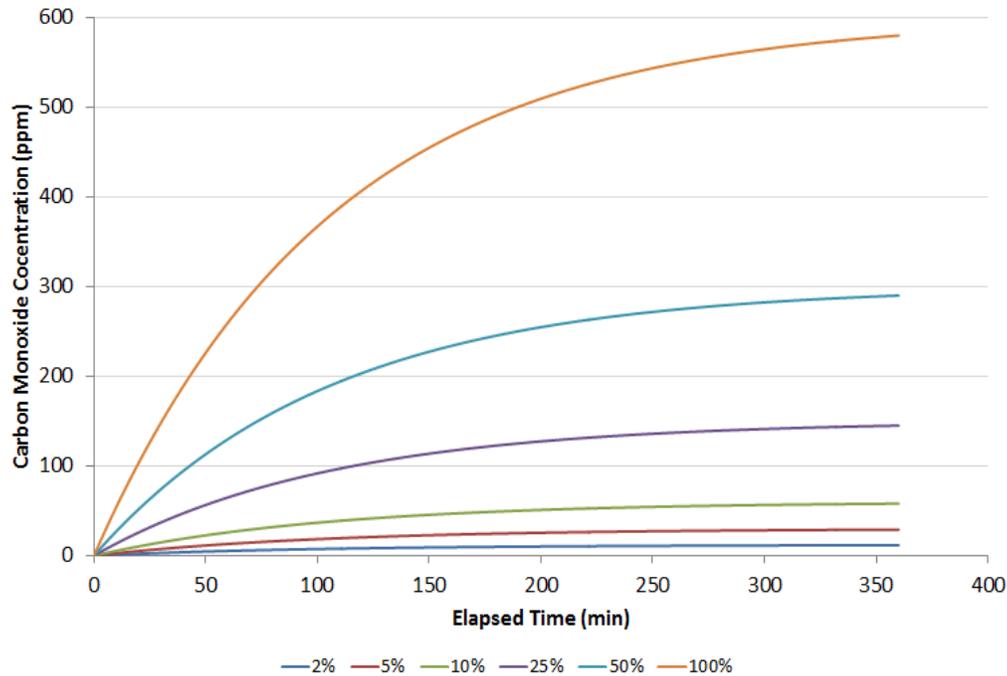


Figure 6: Increase in 'whole boat' CO concentration for different degrees of exhaust plume re-ingestion

| 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

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.

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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Integrated Atmosphere Management

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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.

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

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Abstract

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. electrolyzers). 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 damage 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 analysis³. 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 Haslar⁴. 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 Instruction⁵ 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.

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

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

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 regime 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

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Long-Term Demonstration of an Optical Multi-Gas Monitor on the International Space Station

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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 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 Russian 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 is 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 20 months of operation are presented and future applications including combustion product monitoring are discussed.

INTRODUCTION

NASA has invested in environmental monitoring applications of tunable diode laser spectroscopy (TDLS) for more than 10 years through the Small Business Innovation Research (SBIR) Program, which funds cutting edge research and development entities to solve problems of interest to the space program. The immediate interest of the Environmental Sciences Branch at NASA-Johnson Space Center (NASA-JSC) in Houston, Texas is to develop hand-held battery powered gas monitors both to replace outdated gear and to augment the monitoring capability available on board the

International Space Station (ISS). To that end, we have identified and partnered with promising SBIR derived technology vendors to address existing requirements to monitor certain target gases associated with emergency scenarios such as combustion, system chemical leaks and loss of central air monitoring. Low power consumption and size of the sensor package are key factors in the development along with detection range and selectivity. Currently, commercial off-the-shelf (COTS) electrochemical sensor based hand-held monitors and Draeger tubes are used on ISS with mixed success. The goal of the TDLS development is to replace these with a few devices that are calibrated once on the ground and placed in service for 5 years or more. These will provide better/faster emergency response data, save a tremendous amount of hardware manifest (launch and return “traffic”) and conserve precious crew time. Previous SAMAP presentations described the current on-board gas monitoring devices and plans to replace obsolete equipment with TDLS based technology. This paper reports on progress made since then, including the results of a technology demonstration flight experiment of a TDLS based 4 gas Multi-Gas Monitor (MGM) on the ISS, and describes new follow-on projects for monitoring target gases required by ISS and the Orion capsule.

MULTI-GAS MONITOR FLIGHT EXPERIMENT

In 2011, we identified 4 target gases (Table 1) that could be readily measured via TDLS and built a functional breadboard called Optical Life Gas Analyzer (OLGA). In 2012, we built a battery powered OLGA for ground demonstration. The ISS program management was keenly interested in better technology for the measurement of ammonia, so in November 2012, we requested and received funding for a flight experiment, a technology demonstration (“Tech Demo”) to be operated on ISS for at least 6 months. The objective of the ISS Tech Demo was to prove long term reliability of the sensor for the 4 target gases, at least 2 of which we could compare with other assets on board. The resulting flight unit is pictured in Fig 1. Note the display shows the 4 gases plus temperature and pressure. The OLGA name was changed to Multi-Gas Monitor as the official “opnom.”

Table 1. Multi-Gas Monitor Target gases and ranges

| Gas | Concentration Range |
|-----------------------------------|---------------------------|
| Ammonia (NH ₃) | 5 – 20,000 ppm |
| Carbon Dioxide (CO ₂) | 250 – 30,000 ppm |
| Oxygen (O ₂) | 4 – 36% |
| Water vapor (H ₂ O) | 5 – 90% Relative Humidity |



Figure 1. Photos of MGM with power/data cables, flange and display.

The MGM can be powered multiple ways to give it operational flexibility. While in the rack, it is powered by 5V USB cables plugged into the Nanoracks Frame, which also serve as the data connection. With internal rechargeable lithium ion batteries, the unit can be deployed by the crew for up to 20 hours. The 3rd power option is a 28V connector which is useful for deploying anywhere there is an available EXPRESS outlet on ISS. The sensor draws only 2.5W. A timeline of the flight experiment to date is given in Table 2. Calibration was conducted at NASA-JSC in July 2013. No inflight recalibration is possible, or as it turns out, necessary. MGM was shipped to Russia in August and launched on a Soyuz vehicle in November 2013. MGM was installed in the Nanoracks frame (Fig 2a) in the Japanese Experiment Module (JEM) in February 2014 and spent the majority of the 20 months (as of Oct 2015) running continuously with weekly data downlink managed by ground controllers. The experiment required no crew interaction except for testing the ammonia channel with a medical inhalant in July 2014, a manual reset (Fig 2b) in December 2014, and the deployments outside of JEM in August and September 2015. One of the unplanned tests was detecting CO₂ thruster firings from the unrelated Synchronized Position Hold Engage Reorient Experimental Satellites (SPHERES) experiment (Fig 3). Fig 4 shows a typical day of data from MGM. All of these activities serve to demonstrate capabilities and prove out the technology.

Table 2. MGM Flight Experiment Timeline

| Date | Event |
|---------------------|---|
| Jul 22-30, 2013 | MGM calibrated at NASA-JSC |
| Nov 7, 2013 | MGM launched on 37 Soyuz |
| Feb 3, 2014 | Installation, activation and check out |
| Feb 11, 2014 | SPHERES CO ₂ unplanned “challenge” |
| Jul 25, 2014 | Ammonia inhalant test |
| Dec 15, 2014 | Crew manual reset |
| Jan 14, 2015 | Thermal control ammonia false alarm |
| Jan 16-17, 2015 | SPHERES CO ₂ unplanned “challenge” |
| Aug 25-26, 2015 | Deployed on battery power to Node 3 |
| Aug 28-Sep 28, 2015 | Deployed on 28V power to US Lab |
| Sep 28 - present | MGM back in JEM Nanoracks |



Figure 2a. MGM installed nose out in the Nanoracks Frame in a JEM EXPRESS rack
 Figure 2b. MGM being held by crewmember on ISS, right after a manual reset

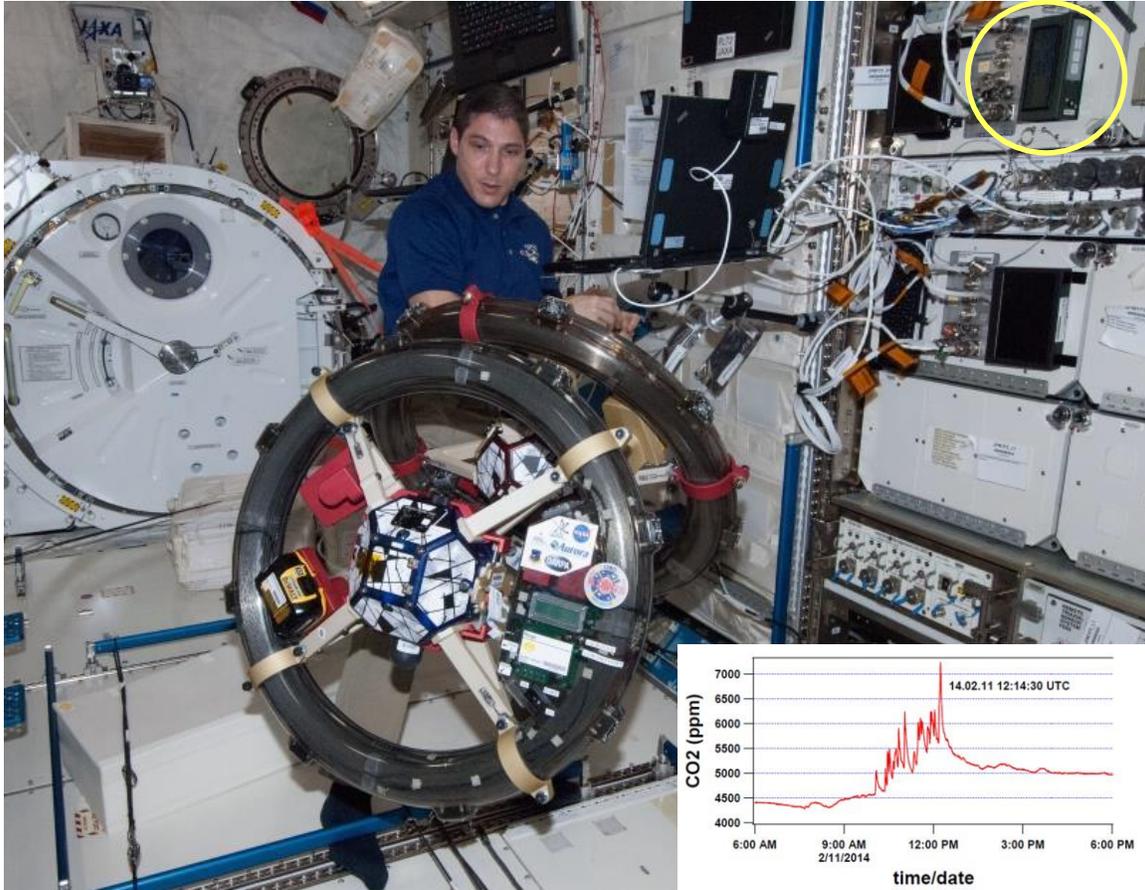


Figure 3. MGM (in yellow circle) detecting CO₂ thruster fire from unrelated SPHERES experiment, with inset MGM CO₂ data plot showing spikes of 5000-7500 ppm.

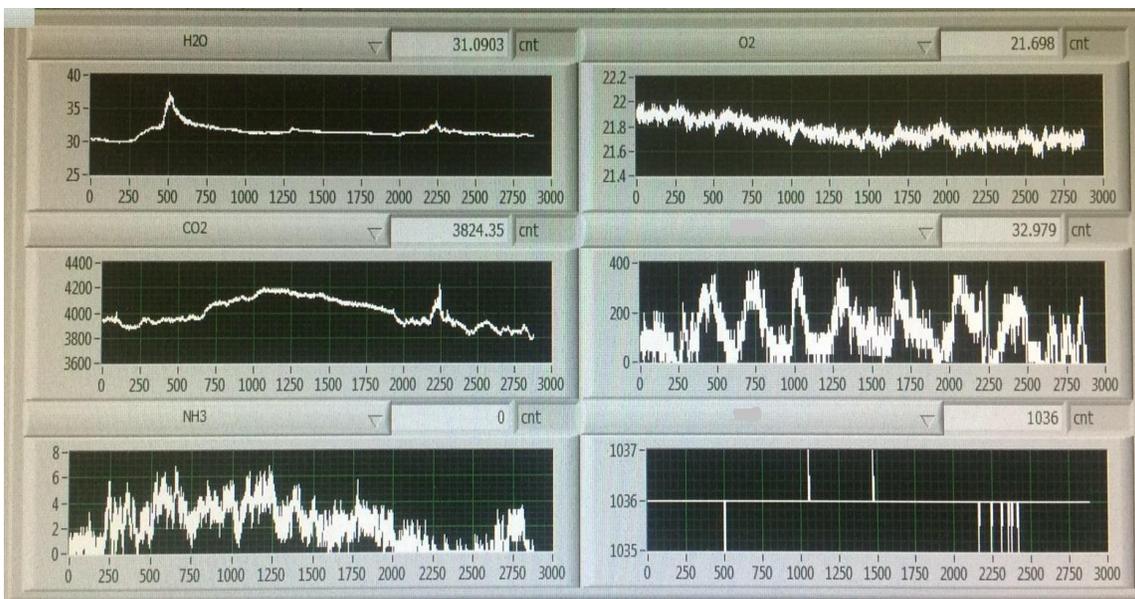


Figure 4. One day (10/2/15) of MGM flight data displayed on the ground Labview GUI

The weekly downlinks of data from MGM are checked via the Labview Graphical User Interface (GUI) and compiled together for comparison with other assets on board ISS. The Major Constituents Analyzer (MCA) is a centralized mass spectrometer similar to a submarine CAMS that sequentially samples air via tubing from all of the modules in the US segment of ISS. MCA measures O₂ and CO₂ among other permanent gases. MCA data specifically for the JEM is extracted and compared with MGM data. Plots of O₂ and CO₂ in Figs 5 and 6 demonstrate the two instruments track quite well. MCA benefits from periodic calibration using a built-in gas standard, which may account for the narrowing of the difference in the CO₂ data over time in Fig 6.

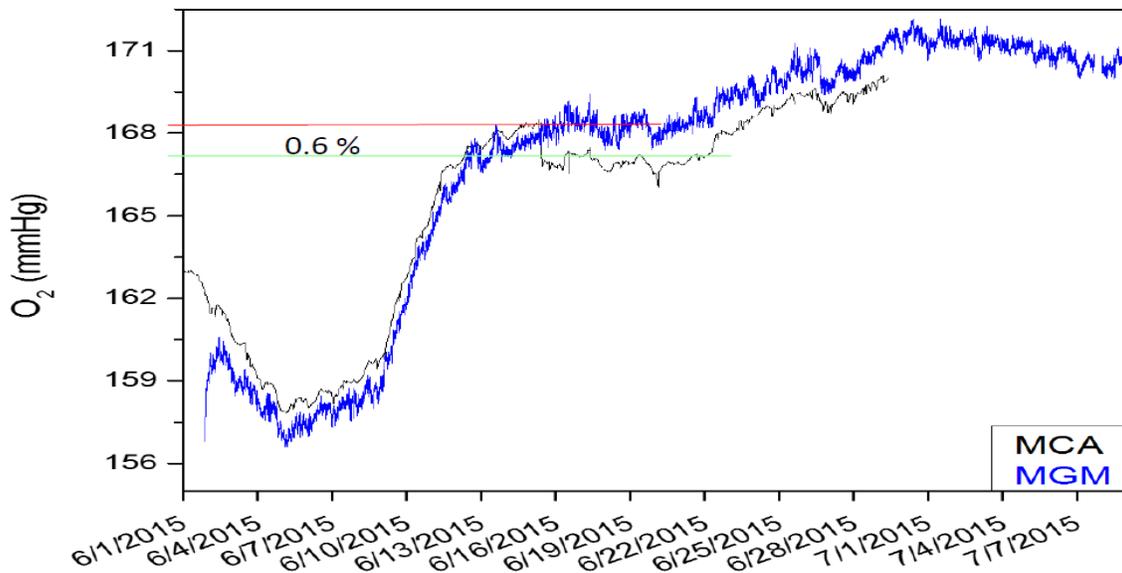


Figure 5. Comparison of O₂ measured by MGM and MCA

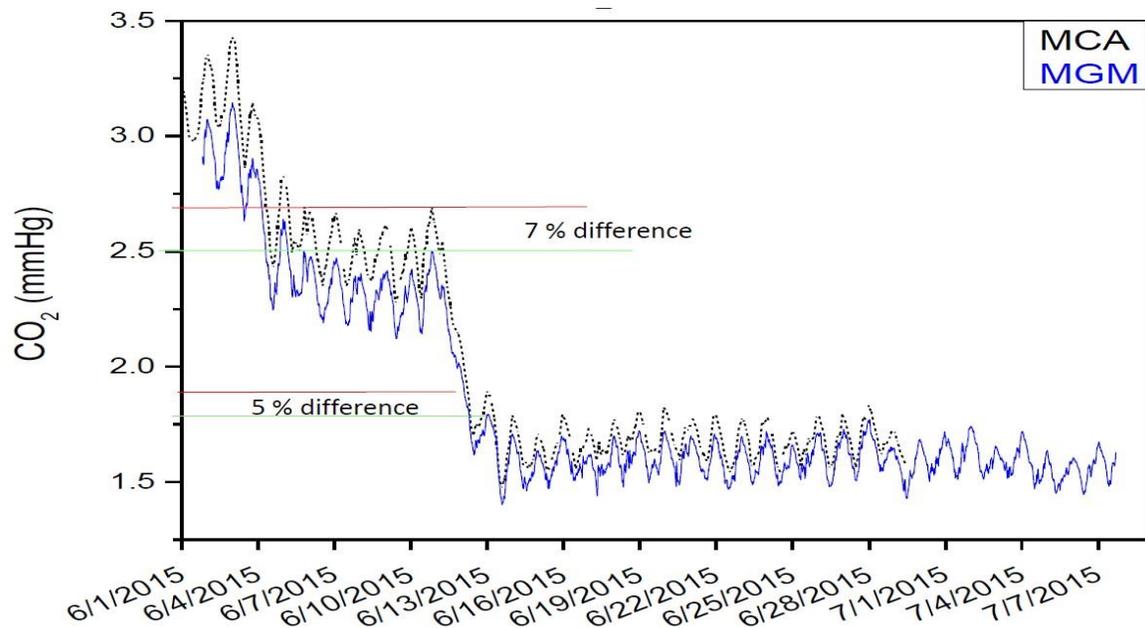


Figure 6. Comparison of CO₂ measured by MGM and MCA

MGM's other 2 channels, water and ammonia, are more difficult to check for accuracy on orbit. The Columbus module of the ISS, however, has a dew point sensor, which registered a dew point average of 48F (36% RH at 25C/1Atm) in 2014 vs. MGM's average of 12,000 ppm water (or 38% RH at 25C/1Atm) from Fig 7. This is decent agreement, considering the measurements were made in 2 different modules. The NH₃ channel was checked in a qualitative way, with a crewmember opening an ammonia inhalant at MGM's air intake (Fig 8). The test gave an immediate response of 75 ppm, a crew call down matching the downlink data file value, which is in line with expectations.

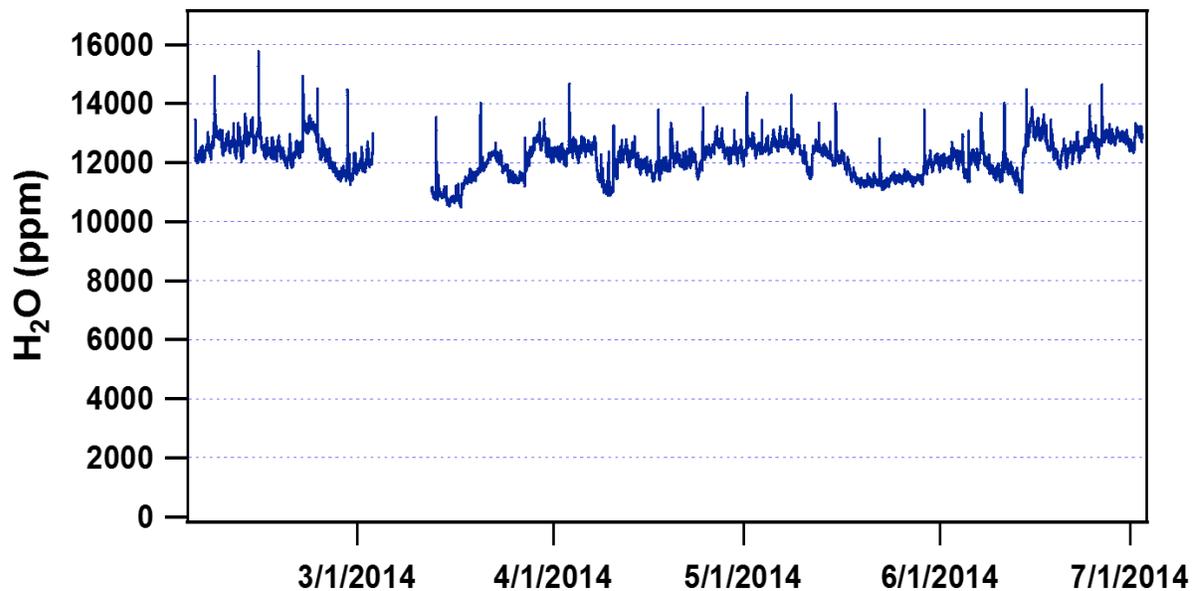


Figure 7. MGM water plot from JEM showing the approximately weekly heat exchanger dry out cycles as spikes. The gap is lost data from a hiccup in MGM's data logger.

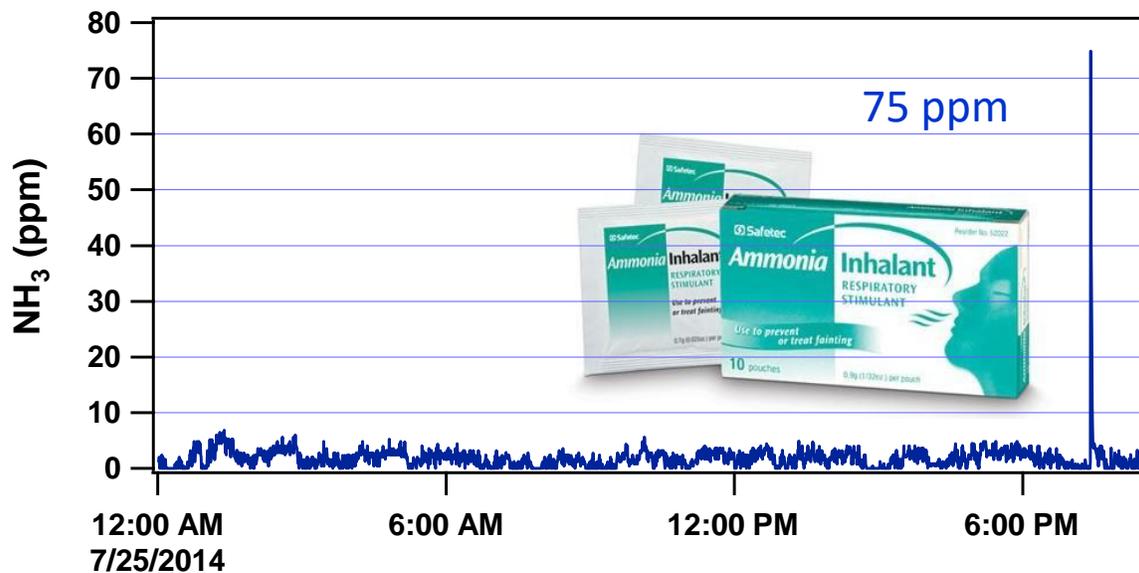


Figure 8. The only way to test the ammonia channel was to expose MGM to an artificial source of ammonia, in this case, an inhalant. Crew called down the peak of 75 ppm.

Conclusions

As of October 2015, the Multi-Gas Monitor technology demonstration flight experiment has shown stable operation of the TDLS sensor over the past 20 months, with no drift or degradation in the quality of the data. The MGM results closely match the central Major Constituent Analyzer's results for O₂ and CO₂. The ammonia channel was tested on orbit using a medical inhalant, and shown to respond rapidly and to recover rapidly. MGM's water channel is consistent with humidity readings in the Columbus module, with spikes matching heat exchanger dry out cycles in the JEM. Occasional MGM data logger hiccups lost a few weeks of data, but the TDLS sensor remains unaffected. Remote power cycling recovers the data logger. Overall, the Multi-Gas Monitor has been a very successful tech demo, and proves the core TDLS technology is ready for "prime time", that is, it is fit for incorporation into hardware designed for operational use and decision making, including critical emergency response scenarios.

Future Directions

A version of the MGM is slated for a sea trial aboard a US submarine in 2016. When introducing new technology to the space program, NASA often follows a "2-step" process involving a "risk mitigation" style flight experiment (tech demo, analogous to a sea trial) followed by a redesign that incorporates any lessons learned from the experiment before the operational version is built and deployed. The MGM represents the successful first step not only for NH₃, CO₂, O₂, and H₂O, but also for combustion products such as CO, HCN, HF, and HCl, and other indoor air quality markers such as formaldehyde. The MGM has spawned two new projects for ISS and Orion to develop (1) Small hand-held ammonia monitors with unprecedented concentration range, and (2) Combustion product monitors that also measure O₂ and CO₂. NASA also has plans in 2017 to demonstrate on ISS a TDLS based formaldehyde monitor built by Southwest Sciences Inc (Santa Fe, NM).

Acronyms

| | |
|---------|--|
| CAMS | Central Atmosphere Monitoring System |
| COTS | Commercial Off-the-shelf GUI |
| | Graphical user interface ISS |
| | International Space Station |
| JEM | Japanese Experiment Module JSC |
| | Johnson Space Center (Houston) MCA |
| | Major Constituents Analyzer MGM |
| | Multi-Gas Monitor |
| RH | Relative Humidity |
| SAMAP | Submarine Air Monitoring and Air Purification Conference |
| SBIR | Small Business Innovation Research |
| SPHERES | Synchronized Position Hold Engage Reorient Experimental Satellites |
| TDLS | Tunable Diode Laser Spectroscopy |

Operational Use of the Air Quality Monitor On Board ISS and Potential for Air Quality Monitoring On Board Submarines

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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 generally 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 potentially affecting water recycling equipment (excess ethanol). In the latter case, data from water samples and the AQM were compared to understand an issue with the water processor assembly. 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.

INTRODUCTION

The NASA toxicologist is charged with assessing the air quality aboard the International Space Station (ISS) to ensure there are no negative impacts to crew health. The air quality monitor (AQM), which has been operational on ISS since January 2014, provides quantitative data on a target list of volatile organic compounds (VOCs). This information is a key part of the toxicologist's assessment of air quality. The importance of the AQM has greatly increased as the number and frequency of archival grab sample containers (GSCs) – returned to the Earth for analysis – have been significantly reduced. Additionally, the time between the archival sample acquisition and the return and analysis of the sample can be more than 3-5 months. The AQM also proved useful for troubleshooting Environmental Control and Life Support Systems

(ECLSS) and would be invaluable for monitoring clean-up efforts following a contingency event (i.e., leak, spill, or fire).

The AQM's target compound list (Table I) was selected based upon results from years of archival air sample analysis from Shuttle, Mir, and ISS. Target compounds had one or more the following characteristics: (a) They were frequently detected in spacecraft atmospheres (ethanol, acetone, xylenes), (b) They had significant toxicity at low concentrations, although they were seldom detected in spacecraft air (benzene), and c) They had a negative effect on ECLSS (siloxanes and 2-propanol). Ammonia detection is only qualitative (not present, present low concentration, or present high concentration). The target list is fluid and may be modified based upon experience and/or changes in materials of construction or ECLSS. The AQM's analytical capabilities extend far beyond the current target list, but the goal is to focus on the compounds that have the most impact on crew health and ECLSS. Additionally, the AQM's analytical runs are prescribed such that unexpected compounds (i.e., nontargets) are detected and available for analysis.

Table I. AQM Target Compounds

| Target Compounds | Unit 2218 | Unit 2221 | Target Compounds | Unit 2218 | Unit 2221 |
|------------------|-----------|-----------|------------------------------|-----------|-----------|
| Methanol | X | | Trimethylsilanol | | X |
| Acetaldehyde | | X | Benzene | X | |
| Acrolein | X | | n-butanol | | X |
| Ethanol | | X | Toluene | X | X |
| Acetone | X | | Hexanal | X | |
| 2-Propanol | X | | Hexamethylcyclotrisiloxane | X | x |
| Dichloromethane | | X | m/p-Xylene | X | X |
| Hexane | X | | o-Xylene | X | X |
| Dichloroethane | X | | Octamethylcyclotetrasiloxane | X | X |
| 2-Butanone (MEK) | | X | Decamethylcyclopentasiloxane | X | X |
| Ethyl Acetate | | X | Ammonia | | X |

Note: Two units are used to detect all compounds with detection of some compounds on both units for redundancy.

EXPERIMENTAL

A key feature of the AQM is that the gas chromatograph (GC) carrier and detector make-up gases are recirculated air that is continually processed through molecular sieve scrubbers. The 3 small scrubbers, requiring replacement about every 6 months, are the only on-orbit maintenance needed for the 2 AQMs in service. In addition to maintaining the flow of gases, the recirculation pumps also provide the GC column head pressure required to separate compounds on the GC column. Just before sampling, 1 valve switches to stop air circulating through the preconcentrator (Carboxen 1000 and Carbotrap B) thereby allowing the sample pump to pull an ambient air sample through the preconcentrator. A 3-way valve near the inlet then switches to

allow ambient air to be pulled through a molecular sieve scrubber removing water and organics before it flows through the preconcentrator and out via the sample pump. This part of the sample process is called the “purge” because the dry ambient air removes most of the water deposited on the preconcentrator during the initial sample intake. The purge helps to improve the quantitative accuracy for low molecular weight compounds such as methanol and acetaldehyde.

Once the sampling is completed, the 2 valves switch again to restore the recirculated flow through the preconcentrator, the GC column, and the detector. Simultaneously, the preconcentrator is ballistically heated to 300°C to desorb the organic compounds. Desorbed organics flow into the GC, where a heat ramp profile helps separate the compounds to be presented to the detector. The GC column in one unit has a VF-624S coating that separates low molecular weight polar compounds, while the other column has a DB5-MS coating for quick separation of higher molecular weight compounds.

The differential mobility spectrometer (DMS) detector further separates the compounds by applying oscillating asymmetric radio frequency (RF) fields. The detector gas flow moves the ions toward the Faraday plate detector. However, most ions will not make it to the detector when the RF fields are applied. Ions move perpendicular, at different rates, to the gas flow within the DMS. Unless a “compensating voltage” (V_c) is applied, most ions will be neutralized on the electrodes of the DMS before reaching the detector. The separation of ions in the RF field is a function of differing mobility of ions in the RF field. It is the combination of GC retention time and V_c for an ion that provides the desired high selectivity in the AQMs. A more detailed explanation of the AQM theory and technical specifications can be found elsewhere.¹⁻³

The AQM data are collected and presented in two formats: scan (Figure 1) and GC (Figure 2). The scan mode shows all V_c throughout the GC run. This provides the means to establish the GC retention time and V_c for each compound that is used in the GC format.

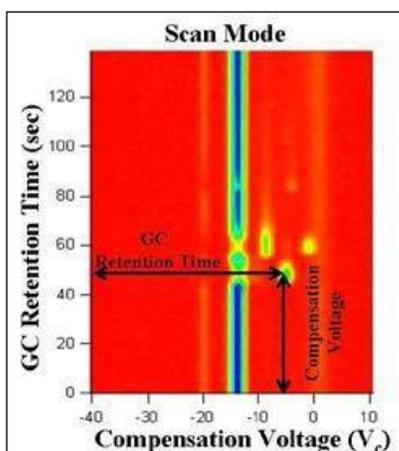


Figure 1. Scan format.

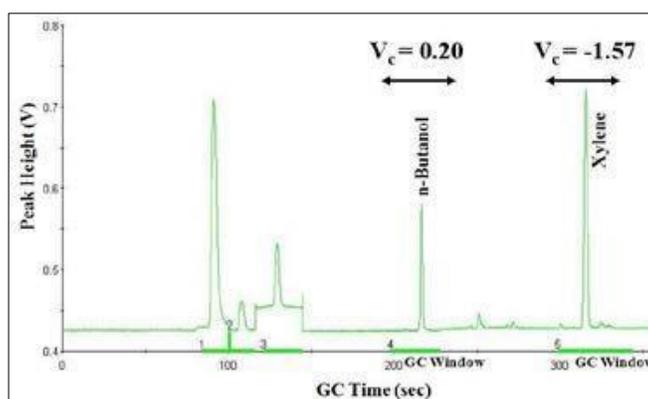


Figure 2. GC format.

Additionally, the scan mode can be used to manually quantify compounds and to detect and help identify nontarget compounds in the sample. The GC format is the mechanism for identification and quantitation of target compounds. The information in the scan mode is used to establish “windows” for each target compound. The windows combine specific GC retention time, RF

voltage, V_c voltage, and ion polarity to provide excellent selectivity for each target compound. This combination of window parameters prevents interference from other compounds in the sample. Each GC peak is integrated and the area is compared to a look up table, developed during calibration, to determine the concentration (mg/m^3) for each compound. The GC mode leads to an automatic display of results (Figure 3) on the AQM after completion of a sample run.

Results and data can also be transferred wireless to the ISS server for transmission to the ground. Additionally, the AQM can always be controlled from the ground by remote desktop.

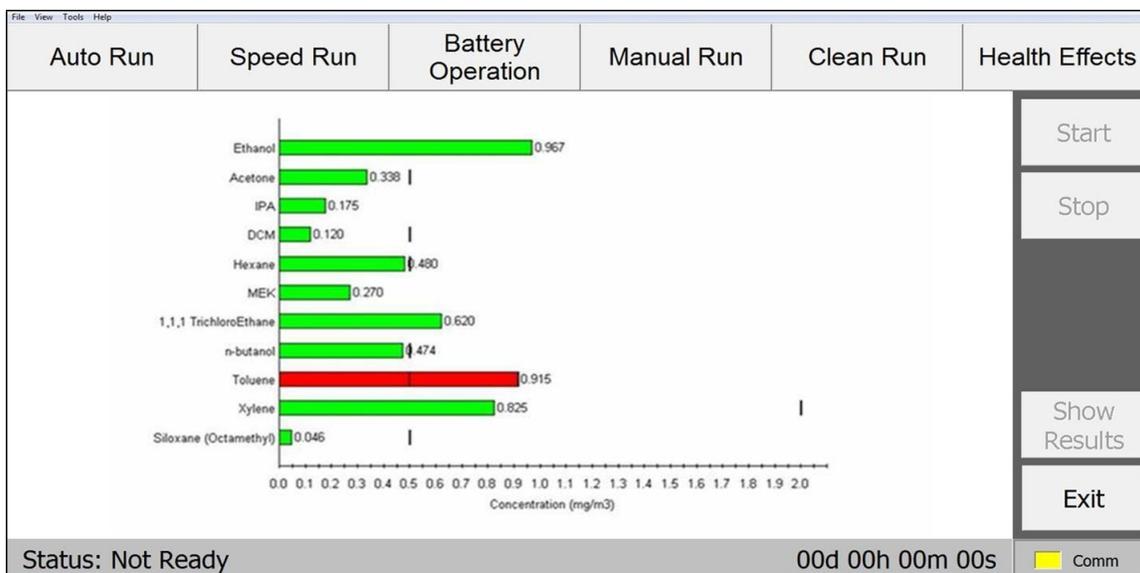


Figure 3. Display of results on the AQM graphical user interface (GUI).

RESULTS AND DISCUSSION

One of the unique features of the AQMs has been their ability to maintain calibration in excess of 2 years for target compounds (Table II). There has been no recalibration since the initial ground calibration in the year before they arrived on ISS. After validation was completed in 2013, by comparison of AQM results and archival grab sample containers (GSCs)⁴, returning GSCs were compared to AQM results, just to establish calibration lifetime. The requirements for a successful match are as follows: $\pm 40\%$ when the concentration is $> 0.5 \text{ mg}/\text{m}^3$, $\pm 50\%$ if the concentration is $< 0.5 \text{ mg}/\text{m}^3$, and $\pm 0.05 \text{ mg}/\text{m}^3$ if the concentration is $< 0.1 \text{ mg}/\text{m}^3$. Trace and non-detected (ND) are also a match.

Table II shows that AQM and GSC values matched most of the time for all compounds over a 2-year period, except for 2 siloxanes and n-butanol. It was believed that all 3 of the exceptions can be corrected with improved preflight calibration procedures, (calibration procedures for the AQMs are available elsewhere⁵) specifically, using the calibration standards within a few days of their creation to avoid wall losses. All 3 compounds are known to have significant losses to the walls of canisters and the results (higher values than GSCs) from the AQM supports this theory. Decamethylcyclpentasiloxane (DMCPS) was designated as a trending compound, but the other 2 compounds were used in the determination of the health effects. The next set of AQMs (started operating in February 2016) were calibrated using improved procedures and the first 3 comparisons to GSCs now show good matches for these compounds (Trimethylsilanol-TMS, DMCPS, and n-butanol).

Table II. Compounds from December 2014 and February 2015 Comparisons

| Target Compound | AQM* | GSC* | %Diff | Matches/#GSCs | Target Compound | AQM* | GSC* | %Diff | Matches/#GSCs |
|------------------------------|-------|------------|-------|---------------|------------------------------|-------|------------|----------|---------------|
| Ethyl Acetate | 0.05 | 0.03 | Match | 14/15 | 2-Propanol | 0.15 | 0.28 | 46 | 11/12 |
| Hexamethylcyclotrisiloxane | 2.0 | 2.3 | 12 | 13/15 | 2-Butanone | Trace | Trace | Match | 15/15 |
| Hexanal | ND | ND | Match | 12/12 | Acetaldehyde | 0.28 | 0.26 | -8 | 12/15 |
| Hexane | ND | ND | Match | 12/12 | Acetone | 0.23 | 0.37 | 38 | 11/12 |
| Methanol | 0.38 | 0.37 | -3 | 12/12 | Acrolein | ND | ND | Match | 12/12 |
| m,p-Xylene | ND | ND-0.01 | Match | 15/15 | Benzene | ND | ND | Match | 12/12 |
| n-Butanol | 0.12 | 0.06 | -111 | 2/15 | Decamethylcyclopentasiloxane | 2.88 | 0.58 | -397 | 0/15 |
| Octamethylcyclotetrasiloxane | Trace | 0.08 | Match | 15/15 | Dichloroethane | ND | Trace-0.02 | Match | 12/12 |
| o-Xylene | Trace | TRACE-0.02 | Match | 14/15 | Dichloromethane | ND | Trace | ND-Trace | 15/15 |
| TMS | 0.32 | 0.12 | -167 | 0/15 | Ethanol | 5.9 | 8.5 | 31 | 14/15 |
| Toluene | ND | ND | Match | 15/15 | | | | | |

Note: ND=below the minimum detection limit and trace is a concentration above the ND, but below the minimum quantitation limit.

Following the validation of the AQMs in 2013, a survey of the Columbus and JPM (aka JEM) modules was undertaken to determine if the ISS is a well-mixed atmosphere. Nominally, both AQMs resided in the LAB Modules; however, comparison of the air contaminants in the LAB to the other modules could be accomplished by moving 1 AQM for 60 days to JPM or Columbus. The 60 days in each module gave an opportunity to collect a GSC sample in that location and to collect sufficient data for a good profile of contaminants. GSC samples were an independent means to affirm the survey results. Figure 4 shows the position of the AQMs in Columbus and JPM Modules.

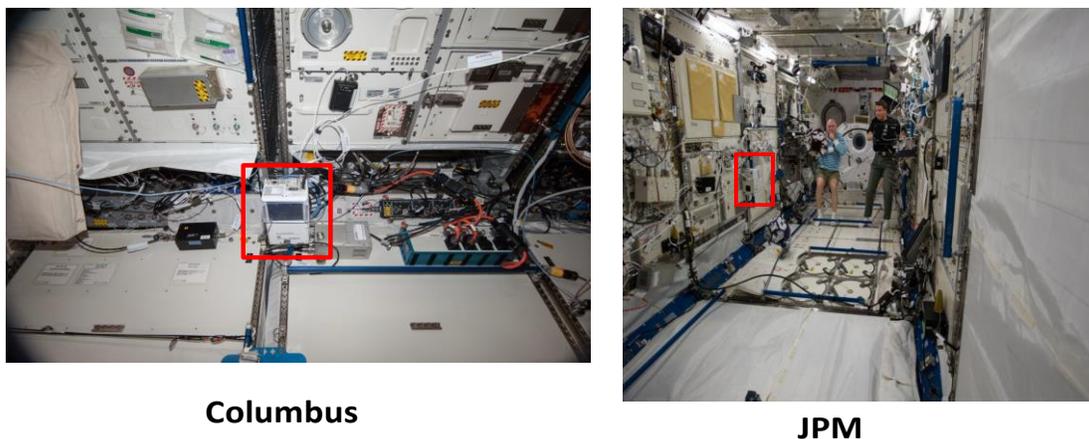


Figure 4. AQM (red boxes) in Columbus and JPM.

The two graphs shown in Figure 5 are representative of the results from AQM module survey. The graph of methanol shows the concentration detected was relatively constant in all 3 modules. O-xylene is detected on both units and the graph of this compound shows the comparison between the 2 units during the survey. The concentrations are low, but generally there is good agreement between the 2 units, and once again this is representative of the other target compounds. The docking of a Russian vehicle always increases the concentration of o-xylene in the nearest module (LAB), therefore some of the differences seen are real and explainable. The conclusion from the survey was that the ISS is

well mixed, which agreed with GSC results, and that representative samples could be obtained by leaving the AQMs in the LAB Module.

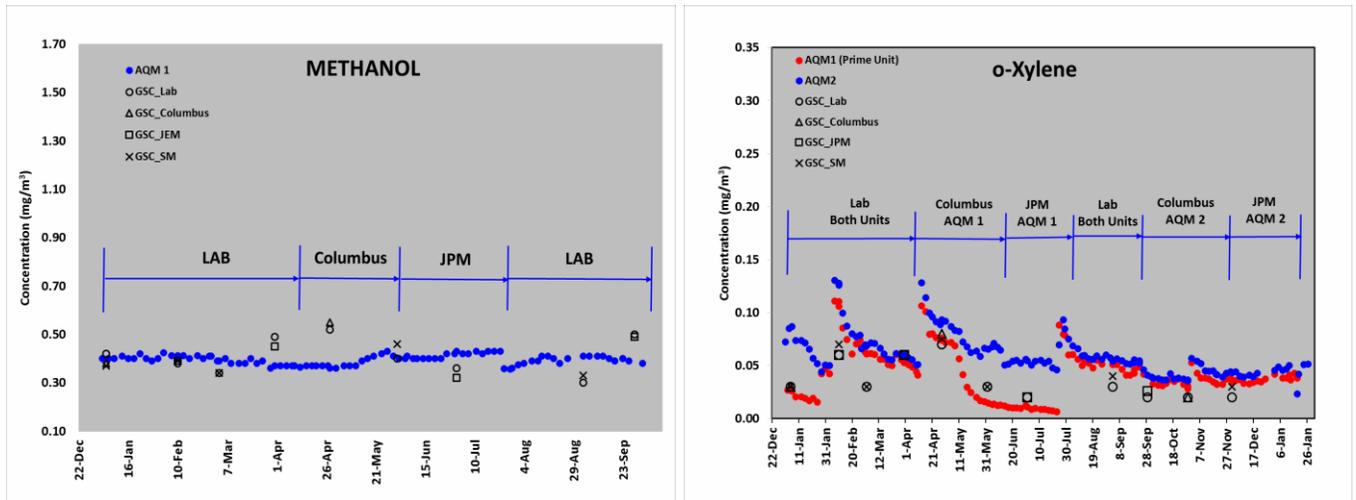


Figure 5. AQM module surveys. Location where the GSC was acquired is shown (i.e., GSC-Columbus).

Historically, ethanol concentrations in the ISS air had hovered around 2-3 mg/m³, with an occasional spike to 5-6 mg/m³ that lasted a few days. Then, the concentrations began to increase for long periods starting in April 2014. The following year, the water sensors began to detect a large conductivity increase in processed condensate water. Analysis of returned water samples showed high concentrations of ethanol in the condensate water, but none in the processed water. Although a definitive link between ethanol and the high conductivity was not established, the ECLSS engineers now receive weekly data from AQM to monitor the levels of ethanol in the air. A possible connection between ethanol levels in air and the condensate water conductivity is shown in Figure 6. The collection times for condensate water samples and when condensate was being processed tend to make the comparison more difficult, but the pattern of mutual increases for ethanol in air and water are still visible. Ethanol concentrations from AQM continued at relatively high levels through August of 2015. Engineers also monitor several other compounds in the ISS atmosphere including siloxanes that may lead to increases in total organic carbon.

One of the most potentially serious events started on January 14, 2015 when an ECLSS sensor indicated a large leak of ammonia near Node 2. Potentially, the leak could reach 0.5% to 1% ammonia in the atmosphere. The crew was quickly evacuated to the Russian Module (SM), and the hatch was sealed between the Russian Module and the other ISS modules. Pressure fluctuations in the LAB Module sensor indicated a leak; however, once in the safe haven the crew reported no symptoms or smell of ammonia while in the LAB Module.

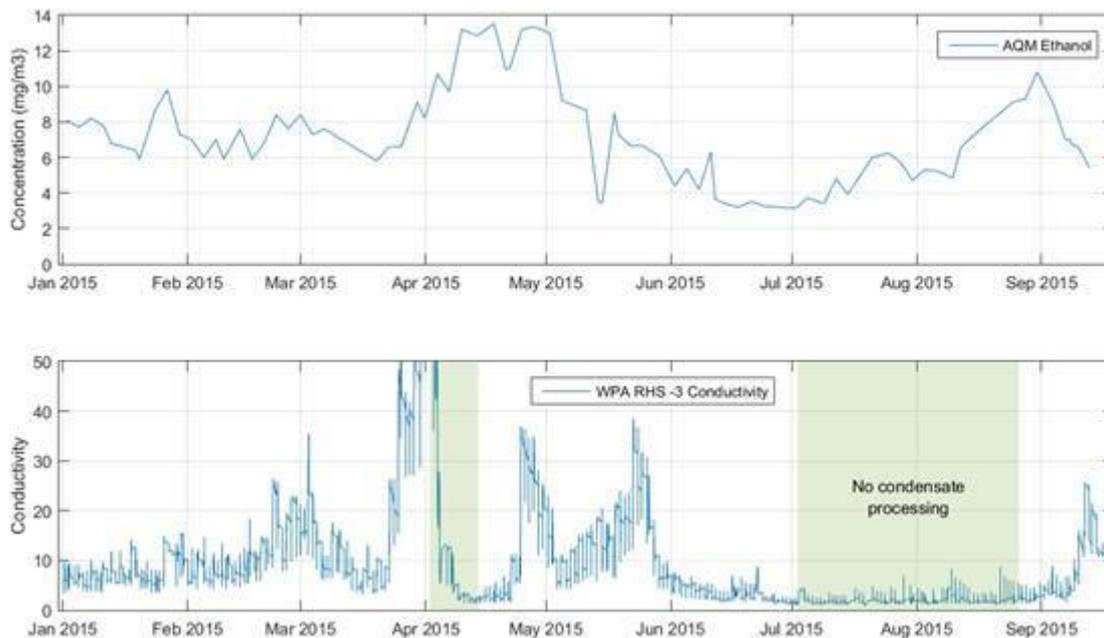


Figure 6. Comparison of ethanol data from AQM and water processor sensor.

The ECLSS engineers reviewed the data and were postulating it was a false alarm. There were only two ways to verify if ammonia had leaked: send the crew, with protective gear, into the unknown LAB atmosphere to acquire Draeger tube measurements or control the LAB AQM from the ground to analyze the atmosphere and downlink the data. As stated previously, the AQM would provide qualitative data and certainly could distinguish between no ammonia, nominal ammonia, or an ammonia concentration that was a danger to crew health and safety. The advantage of the AQM option was that the crew did not have to enter the LAB, where it was unknown if the protective gear would be sufficient, and movement to the LAB would also endanger the safe haven when the hatch was opened.

A decision was made to run the AQM that indicated there was no ammonia beyond nominal levels present in the atmosphere. Two runs, taking a couple of hours, were completed for absolute verification. After the AQM results, the crew did enter the LAB Module with protective gear to take Draeger tube samples, which also showed there was no ammonia leak. The AQM provided the data to confirm the ECLSS engineers' view that it was a false alarm without putting the crew in an unknown and potentially dangerous environment. The crew was able to enter the LAB Module with a high degree of confidence that there was no ammonia in the module. This is an excellent example of how the AQM is used to protect crew health and safety.

CONCLUSIONS

Over the past 2.5 years on ISS, the AQM has demonstrated its ability to remain in calibration for years and to be a reliable instrument, always available to address issues related to the atmosphere and crew health. The AQM experience on ISS demonstrates that the AQM could be valuable in other closed environment situations such as submarines. Furthermore, as on ISS, a script can be developed to run the AQM at prescribed times with no crew interactions. Data can be displayed on the instrument's GUI after a run or transferred wirelessly to a server or computer. Buttons on

the instrument GUI allow for multiple types of manual runs, if necessary. The only maintenance required is the replacement of the 3 sieve packs approximately every 6 months. This process takes only a few minutes. The data provided by AQM can verify that ECLSS is meeting requirements for submarines or other closed environments. Finally, the AQM aboard a submarine could be used to confirm other sensor readings and to contribute data to troubleshooting activities related to ECLSS or other submarine systems.

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