PROCEEDINGS

SAMAP

Submarine Air Monitoring Air Purification Conference

Resurgence in Submarine Shipbuilding

4th - 6th November 2019

Crowne Plaza Newcastle, Newcastle, UK

Sponsored by

ANALOX

CONTENTS

WELCOME LETTER

On behalf of the organising committee, it is my pleasure to invite you to join in the 12th Submarine Air Monitoring and Air Purification conference 4-6th November 2019 in Newcastle upon Tyne, in the heart of Geordie country. A city with a long and varied history synonymous with the 19th century Industrial Revolution, coal mining and shipbuilding. It also prides itself with a rich cultural heritage, flourishing liberal arts and a first-rate university. It is the eighth most populous city in the UK situated 166 km south of Edinburgh.

The SAMAP conferences are held every second year, alternating between Europe and North America. The aim of the conference is to bring together advances in research and technology related to the maintenance of a physiologically acceptable atmosphere in submarines and other enclosed environments. This involves a multidisciplinary approach encompassing analytical chemistry, toxicology, physiology, human performance and engineering. In this eclectic context, where possible the presentations are grouped according to the categories: air monitoring, air purification or health effects.

Historically, there has been some collaboration between submarine atmosphere research and air quality management in manned space vehicles due to the requirement for long-term isolation in an enclosed environment. Therefore input from space programs is relevant and always welcome at SAMAP.

The detailed organisation of each SAMAP conference is voluntarily undertaken by a local organisation or business with a long history of association with SAMAP. This year Analox and Sonistics, Ltd have undertaken the arduous task of organising this year’s conference, providing staff and financial resources to ensure a successful meeting. Thus we are particularly indebted to Vicky Pigg and Michelle Wilson of Analox, Stokesley UK and Sam Hopkins of Sonistics Ltd, Bath, UK.

Wally Mazurek, Australia.

(Convenor)

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KEYNOTE LECTURE

Tom Limero

Wyle Laboratories Inc., JSC, Houston, USA.

Thomas Limero hails from Springfield, Massachusetts and he received a Bachelor of Science degree in Zoology from the University of Massachusetts in 1969. He earned a Ph.D. in Analytical Chemistry from the University of Houston in 1988, where his doctoral work centered on development and characterization of a non-radioactive source for electron capture detector. Tom was the supervisor of the Toxicology Laboratory at JSC for 28 years. Under his guidance the laboratory developed new samplers, adopted EPA analysis protocols for archival samples, and developed, with commercial partners, real-time monitors to measure combustion products and volatile organic compounds aboard spacecraft. Over the past 3 years, Tom has taken on the role of subject matter expert (SME) in chemistry and continues investigate technologies for use aboard spacecraft, which now include nano-HPLC for biomarker detection.

OPENING ADDRESS

Waldemar Mazurek

CV Sept 2019

Waldemar (Wally) Mazurek joined the Department of Defence, Defence Standards Laboratories, DSL (subsequently renamed as the Materials Research Laboratories, MRL and later, the Defence Science and Technology Organisation, DSTO) in 1967 and worked in many chemistry disciplinary groups including textiles, paints, sealants and general chemistry. In 1991 he was appointed as the head of a new group on submarine atmospheres and in the same year he spent 13 months on attachment to the UK (DERA) MoD at Holton Heath, UK in the Submarine Atmospheres Group headed by Paula Dibben.

On return to the Australian Department of Defence he developed a research program in submarine atmospheres as well as collaborative research and information exchange programs with the USN, RN, the French Navy, Swedish MoD and the Netherlands MoD. In 1994 he organised the first Submarine Atmosphere Monitoring and Air Purification (SAMAP) conference in Adelaide, Australia and subsequently acted as convenor for SAMAP conferences in Europe and North America in collaboration with local colleagues and defence organisations.

During this period his group hosted two visiting scientists (UK and Sweden) as well as providing training for the USN in submarine diesel exhaust measurements.

In addition to the submarine atmosphere research, his group was also involved in air quality issues in surface ships, military aircraft and armoured military vehicles. He has published in the open scientific literature as well as internal publications and reports.

In 2014 he retired from DSTO but has maintained an active interest in the SAMAP conferences.

He holds an MSc and a PhD degree in chemistry, from La Trobe University, Melbourne, Australia.

PROGRAM OF EVENTS

Sunday 3rd November

13:00 - 17:00	Registration desk

Monday 4th November

07:30 - 08:30	Registration desk and refreshments
08:45	Welcome address by Cpt Martyn Boyes Royal Navy and Wally Mazurek
09:00	Keynote speaker Dr Tom Limero, Johnson Space Center, Houston USA
10:00 - 15:30	Speaker sessions

17:00	Coach leaves for Evening reception Boat Ride along the Tyne
17:30	Boat boarding
18:00	Sail time
20:00	Return to hotel

Tuesday 5th November

09:00 - 13:00	Speaker sessions
14:00	Bus departs for HMS Trincomalee Visist
16:00	Return to host hotel, evening at your own leisure

Wednesday 6th November

09:00	Speaker sessions
14:00 - 15:00	Closing comments and finish

ABSTRACTS

SUBS IN SPACE

Tom Limero

Wyle Laboratories Inc., JSC, Houston, USA

The collaborations between NASA and the U.S. Navy date back to the very beginnings of NASA in 1958. This presentation provide a time line of activities and collaborations from the earliest days to the present. Joint projects ranged from rockets to environmental controls, monitoring equipment, and air quality standards. Also, starting in the early 1990s NASA began discussions with the U.K. Navy and by the early 2000s, a joint project was initiated that involved NASA, the U.K. Navy, and the U.S. Navy. SAMAP has provided a forum by which NASA and the navies of the world have an opportunity to exchange ideas and innovations that have led to continued discussions and sea trials. NASA and the navies of the world face some similar issues with their partial closed environments and although differences in operational scenarios and logistics do exist, there is still good reason to share ideas and collaborate now and in the future.

A BRIEF HISTORY OF SUBMARINE AIR QUALITY

W. Mazurek, Australia.

The development of submarines is inextricably linked to the maintenance of a physiologically compatible internal atmosphere. The first submarine deployed during the American Civil War was man-powered and while submerged, lime was used to remove the carbon dioxide generated by the crew.

Early twentieth century submarines, powered by combustion engines were essentially semi-submersibles and dived for short periods to avoid visual detection. The development of radar during WWII facilitated the early detection of submarines requiring longer dive times for effective deployment. Although initially, atmosphere control was limited to maintaining acceptable levels of oxygen and carbon dioxide but as the demand for longer dive times increased, the maintenance of general air quality became necessary. This was particularly important with the advent of nuclear-powered submarines with dive times of several weeks or more. In fact the length of the dive was limited by the air quality. This necessitated monitoring of numerous air contaminants and the development of various air purification technologies. Furthermore, new methods of oxygen generation and carbon dioxide removal were required.

While modern conventionally powered submarines rarely staydivedbelow snorting depth for more than 3 days, the maintenance of air quality has become an occupational health and safety issue.

The presentation reviews the various air purification and air monitoring technologies deployed in early submarines until recent times.

ATMOSPHERE MONITORING – ASSESSING FUNCTIONAL LIMITS OF DETECTION

Mr Alan Chapman
Maritime Life Support, QinetiQ, Haslar Marine Technology Park,
Gosport, Hampshire, PO12 2AG, UK.

The UK Ministry of Defence has developed its own regulations for atmosphere control in submarines (BR1326). The UK Health & Safety Executive, and the European Union, continues to drive down chemical exposure limits for Industry and these are published in The Health & Safety Executive UK EH40 guidance document. Submarine Maximum Permissible Concentration (MPC) action levels for atmosphere contaminants must be reviewed when revised evidence of the risk to health of exposure becomes available.

Understanding the Limit of Detection (LoD) and Limit of Quantification (LoQ) achievable by on-board monitoring techniques is particularly important for Royal Navy submarines because continuous MPC action levels are typically lower than Workplace Exposure Limits and consequently are more challenging for monitoring techniques to achieve. Typically the upper limits of detection and quantification are less critical in the submarine environment and these are not addressed in this paper.

A number of alternative methods of assessing the lower operation limit of analytical techniques are routinely used. For direct reading toxic gas monitors sold in Europe this is most commonly performed to EN 45544:2015 [1] whilst retrospective analysis techniques are typically based on the in-house quality requirements of the individual laboratories. Eurachem Method Validation Working Group give guidance on how to determine LoDs and LoQs in their guide, The Fitness for Purpose of Analytical Methods [2]. This paper looks at the process used in both the EN 45544 and Eurachem methodologies and how this affects the confidence in the lower operating limit. It is especially important to use a single methodology for assessing the functional limits of methods when comparing real-time monitoring techniques against retrospective methods to allow a fair unbiased assessment.

NOVEL APPROACHES FOR THE INVESTIGATION OF SUBMARINE AIR QUALITY

A.V. Qualley[1], B Vaught[2], L.A. Beardslee[2], D.M. Fothergill[2] & H.M. Rubenstein[3]

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[2] United States Navy Naval Submarine Medical Research Laboratory, Naval Submarine Base, Bldg. 141, Trout Ave, Groton, CT 06349, USA
[3] United States Air Force 711th Wing – Air Force Research Laboratory, 711th Human Performance Wing/RHMO, 2510 Fifth Street, Area B, Building 840, Wright-Patterson AFB, OH 45433, USA

Introduction: Current passive dosimeter methodologies require the use of several different types of media and multiple analytical strategies for sampling and measuring airborne volatile organic compounds (VOCs). Here, the use of two non-traditional dosimeters, silicone wristbands (SWB) and mesoporous silica (MPS) tokens, were evaluated as universal passive dosimeters for contaminants present in the isolated atmosphere onboard a US nuclear submarine. The data presented describes our initial steps in exploring the technical feasibility of conducting individual longitudinal exposure monitoring for submariners using a universal passive dosimeter.

Methods: Surveillance sampling of airborne contaminants was conducted onboard a fast attack US Navy submarine using the new SWB and MPS dosimetry media and a currently used sorbent sampler produced by Assay Technologies, Inc. All media were exposed at eye level at 6 locations for a period of 22 days while the submarine was underway. Control media were brought aboard and remained isolated from the atmosphere for the duration of the study. Off-line thermal extraction with conventional thermal desorption gas chromatography/mass-spectrometry (TD-GC/MS) was used to measure 16 VOCs of interest adsorbed to the novel sampling media (MPS, SWB). Additionally, newly acquired modified off-the-shelf (MOTS) instrumentation (SIFT-MS) was investigated for the ability to expand the analyte range for each individual analysis.

Results: We were able to detect 13 out of 16 VOCs in the SWB and 11 out of 16 compounds in the MPS that were above the background levels measured on the control media. The amounts of the various VOCs measured was generally higher in the aft compartments (engine room) compared to the forward compartments but showed consistency in the relative amount between the different media except for benzene which was higher in the Assay badges. Our preliminary findings indicate that the MOTS SIFT-MS is capable of analyzing all of the 19 target VOCs simultaneously and that both MPS and SWB samplers can be used to introduce analytes into the SIFT-MS, albeit with differing levels of background interferences.

Conclusions: Novel media (SWB and MPS) demonstrated the ability to differentiate between separate compartments onboard the vessel based upon the spectrum of collected VOCs and showed good agreement between SWB, MPS and a legacy sorbent sampler produced by Assay Technologies, Inc. for most of the VOCs measured. We also demonstrated that SIFT-MS is capable of analyzing all of the target VOCs simultaneously. Preliminary findings indicate that both MPS and SWB samplers can be used to introduce analytes into the SIFT-MS via an automated TE step, albeit with differing levels of background interferences. Future experiments will determine sampling rates for the novel sorbent materials and evaluate the SIFT-MS as an alternative to TD-GC-MS based strategies.

(Funded by the U.S. Defense Health Agency, US Navy J9 Restoral and Joint Program Committe-5 Military Operational Medicine Research Program)

CONTAMINANT DETECTION IN THE SUBMARINE ENVIRONMENT

M. Leist, Defence Science & Technology Group

506 Lorimer St, Fishermans Bend, Victoria 3207, Australia

Submarine extended underwater endurance places a significant limitation on the ability to exchange contaminated air with fresh air. To ensure submarine operations do not pose a risk to crew health or damage to the platform, a thorough understanding of the levels and types of contaminates present is essential.

The measurement of contaminates within the submarine environment can be a complex task. The chemical composition of the submarine atmosphere can differ significantly from other industrial workplaces thereby creating unique analytical challenges. In addition, any chemical sensors installed must also be sufficiently robust and reliable to avoid increasing the workload of the crew, or the maintenance schedule of the submarine. The challenges facing the measurement of both gas and particulate matter will be discussed.

Originally at the request of the Royal Australian Navy (RAN), the Defence Science and Technology Group commenced a program to develop a prototype Tunable Diode Laser (TDL) sensor for the detection of Carbon Monoxide. Carbon Monoxide has been historically challenging to detect due to the elevated levels of hydrogen present in the Collins Class Submarine atmosphere. An update on the development of the sensor that is aimed to meet both the analytical and environment challenges will be provided and compared with current alternatives.

While the international Agency for Research on Cancer (IARC) have concluded that there is sufficient evidence for the carcinogenicity of engine exhaust, it is also important to be able to determine Diesel Particulate exposure to minimise lesser non-malignant potential health effects such as cardio vascular effects and inflammation effects in airways. The ability to determine crew exposure to diesel particulate matter in the submarine will also be discussed and atmosphere data presented.

ACUTE EXPOSURE TO DIESEL EXHAUST EMISSIONS: IRRITANTS

W. Mazurek

Australia

Diesel exhaust emissions are a major source of pollution in conventionally powered submarines in terms of both fugitive emissions from the engine and intake of exhaust emissions through the snorting tube. Exposure monitoring is largely confined to diesel particulate matter (DPM) measurements in real-time and retrospectively in addition to CO and NO_x measurements under steady-state engine running conditions. In the case of submarines, the engines are run at constant speed and constant load during battery charging with little variation in combustion conditions. However engine starts represent entirely different combustion conditions which affect the composition of the exhaust emissions. This is true of all combustion engines and where engine loads and speeds are variable the composition of the exhaust emissions is also likely to vary.

During the course of measuring engine exhaust emissions from a variety of military platforms, it became apparent that personnel exposure during engine idling resulted in eye nose and throat irritation. It is well known that the combustion process can produce lachrymatory compounds such as formaldehyde, acetaldehyde and acrolein. However, these compounds are not mentioned in exhaust emission regulations nor are they generally measured. This is generally because modern engine management technology has resulted in a significant reduction in the emission of these compounds. Unfortunately, military platforms tend to retain their engines for up to 20 years or more and the configuration of the exhaust may enhance exposure to personnel compared to civilian applications. Furthermore, in the case of submarines, the engines are custom built and are not covered by engine emission regulations.

The aim of this presentation is to illustrate the nature and concentrations of irritants produced by diesel combustion engines and the sampling and analytical techniques that can be deployed for the monitoring of these compounds.

CARBON MONOXIDE RELEASE FROM WHOLE BEAN ROASTED COFFEE IN STORAGE

Alan McCarrick and Benjamin Letter
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Shannon O'Dwyer
Naval Surface Warfare Center Philadelphia Division, Phila, PA
and Drexel University, Phila, PA

Matthew Knighton
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and Rowan University, Glassboro, NJ

Sara Jane Neal
Naval Sea Systems Command, Washington, DC

The process of roasting coffee beans produces carbon monoxide (CO) and carbon dioxide (CO_2) as unwanted byproducts along with the multiple flavor and odor compounds that become trapped within the coffee beans as they cool from the high roasting temperatures. After roasting is complete, these gasses begin to diffuse out of the beans. Roasted beans are normally kept for several hours to days to "temper" by releasing some gases before packaging. Coffee beans packaged in flexible, sealed bags with one-way vent valves slowly release these gases to the surrounding storage area. As the gasses diffuse out of the beans and the vent valve opens, all gaseous components are released into the surrounding atmosphere. Our data indicates that storage of roasted coffee beans in non-ventilated spaces can potentially raise concentrations of CO to dangerous levels. The Navy has an interest in determining the CO off-gassing rate and total capacity as it applies to shipboard storage involving large quantities of bagged coffee in order to ensure the safety and wellbeing of Navy sailors. An environmental chamber was configured to mimic the chamber volume to coffee mass ratio of storage aboard some US Navy ships. Increases in CO and CO_2 concentrations were measured over time for three different nominal temperatures: 40°F, 70°F, and 100°F. Off gassing rates were capable of generating hazardous levels of CO at rates significantly affected by temperature. Diffusion occurred more rapidly with increasing temperature. A second test at room temperature released CO at much higher rates than the first test. Further investigation indicated that the beans used for the second room temperature test had been shipped significantly closer to the roasting date than the manufacturer claims. This confirms that the rate of CO release is substantially higher immediately soon after roasting.

AN EVALUATION OF MONOETHANOLAMINE (MEA) DEGRADATION AND MITIGATION UNDER THE CONDITIONS USED IN SUBMARINE CARBON DIOXIDE REMOVAL PLANTS

Charles Cummings, Timothy Taylor

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The current carbon dioxide (CO_2) removal technology utilised on Royal Navy submarines is based on the amine, monoethanolamine (MEA). This reversibly binds CO_2 under ambient conditions and releases it when heated. However, this amine degrades within the plant yielding hazardous compounds such as ammonia (NH_3). In this study a laboratory test apparatus was used to evaluate MEA solutions containing a range of inhibitor additives to determine which experienced the least degradation. A series of additional experiments were carried out to optimise the sorbent used to remove reaction adducts and metal impurities from the MEA within the system. These investigations concluded that the existing inhibitor additive was the most appropriate based on performance, cost, and exposure hazard but improvements could be achieved by using alternative sorbent media. The methodology presented can be applied to new CO_2 removal technologies including solid amines which also degrade to release NH_3.

VOLATILE ORGANIC COMPOUNDS (VOC) INTERACTION WITH HIGH AND LOW TEMPERATURE CARBON MONOXIDE/HYDROGEN OXIDATION CATALYSTS

Gareth Toft[1], Charles Cummings[1] & Tina Goodall[2]

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Under its duty of care the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere. A key component in this is the high-temperature carbon monoxide (CO)/hydrogen (H_2) burner. This employs a bed of Moleculite®, a copper oxide/manganese dioxide oxidation catalyst at elevated temperature. Although the primary function of the burner is the removal of H_2 and CO an important secondary role is the removal of Volatile Organic Compounds (VOC). This paper presents the finding of an investigation to determine the removal performance of Moleculite® for several submarine atmosphere VOC. Removal of between 61 and 76 % total VOC content was found, suggesting that the CO/H_2 burner has a significant impact on the level of atmospheric VOC. Whilst Moleculite® has been the catalyst of choice for many years, other materials which operate at lower temperatures are of growing interest. Use of these alternatives would provide significant power savings. Low-temperature catalysts have the potential to be poisoned by submarine atmosphere contaminants. The laboratory evaluation of two Johnson-Matthey precious metal catalysts is reported. Results showed that VOC had only a minimal effect on CO and H_2 oxidation performance and that these catalysts had an average VOC removal of 78.5 %. Low-temperature catalysts have potential to replace the currently used high-temperature catalyst with no adverse effect on either CO/H_2 or VOC removal performance.

DESIGN IMPROVEMENTS TO THE MPOG OXYGEN GENERATOR

Pete Hutchinson

Air purification, Survival in disabled submarine

Molecular Products is a world leader in the design and manufacture of life critical devices for the treatment of breathable gases and the filtration of hazardous or harmful emissions. Where there is a finite quantity of air, Molecular Products' leading-edge technologies will sustain human life independently, or collectively, to maintain a breathable environment

Over the past decade Molecular Products has developed the newest additions to their oxygen portfolio; the MPOG and EO2-30. These oxygen generators are used globally to provide breathable oxygen in closed environments; primarily submarines, mines and safe havens. The subtlety of the technology comes from the concentrations of iron and sodium chlorate in the chemical formulation to control the rate of the reaction and the oxygen volumes produced. Sodium chlorate chemistry has been commercially proven over decades of use and has been relied on in some of the harshest environments to generate breathable oxygen since the early 1900s.

In the MPOG and EO2-30, Molecular Products has designed intrinsically safer through-life products, driven by an extensive development programme and a comprehensive understanding of their lifecycle. But design and development are a continuous process that relies on consistent feedback and collaborative relationships with customers. And it is these two things that are pivotal in ensuring that Molecular Products remains at the forefront in the manufacture of life support devices for some of the world's most inhospitable environments.

When launched in 2011, the MPOG was a new evolution of oxygen generator that offered improved user experience and better protection. In this presentation, Molecular Products will discuss how a close working relationship with users and honest feedback has led to design improvements to the product. Including changes to chemical classifications that resulted in replacement material being sourced, to ensure a safe product is supplied. We will talk through the test regime, performance criteria and design changes that have led to the MPOG Mk2.

MONITORING THE CO2 LEVELS WITHIN A CO2 SCRUBBER TO GIVE AN INDICATION AS TO WHEN TO CHANGE THE SCRUBBER MEDIA

M. Richardson
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Stokesley, North Yorkshire, UK, TS9 5PT

Active CO2 scrubber systems using CO_2 canisters or CO_2 scrubbing packs, operate by forcing atmosphere through multiple scrubber media, often installed in parallel. This means airflow from a drive pump/fan is branched, with each branch passed through a set of scrubber media, following which the branches are recombined before the scrubbed atmosphere is distributed to the vessel.

In general these systems are operated by changing out the CO_2 scrubber media in the system at a set time period calculated previously from information of the usage rate of the scrubbers. This may result in a situation that some of the media still have usable life left due to the possible differences in flow distributed to each scrubber medium installed in parallel and the variation of usage rates due to activity within the boat. This situation may be further complicated by a boat having multiple active scrubber systems installed in different areas of the boat, with each system potentially being exhausted at a different rate.

The early replacement of scrubber media means that more need to be carried on a vessel than are necessarily required, or with a given stock the ability of the submarine to stay submerged without taking in fresh air, by snorting, is reduced.

Analox proposes that the efficiency of the scrubber media use could be improved by the instrumentation of the scrubber system, to check in real time the usable life left in each scrubber media. To test this hypothesis we intend to instrument an active scrubber system to measure the relative usage rate of scrubber media to determine the magnitude of the efficiencies that could be gained by fully utilising each scrubber medium and replacing them only when they become exhausted, rather than replacing all scrubber media onboard when the CO_2 level across the vessel reaches a set level or a predetermined estimated time expires.

This measurement of the potential benefit of fully utilising each scrubber medium will then be used to build a set of proposed actions that could be taken to improve submarine active scrubber system performance.

TEST RESULTS OF TWO NEW NON-REGERNERATIVE CARBON DIOXIDE SCRUBBERS

Peter Row[1] and Thomas Daley[2]
[1]TPG Maritime Ltd. UK
[2]Micropore Inc. USA

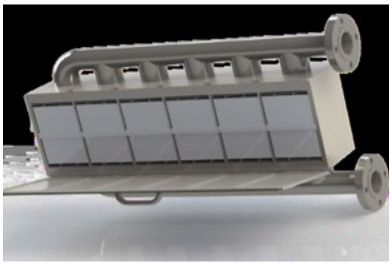
Micropore has teamed with TPG Maritime to develop a new series of non-regenerative carbon dioxide (CO_2) scrubbers. These units are intended for atmosphere control applications such as submarines, hyperbaric chambers and small submersibles. TPG maritime has a long history of design, build and support of submarine atmosphere control systems. Micropore developed and manufactures a proprietary CO_2 adsorbent that encapsulates fine alkaline powder into a solid sheet. Integrating Micropore PowerCube® adsorbent into a family of custom designed scrubbers allows for optimal utilization of adsorbent in a space and power optimized design.

The first commercially available scrubber was the single cube CO2RE (Carbon Dioxide Removal Equipment) scrubber. This scrubber has an installed fan (AC or DC powered) and the option of inlet and outlet infrared CO_2 analyzers for automated operation. The power requirement is low (several watts) due to low airflow resistance through the scrubber and adsorbent. This paper will report on the performance test results over the typical range of submarine ambient CO_2 concentrations.

The second scrubber offered by TPG Maritime is a 6 cube unit with multiple arrangements. This scrubber is intended for back-fit or new construction diesel electric submarines. These scrubbers offer 6 cubes in either two banks with parallel flow or all 6 cubes in parallel. Due to the low pressure drop, airflow can be provided by existing ventilation system or by a dedicated fan. Performance test results for these cubes is reported in this paper.


CO2RE Single Cube


6 Cube Scrubber
for retro-fit


Inline 6 Cube
Scrubber

A HISTORY OF CO_2 SCRUBBING ON BOARD WALRUS CLASS SUBMARINES

Toon Mariën

Ministry of Defence, NL

An overview of CO_2 scrubbing on board Walrus class throughout the years.

During the build of the Walrus class, 8 scrubbers for scrubbing CO_2 were build and implemented. Two scrubbers were installed on each Submarine, positioned in Wardroom and Torpedo storage room. These scrubber made use of canisters filled with Sodalime Granuals.

Already during the first few years it became clear that the scrubbers were not performing as expected. So throughout the years RNLN made small changes, as air flow rate and internal cannister changes by OEM. In 2007 there was a study upon improving CO_2 scrubbing, one of the conclusions was that more volume of adsorbing material was needed, even with 100% use of the canisters in the two existing scrubbers. **This resulted in a 3rd scrubber**. The third scrubber gave a slight but not sufficient improvement so further research was done.

From start of operating Walrus class until 2013/2014, the MAC values of CO_2, were a maximum level of 1.5% (no designated time limit), and a 24 hours maximum level of 2%.

With a new POR for new canisters the responsible department of the Defence Material Organization was triggered on the MAC levels. At the end of 2013 a research was initiated on admissible CO_2 levels, this resulted in new MAC levels for CO_2 on Netherlands submarines

After a study on values to be in forced on submarines RNLN decided that we had to go down with .5% on our values now resulting in a CO_2 operational maximum for 1%, and a 24 hours maximum level of 1.5%.

During 2014 and 2015 RNLN did several tests, first test (Power cube test) was presented at SAMAP 2015. This made RNLN switch from granual canisters to the Power cube adapter and the CaOH power cubes. A other test was ("The Nesquick" test) on the internal airflow on the original two scrubbers. Also presented at SAMAP 2015 (by Barend van der Giesen)

RNLN, together with manufacturer of the Power cube adapter and the 2 different Power cube blocks wanted to perform an on board test. So in 2014 RNLN performed a test on board submarine Dolfijn. During the power cube test RNLN made use of the Power cube adapter and 2 different kinds of scrubbing material blocks (CaOH- and LiOHPowerCube). This was presented at SAMAP 2015

Continued overleaf

The combined conclusions of these test were:

- Install a third scrubber
- Use the Micropore powercube adapters in combination with the Micropore calcium hydroxide blocks (Powercube)
- Improve airflow through the two existing scrubbers

After implementing the first two conclusions the CO_2 levels on board submarines improved and even became lower than expected. Although RNLN did not perform an endurance test up to this moment.

The third conclusion is work in progress. In 2018 a company performed CFD analysis on both old scrubbers and were asked for suggestions on improving the internal airflow, after some modelling and calculations the conclusion was that a suggested small change, would make a big difference and was the best solution for both scrubbers.

With this small change on a part of the scrubber the airflow could be improved to get an almost evenly airflow through all power cubes.

The average deviation on the torpedo storage room scrubber changed from 5.44% to 0.53%. The Ideal airflow is 16.67% through each of the six power cubes.

The improvement on the Wardroom scrubber was significant less than the improvement on the Torpedo storage room scrubber. Never the less RNLN made the change on both scrubbers.

The Average Deviation on the wardroom scrubber is under 1%. No graphs or pictures on the Wardroom scrubber about air flow are available in this presentation.

RNLN implemented this improvement on one of the submarines and is looking for an opportunity for testing.

What now?
So RNLN has mounted a third scrubber (final design) and made the changes to the two existing scrubbers on one of our submarines. This coming fall RNLN will implement the changes to the two scrubbers on the second submarine and have to plan and perform a quayside - and sea trial.

PLAN:
1st, Perform a static quayside trial, like RNLN did before, find a few a bit crazy guys, Put these guys in a closed down submarine, give them fire extinguishers, have them discharge aprox 2.8 kg CO_2 /hour into the submarine for simulating a crew of 62 and let them measure: CO_2, O_2, temperature, humidity and 2nd Perform sea trial to look at the performance under real life submarine conditions.

WHY USE A DSVDS FOR SUBMARINE RESCUE?

Jos Bogaert
SMERAS Consultant. Den Helder, The Netherlands.

Every scenario of distressed submarine is different, but critical parameters that may limit survivability of the crew are always the same:
- Pressure rise
- Toxic atmosphere
- Loss of life support capability
- Time

In an ideal world, it should be possible to undertake:
- Fast mobilization of rescue elements
- Fast localisation and environment assessment
- Safe & fast rescue intervention
- Immediate medical treatment for sub’s crew

A lot of rescue systems like NATO NSRS (or equiv.) are available.
Most of these systems have the following functions :
- Transportable full rescue system
- TUP facilities
- On-board decompression chambers & medical experts

In some cases, SRS intervention may be difficult, or even impossible:
- System not available (maintenance…)
- Longer mobilization of system
- Technical failure before or during operation
- Bad sea conditions
- Sub/SRS interface unreachable by SRS or damaged
- Sub/SRS interface unreachable by sub’s crew

In such situations ADDITIONAL TIME is needed

To increase significantly preparation and intervention time, the following problems must be addressed :
- Avoid toxic atmosphere inside Sub by regeneration/ventilation
- Continuous monitoring and control of inside pressure
 Ventilation and Depressurization System (DSVDS)
- Ensure life support for the ELSS Pod posting

Continued overleaf

Background

A DSDVS provides the means of remotely de-pressurising and / or ventilating a DISSUB compartment that is subject to elevated internal pressure, or has an atmospheric specification beyond breathable limits.

A DSDVS therefore has two purposes; firstly to control pressure /de-pressurise, and secondly to ventilate.

The former would either be able to maintain pressure within survivable limits (against for example a rising pressure gradient) or to lower the pressure to reduce the surface decompression obligation.

The latter would supply air and remove waste gases.

DISSUB Internal Pressure

Of all the factors influencing the system capabilities, the target pressure (and airflow) in the DISSUB is arguably the most critical. It is from this point that the rest of the system must be matched and sized

When looking at a system that supplies breathing air, too high a DISSUB internal pressure demands a high flow to provide sufficient refreshing of the atmosphere to accommodate the submariner's life support consumption rates – whilst the higher internal pressure aids recovery of the exhaust gasses, the size of the recovery hose this may entail on the recovery side could hamper system mobilisation.

The consequent increase in supporting equipment quickly adds to the overall size of the rescue spread.

Too low a target pressure reduces the differential available to exhaust spoiled air at the surface.

Flow Rate Limitations

The flow rates required to maintain the atmosphere within habitable bounds are a function of:

- the consumption rates of the submariners
- the pressure of the chamber
- the size of the chamber
- any contaminated air to be removed and production sources of contamination
- the smallest restriction in the line

It is also worth noting that the flow rates may produce problems at entry to the DISSUB –there is a physical limit to the velocity with which air may enter and exhaust through a salvage point. A restriction at this point, should be investigated with respect of orifice size and internal layout. This will then have an impact on the system. Although it is possible to increase mass flow rate with pressure, the velocity shall remain constant, the point at which this occurs on a submarine requires understanding ahead of purchasing a system as it may affect internal pressures

Transportation

The system has to be air transportable, and the items specified comply with JADTEU guidelines.

It is worth noting however that standard 20ft ISO specified size of shipping container disqualifies use of certain common 747 transport planes. These planes have historically been the most readily available means of air mobilisation and form the basis of many designs.

If a specific set of air transport guidelines or the details of the most readily available air transporter were available, the design may be specifically tailored to this.

Continued overleaf

Medical Air / Oxygen

A system capable of introducing oxygen, coupled with ELSS pod posting of LIOH Curtains or similar would offer additional system flexibility at extremes of operation.

Integration of such facility is a relatively small cost when considering the purchase of a system but adds an additional layer of capability and the ability to extend the habitable environment in certain scenarios.

A system capable of supplying oxygen must be designed with this in mind at the outset and material and safety considerations applied throughout as standard.

Umbilical System Deployment

The means of deploying the umbilical, requires thoroughly integrated and must be considered as the system develops. Historically this is one of the most challenging aspects when providing a rescue ready DSDVS.

Regard for factors such as deck handling, splash zone transition, submarine interface, ROV and diver interface and surface ship stability are critical. Whilst a large diameter umbilical facilitates the flow rates, were it also load rated, its stiffness would demand a winch of such dimensions that it would severely limit deployment and mobilisation.

DSVDS Exercises

- Although there are several systems in use with different Navies, knowledge of the working of the systems is minimal
- Every exercise a successful coupling of the hoses is performed and when air is flowing the exercise stops
- All these exercises take place at limited depths while the real challenge is to do it deep
- Also not much thought is given how to deal with partial pressure of oxygen / CO2 and what mixture to supply to the submarine

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Thomas Limero, PhD
KBR/NASA Johnson Space Center

NASA/Navy Collaboration
The Early Years

- The Naval Research Laboratory (NRL) was deeply involved in development of rockets after World War 2
- NRL funded development of the Aerobee sounding rocket
  - Sounding rockets sent instruments beyond Earth's atmosphere to collect data for a short period of time
  - The Aerobee rocket launched the first mass spectrometer (Bennett MS) into low earth atmosphere to study radiation above the Earth's atmosphere
- Almost the entire work force (47) at NRL involved in the Aerobee work was transferred to NASA upon its formation in 1958 to build the space science and sounding rocket programs at Goddard
- NASA launched almost 150 Aerobee rockets per year during the early 1960s to study cosmic rays and other radiation impacting Earth

NASA/Navy Collaboration
The Early Years: Apollo Era

- Similarities
  - Partially closed environments
  - Escape is not possible by opening a door or hatch
  - Continuous exposure to the atmosphere (24/7)
  - Crew relies on air scrubbing for acceptable environment
  - Both have emergency escape options (ISS-Soyuz and submarines- surface or dissub scenarios)
- Differences
  - Crew size is drastically different
  - Differences in volume
  - Cooking-real food
  - Environment: microgravity vs. pressurized volume
  - Scrubbing is more robust on submarines
- Sounding rockets continued to launch for NASA under the guidance of the personnel transferred from NRL
- In the 1960s, a recognition of similarities between the closed environments of submarines and spacecraft led to collaboration on setting spacecraft limits on contaminants

NASA/Navy Collaboration
The Early Years: Apollo Era

- In 1968 NASA began to explore setting maximum allowable concentrations (MACs) for the expected longer duration missions to come
- NASA requested the NRC's Space Science Board to organize a panel on Air Standards for Spaceflight
  - The task was to evaluate the effect on contaminants on the health and performance of crews for long-term missions and short-term emergency limits
- Approximately 200 contaminants had been identified based upon offgas tests and simulated spacecraft environments.
- Of the 200 contaminants, 23 had contaminant limits of 90 days established by the NRC's Committee on Toxicology (COT) for submarine environments.
  - The Space Science Board recommended the established limits for these 23 compounds be used for spacecraft
  - NASA recommended 11 more compounds that required contaminant limits, plus 5 others that were required to have emergency limits

NASA/Navy Collaboration The Early Years: Apollo Era

90- Day Limit

Contaminant	mg/m^3	Contaminant	mg/m^3
Acetone	71	Methane	3300
Acetylene	2700	Methyl alcohol	13
Ammonia	17	Methyl chloroform	3000
Benzene	3	MEA	1
Carbon Monoxide	29	Nitrogen dioxide	1
Chlorine	0.3	Ozone	0.04
Freon 12	5000	Phosgene	0.2
Freon 114	7000	Sulfur dioxide	2.6
Ethyl alcohol	115	Toluene	188
Hydrogen	245	1,1,1 trichloroethane	1100
Hydrogen chloride	1.5	Xylene	217
Hydrogen fluoride	0.1		

Provisional Spacecraft Limits (mg/m^3)

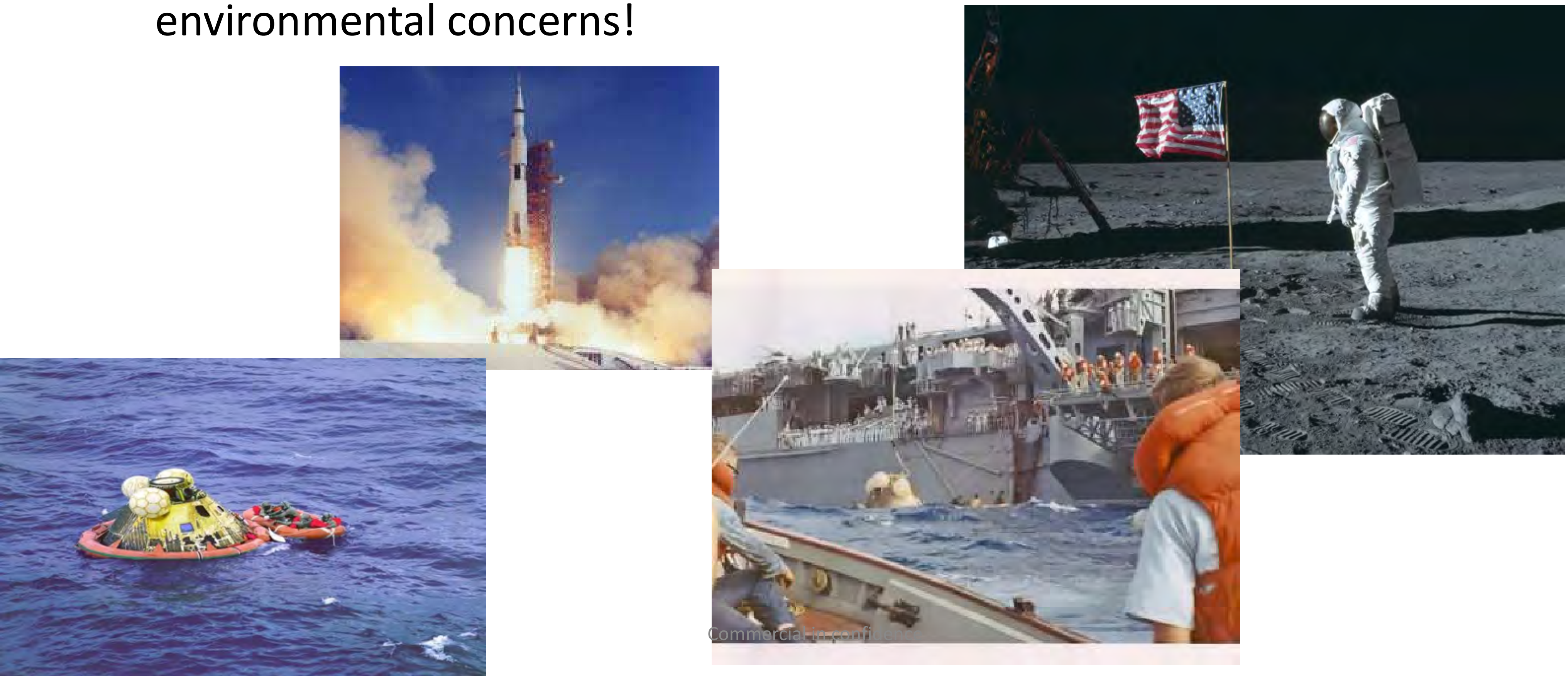
Contaminant	90 Days	1,000 Days
n-Butanol	30	30
2-Butanone	58	59
Carbon Monoxide	17	17
Chloroform	24	5
Dichloromethane	105	21
Dioxane	36	7
Ethyl Acetate	144	144
Formaldehyde	0.12	0.12
2-MethylButanone	82	82
Trichloroethylene	54	11
Freon 113	161	N/A

Provisional Emergency Limits

Contaminant	mg/m^3 (60 min)
2-Butanone	294
Carbonyl fluoride	67
Ethylene glycol	253
2-Methylbutanone	409
Freon 113	1612

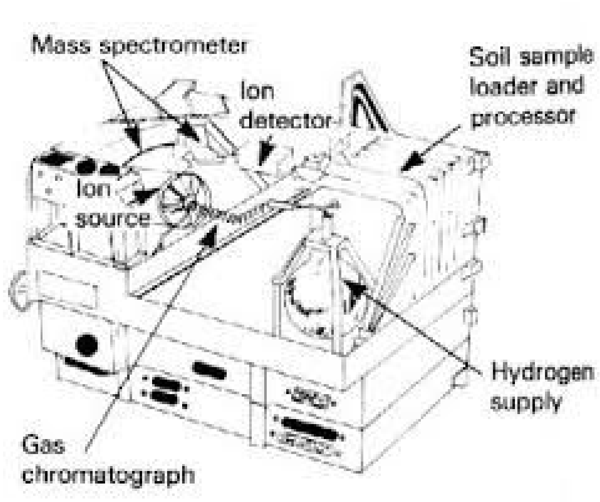
NASA/Navy Collaboration
The Early Years: Apollo Era

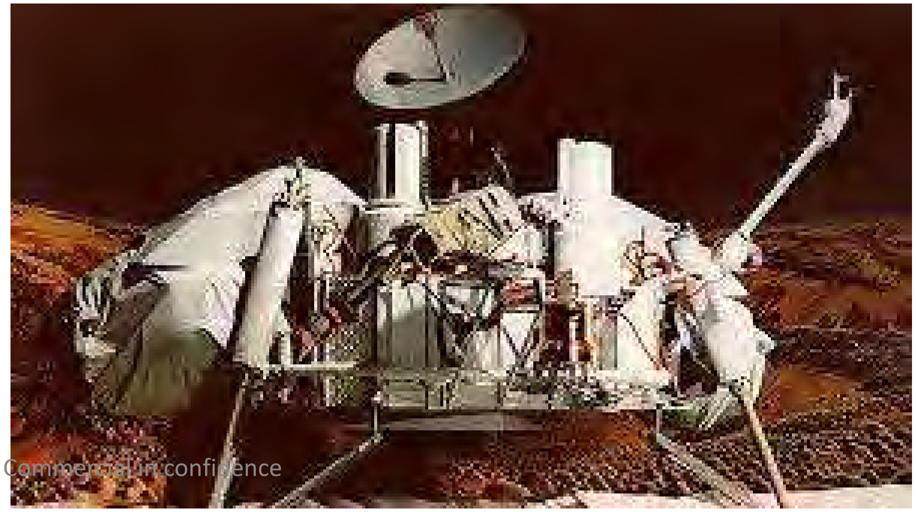
- And of course the Navy and NASA had collaborations beyond environmental concerns!



NASA/Navy Collaboration
The Early Years: 1970s

- The first robotic mission to Mars was called the Viking Lander
- Viking Lander had among its suite of instruments a very unique gas chromatograph-mass spectrometer (GC/MS)
- The mass spectrometer was a robust magnetic sector instrument that used an ion pump to maintain the vacuum
- This instrument's reliability and small size drew the interest of the NASA medical community and the U.S. Navy





NASA/Navy Collaboration
The Early Years: 1970s

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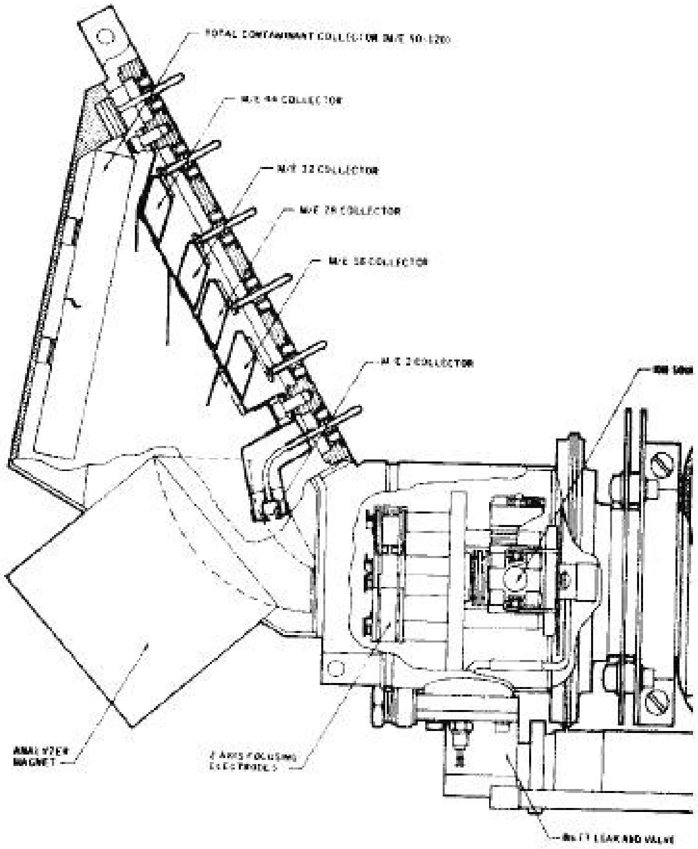


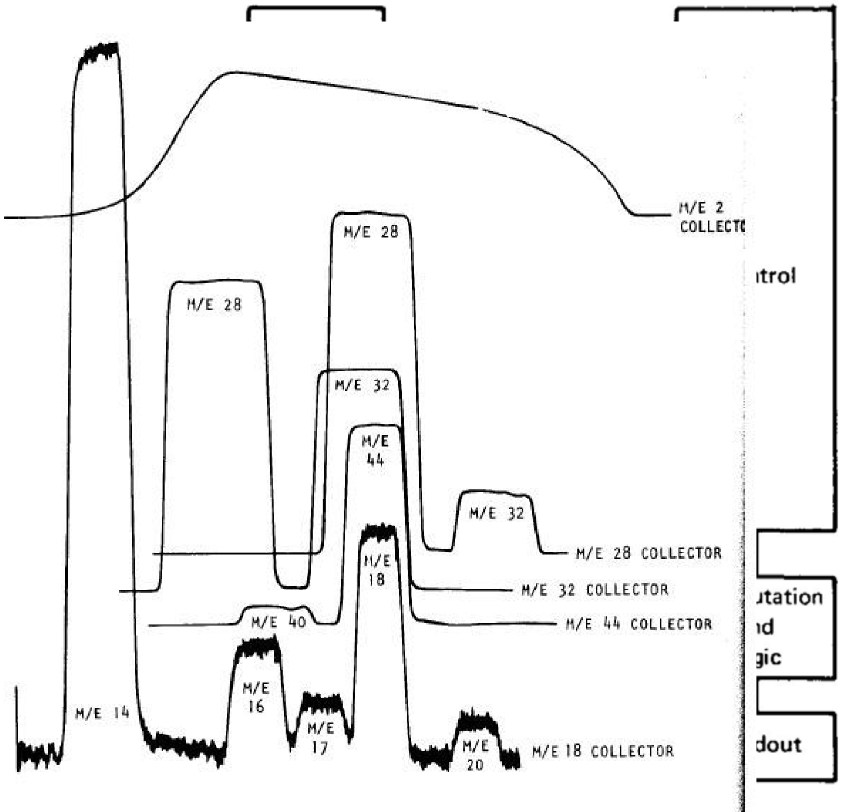


FIGURE 3. Typical Mass Peaks and Collector Alignment

NASA/Navy Collaboration
The Early Years: 1970s

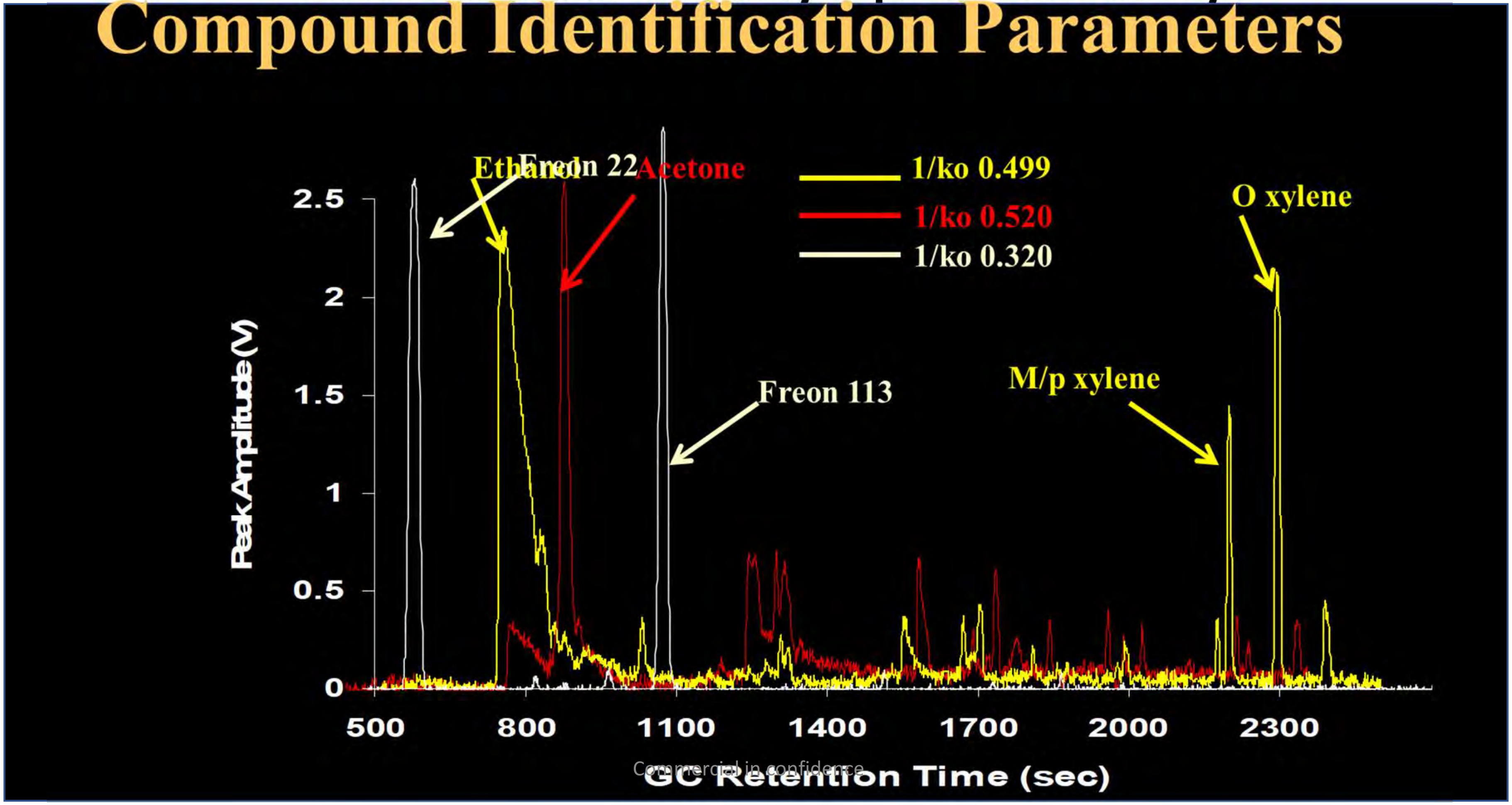
NASA/Navy Collaboration
1990s

- In the early 1990's the NASA toxicology group had discovered ion mobility spectrometry and was considering what uses it might have for spaceflight
- The first application of this new technology was as an experiment for detecting hydrazine onboard spacecraft.
  - The hydrazine monitor was a modified Graseby Chemical Agent Monitor (CAM)
  - Although the flight of the unit was successful, it became a victim of funding cuts in the space station program

NASA/Navy Collaboration
1990s

- During the initial work with the hydrazine monitor we began to think if, a gas chromatograph were interfaced to the detector and there was no dopant, would it be possible to measure trace organic compounds in the air
- The new ISS was going to require monitoring of trace contaminants in the air, but gas chromatography/mass spectrometry did not seem to the answer during this time.
- The advantages of this technology, ion mobility spectrometry, was that no vacuum pump was required and there was potential for reliable long-term operation and no periodic calibration

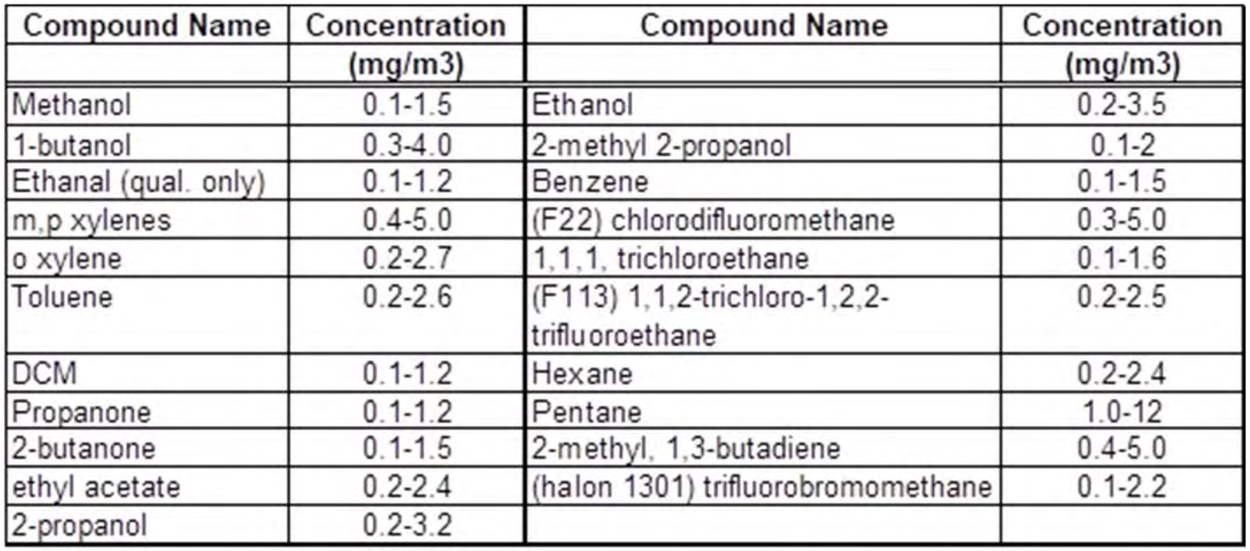
NASA/Navy Collaboration
1990s: Ion Mobility Spectrometry



Compound Identification Parameters

NASA/Navy Collaboration
1990s

- Target compounds for the VOA



Compound Name	Concentration (mg/m3)	Compound Name	Concentration (mg/m3)
Methanol	0.1-1.5	Ethanol	0.2-3.5
1-butanol	0.3-4.0	2-methyl 2-propanol	0.1-2
Ethanal (qual. only)	0.1-1.2	Benzene	0.1-1.5
m,p xylenes	0.4-5.0	(F22) chlorodifluoromethane	0.3-5.0
o xylene	0.2-2.7	1,1,1, trichloroethane	0.1-1.6
Toluene	0.2-2.6	(F113) 1,1,2-trichloro-1,2,2-trifluoroethane	0.2-2.5
DCM	0.1-1.2	Hexane	0.2-2.4
Propanone	0.1-1.2	Pentane	1.0-12
2-butanone	0.1-1.5	2-methyl, 1,3-butadiene	0.4-5.0
ethyl acetate	0.2-2.4	(halon 1301) trifluorobromomethane	0.1-2.2
2-propanol	0.2-3.2		

  - Frequently detected in archival samples from spacecraft at measurable concentrations (i.e., ethanol)
  - Although rarely detected in spacecraft air, the compound has moderate to high toxicity (i.e., benzene)
  - Can affect the performance of the ECLS systems (i.e,., 2-propanol)

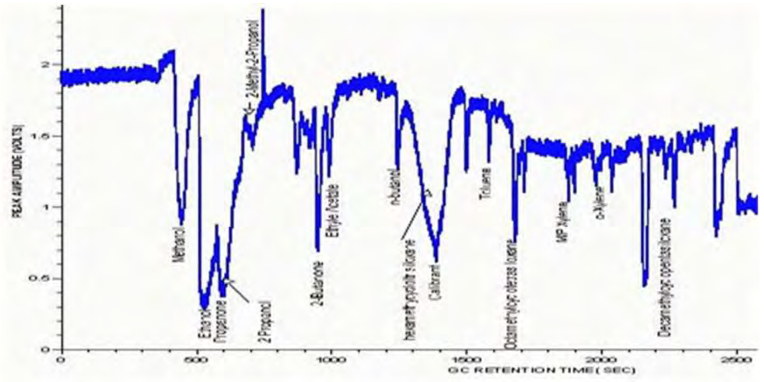
NASA/Navy Collaboration
1990s

- The Volatile Organic Analyzer (VOA) was selected as the trace contaminant monitor for ISS
- NASA initiated a risk mitigation program to test potential ISS hardware and the VOA risk mitigation experiment (VOA/RME) flew on two Shuttle missions

VOA/RME on STS-89 Shuttle Mission

NASA/Navy Collaboration 1990s

- More on the VOA/RME in a few minutes, BUT FIRST
- The data from the VOA/RME experiments showed excellent results in comparison with archival grab sample container collections
- Important lessons were learned
  - The sample volume used was too large as the VOA/RME was sensitive to trace organic compounds
  - Most importantly, a few peaks appeared in all runs. After reviewing the drift time of the peaks and the GC retention time, plus review of the GC/MS data for the archival samples it was thought they were siloxanes. Standards verified that indeed the peaks were siloxanes and they were added to the target list.



NASA/Navy Collaboration
1990s

A FORCE OF NATURE!

- In 1994, Hilary and I discovered that we were both working with ion mobility spectrometry for use in closed environments. Hilary on submarines and me on spacecraft
- We continued having discussions and following each other's progress throughout the 1990s at the ISIMS conferences, and via occasional visits and discussions
- Hilary told me about SAMAP and I attended my first conference in 2000
- I was at Hilary's house with Mike and a colleague on 9/11/2001, as we had met to discuss a possible submarine trial using the VOA/RME

NASA/Navy Collaboration
1990s

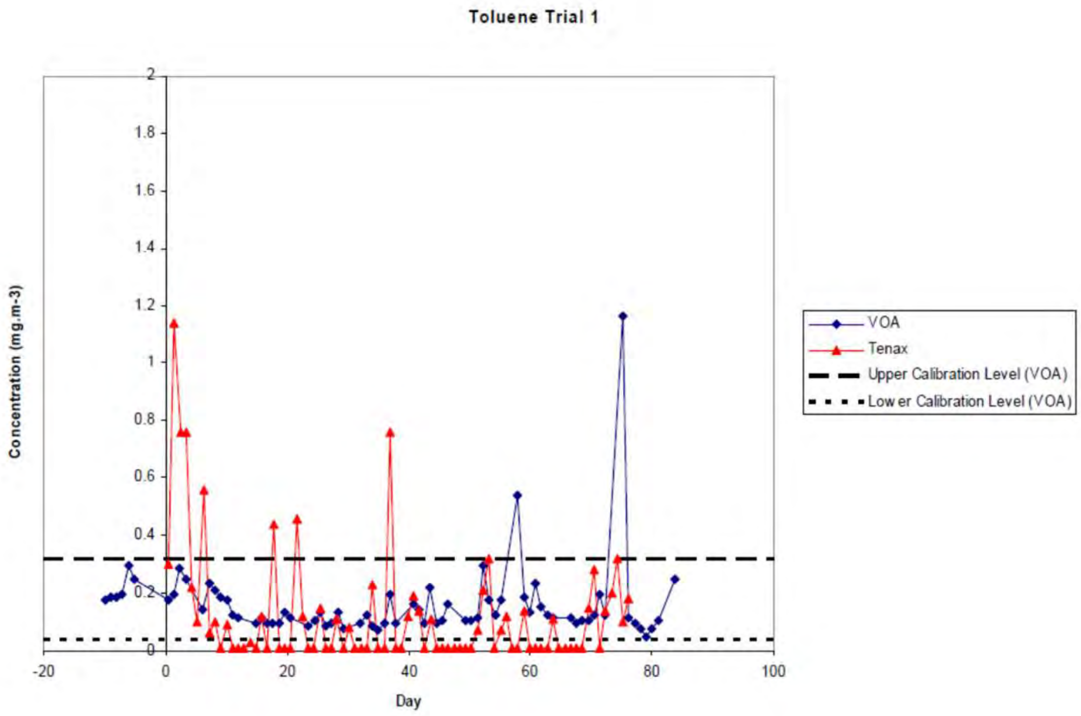
- Getting the VOA/RME to the UK Navy for a sea trial was not straight forward: What you would think it would be

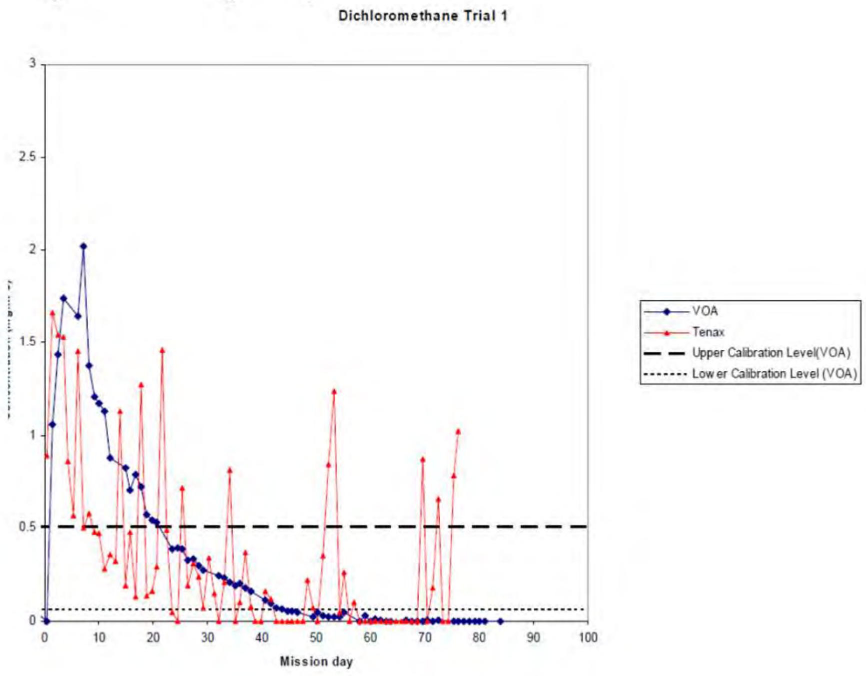
- At the SAMAP meeting in 2000, Dr. Bollan was able to bring together the U.S. Navy, U.K. Navy, and NASA. A process was created to allow the transfer of the VOA/RME to the U.K. Navy for a submarine trial

NASA/Navy Collaboration
2000s: VOA/RME submarine Trials

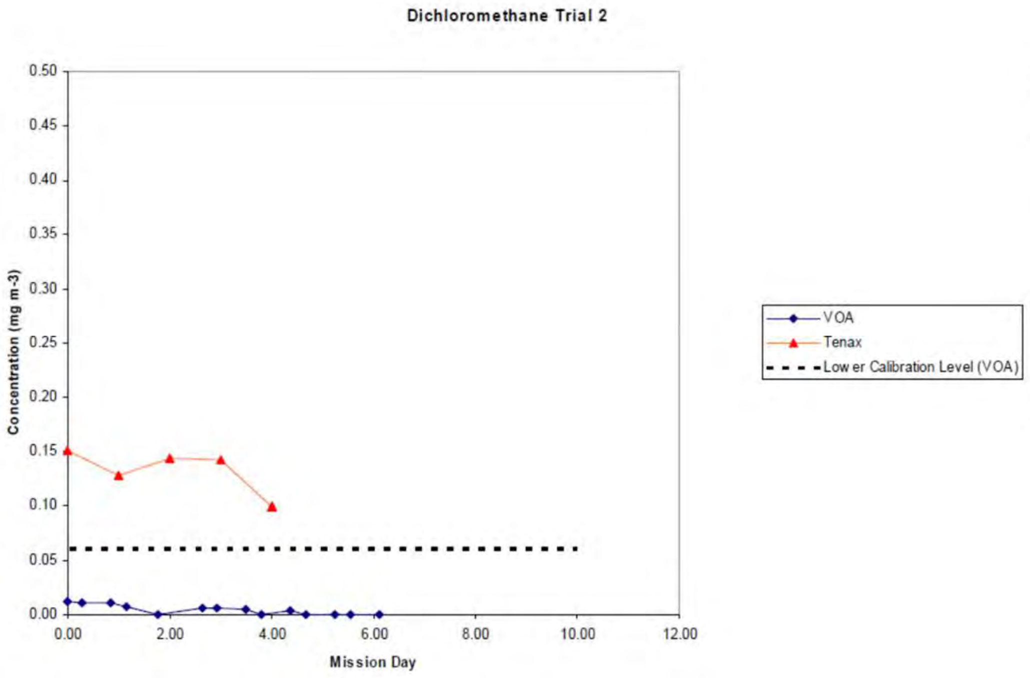
- The installation and first sea trial of the VOA/RME occurred in 2001
- Two objectives of the trial were to learn more about the dynamics of the contaminants in the atmosphere and to assess the data acquired via retrospective samplers
  - The retrospective samplers were glass tubes filled with Tenax that were sealed via torch after the sample was collected.

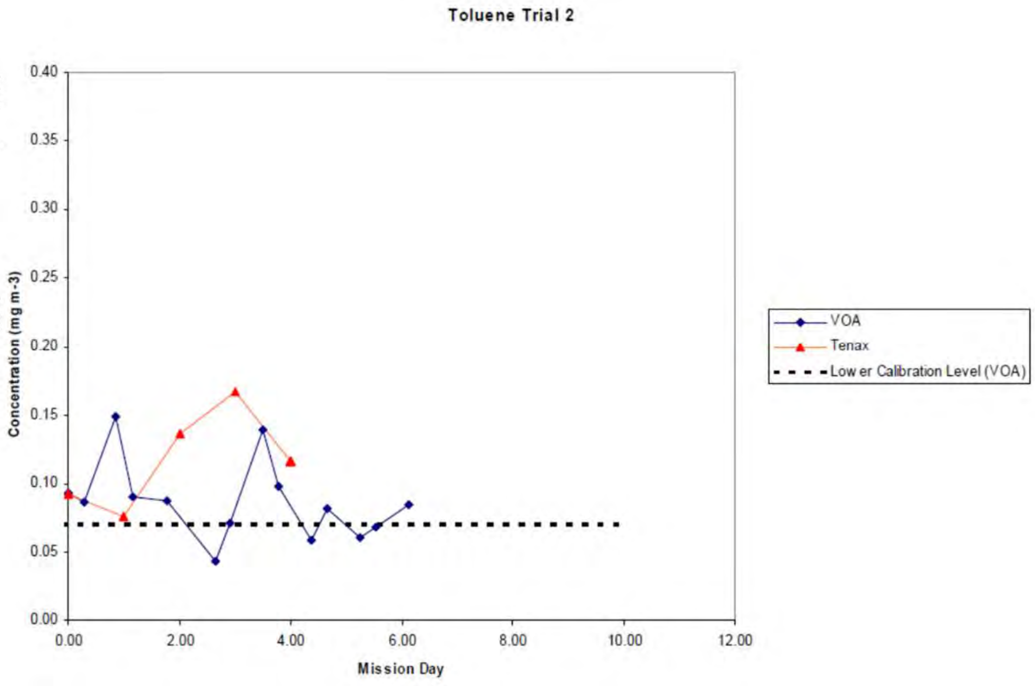
NASA/Navy Collaboration
2000s: VOA/RME submarine Trials





NASA/Navy Collaboration
2000s: VOA/RME submarine Trials

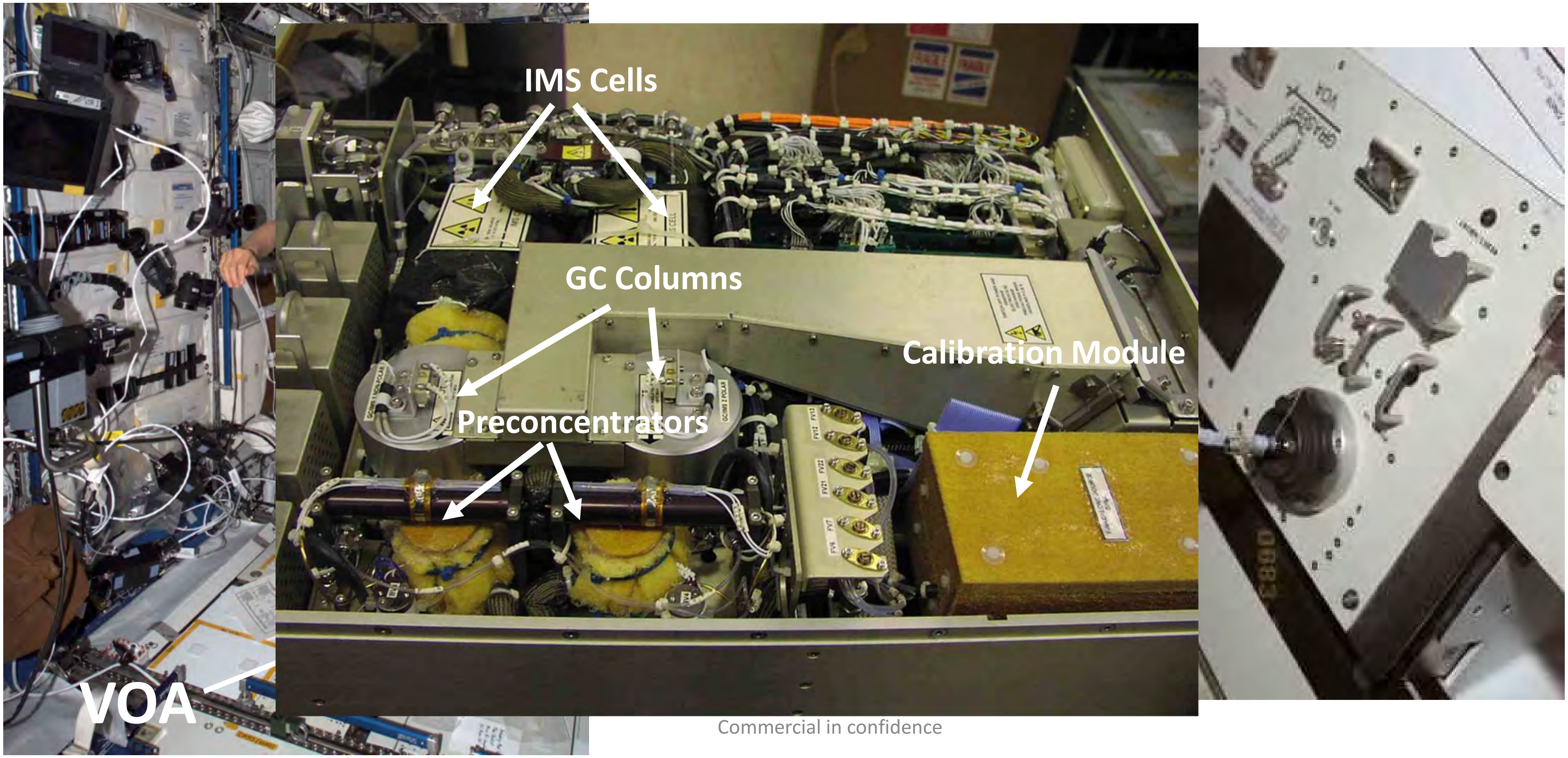




NASA/Navy Collaboration
2000s: VOA/RME submarine Trials

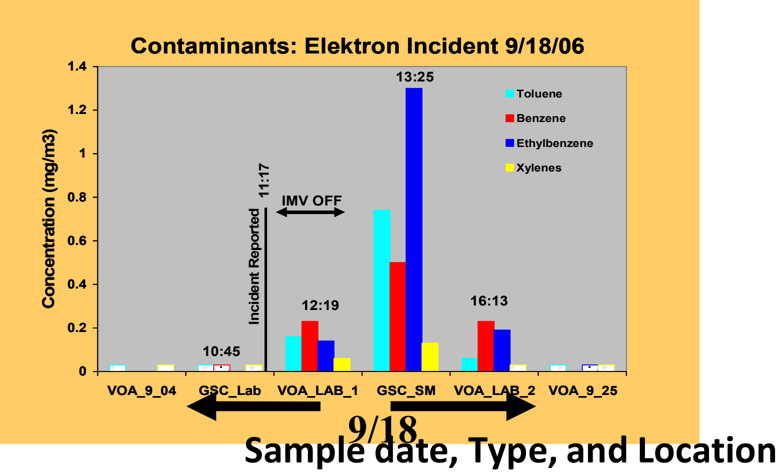
- I believe the VOA/RME is the first instrument to be in space and below the waters of the ocean
- The stainless steel tubes showed more consistent results than the glass sealed tubes
- The levels of ethanol were higher with the VOA/RME, but this is because ethanol is not trapped efficiently on Tenax
- Concentrations of contaminants are not necessarily steady for the entire patrol
- The compounds and their relative concentrations were remarkably similar for submarine and ISS
- Older submarines are no dirtier than newer submarines
- The air contaminant concentrations are well below specified limits
- The air tends to be very clean on submarines and on spacecraft

NASA/Navy Collaboration
2000s: VOA on ISS



NASA/Navy Collaboration
2000s: VOA on ISS

- The VOA had a fuse issue, which was repaired on orbit, an Elektron (oxygen generator) occurred within 6 months of the repair.
- The VOA monitored the concentration of the compounds released, which included ethylbenzene, a non-target compound



NASA/Navy Collaboration
2000s: Carbon Dioxide

- NASA used lithium hydroxide for the CO_2 scrubbing on the Apollo missions and on Shuttle
- Molecular sieve beds plus the Russian scrubber (Vozdukh), are used on ISS to scrub CO_2
- MEA is not used on ISS, although I suspect (not confirmed) that the Russian CO_2 scrubber uses a version of their submarine CO_2 scrubber, replacing the liquid with a solid amine
- NASA is currently testing amine swing beds on orbit
- NASA brought forward some new research on CO_2 that suggested the concentrations in spacecraft and submarines is too high

NASA/Navy Collaboration 2000s: Carbon Dioxide

- Dr. John James provided the following information at the 2013 SAMAP conference
    - Apollo & Shuttle: 7.6 mmHg (10,000 ppm)
    - ISS: 180 day SMAC = 5.3 mmHg
    - Exploration: 1000d SMAC = 3.8 mmHg
    - ISS Chit constraint: 4 mmHg
    - US Submariner & industrial limits = 3.8 mmHg
    - UK Submariner limit = 5.3 mmHg
    - ASHRAE standard for buildings = 0.8 mmHg
- A study by Satish showed a degradation in performance ~1.9 mmHg

NASA/Navy Collaboration
2000s: Carbon Dioxide

- Dr. James’ presentation generated much discussion that is still ongoing
  - Do humans adapt to the higher levels of CO_2 and eventually mitigate the effect?
  - After more than 5 years, studies are still continuing and NASA is actively involved in pursuing methods to measure CO_2 in the blood on orbit and to determine where the CO_2 levels begin to effect performance
  - For the present, NASA has lowered the long-term CO_2 limit to an average of 3 mmHg or below over 24 hours

NASA/Navy Collaboration 2000s: Oxygen Generators

- Various types of oxygen generators, generally known as self-contained oxygen generator (SCOG) are used in a variety of military and aerospace applications
  - Submarines
  - Airplanes
  - Spacecraft
- NASA became aware of the potential hazards of SCOG in 1997, when upon activation, a SCOG burned uncontrollably for 10-20 min in the MIR spacecraft before it became exhausted
- Fortunately, there were no injuries or significant damage to the MIR spacecraft
- However, one look at the SCOG shows that it easily have been much worse!

NASA/Navy Collaboration 2000s: Oxygen Generators

- NASA assisted the Russian’s investigation into the SCOG failure and determined it was due to contamination

- The HMS Tireless at sea under the Polar ice cap when a crewmember activated a SCOG
- Within a short period of time the SCOG exploded and 2 crewmembers were killed

NASA/Navy Collaboration 2000s: Oxygen Generators

- NASA's White Sands Facility and the NASA Engineering and Safety Center (NESC) offered their expertise to investigate the failure
- It was discovered that the briquette was internally contaminated with liquid oil and this can result in a runaway pressure event
- Furthermore it was postulated that the briquette might have been cracked due to rough handling
- This was an example of shared expertise to improve the safety of both submariners and astronauts

NASA/Navy Collaboration 2010s

- The Toxicology Environmental Chemistry (TEC) laboratories have worked on two major projects in the last 10 years that have crossed over into collaboration with the U.S. and U.K. Navies
    - The Air Quality Monitor (AQM), which was the replacement for the VOA
    - The Multi-Gas Monitor (MGM) and Anomaly Gas Analyzer (AGA) which measure major constituent gases (O2, CO2), combustion products (CO, HCl, HCN, and HF), and others (water, ammonia and hydrazine)
- The AQM (Draper Labs, MA) is based upon a slightly different version of the VOA technology. Think VOA (time of flight MS) and AQM (quadrupole MS)
- The MGM and AGA (Vista-Photonics, NM) use laser and photoacoustic spectrometry
- Both the AQM and MGM have flown on ISS and were used in a submarine sea trial with the U.S. Navy

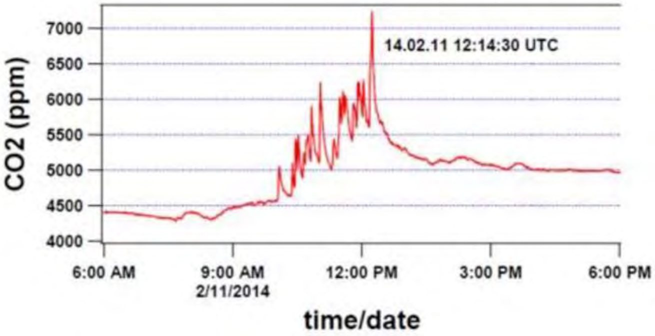
NASA/Navy Collaboration 2010s: AQM Submarine Trial

- Discussions of AQM performance on ISS at Technical Interchange Meeting led to development of a plan for AQM (and MGM) trial on a U.S. and/or U.K. submarine
  - SAMAP AND ICES meetings provided a venue for discussions
  - Furthermore, “Subs in Space” meetings in Houston in 2015 and 2017 were important for collaboration discussions between NASA and the UK and US navies
- This trial occurred on a U.S. submarine and was to evaluate the potential of the AQM (Air Quality Monitor) and MGM (Multi-Gas Monitor) to update the U.S. submarine’s monitoring suite for a new class of submarine under design
- Although ISS has two AQMs onboard to enhance quantitative accuracy, it was believed that the U.S. Navy’s target list could be covered by one unit.
- The slightly polar 624 GC column was selected as it seemed best suited for the target compounds
- The AQM was scripted to collect data every 8 hours and data was stored on the unit
- Five archival GSCs (similar to those used on ISS) and SAHAP badges were also present to take samples during the submarine trial

NASA/Navy Collaboration
2010s: MGM on ISS

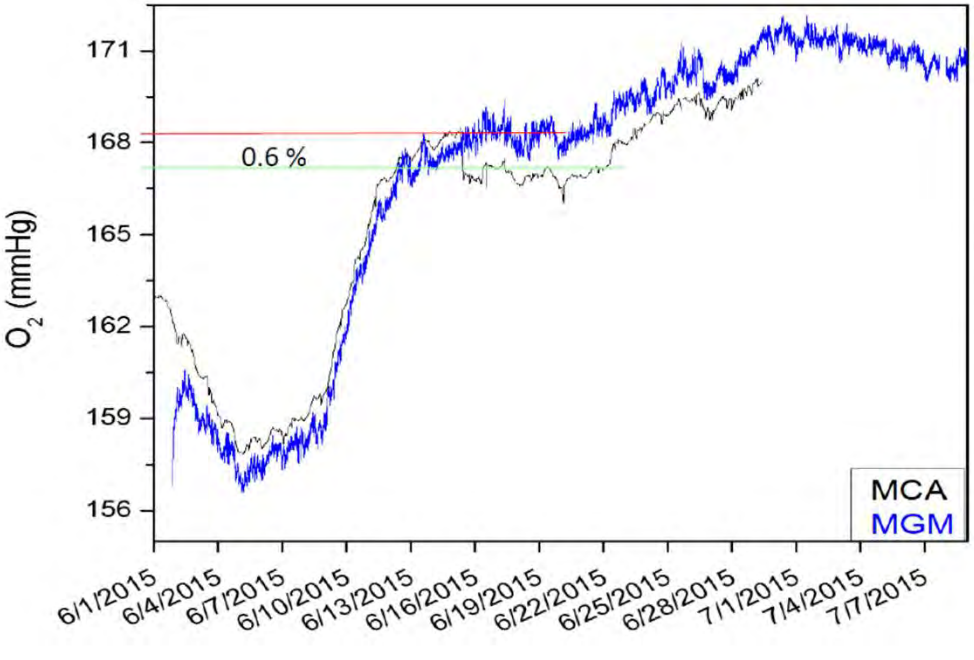
- The multi-gas monitor (MGM) launched to ISS as an experiment in November 2013
  - MGM measures 4 gases: oxygen, carbon dioxide, ammonia, and water vapor
  - Four tunable diode lasers measure the four gases every few seconds and records a 30 second rolling average
  - Total power draw is approximately 2.5 watts
  - Once calibrated, accuracy is maintained for years

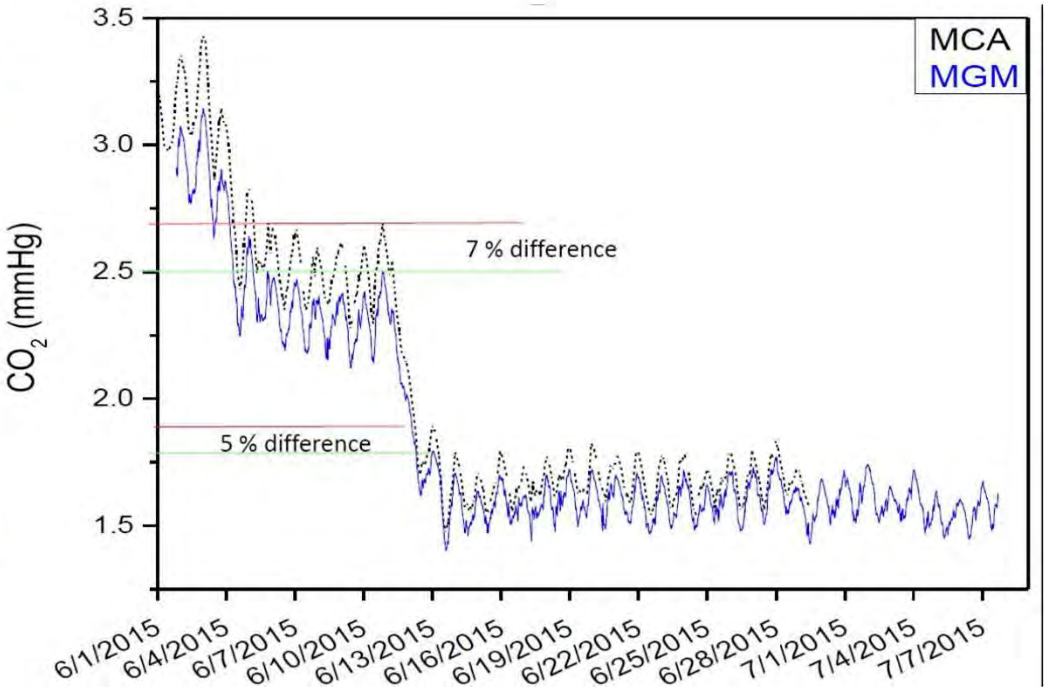
NASA/Navy Collaboration
2010s: MGM Experimental Results on ISS



MGM (yellow circle) detecting thruster release from the SPHERES experiment

NASA/Navy Collaboration
2010s: MGM Experimental Results on ISS
Compare MGM data to the onboard MCA data

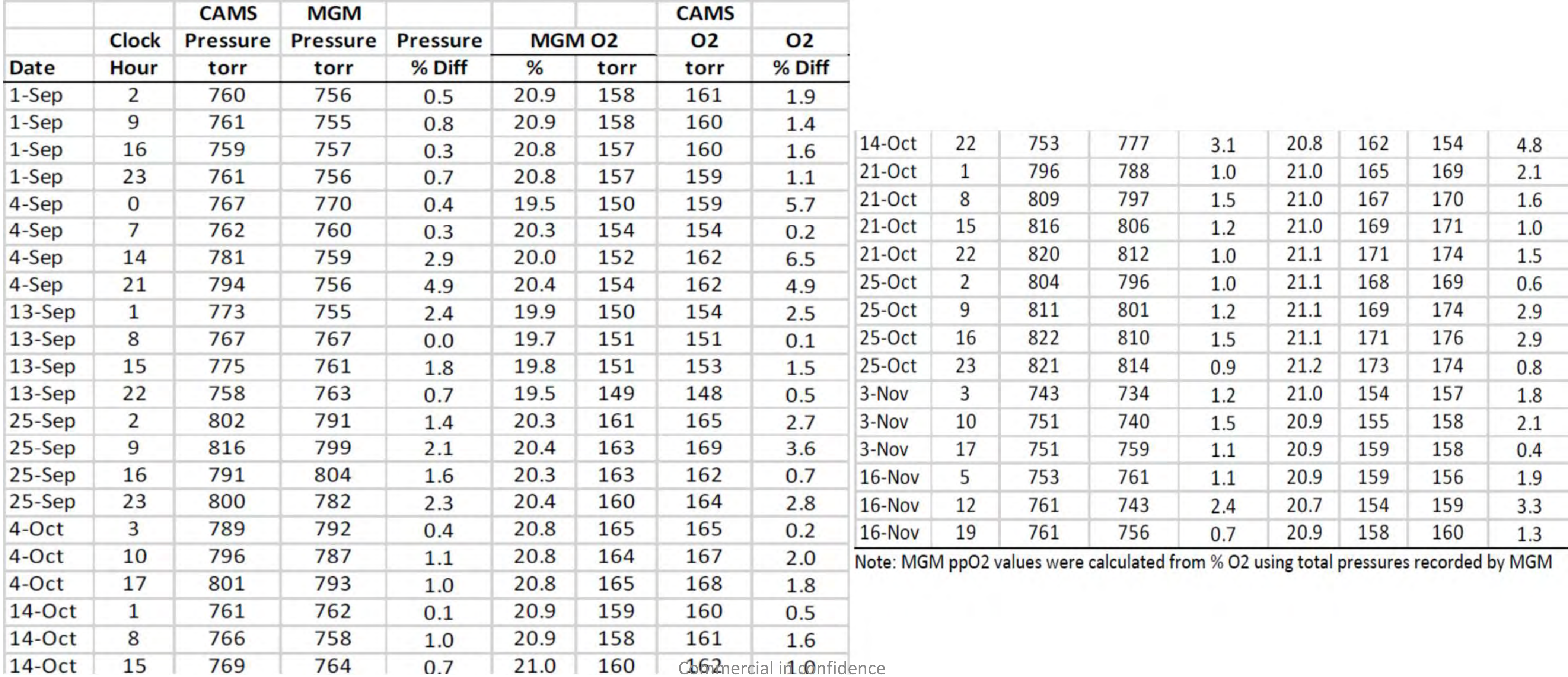




NASA/Navy Collaboration
2010s: MGM Submarine Trial

- The submarine trial was 76 days in duration
- A slightly different version of the MGM was used for the submarine trial, but the core (i.e., sensors) were the same
- The unit was calibrated and checked in the Toxicology laboratory at JSC prior to deployment
- Once installed the only crew intervention would be if the screen went blank; however that did not happen and no crew intervention was necessary
- In addition to the 4 gases monitored by the other instrument, this one also independently measures pressure, temperature, and water vapor
- When installed on the submarine the CO_2 and water vapor were checked against the CAMS Mark II and compared favorably. The CAMS calibration is checked weekly

NASA/Navy Collaboration
2010s: Results: MGM Submarine Trial



Date	Clock Hour	CAMS Pressure torr	MGM Pressure torr	Pressure % Diff	MGM O2 %	MGM O2 torr	CAMS O2 torr	O2 % Diff
1-Sep	2	760	756	0.5	20.9	158	161	1.9
1-Sep	9	761	755	0.8	20.9	158	160	1.4
1-Sep	16	759	757	0.3	20.8	157	160	1.6
1-Sep	23	761	756	0.7	20.8	157	159	1.1
4-Sep	0	767	770	0.4	19.5	150	159	5.7
4-Sep	7	762	760	0.3	20.3	154	154	0.2
4-Sep	14	781	759	2.9	20.0	152	162	6.5
4-Sep	21	794	756	4.9	20.4	154	162	4.9
13-Sep	1	773	755	2.4	19.9	150	154	2.5
13-Sep	8	767	767	0.0	19.7	151	151	0.1
13-Sep	15	775	761	1.8	19.8	151	153	1.5
13-Sep	22	758	763	0.7	19.5	149	148	0.5
25-Sep	2	802	791	1.4	20.3	161	165	2.7
25-Sep	9	816	799	2.1	20.4	163	169	3.6
25-Sep	16	791	804	1.6	20.3	163	162	0.7
25-Sep	23	800	782	2.3	20.4	160	164	2.8
4-Oct	3	789	792	0.4	20.8	165	165	0.2
4-Oct	10	796	787	1.1	20.8	164	167	2.0
4-Oct	17	801	793	1.0	20.8	165	168	1.8
14-Oct	1	761	762	0.1	20.9	159	160	0.5
14-Oct	8	766	758	1.0	20.9	158	161	1.6
14-Oct	15	769	764	0.7	21.0	160	162	1.0
14-Oct	22	753	777	3.1	20.8	162	154	4.8
21-Oct	1	796	788	1.0	21.0	165	169	2.1
21-Oct	8	809	797	1.5	21.0	167	170	1.6
21-Oct	15	816	806	1.2	21.0	169	171	1.0
21-Oct	22	820	812	1.0	21.1	171	174	1.5
25-Oct	2	804	796	1.0	21.1	168	169	0.6
25-Oct	9	811	801	1.2	21.1	169	174	2.9
25-Oct	16	822	810	1.5	21.1	171	176	2.9
25-Oct	23	821	814	0.9	21.2	173	174	0.8
3-Nov	3	743	734	1.2	21.0	154	157	1.8
3-Nov	10	751	740	1.5	20.9	155	158	2.1
3-Nov	17	751	759	1.1	20.9	159	158	0.4
16-Nov	5	753	761	1.1	20.9	159	156	1.9
16-Nov	12	761	743	2.4	20.7	154	159	3.3
16-Nov	19	761	756	0.7	20.9	158	160	1.3

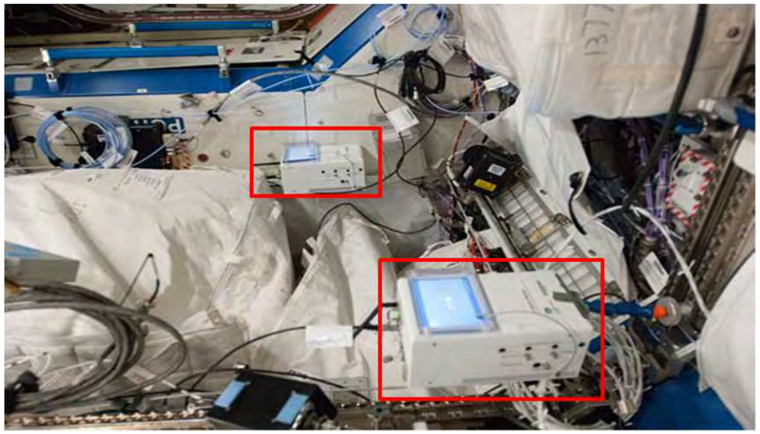
Note: MGM ppO2 values were calculated from % O2 using total pressures recorded by MGM

NASA/Navy Collaboration
2010s: AQM

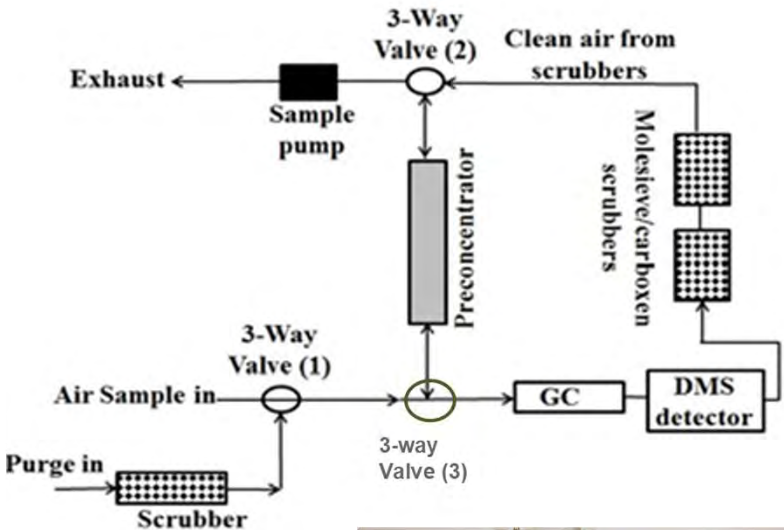
- The first pair of AQMs launched to ISS in early 2013. Two AQMs, each with a different GC column are used to cover all the target compounds

GFE 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



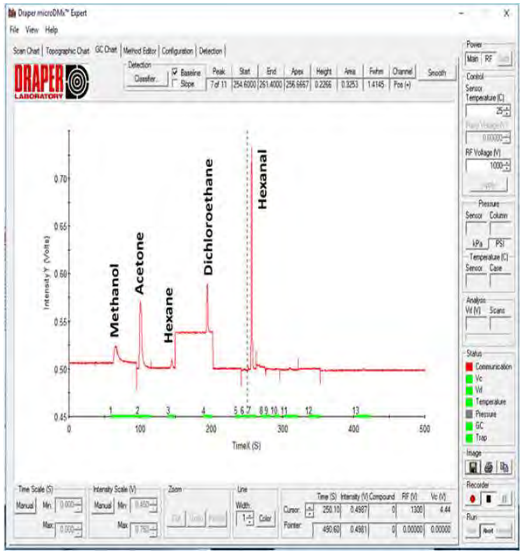
NASA/Navy Collaboration
2010s: AQM



- Each AQM is approximately shoe-box size
- Once calibrated, they remain accurate for a minimum of 3 years
- Although similar to the VOA technology, the AQM uses differential mobility spectrometry (DMS). DMS actually favors detection of smaller molecules (<400 amu)
- The AQM is portable and can run on batteries (VOA was fixed position)
- The AQMs are scripted to run every 73 hours
- Data is saved to an onboard computer then transferred via wireless connection to the ISS server. The data is downlinked to the ground once per week.
- The AQM can be controlled from the ground via remote desktop

Replaceable sieve packs are the only maintenance required (~ 6 months)

NASA/Navy Collaboration
2010s: AQM Operation



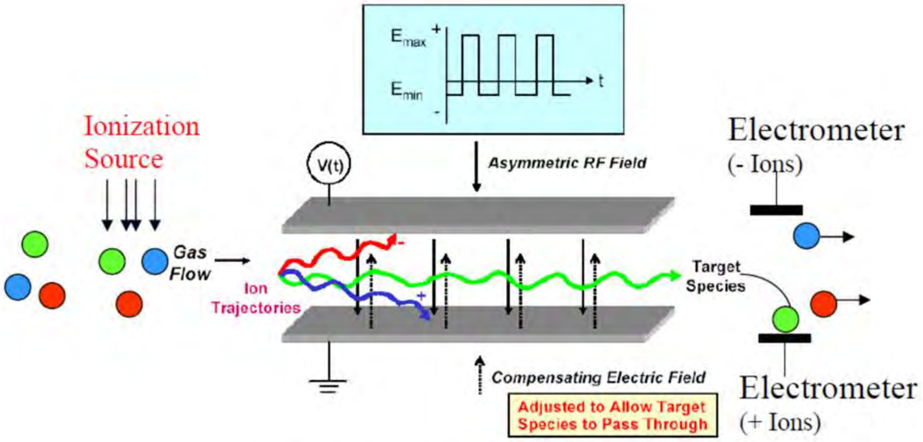
☑ Baseline
☐ Slope

Peak	Start	End	Apex	Height	Area	Fwhm	Channel
7 of 11	254.6000	261.4000	256.6667	0.2266	0.3253	1.4145	Pos (+)

Sensor Temperature (C): 25
RF Voltage (V): 1000

Time Scale (S): Manual Min: 0.000 Max: 0.000
Intensity Scale (V): Manual Min: 0.450 Max: 0.750
Line Width: 1

	Time (S)	Intensity (V)	Compound	RF (V)	Vc (V)
Cursor	250.10	0.4987	0	1300	4.44
Pointer	490.60	0.4981	0	0.00000	0.00000



Draper Labs, microAnalyzer V2.0 Series Product Family Manual

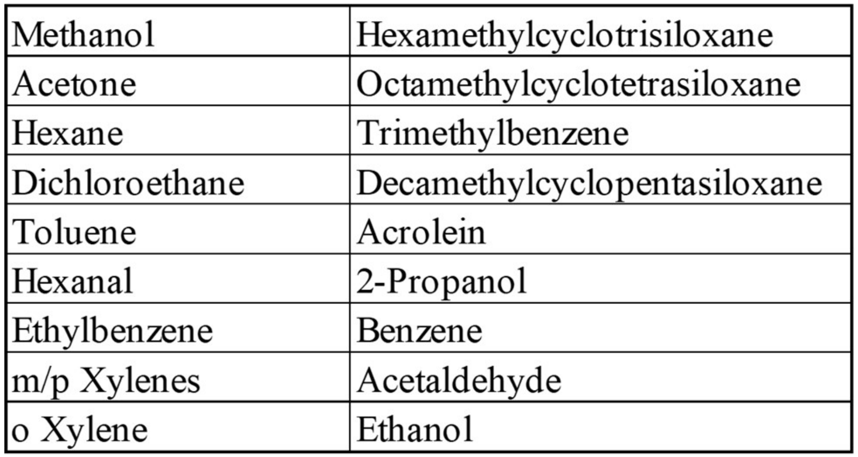
NASA/Navy Collaboration
2010s: AQM On-Orbit Results

Unit 2214 (AQM1)	3-Jan	GSC_Jan3	%Diff_Jan3	14-Feb	GSC_Feb14	%Diff_Feb14	3-Apr	GSC_Apr3	%Diff_Apr3	8-May	GSC_May8	%Diff_May8
Methanol	0.29	0.36	19	0.31	0.34	9	0.29	0.39	26	0.29	0.35	17
Acetone	0.36	0.33	-9	0.28	0.31	10	0.34	0.32	-6	0.38	0.31	-23
Hexane	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND
2_Propanol	0.16	0.17	6	0.35	0.38	8	0.20	0.17	-18	0.15	0.15	0
Dichloroethane	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND
Toluene												
Hexanal	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND
mp- Xylene												
o-Xylene												
Acrolein	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND
Benzene	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND
Octamethylcyclotetrasiloxane												
Decamethylcyclopentasiloxane												
Hexamethylcyclotrisiloxane												
Unit 2225 (AQM2)												
Acetaldehyde	0.11	0.26	58	0.12	0.22	45	0.13	0.24	46	0.10	0.28	64
Ethanol	3.40	5.70	40	2.57	3.10	17	3.88	5.60	31	4.00	6.60	39
Dichloromethane	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND
TMS	0.18	0.18	0	0.14	0.13	-8	0.16	0.16	0	0.17	0.14	-21
2-Butanone	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	Trace	ND-ND
Ethyl Acetate	Trace	Trace	Trace-Trace	ND	ND	ND-ND	0.06	0.037	MATCH	0.060	0.028	MATCH
n_Butanol	0.09	0.09	-3	0.07	0.08	9	0.08	0.067	-19	0.090	0.065	-38
Toluene	ND	ND	ND-ND	ND	ND	ND-ND	Trace	ND	Trace-ND	0.03	Trace	MATCH
mp- Xylene	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND	ND	ND	ND-ND
o-Xylene	Trace	ND	Trace-ND	Trace	ND	Trace-ND	0.03	ND	MATCH	Trace	ND	Trace-ND
Octamethylcyclotetrasiloxane	Trace	ND	Trace-ND	Trace	ND	Trace-ND	Trace	ND	Trace-ND	Trace	ND	Trace-ND
Decamethylcyclopentasiloxane	0.19	0.29	34	0.16	0.18	11	0.17	0.18	6	0.20	0.24	17
Hexamethylcyclotrisiloxane	0.08	0.25	68	0.05	0.27	81	0.07	0.06	-17	0.08	0.17	53

Unit 2214 (AQM1)	**Matches/#GSCs 2016-2017 (Aug)**
Methanol	12/14
Acetone	14/14
Hexane	14/14
2_Propanol	14/14
Dichloroethane	14/14
Toluene	
Hexanal	14/14
mp- Xylene	
o-Xylene	
Acrolein	14/14
Benzene	14/14
Octamethylcyclotetrasiloxane	
Decamethylcyclopentasiloxane	
Hexamethylcyclotrisiloxane	
Unit 2225 (AQM2)	11/17
Acetaldehyde	9/17
Ethanol	15/15
Dichloromethane	15/15
TMS	15/15
2-Butanone	15/15
Ethyl Acetate	15/15
n_Butanol	15/15
Toluene	15/15
mp- Xylene	15/15
o-Xylene	15/15
Octamethylcyclotetrasiloxane	15/15
Decamethylcyclopentasiloxane	15/15
Hexamethylcyclotrisiloxane	12/15

NASA/Navy Collaboration
2010s: AQM Submarine Trial

- Although most target compounds for the submarine trial were the same as ISS target compounds, two compounds (ethylbenzene and trimethylbenzene) were unique to this trial. The AQMs were calibrated for these compounds as well as the other target compounds.
- The AQM was installed in the main fan room, the source of all shipboard air, which should make it representative of the air within the submarine.

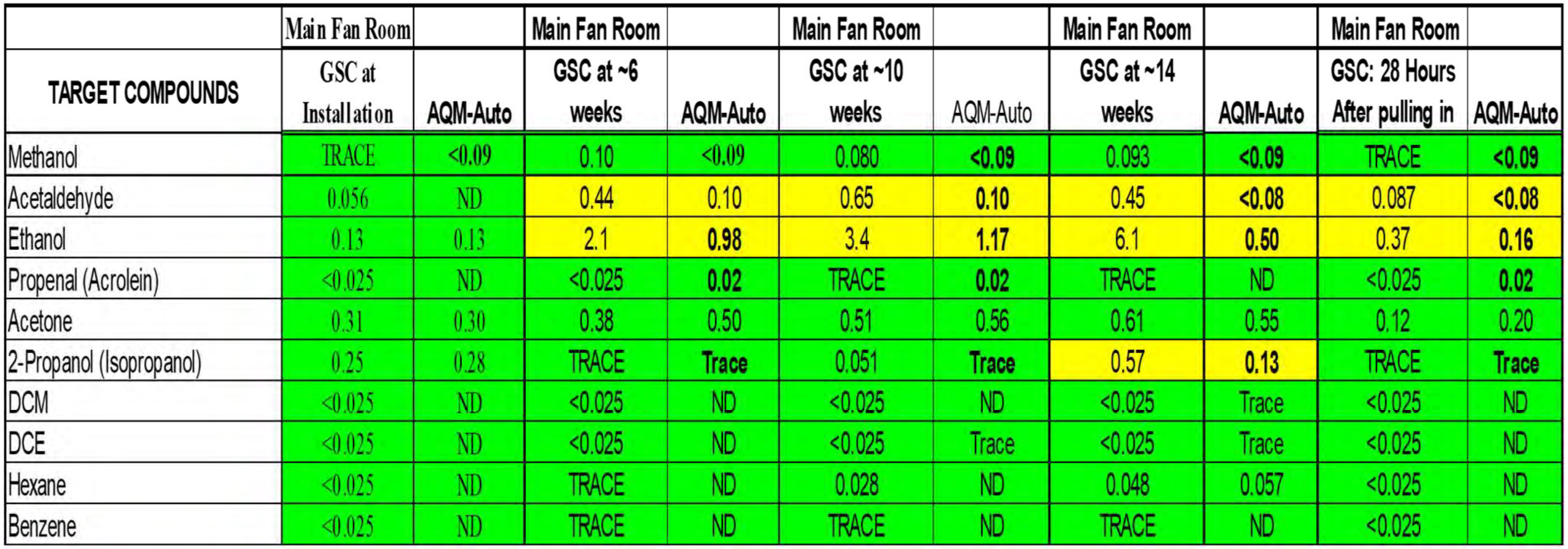


Methanol	Hexamethylcyclotrisiloxane
Acetone	Octamethylcyclotetrasiloxane
Hexane	Trimethylbenzene
Dichloroethane	Decamethylcyclopentasiloxane
Toluene	Acrolein
Hexanal	2-Propanol
Ethylbenzene	Benzene
m/p Xylenes	Acetaldehyde
o Xylene	Ethanol

- **On the left, the AQM is shown in its location in the fan room**
- **On the right is the AQM target list for the submarine trial**

NASA/Navy Collaboration 2010s: AQM Submarine Trial

Results: GSC and AQM Comparison Concentrations (mg/m^3)



	Main Fan Room		Main Fan Room		Main Fan Room		Main Fan Room		Main Fan Room	
TARGET COMPOUNDS	GSC at Installation	AQM-Auto	GSC at ~6 weeks	AQM-Auto	GSC at ~10 weeks	AQM-Auto	GSC at ~14 weeks	AQM-Auto	GSC: 28 Hours After pulling in	AQM-Auto
Methanol	TRACE	<0.09	0.10	<0.09	0.080	**<0.09**	0.093	**<0.09**	TRACE	**<0.09**
Acetaldehyde	0.056	ND	0.44	0.10	0.65	**0.10**	0.45	**<0.08**	0.087	**<0.08**
Ethanol	0.13	0.13	2.1	**0.98**	3.4	**1.17**	6.1	**0.50**	0.37	**0.16**
Propenal (Acrolein)	<0.025	ND	<0.025	**0.02**	TRACE	**0.02**	TRACE	ND	<0.025	**0.02**
Acetone	0.31	0.30	0.38	0.50	0.51	0.56	0.61	0.55	0.12	0.20
2-Propanol (Isopropanol)	0.25	0.28	TRACE	**Trace**	0.051	**Trace**	0.57	**0.13**	TRACE	**Trace**
DCM	<0.025	ND	<0.025	ND	<0.025	ND	<0.025	Trace	<0.025	ND
DCE	<0.025	ND	<0.025	ND	<0.025	Trace	<0.025	Trace	<0.025	ND
Hexane	<0.025	ND	TRACE	ND	0.028	ND	0.048	0.057	<0.025	ND
Benzene	<0.025	ND	TRACE	ND	TRACE	ND	TRACE	ND	<0.025	ND

Match when using ISS criteria

No match when using ISS criteria

Manual analysis

Match: ND/Trace, ±0.05<0.1mg/m^3, ±50 >0.1<0.5mg/m^3, ±40 >0.5mg/m^3

NASA/Navy Collaboration
2010s: AQM Submarine Trial

- The AQM successfully completed the submarine trial
- While not perfect, the data matched reasonably well with the GSCs
  - A new scrubbing material (LiOH) was used in the sieve packs in place of Carboxen to help mitigate some effects from CO_2 that were observed on ISS.
  - Although the testing in lab showed good results, it was clear during the trial there was a contaminant from the LiOH that reduced sensitivity to some compounds.
- It was difficult to compare SAHAP badge results to AQM and GSC data as the SAHAP badges collect a sample over 30 days; whereas AQM and GSC is at a specific point in time

NASA/Navy Collaboration
FUTURE WORK

- Discussions have occurred with the U.S. and U.K Navies about another trial with both the MGM (or possibly the AGA) and the AQM
- The AGA would provide tremendous capability in a small footprint

- The AGA uses the same technology as MGM, but measures more gases. AGA engineering units have been tested and flight units will be ready for launch in late 2020 or early 2021
- In addition to the four gases mentioned above, the AGA also measures combustion products: carbon monoxide, hydrogen chloride, hydrogen fluoride, and hydrogen cyanide. It also targets hydrazine
    - Photoacoustic spectrometry is used for detection of carbon monoxide, hydrogen cyanide, and hydrazine
- This instrument is designed for ISS (replacing several other instruments) and for Orion

Parameter	Measurement Range	Accuracy	Accuracy	Accuracy
Pressure	9.5-15.6 psia	±0.1psia		
Oxygen	14-50%	±1% (absolute) ≤26%	±2% (absolute) >26%	
Carbon Dioxide	0.3-21 mmHg	±10% ≥ 0.8 mmHg	±0.2 < 0.8 mmHg	
Carbon Monoxide	5-1000 ppm	±10% ≥ 5 ppm	±5 ppm < 55 ppm	
Hydrogen Cyanide	2-50 ppm	±25% ≥ 55 ppm	±1 ppm < 5 ppm	
Hydrogen Fluoride	2-50 ppm	±25% ≥ 55 ppm	±1 ppm < 5 ppm	
Hydrogen Chloride	2-50 ppm	±25% ≥ 55 ppm	±1 ppm < 5 ppm	
Ammonia	10-30,000 ppm	±25% ≥ 150 ppm	±10% 20-150 ppm	±20% <20 ppm
Hydrazine	2-10 ppm	±2 ppm		

NASA/Navy Collaboration
FUTURE WORK

- The AQM in the new trial would use scrubbing material in the sieve packs that is identical to that used on ISS
- In the future other collaborations should occur as new technologies are developed in both monitoring and scrubbing systems
- Join investigations of anomalous events will continue in the future
- It is expected that there will also continue to be close work when considering contaminant limits on spacecraft and submarines

NASA/Navy Collaboration

- Stay tuned: there is talk of subs in space to explore planetary moons!!!!

A BRIEF HISTORY OF SUBMARINE AIR QUALITY

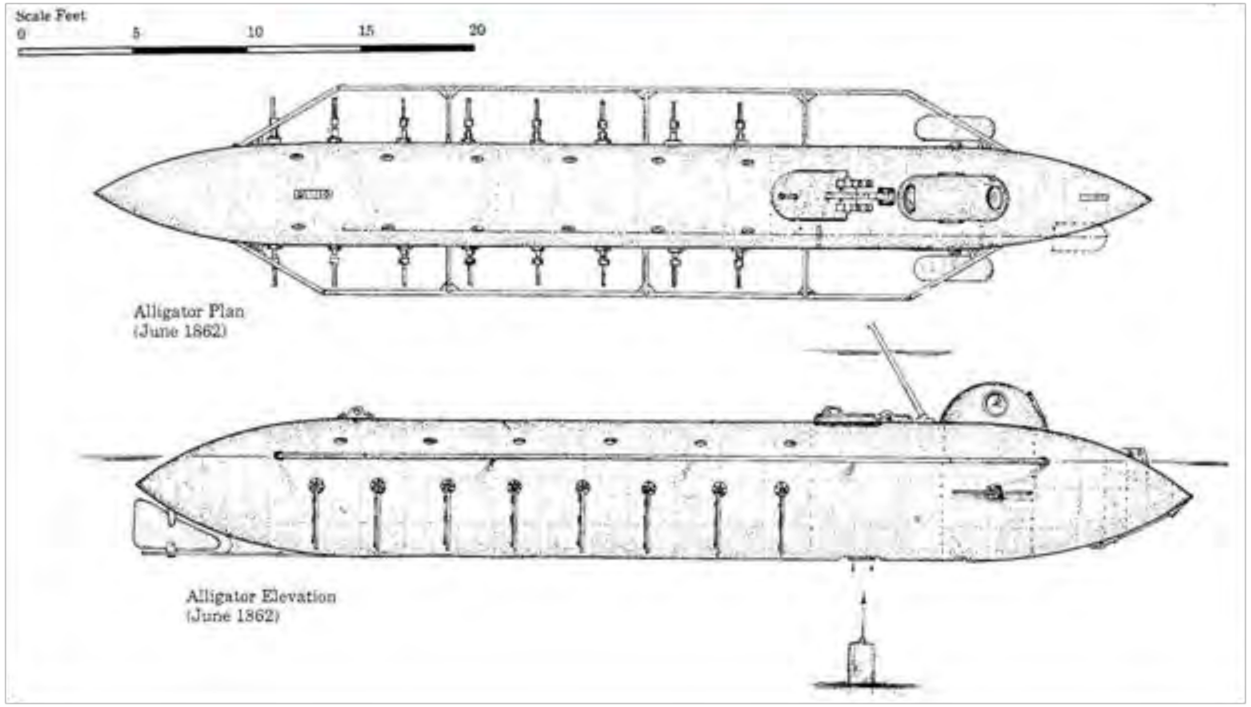
W. Mazurek

AUSTRALIA

ALLIGATOR

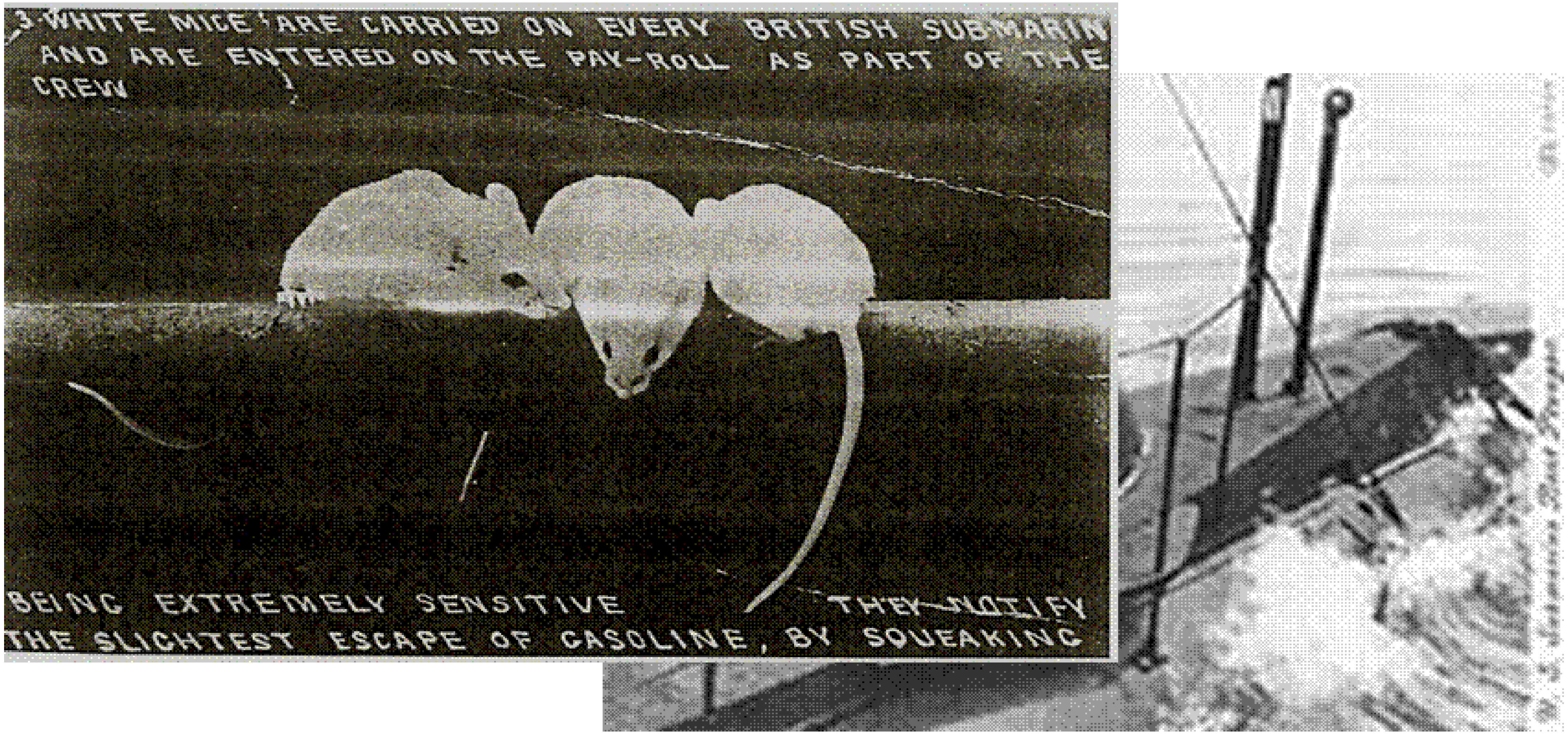
Circa. 1863
Man-powered Submarine
US Civil War
Crew 20(?)

Lime CO_2 Removal System



EARLY SUBMARINE AIR MONITORING SYSTEM

circa 1904 (Post card)



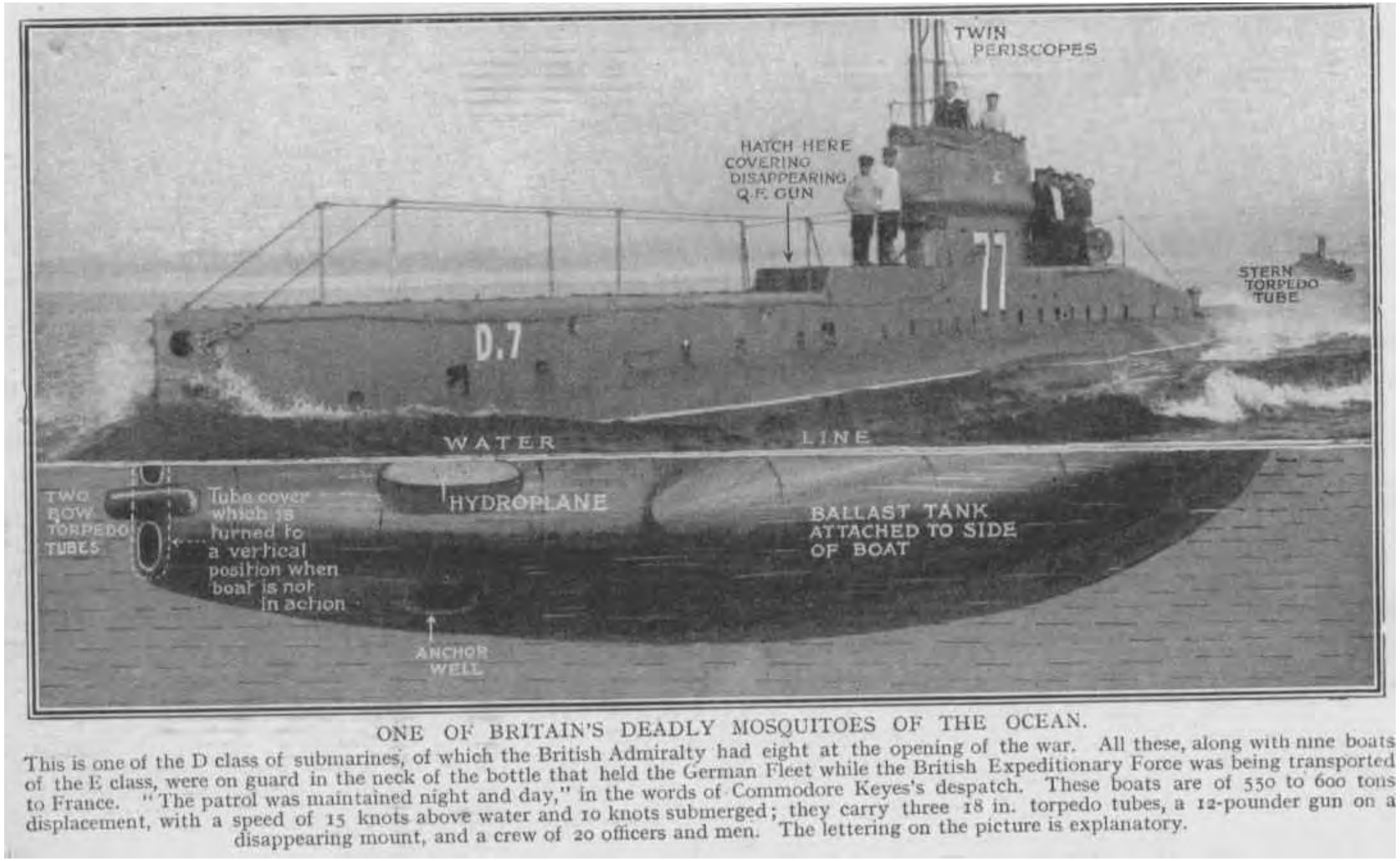
3 WHITE MICE ARE CARRIED ON EVERY BRITISH SUBMARIN
AND ARE ENTERED ON THE PAY-ROLL AS PART OF THE
CREW

BEING EXTREMELY SENSITIVE THEY NOTIFY
THE SLIGHTEST ESCAPE OF GASOLINE, BY SQUEAKING

Peter Evans(MoD), SAMAP 97

RN WWI, D-Class Submarine

(crew=18, 500 tons disp.)



ONE OF BRITAIN'S DEADLY MOSQUITOES OF THE OCEAN.

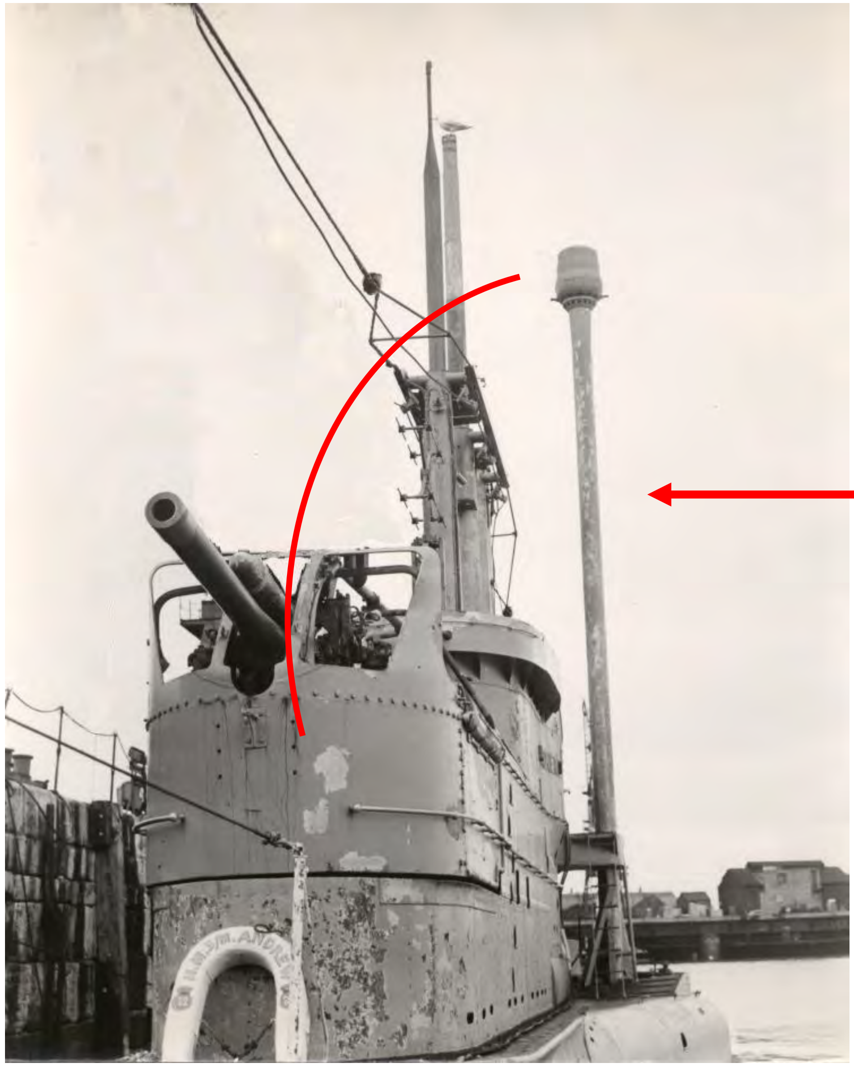
This is one of the D class of submarines, of which the British Admiralty had eight at the opening of the war. All these, along with nine boats of the E class, were on guard in the neck of the bottle that held the German Fleet while the British Expeditionary Force was being transported to France. "The patrol was maintained night and day," in the words of Commodore Keyes's despatch. These boats are of 550 to 600 tons displacement, with a speed of 15 knots above water and 10 knots submerged; they carry three 18 in. torpedo tubes, a 12-pounder gun on a disappearing mount, and a crew of 20 officers and men. The lettering on the picture is explanatory.

WWII SUBMARINES:

Essentially Semi-submersibles with a Keel and no Snorkel

PROCEEDINGS

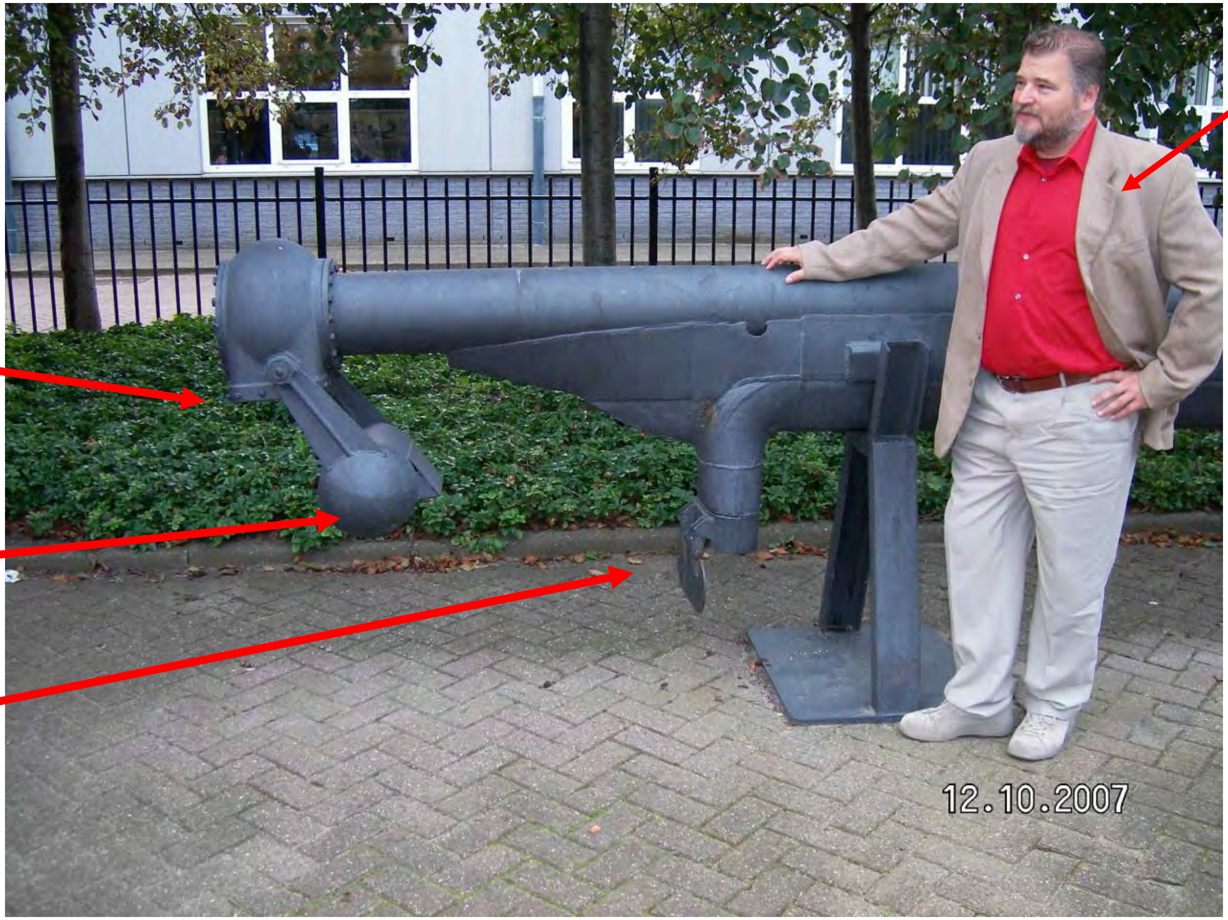
DUTCH FOLDING SNORKEL



SNORKEL

DUTCH FOLDING SNORKEL

(MUSEUM, DEN HELDER)



DUTCHMAN

AIR INTAKE

FLOAT VALVE

EXHAUST

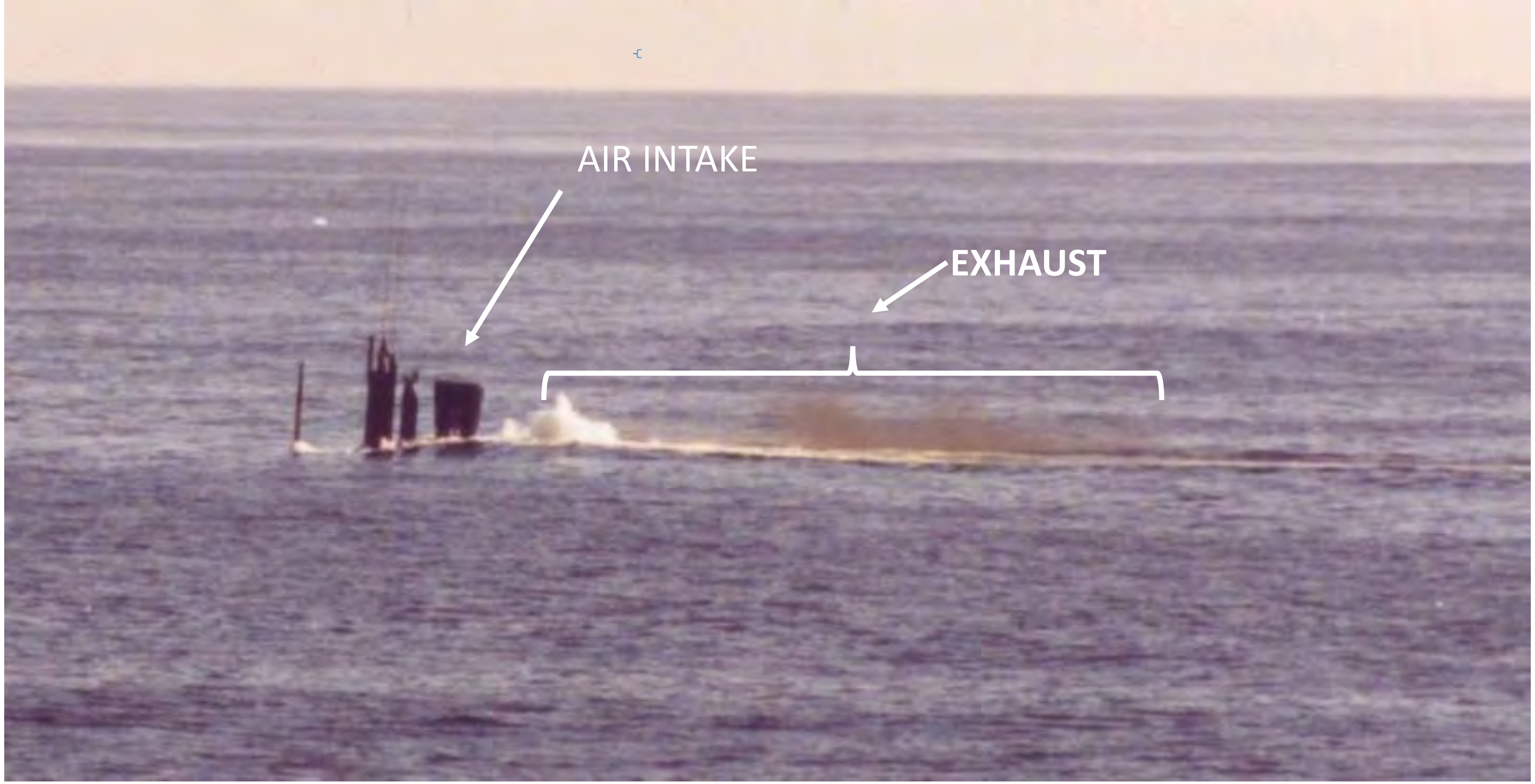
THE ORIGNIAL SNORKEL

Snorkelling

RN EXPERIMENTAL SNORKELS 1950s

Folded Snort Mast *Trespasser*

SNORKELLING SUBMARINE



EFFECTS OF HIGH CARBON DIOXIDE LEVELS (WWII)

- Capt. W.O. Shelford, RN “Subsunk – The sory of submarine escape”, (Harrap, 1960)
- “the brain is being affected before the body is seriously incommoded, so judgement and alertness become blurred and distorted without the crew being aware of their condition”

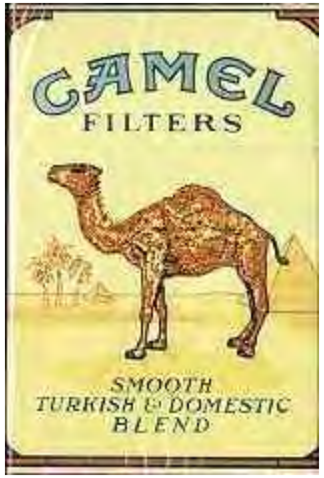
PROCEEDINGS

1945

- ROYAL NAVY BR1326/45: AIR QUALITY
  - OXYGEN 18%
  - CARBON DIOXIDE 3%
  - NO INSTRUMENTATION

- GERMAN and ITALIAN NAVY
  - MONITORING
    - OXYGEN
    - CARBON DIOXIDE
    - HUMIDITY

EARLY GAS DETECTORS



HYDROCARBON/CARBON MONOXIDE SENSOR (1904)

OXYGEN SENSOR (WWII)

PROCEEDINGS

1947

- ROYAL NAVY AIR QUALITY TRIAL

  - OXYGEN
    - PARAMAGNETIC PAULING OXYGEN ANALYSER

  - CARBON DIOXIDE
    - THERMAL CONDUCTIVITY, CAMBRIDGE INSTRUMENT Co

  - CARBON MONOXIDE
    - CHEMICAL CARBON MONOXIDE INDICATOR, FARNBOROUGH

AIR PURIFICATION DIESEL-ELECTRIC SUBMARINES (ie RN OBERON CLASS, 1960s-1980s)

- OXYGEN: CHLORATE CANDLES
- CARBON DIOXIDE: SODA LIME
- CARBON MONOXIDE/ HYDROGEN: PALLADIUM COATED ALUMINA, (HEATED) CATALYST

AIR PURIFICATION IN NUCLEAR-POWERED SUBMARINES

- OXYGEN: ELECTROLYSIS OF WATER
- CARBON DIOXIDE: MONOETHANOLAMINE (MEA) / MOLEULAR SIEVE –REGENERATIVE SYSTEM
- CARBON MONOXIDE/HYDROGEN: HIGH TEMPERATURE CATALYST HOPCALITE (MANGANESE DIOXIDE/ COPPER OXIDE (3:1))

PROCEEDINGS

NUCLEAR POWERED SUBMARINES

AIR PURIFICATION PROBLEMS

1950s

"The Rickover Effect"
Theodore Rockwell, Naval Institute Press (1992) pp218-224.
The Submarine Atmosphere Problem

The Nautilus had just returned from her dramatic eighty-four-hour, thirteen-hundred-mile submerged shakedown cruise to San Juan, and Ebersole had a problem. His voice had an urgent, serious quality to it as he said, "Admiral, this is Ebersole. The air quality on the submarines is terrible. If we don't do something about it before we go to sea again, we'll never be able to stay submerged for very long."

Rickover asked, "Why? What's wrong?"

"The carbon dioxide scrubbers don't work, and the carbon monoxide burners keep exploding and catching fire. It just isn't habitable.

Ebersole was the Medical Officer of Nautilus

ADM Rickover : credited with the development of nuclear-powered submarines for the USN

PROCEEDINGS

NO MORE LOOSE FILLINGS OR SLOW EMBALMING; HOW NAVAL SCIENCE HELPED SUBMARINERS BREATHE EASY

Jeffrey R. Wyatt; UNDERSEA WARFARE, WINTER 2001

"A retired skipper told me once that

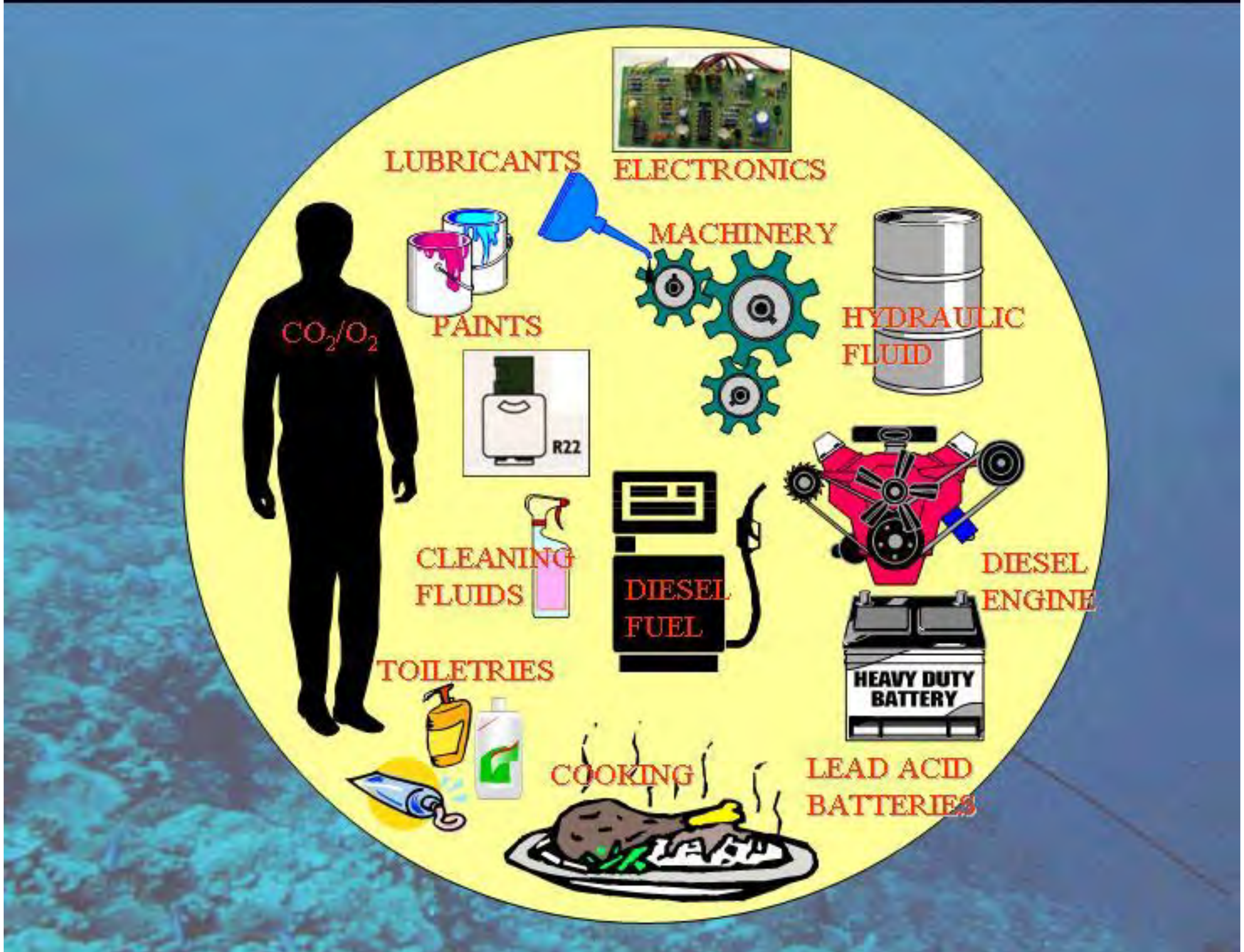
early in his career he was aboard a ………. ship (1960s)

…….. a large refrigerant leak *occurred*. As the refrigerant decomposed, it produced hydrochloric acid. This not only produced significant corrosion throughout the boat, but at the end of the patrol many of the crew (including himself) needed all the fillings in their teeth replaced."

In addition, formaldehyde and phosgene were generated by the hopcalite catalytic "burner"

Jeffrey R. Wyatt (Chemistry Division, U. S. Naval Research Laboratory Washington, DC) Forty Years of Air Monitoring on American Nuclear Submarines, Third Submarine Atmosphere Purification and Monitoring Conference, Toronto Canada, October 11, 2000,

SUBMARINE ENVIRONMENT



1950s

NUCLEAR-POWERED SUBMARINES

- 1954 NAUTILUS
  - PROTOTYPE ATMOSPHERE ANALYSER INSTALLED (MK II)
  - SAMPLES FROM 8 LOCATIONS
    - CARBON DIOXIDE (IR)
    - CARBON MONOXIDE (IR)
    - OXYGEN (PARAMAGNETIC)
    - HYDROGEN (THERMAL CONDUCTIVITY)
    - HYDROCARBONS (IR)
    - FREON (LATER VERSION)

- INSTRUMENTATION TOO COMPLEX AND UNRELIABLE

1980s

NUCLEAR-POWERED SUBMARINES

- CAMS I: MASS SPECTROMETER (MAGNETIC ANALYSER), fixed target compounds based on m/z
    - RELIABLE

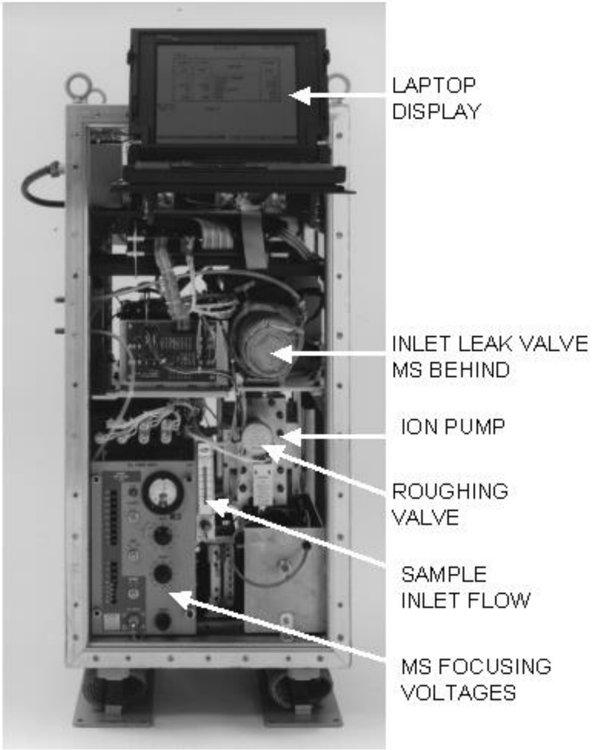
- CAMS II: MASS SPECTROMETER (MAGNETIC ANALYSER), Extended mass range, software selected target compounds

CAMS II capable of monitoring 32 CPDS

RN CAMS

- Early Royal Navy nuclear powered submarines were fitted with an air monitoring system consisting of:
  - Gas chromatograph with 4 separate packed columns for monitoring:
    - hydrogen,
    - oxygen,
    - carbon dioxide and
    - carbon monoxide.
    -
  - Like the early monitors in the US submarines, it also suffered from reliability problems and in 1980 it was replaced with a British version of the US Navy CAMS.
- British CAMS used a quadrupole analyser rather than a magnetic analyser. The quadrupole analysers were more susceptible to drift off calibration. For various reasons the British CAMS proved to be far less reliable than the US equivalent.

MINI-CAMS
designed for diesel-electric submarines



CAMS II 32 CPDS

Instrument Reliability Problems

- Not necessarily due to the technology.
- Installation and maintenance procedures that can lead to these problems.
- The complex and often hostile environment is a challenge to any air monitoring technology.
- There is also is a requirement for continuous operation for 90 days without factory support or calibration.

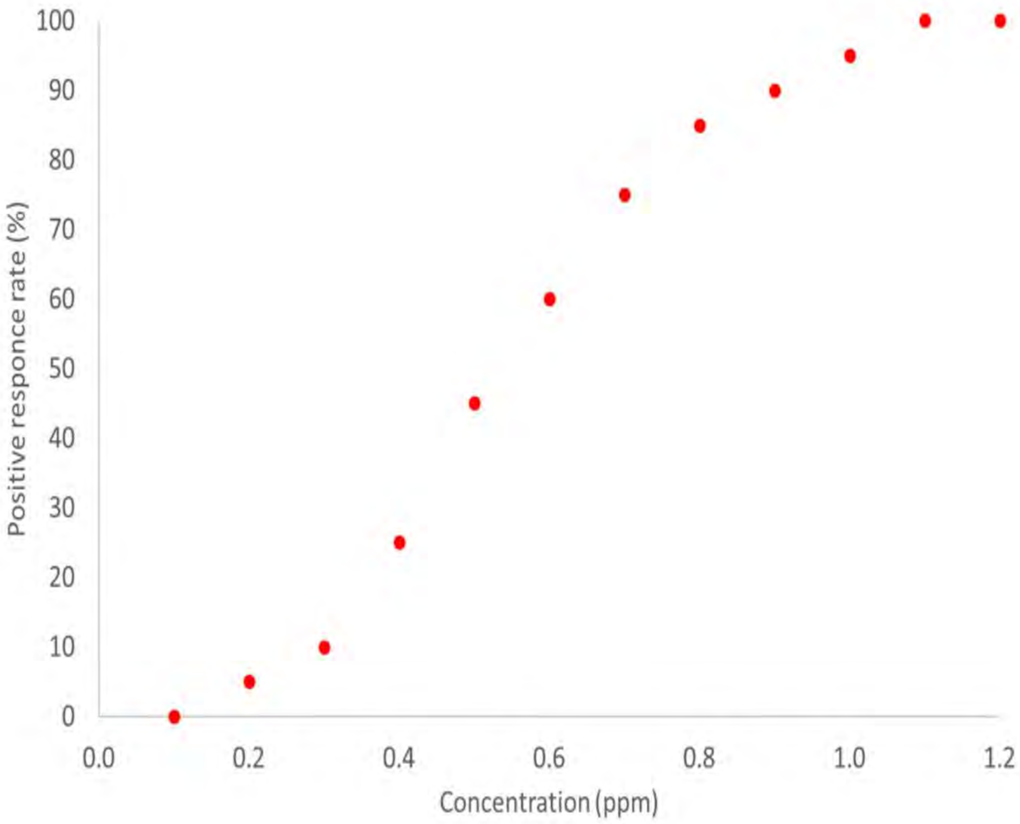
ANY QUESTIONS ?

Atmosphere Monitoring – Assessing functional limits of detection

Alan Chapman
SAMAP 2019
4th – 6th November 2019

QINETIQ

Contents



- Methods of determining lower operating limits of measuring systems
- Direct reading toxic gas monitors lower limit of measurement
- Limits of detection and quantification for laboratory techniques
- Coverage factors
- A practical example of these techniques
- Conclusions

Methods for determining lower operating limits of measuring systems

- Generally in Europe, direct reading toxic gas monitors are validated EN 45544:2015
  - This defines Lower Limit of Measurement (U_{zero}) = ‘*smallest value of the measured quantity within the measuring range’*
- Laboratories performing retrospective analysis are typically working to in-house validation procedure
  - Typically based on Eurachem guide ‘*The Fitness for Purpose of Analytical Methods*’ second edition which defines
    - The Limit of Detection (LoD) = lowest level of an analyte that can be detected, with sufficient confidence, within the sample matrix
    - The Limit of Quantification (LoQ) = lowest level of an analyte that can be quantified, with sufficient confidence, within the sample matrix

Calculation of U_{zero} According to EN 45544:2015

- $ur_{zero} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})}{n-1}}$
- $unr_{zero} = \sqrt{\left(\frac{\bar{x}}{\sqrt{3}}\right)^2 + \left(\frac{x_{res}}{2 \times \sqrt{3}}\right)^2}$
- $u_{zero} = \sqrt{({ur_{zero}}^2 + {unr_{zero}}^2)}$
- $U_{zero} = 2 \times u_{zero}$

Where:
ur_{zero} = Random element of zero uncertainty
x_i = Zero measurement
$\bar{x}$ = Mean of repeated zero measurements
unr_{zero} = Non − random element of zero uncertainty
x_{res} = Resolution of the indicating device
u_{zero} = Total zero uncertainty
U_{zero} = Lower limit of measurement

Calculation of s_0 and s_0' according the Eurachem guide

- $s_0 = \sqrt{\sum_{i=1}^{m} \frac{(z_i - \bar{z})}{m-1}}$
- when readings are not blank corrected
- $s_0{}' = \frac{s_0}{\sqrt{r}}$
- or when readings are blank corrected
- $s_0{}' = \frac{s_0}{\sqrt{\frac{1}{r} + \frac{1}{r_b}}}$
- For a direct reading instrument this simplifies to
- $s_0{}' = \frac{s_0}{\sqrt{1}} = s_0$
- LoD = 3 x $s_0{}'$ and LoQ = 10 x $s_0{}'$

Where:

s_0 = Estimated standard deviation of a reading at or near zero concentration

z_i = Near zero measurements

$\bar{z}$ = Mean of the repeated near zero measurement

m = Number of readings taken

r = Number of replicate readings averaged to produce a final result

r_b = Number of blank replicate readings averaged to produce a final result

$s_0{}'$ = Standard deviation used for calculating LoD and LoQ

Comparison of U_{zero} and s_0'

- $ur_{zero} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})}{n-1}}$, and $s_0{}' = \sqrt{\sum_{i=1}^{m} \frac{(z_i - \bar{z})}{m-1}}$
  - are interchangeable and calculate the random element of the uncertainty
  - ur_{zero} is calculated on zero readings
  - $s_0{}'$ can be calculated on zero or near zero readings

- $\mathrm{unr}_{\mathrm{zero}}$ addresses non-random uncertainty

- EN 45544:2015 uses a smaller coverage factor than Eurachem method
  - U_{zero} is 2
  - LoD is 3
  - LoQ is 10

Selection of coverage factors

- EN 45544:2015 does not explain how the coverage factor for U_{zero} value was derived

- Eurachem Guide explains that the LoD coverage factor
  - Is based on the 95 % confidence interval
  - The 95 % interval for avoiding false positive readings is 1.65.
  - The 95 % interval for avoiding false negative readings is 1.65
  - Therefore the total coverage factor 3.3
  - This is normally rounded down to 3 for the LoD.

- The smaller coverage factor in EN 45544:2015 means there is a lower certainly that false positive or negative readings are avoided.

Instrument evaluation example

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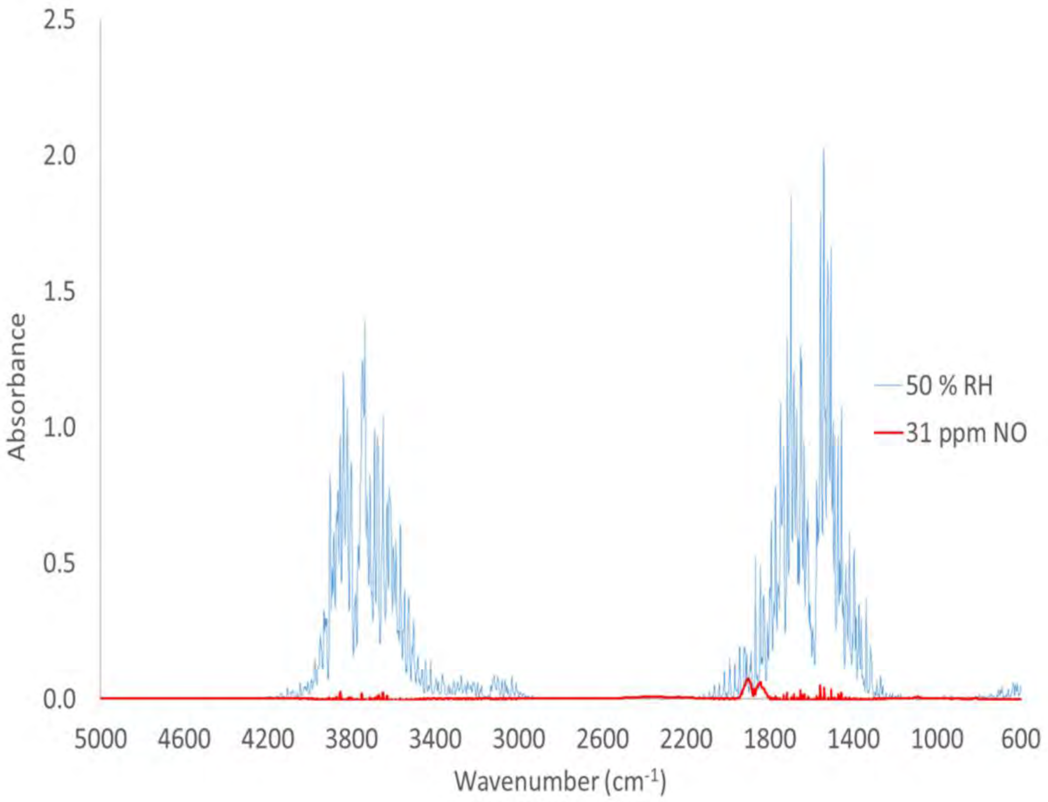
Nitric oxide determination on an FTIR

- Fourier transform infrared analyser (FTIR)
- Determining nitric oxide (NO) and nitrogen dioxide (NO_2)
- Uses a bespoke algorithm
- Evaluation was performed in a mixture of certified and in-house gas standards
- N_2 used was filtered through a scrubber assembly to remove residual NO_x
- Repeated assessments performed with increasing range of co-contaminants
  - H_2O
  - H_2O and carbon dioxide
  - H_2O, carbon dioxide and R134a



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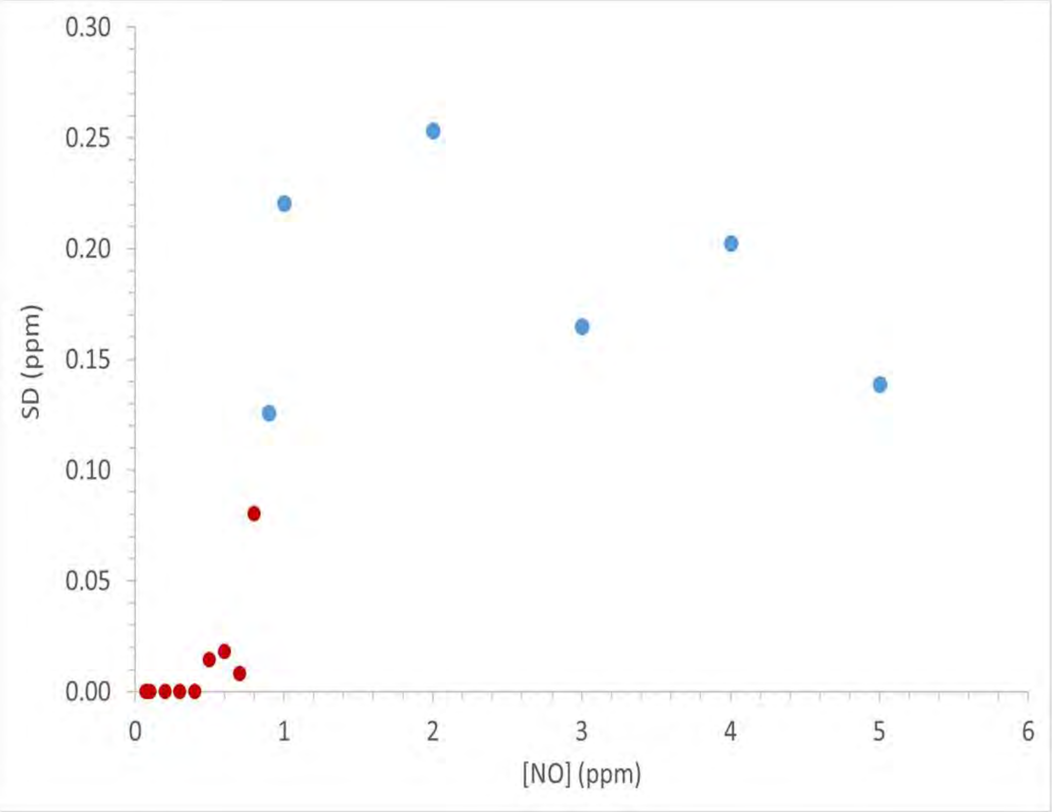
Standard deviation vs concentration

- s_0' vs concentration shows the variance due to the limited number of samples
- The FTIR does not allow the reporting of negative values
- Marked decrease in standard deviation at concentrations < 1 ppm due to false zero readings
- In reagent free gases it is not possible to assess these false zero results.



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Calculated lower operating limits

Challenge gas composition	s_0 (ppm)	U_{zero} (ppm)	LoD (ppm)	LoQ (ppm)
N_2	0.00	0.00	0.00	0.00
1 ppm NO in N_2	0.09	N/A	0.27	0.90
1 ppm NO, 50 % RH in N_2	0.22	N/A	0.66	2.20
1 ppm NO & 0.5 % CO_2 in 50 % RH N_2	0.13	N/A	0.39	1.30
2 ppm NO, 0.5 % CO_2 & 25 ppm R134a in 50 % RH N_2	0.08	N/A	0.24	0.80

- $unr_{zero} = 0.00$
  - Possibly due to processing of negative readings
- NO concentrations selected to avoided false negatives
- High variance in the humidified N_2
  - Observed in all H_2O co-contaminant tests

Conclusions

- Understanding the method the instrument processes negative readings is important
- EN 45544:2015 does not address any matrix effects in setting the Lower Limit of Measurement
- Smaller confidence interval in EN45544:2015 give less certainty that false positive and negative readings are avoided.
- Overall this causes EN45544 to have a Lower Limit of Measurement is not achieved in real world applications.

Acknowledgements

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Submarine
Delivery Agency

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Any questions

?

Novel Approaches for the Investigation of Submarine Air Quality

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Submarine Air Monitoring and Purification Symposium
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AFRL & NSMRL

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Overview

1. Problem Statement:

- Chemically diverse sample has special needs
- Current sampling methods are costly and inefficient

2. Advancement Opportunities

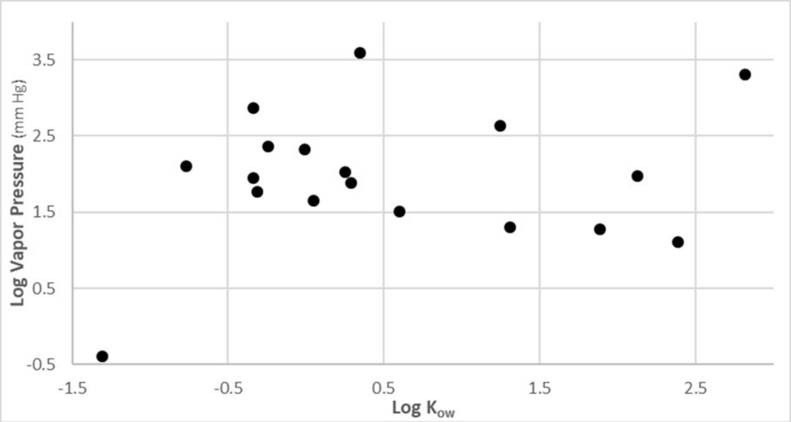
- Evaluation of two new passive sampling devices
- SIFT-MS with automated, online thermal extraction

3. Pilot Field Study

- Dosimeters stationed onboard submarine at multiple fixed locations
- Samplers worn by crew member for comparison

Diverse Analyte Classes Are A Challenge for Analysis

Chemical	BP	Vapor Pressure (mm)	$LogK_{OW}$
Monoethanolamine	170˚C	0.4	-1.31
Methanol	64.6˚C	127.2	-0.77
Acetonitrile	81.6˚C	88.8	-0.34
Acetaldehyde	20.8˚C	740	-0.34
Ethanol	78.4˚C	59.3	-0.31
Acetone	56˚C	231	-0.24
Acrolein	53˚C	210	-0.01
Isopropanol	82.5˚C	45.4	0.05
Acrylonitrile	77.3˚C	107.8	0.25
2-butanone	80˚C	77.5	0.29
Formaldehyde	-19˚C	3890	0.35
Crotonaldehyde	100˚C	32	0.6
Dichloromethane	39.6˚C	435	1.25
MIBK	118˚C	19.9	1.31
1,1,2-trichloroethane	110˚C	19	1.89
Benzene	80˚C	95.1	2.13
1,1,1,2-tetrachloroethane	130.5˚C	13	2.39
1,2-dichlorotetrafluoroethane	3.5˚C	2014	2.82



- Alcohols
  - Methanol (low MW)
- Aldehydes (labile compounds)
  - Formaldehyde

- Alkanolamines
  Ethanolamine (Polar)
- Halocarbons
- Hydrocarbons

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Characteristics of Current Approaches

- SAHAP (Submarine Atmosphere Health Assessment Program) Badge (Assay Technologies, Inc.)
    - Developed under SBIR
    - Multiple components incorporated
    - Multiple analyses required
    - Time-weighted average of calibrated components

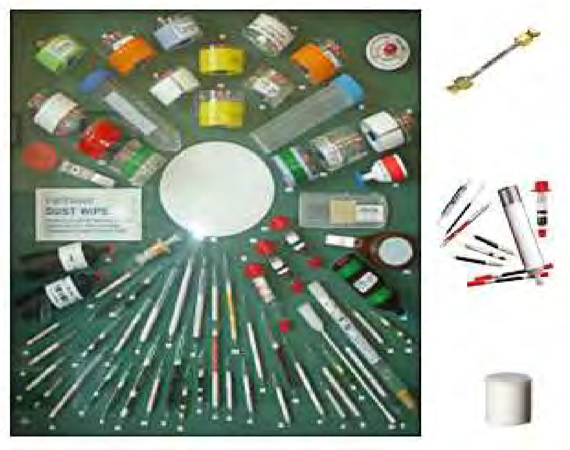


Photo courtesy of Wisconsin Occupational Health Lab

- Active Sorbent Sampling
    - Pumping required – power supply needed
    - More restricted duration vs. passive samplers
    - Can measure concentrations
    - Requires multiple sorbent types for coverage
    - Polar and reactive analytes problematic

SAHAP BADGE

Multiple Chemistries

- Alcohols
- Aldehydes
- Alkanolamines
- Flourohydrocarbons
- Halocarbons
- …others

Pros

- Gold-standard sampling device
- Broad spectrum (multiple chemistries)
- Commercial analysis pipeline

Cons

- Higher per unit cost
- 2 units for all 19 targets!
- Cumbersome form factor – not suitable for crew monitoring

Our Goals…

Validation of a Universal Passive Dosimeter

- Current goals: Verify collection of target constituents of concern
    - Collection of other VOCs for surveillance sampling
    - Establish universal extraction and analysis methods
    - Determine sampling rates for targets (to determine conc.)
- Long-term goal: Provide **individual** longitudinal exposure records

Silicone Wristband Samplers

Sampling Device (MyExposome)

Analysis

- Analysis by thermal extraction -> TD-GC/MS

Pros

- Low cost and easy to obtain
- Non-intrusive wearable
- High-capacity sampler
- VOCs and SVOCs

Cons

- Extensive pre-cleaning required
- Currently require offline thermal extraction
- Confined space requirement for determining **concentration** of VOCs

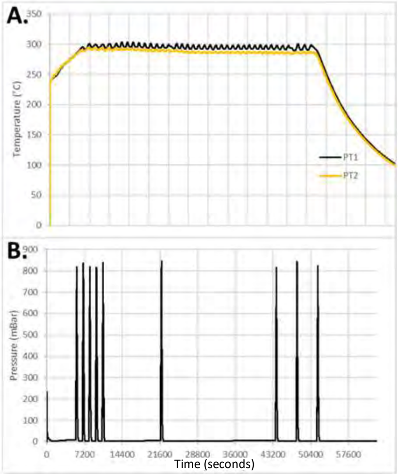
Fick's Law: $N_i = -D_i \nabla C_i$

$N_i = molar\ flux\ (mol \cdot m^{-2} \cdot sec^{-1})$

$D_i = diffusion\ coefficient\ (\underset{\text{surface geometry}}{m^{-2}} \cdot sec^{-1})$

$C_i = concentration\ (\mathrm{mol \cdot m^3})$

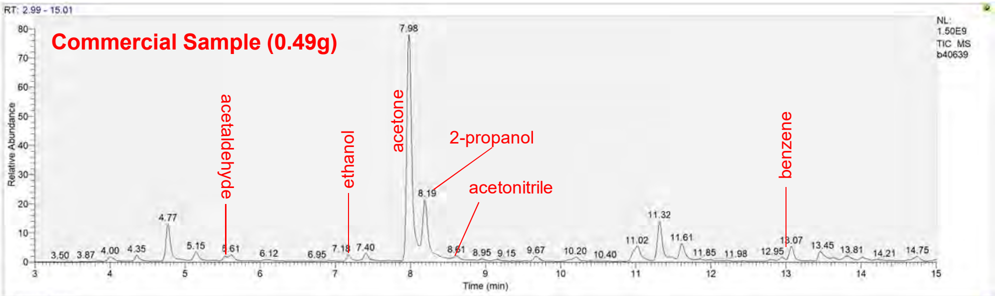
SWB Preparation for Passive Sampling

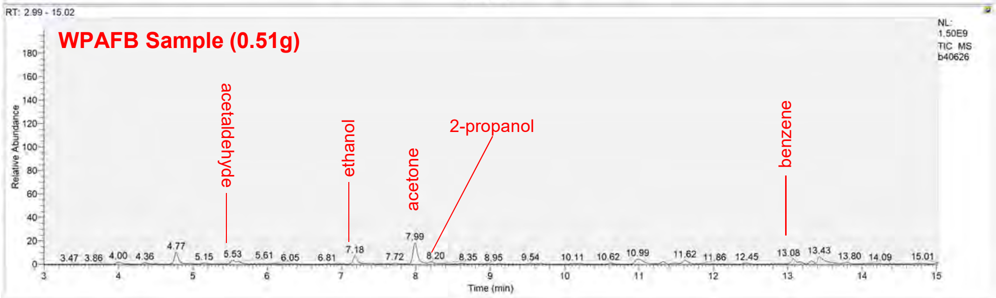


SWB Prep Cycle

- Vacuum oven treatment
- ~300°C/ 2mbar
- 72-96 hours total time
- **Multiple N_2 purge cycles**
- Store under inert gas in glass containers
- Transport/short-term storage in PTFE bags

- SWB are unusable direct from vendor due to high background and contamination of instrument
- Vacuum oven treatment results in ~300mg loss in mass (7-8%)
- High cost of commercially available pre-cleaned SWB led to development of in-house prep method

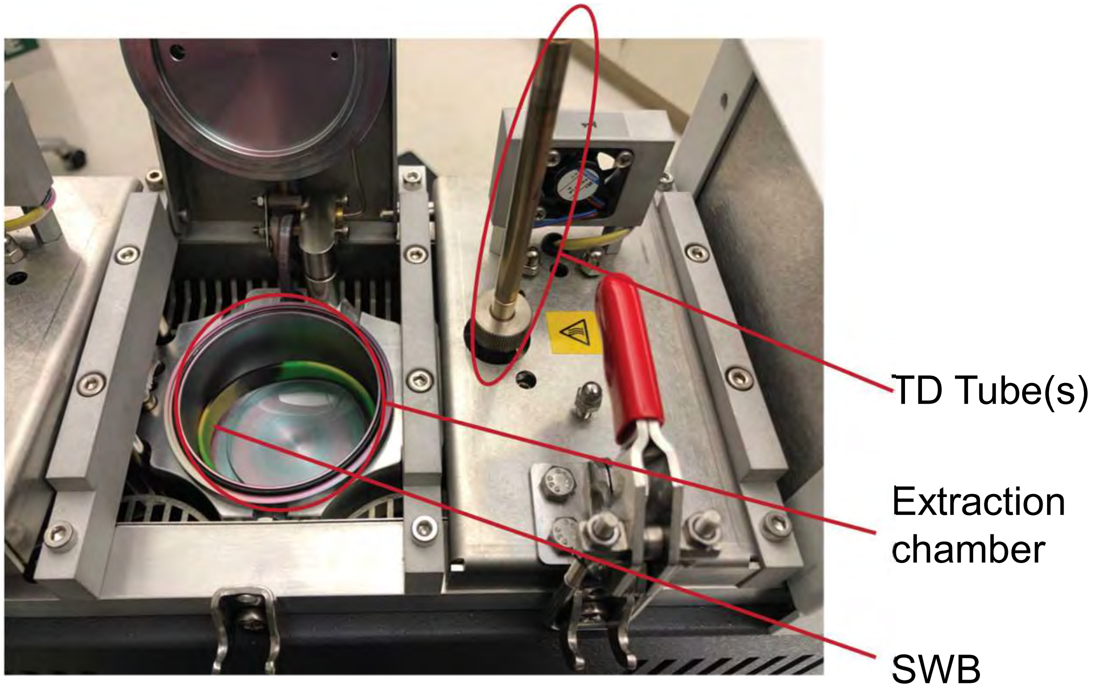




Current methodology yields SWB with lower background contamination vs commercial vendor.

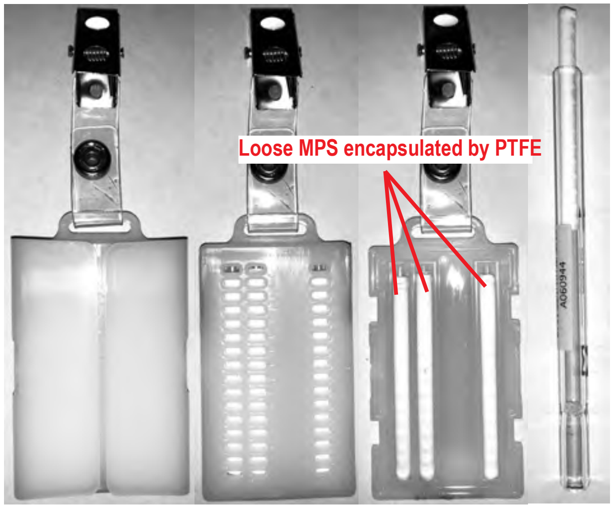
Offline Thermal Extraction of SWB:

- Reduces throughput
- Requires additional equipment
- Increases potential for error



*Method developed by O'Connell and Anderson et al. of Oregon State U

Mesoporous Silica Tokens (Xplosafe LLC)



Sampling Device

- 50mg OSU-6 sorbent inside PTFE sleeve
- Current form factor: Nylon clip-on badge

Analysis

- Direct TD-GC/MS analysis (MPS tokens)

Pros

- No thermal extraction step
- Enclosure enables rate determination
- Potentially 100% reusable
- Integral subtraction control

Cons

- Higher per unit cost (vs SWB)
- Impact of humidity unknown
- Some pre-cleaning required*

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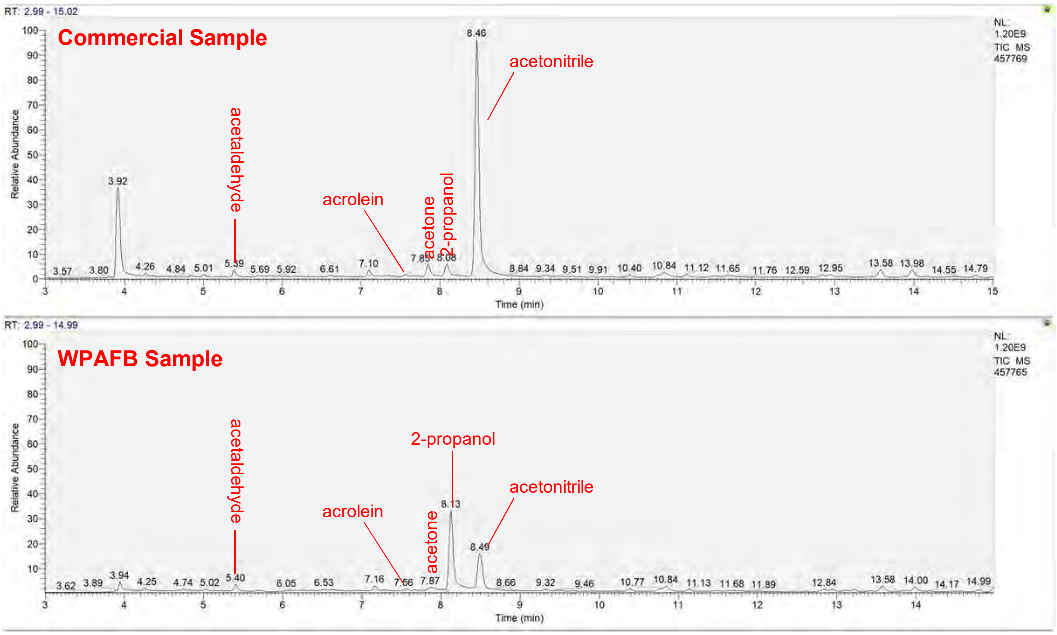
MPS Sampler Preparation by Supercritical CO_2



MPS Prep Cycle

- Supercritical fluid extraction
- Liquid CO_2 extraction under 300 bar pressure
- 3 hr treatment in vacuum oven at 200°C
- SFE prep reduces interfering contaminants from manufacture

*Note: Commercial product is still in R&D. Batch to batch variability can be attributed to improvements and changes to cleaning processes by commercial vendor.

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Pilot Study – 22 Days Aboard Fast-Attack Submarine

Ethanol

	SAHAP	SWB	MPS
F1	96200	19117	606
F2	128000	42669	1435
F3	112000	38342	1125
A1	70000	35976	0
A2	120000	38770	486
A3	104000	30962	0

Acetone

	SAHAP	SWB	MPS
F1	16300	17561	1537
F2	17000	20322	1266
F3	15900	20425	1764
A1	20400	31903	2082
A2	25300	31609	2406
A3	23800	33555	2270

2-propanol

	SAHAP	SWB	MPS
F1	42400		2451
F2	37800		3322
F3	39400		1702
A1	55000		3709
A2	61800		4490
A3	55000		4030

Benzene

	SAHAP	SWB	MPS
F1	7250	990	38
F2	5870		7
F3	6660		12
A1	14000	213	7
A2	14000		7
A3	13100		7

2-butanone

	SAHAP	SWB	MPS
F1	7330		1568
F2	5590	128	2208
F3	6430	109	787
A1	7950	235	1469
A2	7720	292	980
A3	7880	225	1292

Acrolein

	SAHAP	SWB	MPS
F1	0		
F2	667		46
F3	657		76
A1	523	469	8
A2	589		34
A3	639		57

Methyl isobutyl ketone

	SAHAP	SWB	MPS
F1	0		1013
F2	0		980
F3	0	27	1094
A1	782	58	1562
A2	803	27	1575
A3	782	69	1398

Sample Key

F1 – Aux machine room
F2 – Crew's mess
F3 – Fan room (aft bh)
A1 – Engine room LL aft
A2 – Engine room LL fwd
A3 – Engine room maneuvering

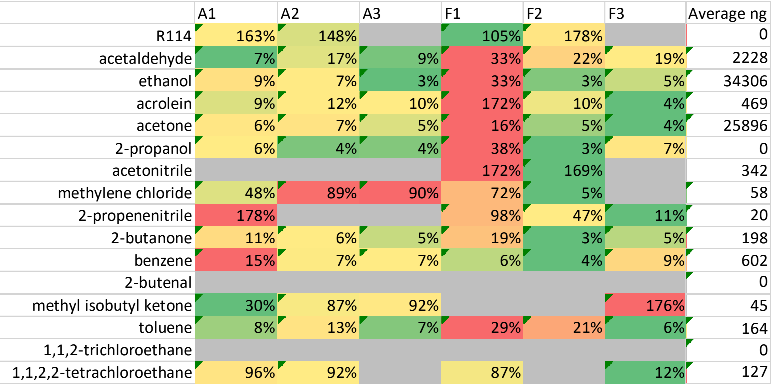
SWB	F1	F2	F3	A1	A2	A3
Acetaldehyde	1032	3020	3634	4409	4051	3782
Acetonitrile	538	143	0	0	0	0
Methylene chloride	73	42	32	115	77	87
2-propenenitrile	90	44	33	40	0	0
2-butenal	0	0	0	0	0	0
Toluene	168	285	274	192	247	235
1,1,2,2-tetrachloroethane	114	0	206	280	163	0

MPS	F1	F2	F3	A1	A2	A3
Acetaldehyde	28032	531	1797	324	444	273
Acetonitrile	**235**	0	0	0	0	0
Methylene chloride	3	5	7	9	8	7
2-propenenitrile	260	9	26	12	9	4
2-butenal	0	**121**	0	0	0	0
Toluene	31	40	46	24	25	17
1,1,2,2-tetrachloroethane	0	0	0	0	0	0

- **Nanograms on 1 SWB or 1 MPS token**
- 1 SWB = ~3.75g; 1 MPS = 0.3g
- Good agreement between different media (presence/absence; rel. abundance)
- High background of SWB reduces sensitivity

Reproducibility of Quantitation by Sampler Type

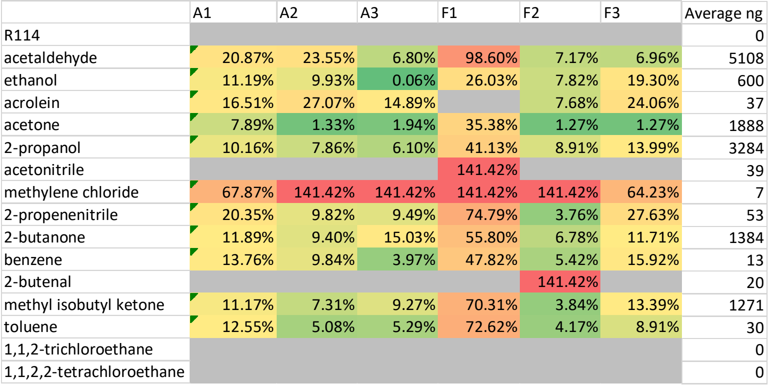
SWB



	A1	A2	A3	F1	F2	F3	Average ng
R114	163%	148%		105%	178%		0
acetaldehyde	7%	17%	9%	33%	22%	19%	2228
ethanol	9%	7%	3%	33%	3%	5%	34306
acrolein	9%	12%	10%	172%	10%	4%	469
acetone	6%	7%	5%	16%	5%	4%	25896
2-propanol	6%	4%	4%	38%	3%	7%	0
acetonitrile				172%	169%		342
methylene chloride	48%	89%	90%	72%	5%		58
2-propenenitrile	178%			98%	47%	11%	20
2-butanone	11%	6%	5%	19%	3%	5%	198
benzene	15%	7%	7%	6%	4%	9%	602
2-butenal							0
methyl isobutyl ketone	30%	87%	92%			176%	45
toluene	8%	13%	7%	29%	21%	6%	164
1,1,2-trichloroethane							0
1,1,2,2-tetrachloroethane	96%	92%		87%		12%	127

- 2 devices hung at each sampling location onboard submarine
- From each device – 2 technical replicates
- Net = 4 quantitative measurements
- Average and RSD are <u>of those 4</u> measures

MPS

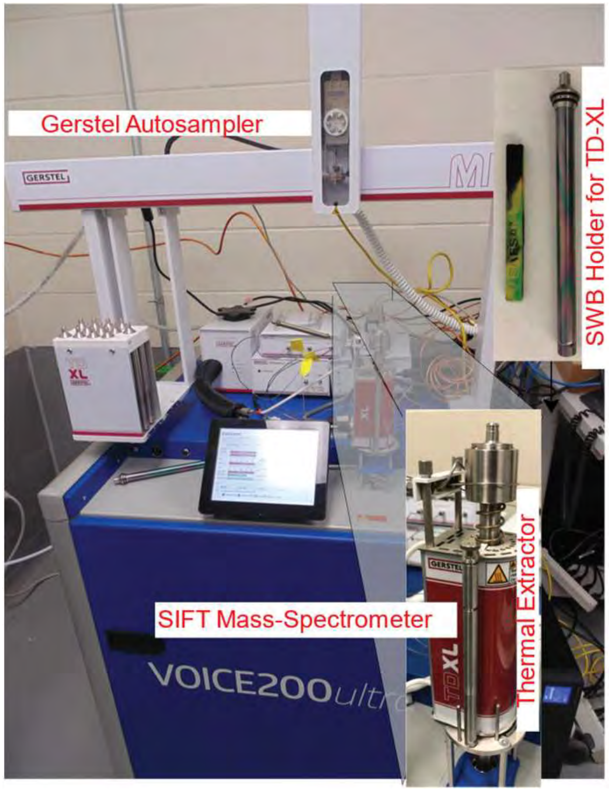


	A1	A2	A3	F1	F2	F3	Average ng
R114							0
acetaldehyde	20.87%	23.55%	6.80%	98.60%	7.17%	6.96%	5108
ethanol	11.19%	9.93%	0.06%	26.03%	7.82%	19.30%	600
acrolein	16.51%	27.07%	14.89%		7.68%	24.06%	37
acetone	7.89%	1.33%	1.94%	35.38%	1.27%	1.27%	1888
2-propanol	10.16%	7.86%	6.10%	41.13%	8.91%	13.99%	3284
acetonitrile				141.42%			39
methylene chloride	67.87%	141.42%	141.42%	141.42%	141.42%	64.23%	7
2-propenenitrile	20.35%	9.82%	9.49%	74.79%	3.76%	27.63%	53
2-butanone	11.89%	9.40%	15.03%	55.80%	6.78%	11.71%	1384
benzene	13.76%	9.84%	3.97%	47.82%	5.42%	15.92%	13
2-butenal					141.42%		20
methyl isobutyl ketone	11.17%	7.31%	9.27%	70.31%	3.84%	13.39%	1271
toluene	12.55%	5.08%	5.29%	72.62%	4.17%	8.91%	30
1,1,2-trichloroethane							0
1,1,2,2-tetrachloroethane							0

<u>Sample Key</u>
<u>F1</u> – Aux machine room
<u>F2</u> – Crew's mess
<u>F3</u> – Fan room (aft bh)
<u>A1</u> – Engine room LL aft
<u>A2</u> – Engine room LL fwd
<u>A3</u> – Engine room maneuvering

AFRL & NSMRL

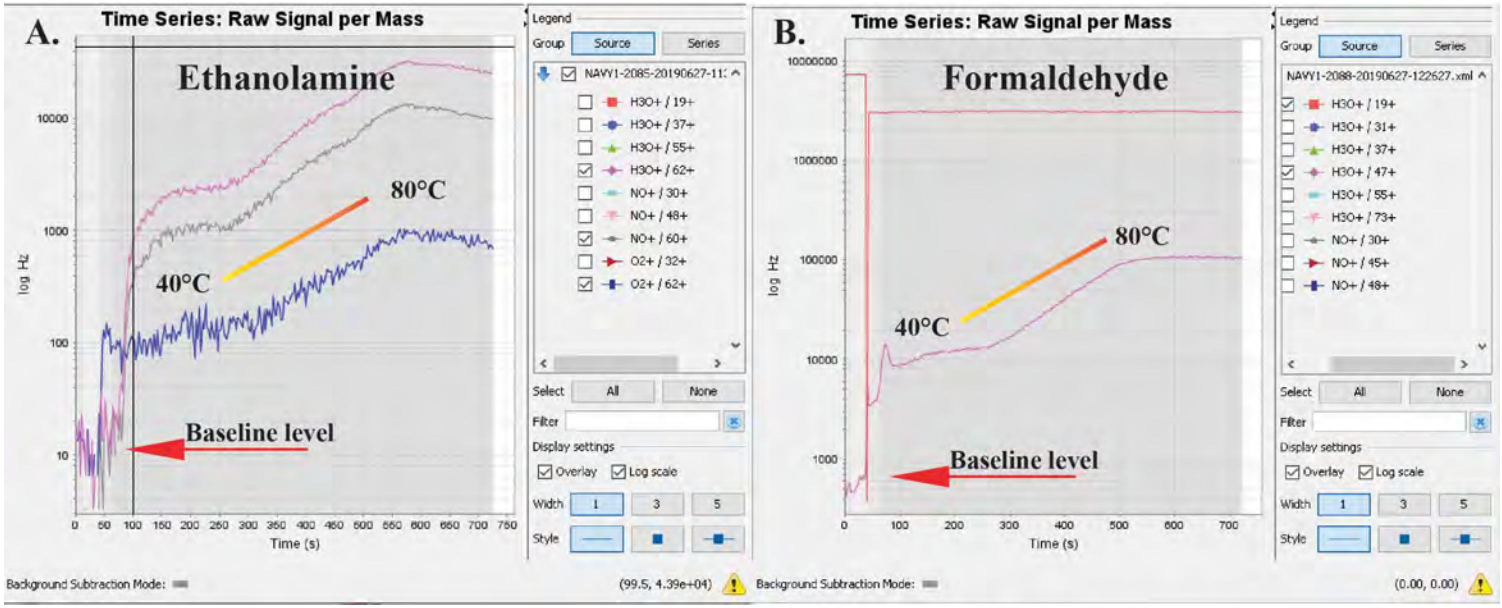
Novel MOTS Instrumentation – TE-SIFT-MS



- Custom Gerstel autosampler and thermal extractor
- Fully automated thermal extraction and analysis of up to 30 samples
- Rapid thermal gradient (120°C/min)
- Analysis ~ 10-15 min/sample
- SIFT-MS amenable to methanol and formaldehyde analysis
- No limitations for polar/non-polar compounds

AFRL & NSMRL

Example SIFT-MS Analysis



Legend (A), Group: Source
☑ NAVY1-2085-20190627-11:
☐ H3O+ / 19+
☐ H3O+ / 37+
☐ H3O+ / 55+
☑ H3O+ / 62+
☐ NO+ / 30+
☐ NO+ / 48+
☑ NO+ / 60+
☐ O2+ / 32+
☑ O2+ / 62+

Display settings: ☑ Overlay ☑ Log scale; Width: 1

Background Subtraction Mode:

(99.5, 4.39e+04)

Legend (B), Group: Source
NAVY1-2088-20190627-122627.xml
☑ H3O+ / 19+
☐ H3O+ / 31+
☐ H3O+ / 37+
☑ H3O+ / 47+
☐ H3O+ / 55+
☐ H3O+ / 73+
☐ NO+ / 30+
☐ NO+ / 45+
☐ NO+ / 48+

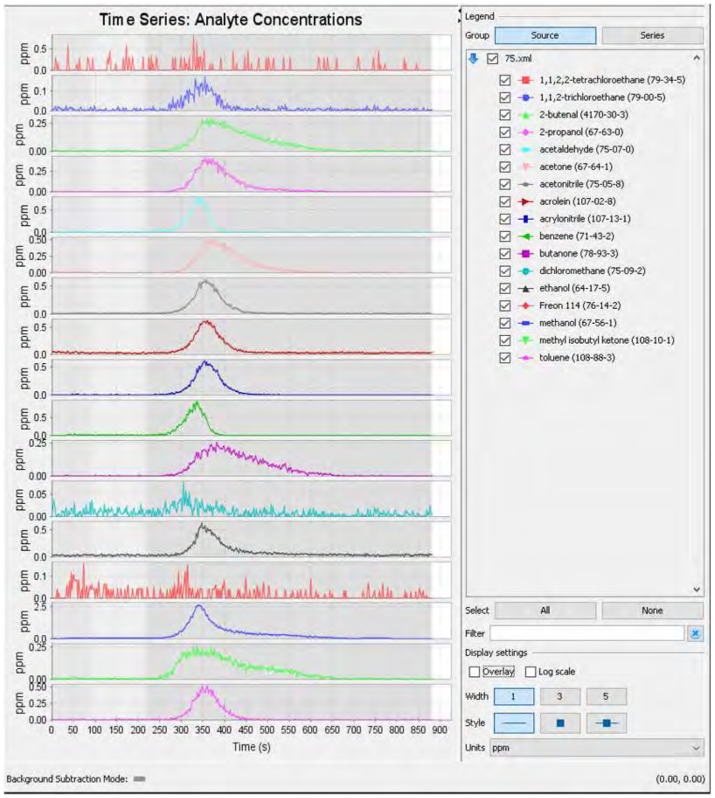
Display settings: ☑ Overlay ☑ Log scale; Width: 1

Background Subtraction Mode:

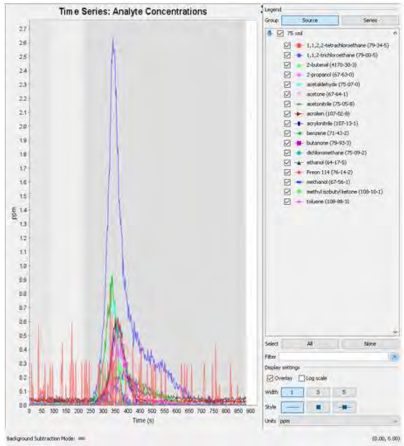
(0.00, 0.00)

- Permeation tubes introduced VOCs via thermal extractor
- Thermal gradient demonstrates emission increase as function of temperature
- Emission ranges from 30-200ng/min over gradient

Simultaneous Analysis of 17 Targets vis SIFT-MS



- Mixture of 17 compounds* loaded to Xplosafe sorbent token
- Token desorbed using TD-XL system
- Simultaneous SIM scan of targets



SIFT-MS uses unique reaction chemistries to provide target ID confirmation and qualitative info for unknowns

*Xcel+ tokens appear to have poor affinity for R-114 and 1,1,2,2-TCA

AFRL & NSMRL

Summary

- Current (gold-standard) samplers are bulky and require multiple, independent analyses to yield data
- New methods developed to prepare 2 novel sorbents for passive sampling of VOCs
- Novel sorbents used for sampling onboard submarine
- Collection of multiple classes of organic compounds on single media
- Both sorbents differentiated between sampling locations while underway
- Good agreement between novel sorbents and legacy device
- Development of new analytical technologies to allow analysis of multiple classes of analytes using one instrument/method

Acknowledgments

- Work was funded by Defense Health Agency Funds
  - US Navy J9 Restoral Funds (work unit F1808)
  - Defense Health Program (Joint Program Committee 5, Military Operational Medicine Research Program, work unit F1604)

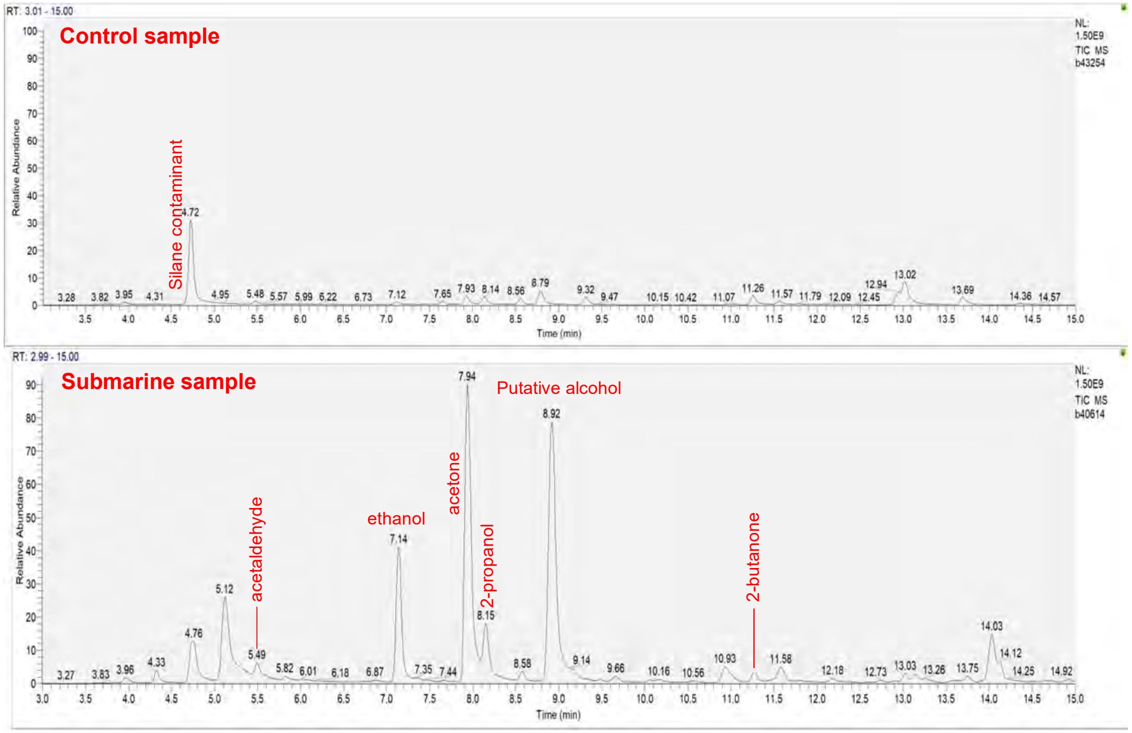
- Special thanks for the on-going collaboration among government and industrial partners
  - Gerstel
  - SYFT Technologies, Inc.
  - XploSafe
  - MyExposome

PROCEEDINGS

AFRL


USS Connecticut (SSN-22) departing on her first scheduled deployment on 1 May 2002

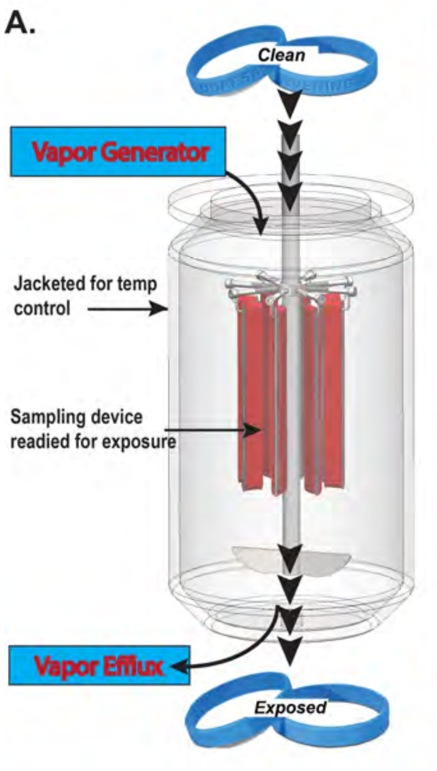
SWB Extract – Comparing Control to Submarine Sample



SWB Control Sample:

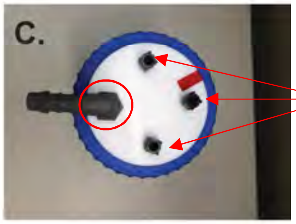
	SWB
acetaldehyde	1551
ethanol	2521
acrolein	685
acetone	13383
2-propanol	9787
acetonitrile	195
methylene chloride	16
2-propenenitrile	31
2-butanone	723
benzene	2204
2-butenal	0
methyl isobutyl ketone	3
toluene	69
1,1,2,2-tetrachloroethane	0
	*Values in ng

Determine Rate of Absorption



Air-tight PTFE cap

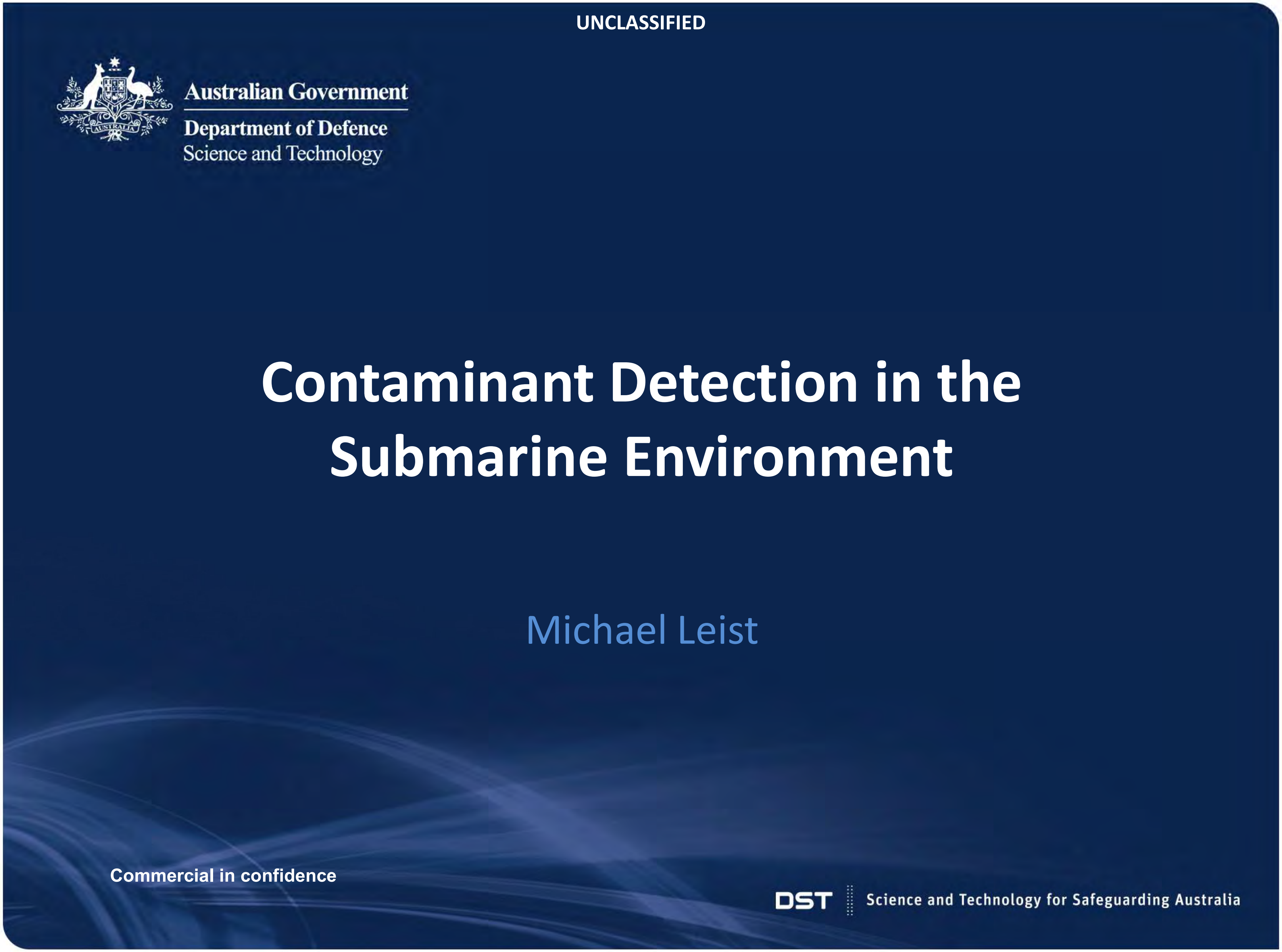
MPS badge



Multiple ports for gas flow

<u>Dosing Process</u>

1. Dosimeter(s) enclosed in chamber
2. Chamber purged with pure N_2
3. Timed application of:
   - -Continuous flow of VOCs <u>or</u>
   - -Static VOCs concentration
4. Chamber purged with N_2
   - -Collect remaining VOCs by TD for mass-balancing
5. Sample extraction and analysis



UNCLASSIFIED

Australian Government
Department of Defence
Science and Technology

Contaminant Detection in the Submarine Environment

Michael Leist

Commercial in confidence

DST Science and Technology for Safeguarding Australia

Carbon Monoxide

Contaminant Detection in the Submarine Environment

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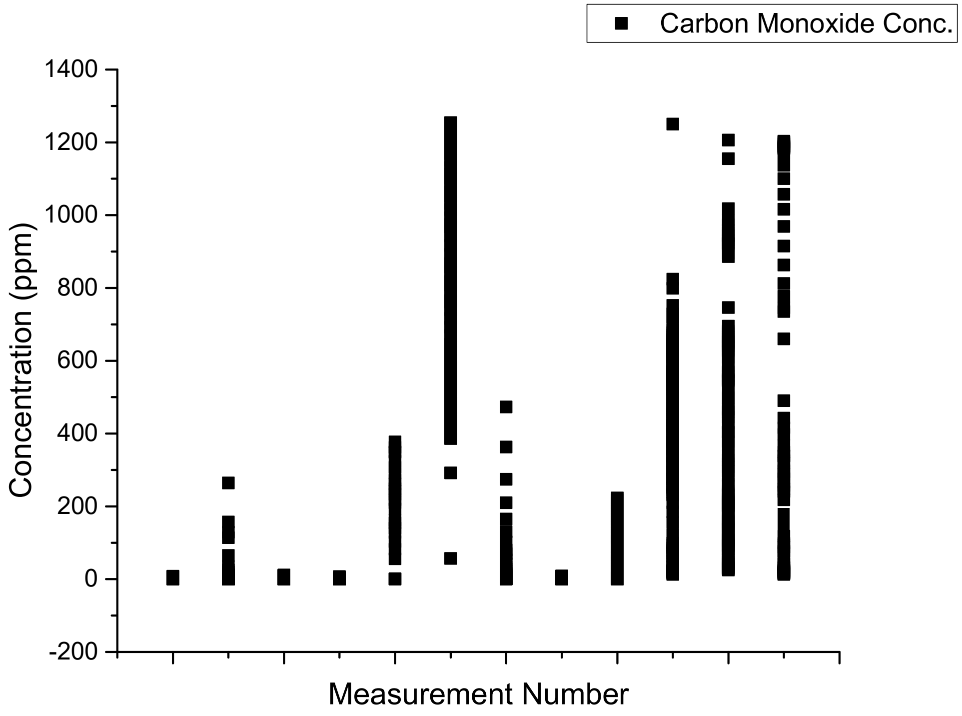
Submarine Atmosphere Contaminant Detection

- Real time instrumentation
  - Distributed Sensor Network
    - Sensors distributed throughout the submarine
- Sensors must satisfy analytical requirements
  - Limits of Detection
  - Accurate
    - Free from cross sensitivities
  - Robust and reliable
    - Maintenance / boat schedules

Submarine Atmosphere Contaminant Detection

Is it feasible to use low cost EC sensors to monitor toxic gases in a submarine?



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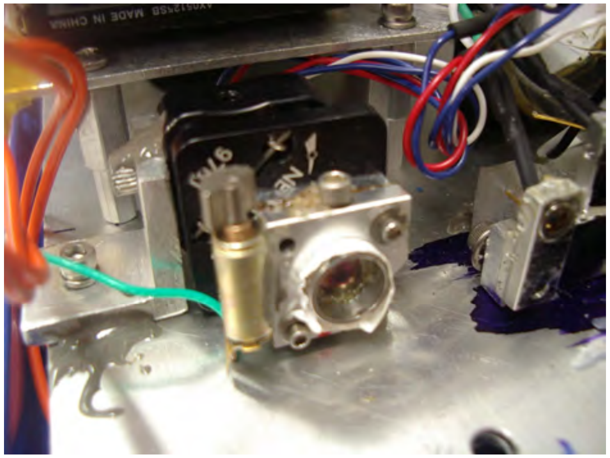
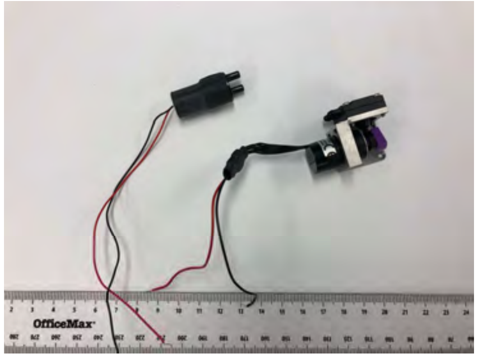
Submarine Atmosphere Contaminant Detection

- DST Prototype Tunable Diode Laser (TDL), Carbon Monoxide
- SAMAP 2015
  - Permanent mounting or portable use
  - Light weight, battery or boat power
  - Sensitivity, Stability, Selectivity,

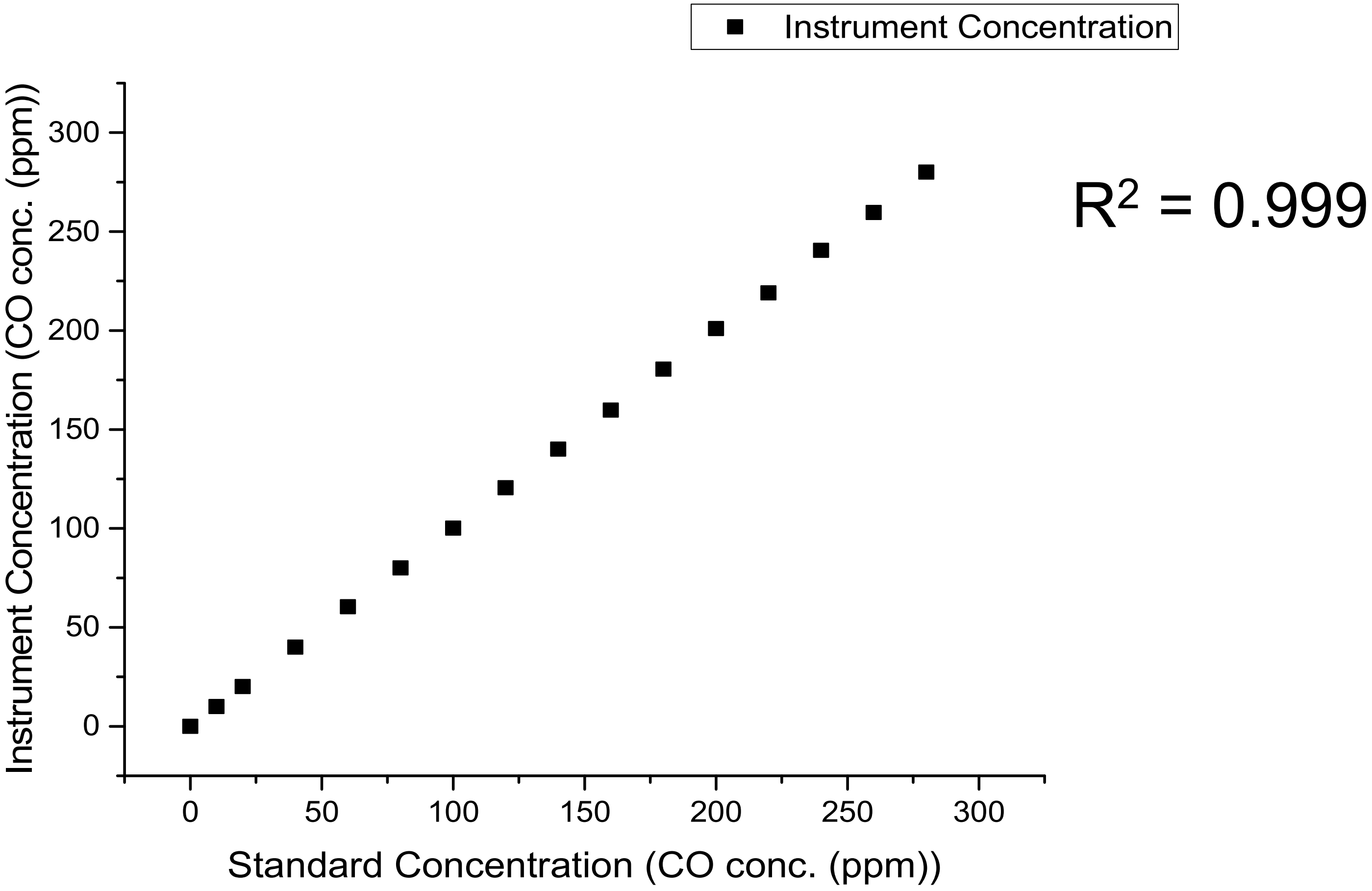


Submarine Atmosphere Contaminant Detection

- DST TDL Continual Development of the Instrument
  - Software/firmware modifications
  - Improved stability
    - Changes made to the TDL
  - Improving the longevity of the air intake pumps
  - Protection of the instrument from the Submarine environment



Submarine Atmosphere Contaminant Detection

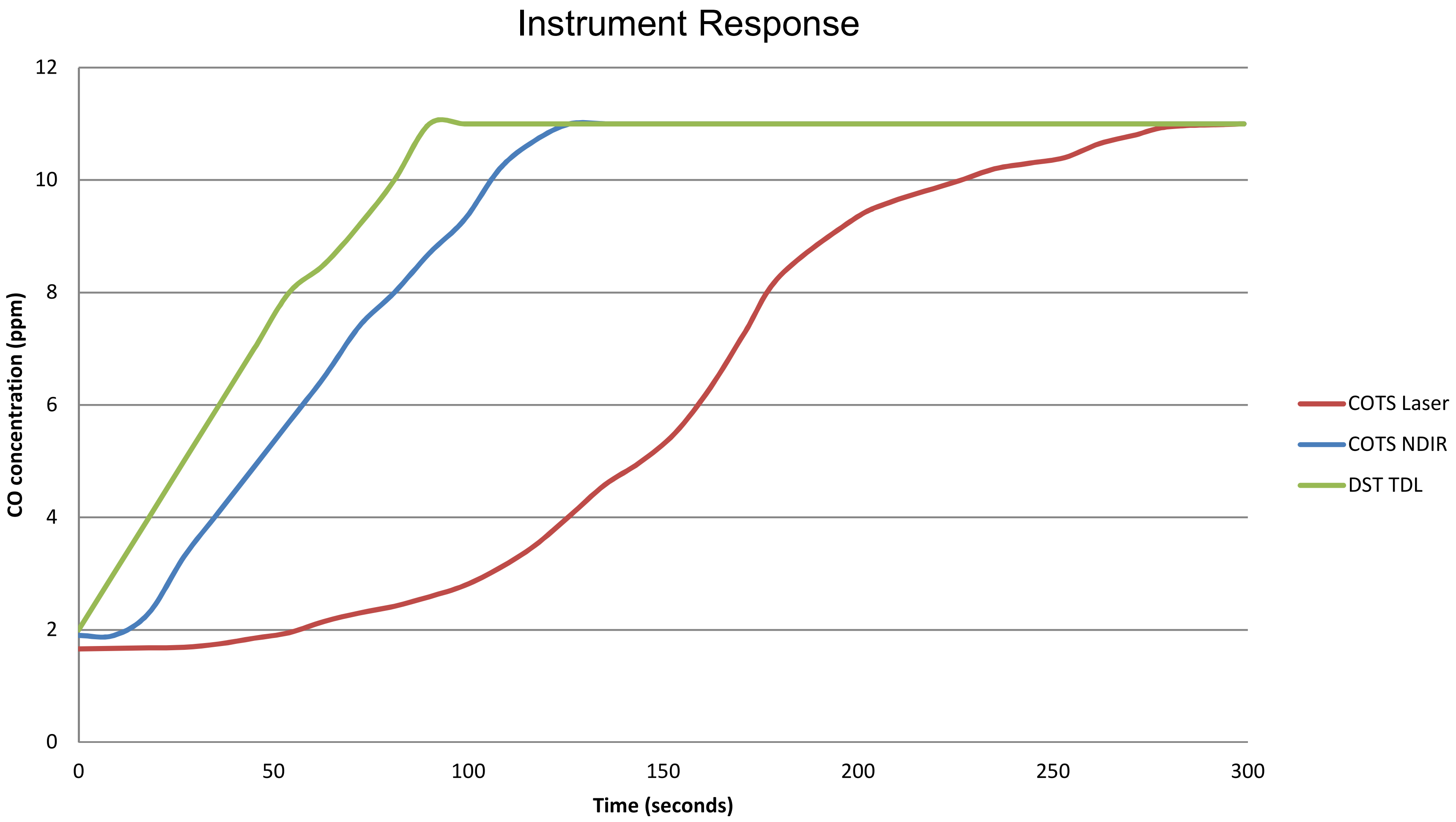


Submarine Atmosphere Contaminant Detection

- DST TDL Compared with COTS options
  - Laser Based Instrument
  - Nondispersive Infrared (NDIR)

- COTS options are;
  - Less flexible
    - Boat Power Only,
    - Higher Power Consumption,
    - Larger Footprint

Submarine Atmosphere Contaminant Detection



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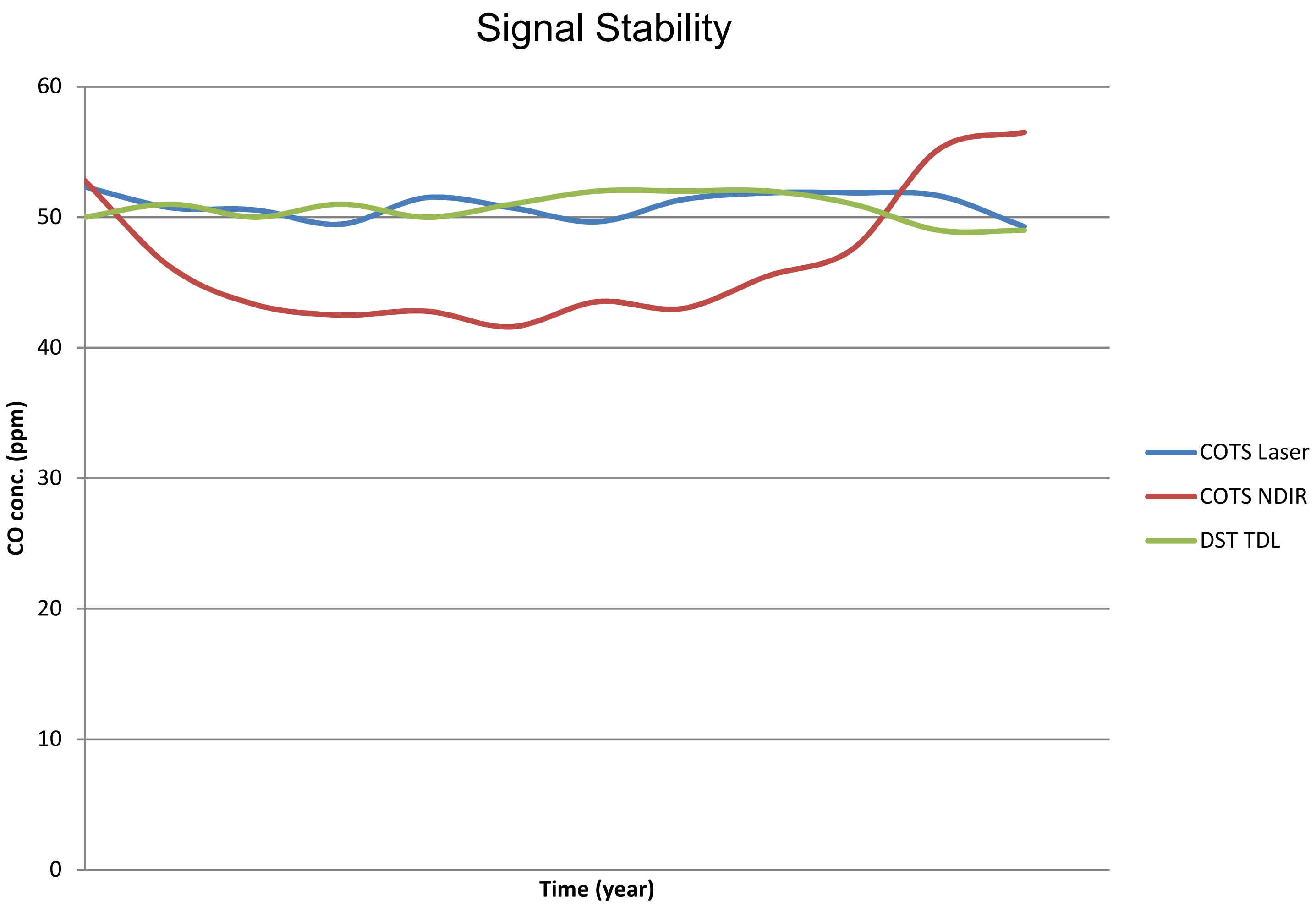
Submarine Atmosphere Contaminant Detection



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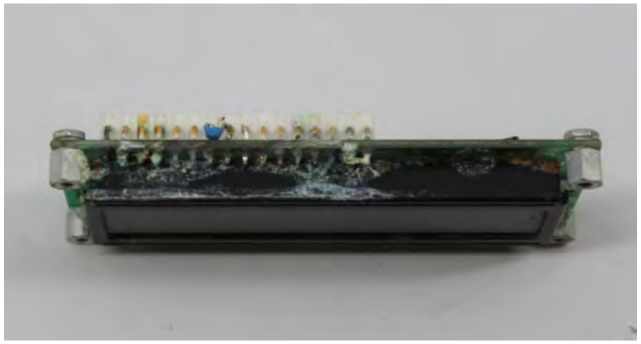
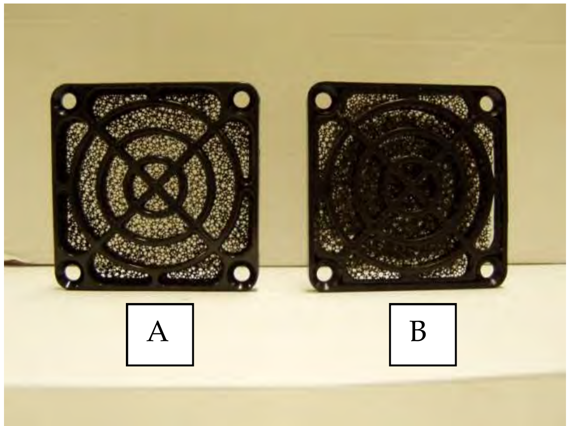
Submarine Atmosphere Contaminant Detection

DST TDL



COTS Laser Instrument



Particulate screen filter on air cooling
A = Clean, B = ~ 20 days

Diesel Exposure Assessment

Submarine Atmosphere Contaminant Detection

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Submarine Atmosphere Contaminant Detection

- Diesel Exhaust has two fractions
  - Gaseous & vapors
    - Major Components (99%) N_2, O_2, CO_2 & H_20
    - Minor Components (1%) CO, NOx, SO_2
  - Particulate (DPM)
    - DPM = (Organic Carbon, OC) + (Elemental Carbon, EC) + Minerals

Submarine Atmosphere Contaminant Detection

- Elemental Carbon (EC)
  - Often used as a surrogate for DPM
  - Provides the best fingerprint for diesel exhaust
  - Relatively free of interferences
  - Chemically stable.

- EC/TC can vary dramatically depending on ending load, tuning, fuel etc.

- Organic carbon (OC) is not used as a DPM surrogate because other sources of OC (e.g., cigarette smoke)

Submarine Atmosphere Contaminant Detection

- Currently no law in Australia governing DPM exposure
- SAFEWORK Australia yet to release industry standard
  - Exposure Standards currently under review
- AIOH recommendation (2004) 0.1 mg/m^3 EC
- NSW Mines (2006) 0.1 mg/m^3 EC
- WA Draft Guideline (2013) 0.1 mg/m^3 EC

Submarine Atmosphere Contaminant Detection

- NIOSH method 5040 (measurement of EC)
  - A pump is used to draw air through a particle size selector and onto a quartz filter

- Downside of NIOSH 5040
  - Not real time, no feedback to crew
  - Crew involvement in the sampling process
  - Risk of sample degradation or contamination prior to analysis
  - Provides averaged result

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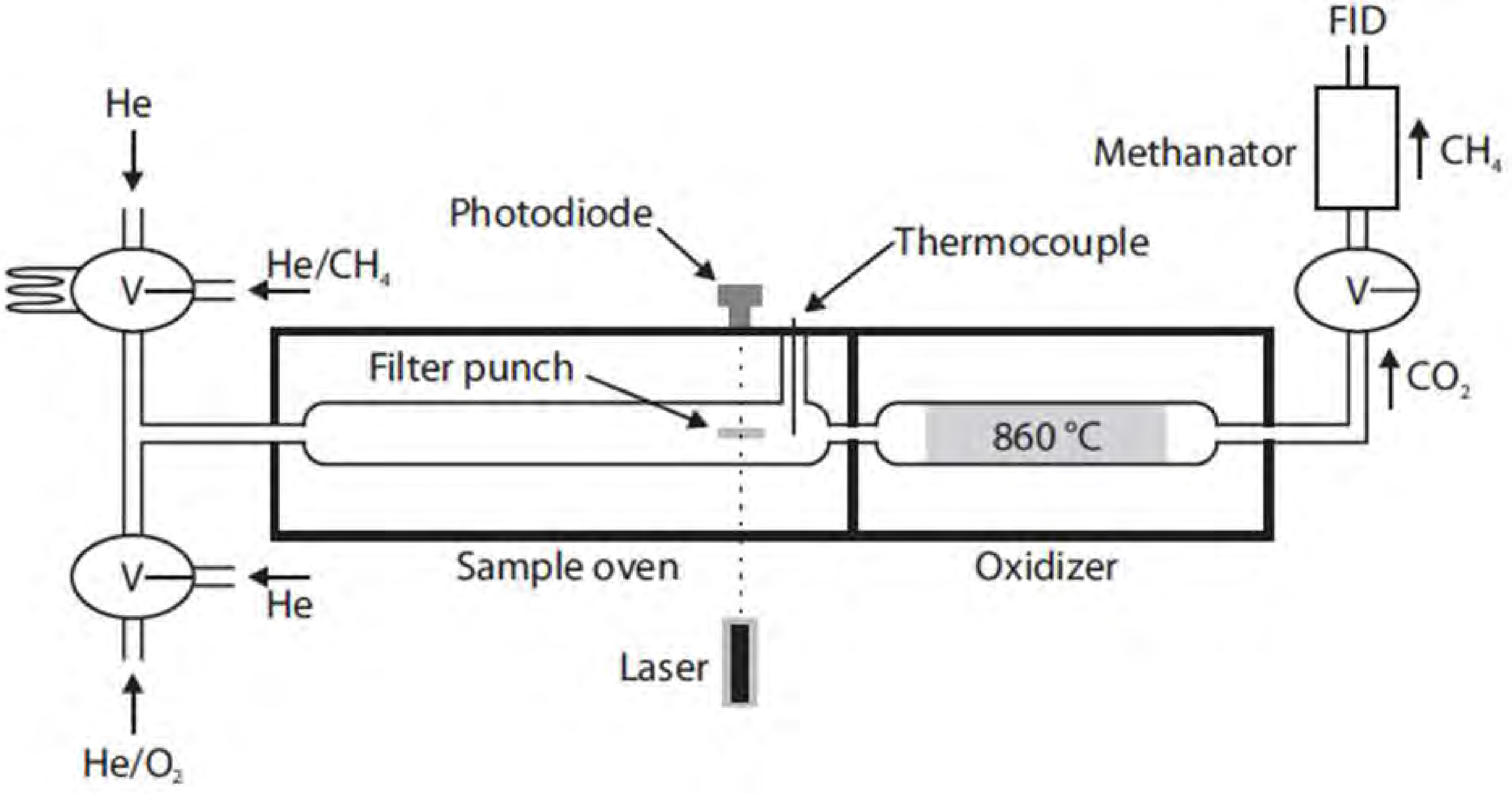
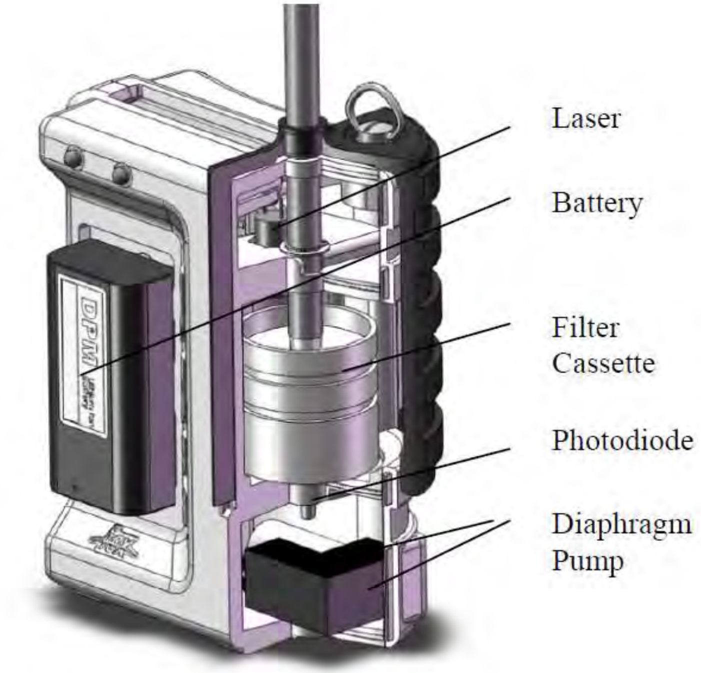
Submarine Atmosphere Contaminant Detection

- NIOSH 5040 - Thermal-optical analysis



Submarine Atmosphere Contaminant Detection

- Airtec Instrument
  - real time DPM (EC)
  - Air drawn into instrument using a diaphragm pump
  - Submircon particles collected on a filter
  - Laser illuminates the filter
  - As DPM particulates accumulate the lasers transmittance decreases



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Submarine Atmosphere Contaminant Detection

External Cyclone (2) is used with the Airtec instrument and connected conductive tubing (1)

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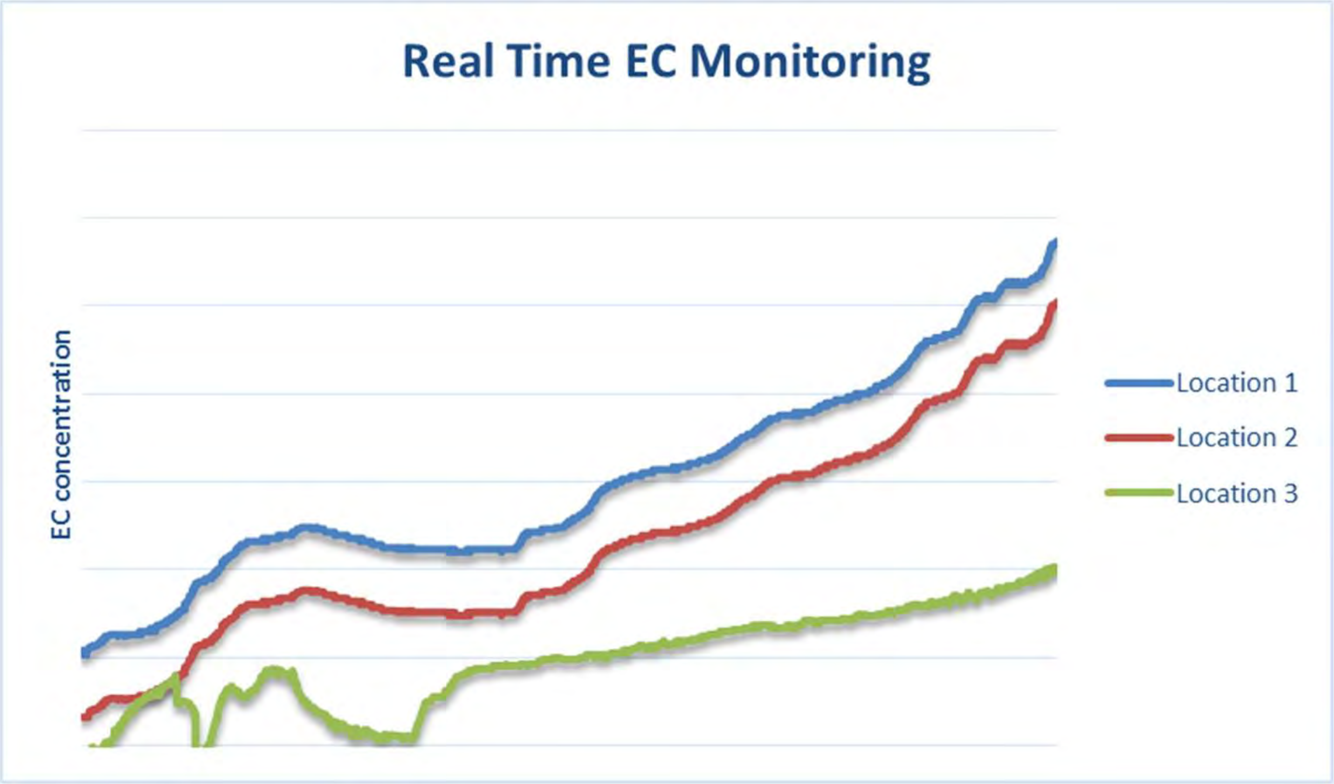
Submarine Atmosphere Contaminant Detection



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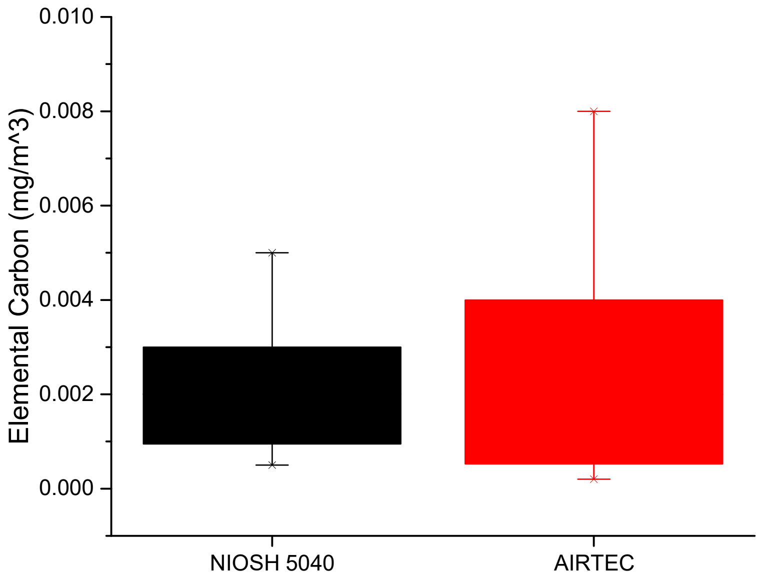
Submarine Atmosphere Contaminant Detection

- Elemental Carbon
  - Method NIOSH 5040 versus Airtec (Realtime)
  - Results obtained from NIOSH 5040 and Airtec are similar



Differences between the two techniques are not statistically significant

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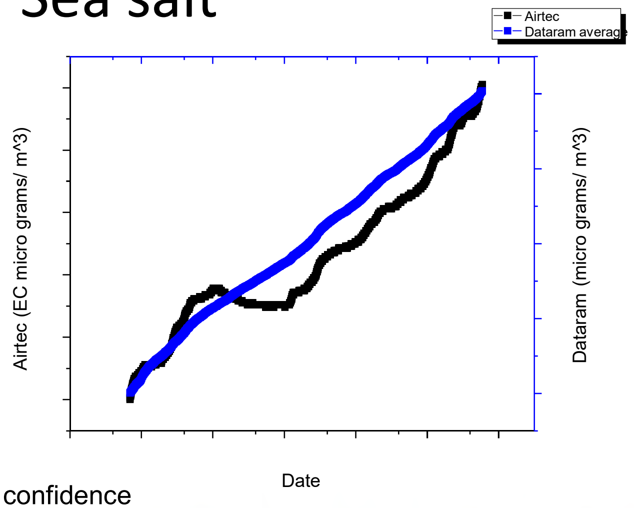
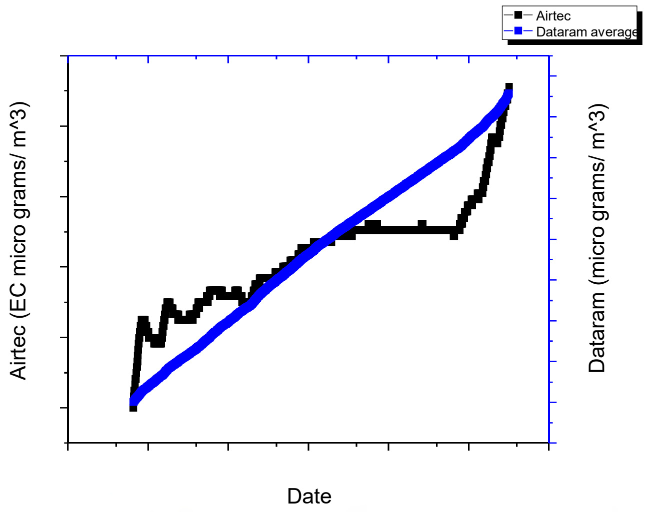
Submarine Atmosphere Contaminant Detection

- Aerosol monitors
  - Not calibrated for DPM
    - Typically Arizona Road Dust or A1 Test Dust
    - DPM has significantly different light scattering properties than of test aerosol
    - A light scattering photometric instrument response will not agree with DPM specific methods

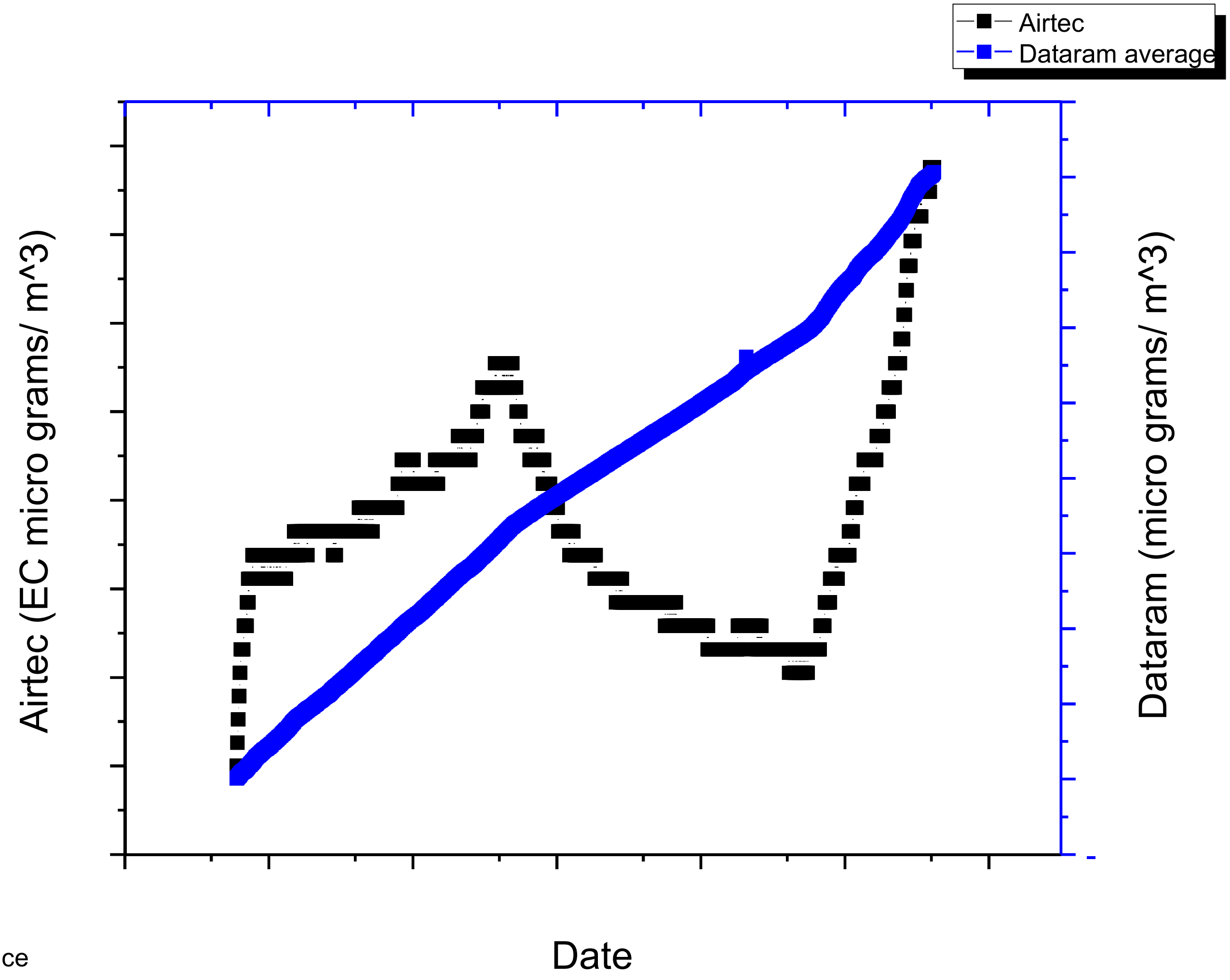
Submarine Atmosphere Contaminant Detection

- Aerosol Monitors Personal DataRam
  - Real time aerosol monitor
  - Passive sampler
  - Measures light scattering
  - No cyclone or filter
  - Sea salt





Submarine Atmosphere Contaminant Detection



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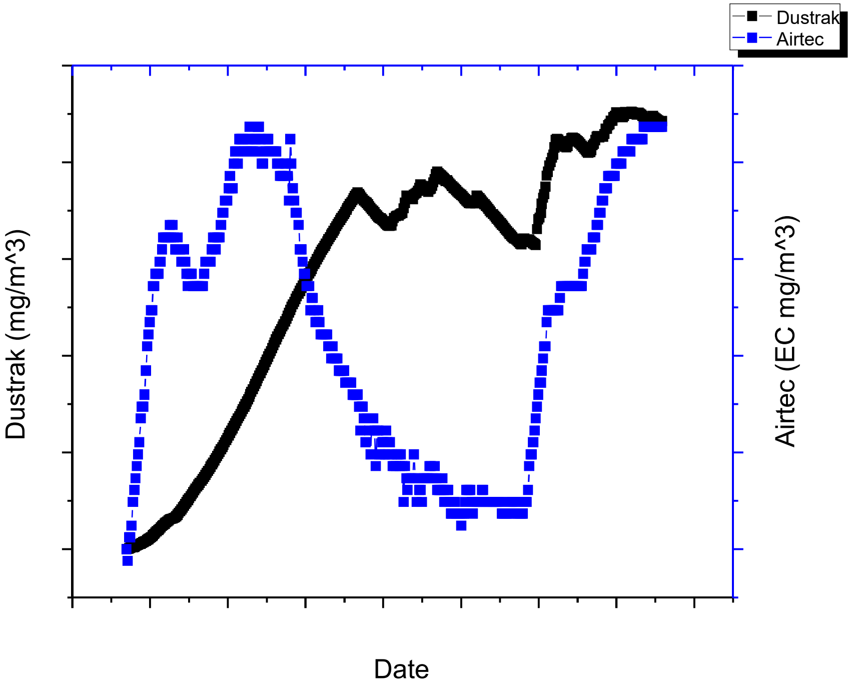
Submarine Atmosphere Contaminant Detection

Dustrak (Aerosols)



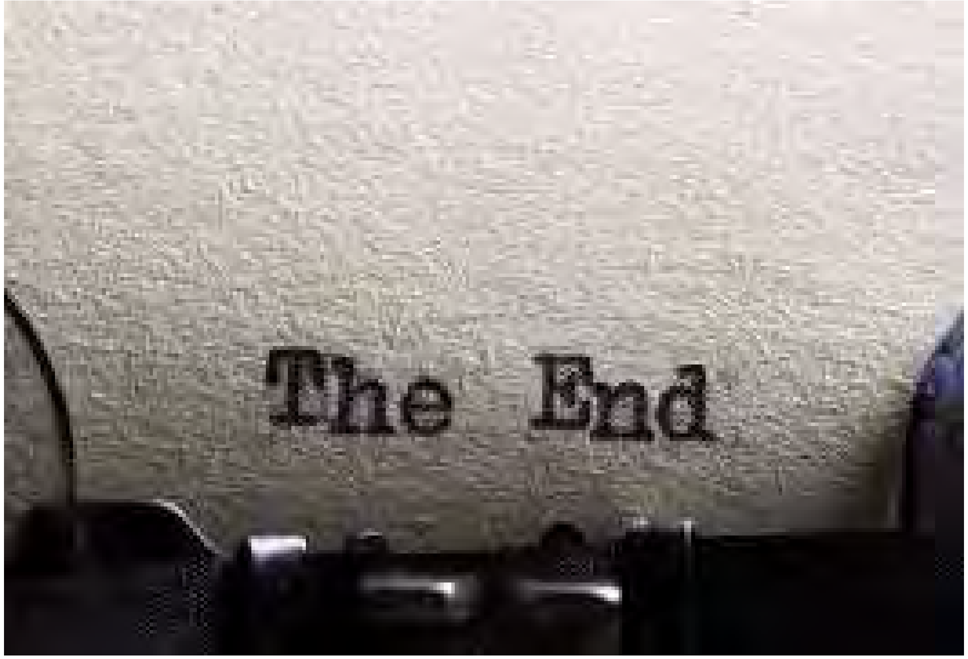
Custom calibration factors used in conjunction with PM1 impactors can improve instrument response

Submarine Atmosphere Contaminant Detection

- Even if we detect EC accurately in the submarine atmosphere…

Are we capturing all potential risks sufficiently?

- Nanoparticle exposure
  - Does low EC guarantee low nanoparticle measurements, Answer = NO


The End

PROCEEDINGS

SAMAP 2019

EXPOSURE TO DIESEL EXHAUST EMISSIONS: IRRITANTS

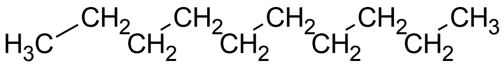
W. MAZUREK

AUSTRALIA

Dedicated to the memory of Peter Hanhela (1950 – 2019) former team member and friend.

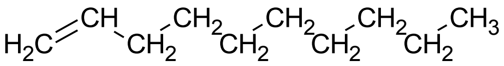
DIESEL FUEL CHEMICAL COMPOSITION: HYDROCARBONS

STRAIGHT CHAIN ALKANES (Paraffins)



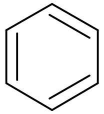
n-Decane $C_{10}H_{22}$

STRAIGHT CHAIN ALKENES

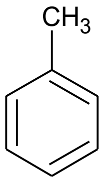


1-Decene $C_{10}H_{20}$

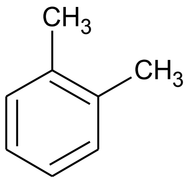
AROMATIC HYDROCARBONS



BENZENE

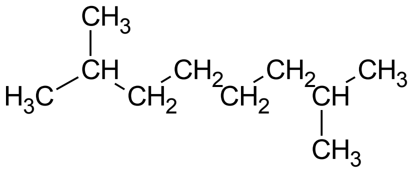


TOLUENE



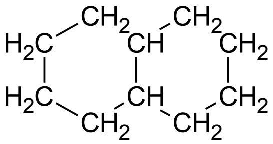
XYLENE

BRANCHED CHAIN ALKANES(Iso-Paraffins)



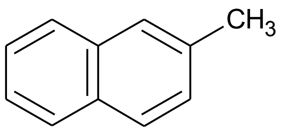
2,7-Dimethyloctane $C_{10}H_{22}$

CYCLIC HYDROCARBONS



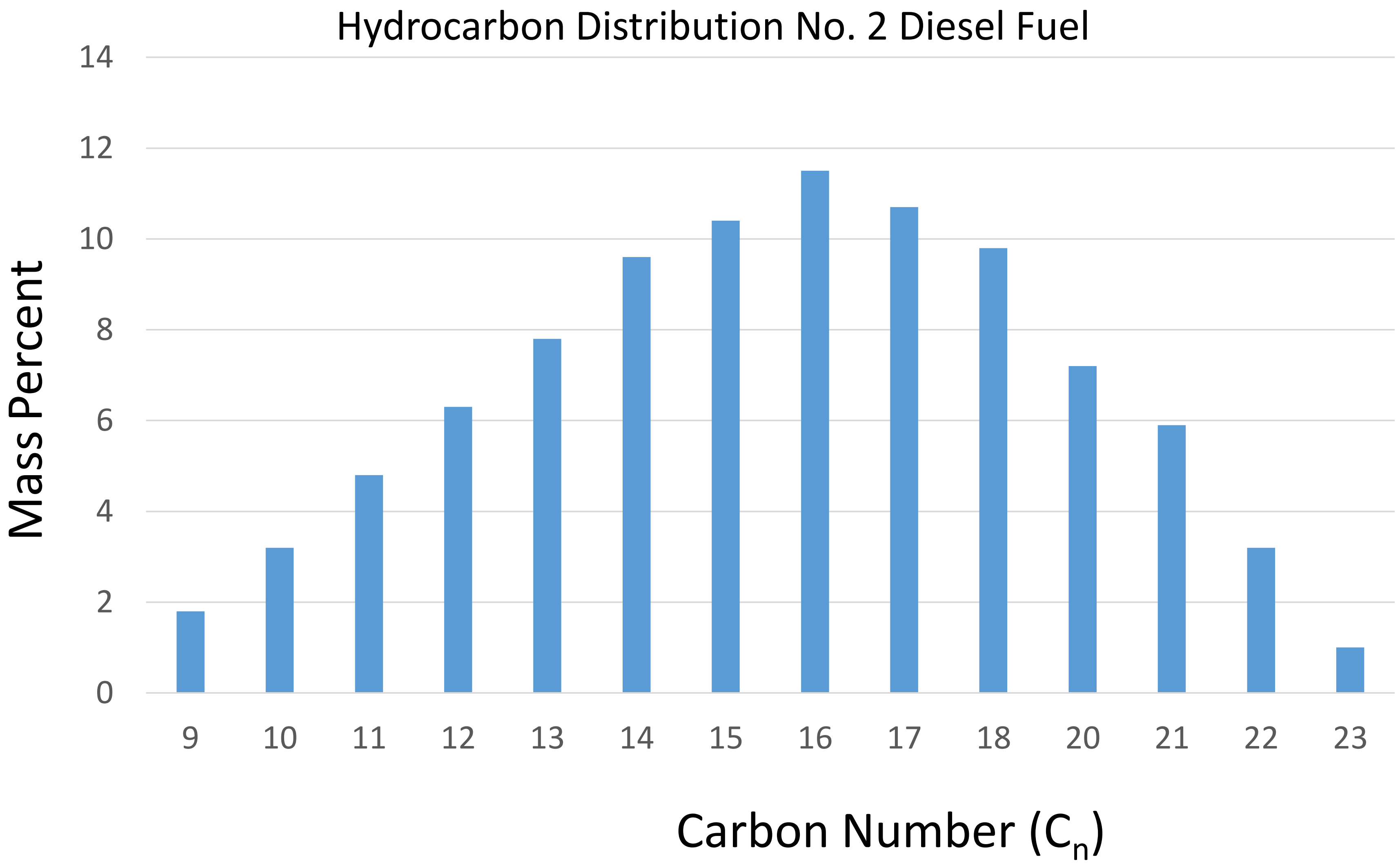
Decalin $C_{10}H_{18}$

POLYCYCLIC AROMATIC HYDROCARBONS



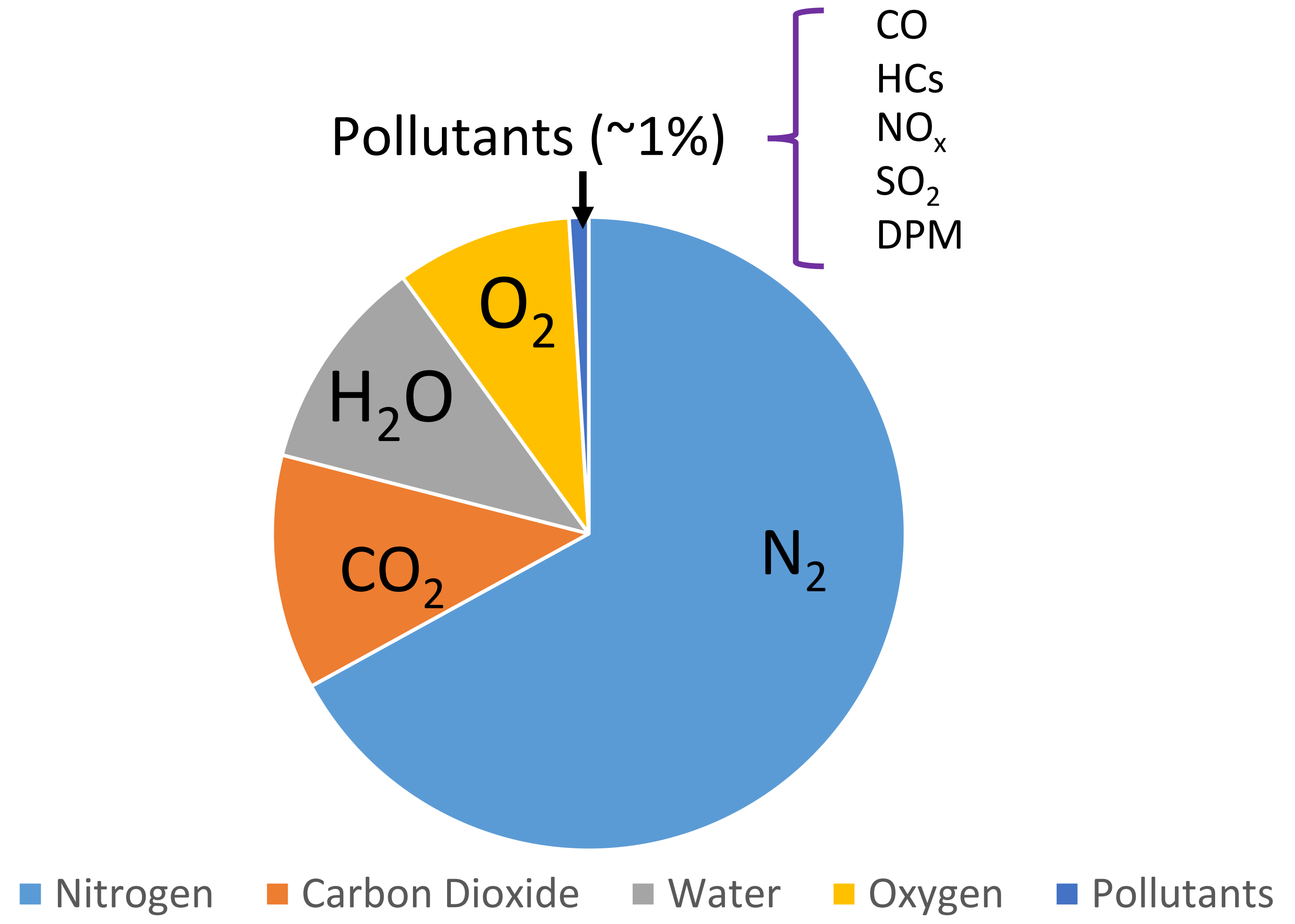
2-Methylnaphthalene

DIESEL FUEL FRACTION



Chevron, 2007, “Diesel Fuels Technical Review” www.chevron.com/products/prodserv/fuels/bulletin/diesel

DIESEL ENGINE EXHAUST EMISSIONS



Uniqueness of Military Diesel Engine Applications

- Length of service (age)
- Designer engines (submarines)
- Exhaust configurations (armoured vehicles, submarines)
- Absence of emission controls

EXPOSURE TO ENGINE EXHAUST IN MILITARY PLATFORMS

- Tanks and Armoured vehicles
- Helicopters
- Submarines

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ACUTE HEALTH EFFECTS OF DIESEL EXHAUST EXPOSURE:

- irritation of the nose and eyes,
- lung function changes,
- respiratory changes,
- headache,
- fatigue and nausea

A. Sydbom, A. Blomberg, S. Parnia, N. Stenfors, T. Sandström, S-E. Dahlén, Health effects of diesel exhaust emissions European Respiratory Journal 2001 17: 733-746

CHRONIC HEALTH EFFECTS OF DIESEL EXHAUST EXPOSURE

- Largely focused on particulates (followed by NO_x , CO, HCs)

Thomas W. Hesterberg, Christopher M. Long, William B. Bunn, Charles A. Lapin, Roger O. McClellan and Peter A. Valberg, Health effects research and regulation of diesel exhaust: an historical overview focused on lung cancer risk, Inhalation Toxicology, 2012; 24(S1): 1–45

EU emission standards for passenger cars (Category M_1*)

Stage	Date	CO	HC	HC+NOx	NOx	PM	PN
		g/km					#/km
Positive Ignition (Gasoline)							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	-	-
Euro 2	1996.01	2.2	-	0.5	-	-	-
Euro 3	2000.01	2.30	0.20	-	0.15	-	-
Euro 4	2005.01	1.0	0.10	-	0.08	-	-
Euro 5	2009.09[b]	1.0	0.10[d]	-	0.06	0.005[e,f]	-
Euro 6	2014.09	1.0	0.10[d]	-	0.06	0.005[e,f]	6.0×10^{11} [e,g]
Compression Ignition (Diesel)							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)	-
Euro 2, IDI	1996.01	1.0	-	0.7	-	0.08	-
Euro 2, DI	1996.01[a]	1.0	-	0.9	-	0.10	-
Euro 3	2000.01	0.64	-	0.56	0.50	0.05	-
Euro 4	2005.01	0.50	-	0.30	0.25	0.025	-
Euro 5a	2009.09[b]	0.50	-	0.23	0.18	0.005[f]	-
Euro 5b	2011.09[c]	0.50	-	0.23	0.18	0.005[f]	6.0×10^{11}
Euro 6	2014.09	0.50	-	0.17	0.08	0.005[f]	6.0×10^{11}

* At the Euro 1..4 stages, passenger vehicles > 2,500 kg were type approved as Category N_1 vehicles

† Values in brackets are conformity of production (COP) limits

a. until 1999.09.30 (after that date DI engines must meet the IDI limits)

b. 2011.01 for all models

c. 2013.01 for all models

d. and NMHC = 0.068 g/km

e. applicable only to vehicles using DI engines

f. 0.0045 g/km using the PMP measurement procedure

g. 6.0×10^{12} 1/km within first three years from Euro 6 effective dates

PN = Particle Number PM= Particle Mass HC = hydrocarbons

REF. DieselNet https://www.dieselnet.com Accessed 15 Jul., 2019

EU DIESEL EMISSION REGULATIONS

EU Stage V emission standards for LOCOMOTIVE engines

Category	Net Power	Date	CO	HC[a]	NOx	PM
	kW		g/kWh			
RLL-v/c-1 (Locomotives)	P > 0	2021	3.50	4.00[b]		0.025

[a] **A = 6.00 for gas engines**

[b] **HC + NOx**

Nitrogen oxides - respiratory tract irritants, lung diseases and lung cancer (

Ibrahim Aslan Resitoglu, Kemal Altinisik, Ali Keskin; The pollutant emissions from diesel-engine vehicles and exhaust after-treatment systems , Clean Techn Environ Policy (2015) 17:15–27)

DieselNet https://www.dieselnet.com Accessed 15 Jul., 2019

PROCEEDINGS

DIESEL ENGINE EXHAUST EMISSIONS: OXYGENATED CPDS

- Nitrogen dioxide
- Sulfur dioxide
- Formaldehyde
- Acetaldehyde
- Acrolein

CARBONYLS

Cernansky, N. P. 1983. Diesel exhaust odor and irritants: a review. J. Air Pollut. Cont. Assoc. 33:97–104.

JULIA A. NIGHTINGALE, RICHARD MAGGS, PAUL CULLINAN, LOUISE E. DONNELLY, DUNCAN F. ROGERS, ROBERT KINNERSLEY, K. FAN CHUNG, PETER J. BARNES, MICHAEL ASHMORE, and ANTHONY NEWMAN-TAYLOR , Airway Inflammation after Controlled Exposure to Diesel Exhaust Particulates, AMERICAN JOURNAL OF RESPIRATORY AND CRITICAL CARE MEDICINE VOL 162 2000 p161-166.

CARBONYLS in DIESEL EXHAUST

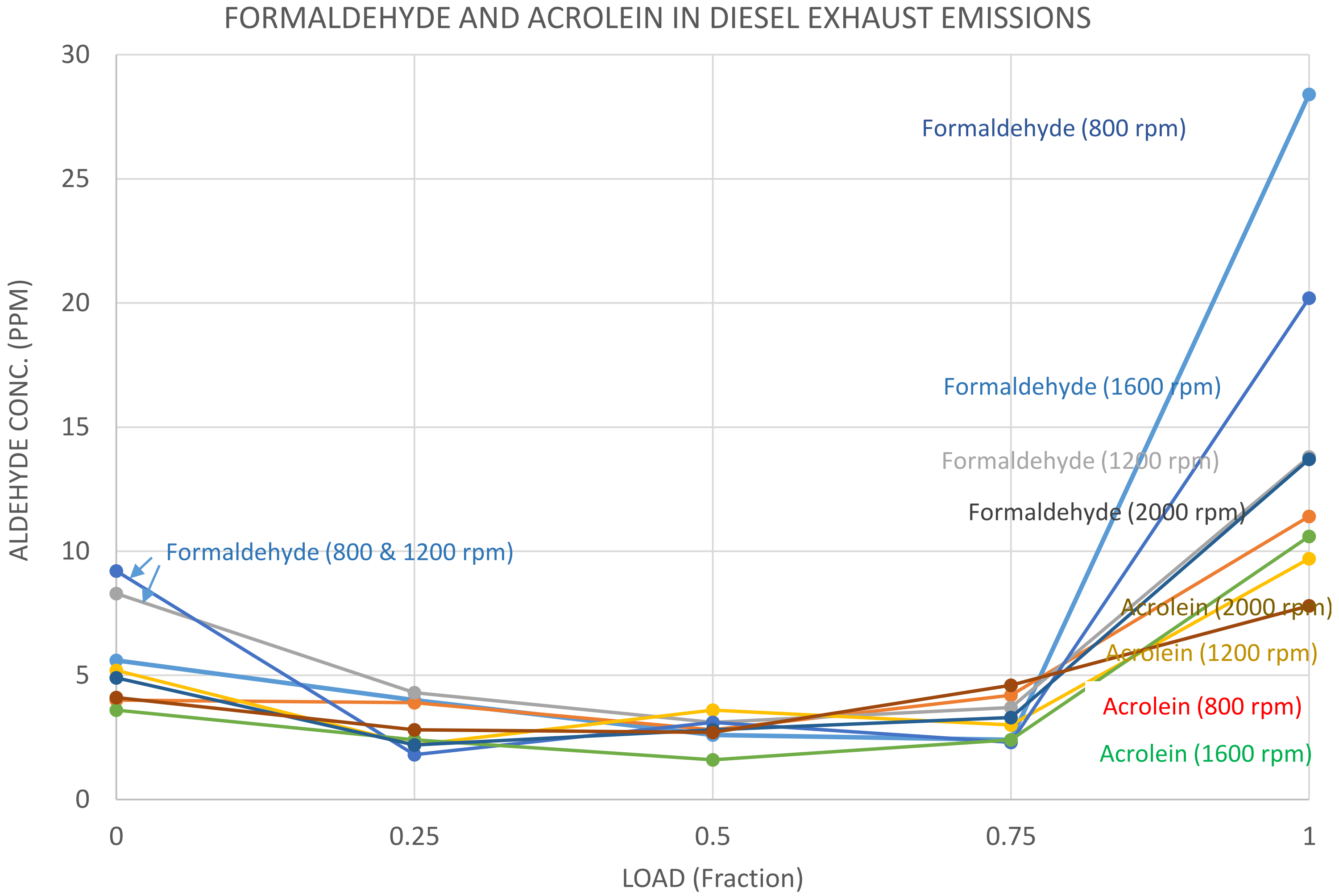
- FORMALDEHYDE
- ACETALDEHYDE
- ACROLEIN

~80% of Carbonyls

- ACETONE
- PROPIONALDEHYDE
- CROTONALDEHYDE
- METHYL ETHYL KETONE
- N-BUTYRALDEHYDE
- METHACROLEIN
- VALERALDEHYDE

Source: Central Pollution Control Board (2010) Study of the Exhaust Gases from different fuel based vehicles for Carbonyls and Methane Emissions, Ministry of Environment, Forest and Climate Change, Govt. of India.

PROCEEDINGS



Diesel engine: 7 L, 6 Cyl, (1962)

R. H. Linnell, W. E. Scott, (1962) Diesel exhaust composition and odor studies, Journal of the Air Pollution Control Association, 12, (1 1), 510-515

DIESEL EXHAUST ALDEHYDES (1962)

	Engine Speed	
Compound	500 rpm (0 Load)	1600 rpm (Full Load)
Formaldehyde	5±0.5 ppm	15±4 ppm
Acrolein	5±0.7 ppm	8±1 ppm

Acrolein was determined by the 4-hexyl-resorcinol method and formaldehyde by the chromotropic acid method. In both methods we collect diesel exhaust directly into the reagent in a fritted glass bubbler

Diesel engine: 7 L, 6 Cyl, (1962)

R. H. Linnell, W. E. Scott, (1962) Diesel exhaust composition and odor studies, Journal of the Air Pollution Control Association, 12, (1 1), 510-515

DIESEL ENGINE EXHAUST EMISSIONS: ALDEHYDES (1983, 2014)

	Diesel Exhaust	Health Effects
FORMALDEHYDE	0.40 mg m^{-3} (0.33 ppm) (2014)[1]	0.16 – 0.54 mg m^{-3} (0.13 – 0.44 ppm) eye irritation[1]
		TLV-TWA = 0.12 mg.m^{-3} (0.1 ppm) ACGIH (2017)[4] STEL = 0.36 mg.m^{-3} (0.3 ppm) ACGIH “
“	4 mg m^{-3} (3 ppm) (1983)[2]	
ACETALDEHYDE	0.20 mg m^{-3} (0.1 ppm) (2014)[1]	TLV - Ceiling = 45 mg.m^{-3} (25 ppm) ACGIH (2014)[5]
ACROLEIN	0.23 mg m^{-3} (0.1 ppm) (1983)[2]	TLV – Ceiling = 0.23 mg.m^{3} (0.1 ppm) ACGIH (2001)

[1] Aneta Wierzbicka ,*, Patrik T. Nilsson , Jenny Rissler , Gerd Sallsten , Yiyi Xu , Joakim H. Pagels , Maria Albin , Kai Österberg , Bo Strandberg , Axel Erikssone , Mats Bohgard , Kerstin Bergemalm-Rynell , Anders Gudmundsson, Atmospheric Environment 86 (2014) 212 – 219 (The diesel exhaust was generated by an idling (900 rpm) Volkswagen Passat TDI)

[2] Cernansky, N. P. 1983. Diesel exhaust odor and irritants: a review. J. Air Pollut. Cont. Assoc. 33:97–104. (engine operating conditions not stated)

[3] JULIA A. NIGHTINGALE, RICHARD MAGGS, PAUL CULLINAN, LOUISE E. DONNELLY, DUNCAN F. ROGERS, ROBERT KINNERSLEY, K. FAN CHUNG, PETER J. BARNES, MICHAEL ASHMORE, and ANTHONY NEWMAN-TAYLOR , Airway Inflammation after Controlled Exposure to Diesel Exhaust Particulates, AMERICAN JOURNAL OF RESPIRATORY AND CRITICAL CARE MEDICINE VOL 162 2000 p161-166.

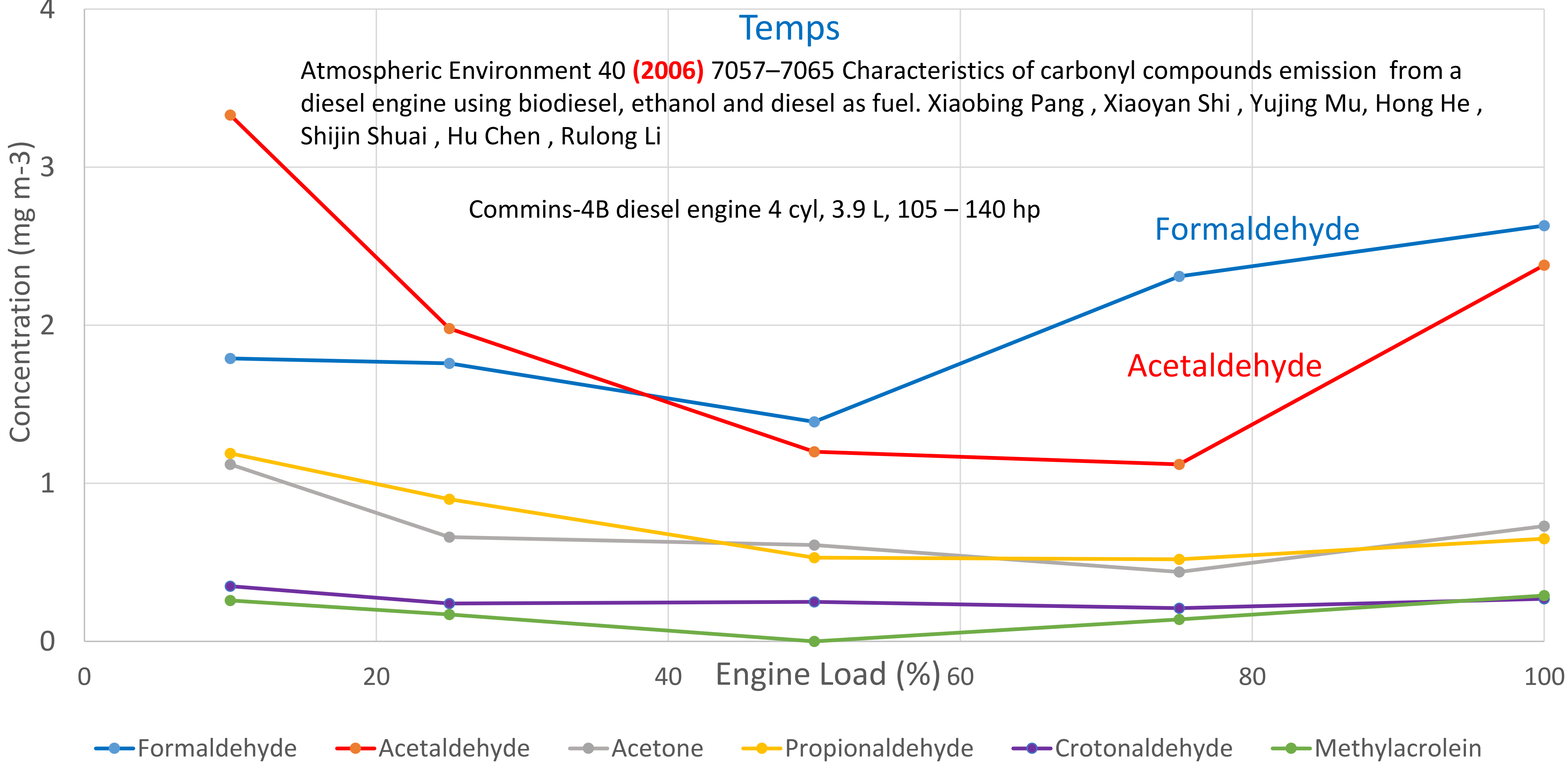
[4] TLV -TWA Threshold Limit Values – Time – weighted Average for 8 h exposure, American Conference of Governmental Industrial Hygienists (ACGIH)

[5] The concentration in air that should not be exceeded during any part of the working exposure.

PROCEEDINGS

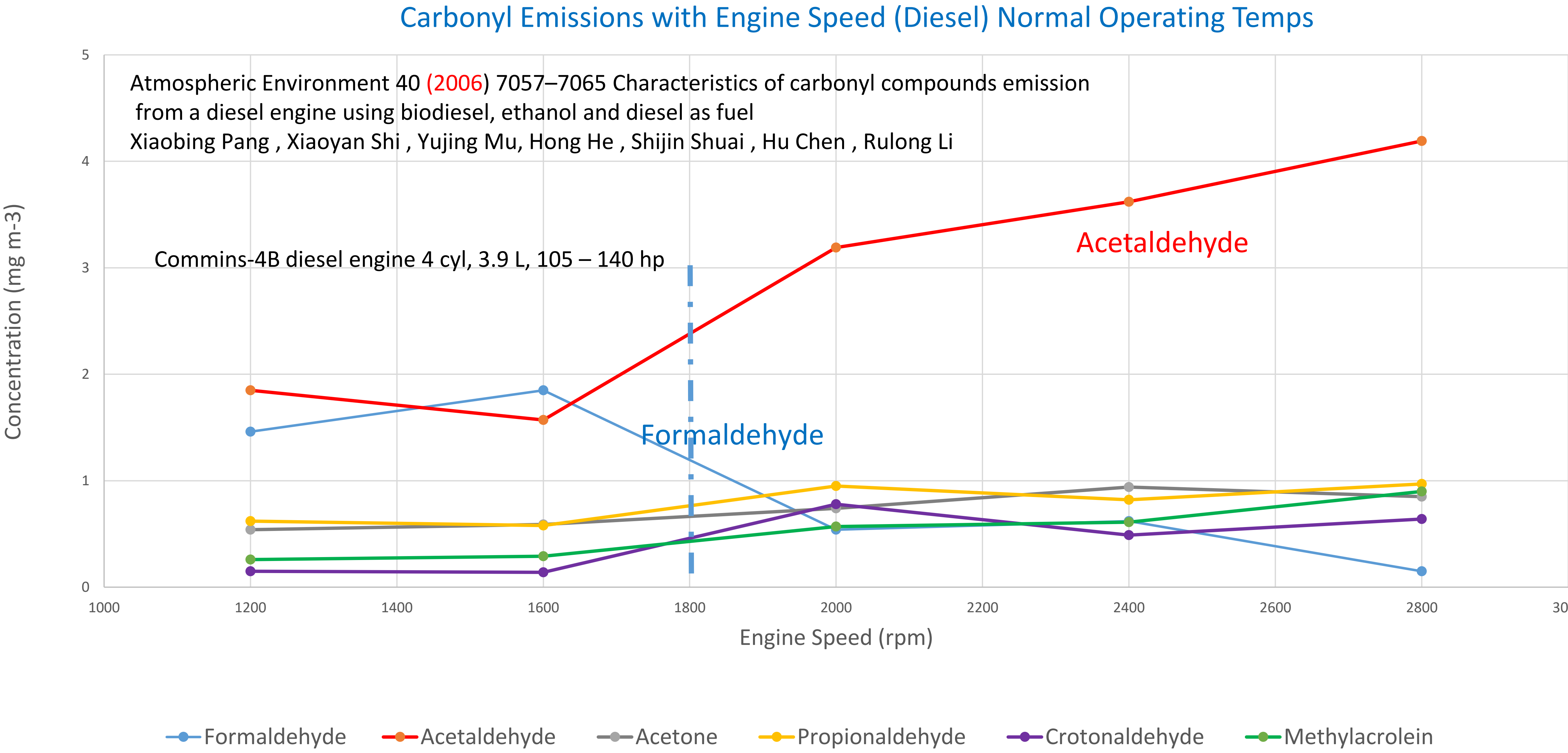
2006

Carbonyl Emissions with Engine Load at 1800 rpm (Diesel) Normal Operating Temps



Atmospheric Environment 40 **(2006)** 7057–7065 Characteristics of carbonyl compounds emission from a diesel engine using biodiesel, ethanol and diesel as fuel. Xiaobing Pang , Xiaoyan Shi , Yujing Mu, Hong He , Shijin Shuai , Hu Chen , Rulong Li

Commins-4B diesel engine 4 cyl, 3.9 L, 105 – 140 hp



Carbonyl Emissions with Engine Speed (Diesel) Normal Operating Temps

Atmospheric Environment 40 (2006) 7057–7065 Characteristics of carbonyl compounds emission
from a diesel engine using biodiesel, ethanol and diesel as fuel
Xiaobing Pang , Xiaoyan Shi , Yujing Mu, Hong He , Shijin Shuai , Hu Chen , Rulong Li

Commins-4B diesel engine 4 cyl, 3.9 L, 105 – 140 hp

PROCEEDINGS

2011

Average emissions from US 2004 compliant (corresponding to EU 1998–2000) and US 2007 compliant (corresponding to EU 2013) heavy-duty diesel engines .

Compound	US 2004 (EU 1998–2000) compliant engines (average ± SD, mg/h)	US 2007 (EU 2013) compliant engines (average ± SD, mg/h)	Reduction of emissions (%)
Carbonyls (including aldehydes)	12,500 ± 3,536	255 ± 95	98

Khalek IA, Bougher TL, Merritt PM, Zielinska B. Regulated and unregulated emissions from highway heavy-duty diesel engines complying with US Environmental Protection Agency 2007 emissions standards. *J Air Waste Manage* 2011;61:427-442.

PROCEEDINGS

Medium-duty diesel truck emissions

(dynamometer study on the Federal Test Procedure urban driving cycle with hot start)

Emission Rates of Gas-Phase

Alkanes	15.8 mg/km (as an example)
Formaldehyde	22.3 mg/km
Acetaldehyde	41.8 mg/km

Alan C. Lloyd and Thomas A. Cackette (2001) Diesel Engines: Environmental Impact and Control, Journal of the Air and Waste Management Association, 51:6, 809-847

ALDEHYDES: SAMPLING AND ANALYSIS

1. 10 Litres Diesel Exhaust sample collected in a sampling bag (eg Tedlar)
2. 20 mL 2,4 Dinitrodiphenyl hydrazine (DMPH) soln. added.
3. 10 µL sample injected into HPLC chromatographed with 1:1 acetonitrile/water

Direct Injection Diesel Engine, 7L (2007)

(sampling at operating temp., 700 rpm)

Formaldehyde: 9-12 ppm

Acetaldehyde: 2.5 – 2.75 ppm

- *M.M. Roy,* HPLC Analysis of Aldehydes in Automobile Exhaust Gas: Comparison of Exhaust Odor and Irritation in Different Types of Gasoline and Diesel Engines, *International Energy Journal 8 (2007) 199-206*

DNPH Cartridge Sampling and Analysis of Aldehydes from Engine Exhaust

Exhaust Sampling:

The carbonyl samples are collected by flowing dilute exhaust (approximately 1.0 liter/min. flow rate) through cartridges (Tejada, 1986). The samples are then brought to the laboratory for analysis.

Extraction and Analysis:

Each cartridge contains an absorbing compound 2,4 Dinitrophenyl Hydrazine (2,4-DNPH) which complexes with the carbonyl compounds to form their dinitrophenylhydrazone derivatives .The cartridges are then extracted with 5.0 mL acetonitrile and analyzed (Tejada, 1986).

Separation and analysis is performed using a High Performance Liquid Chromatograph (HPLC) with an ultraviolet (UV/VIS) detector.

Central Pollution Control Board (Ministry of Environment & Forests) India, (2010) Study of the Exhaust Gases from different fuel based vehicles for Carbonyls and Methane Emissions

An evaluation of monoethanolamine degradation and mitigation

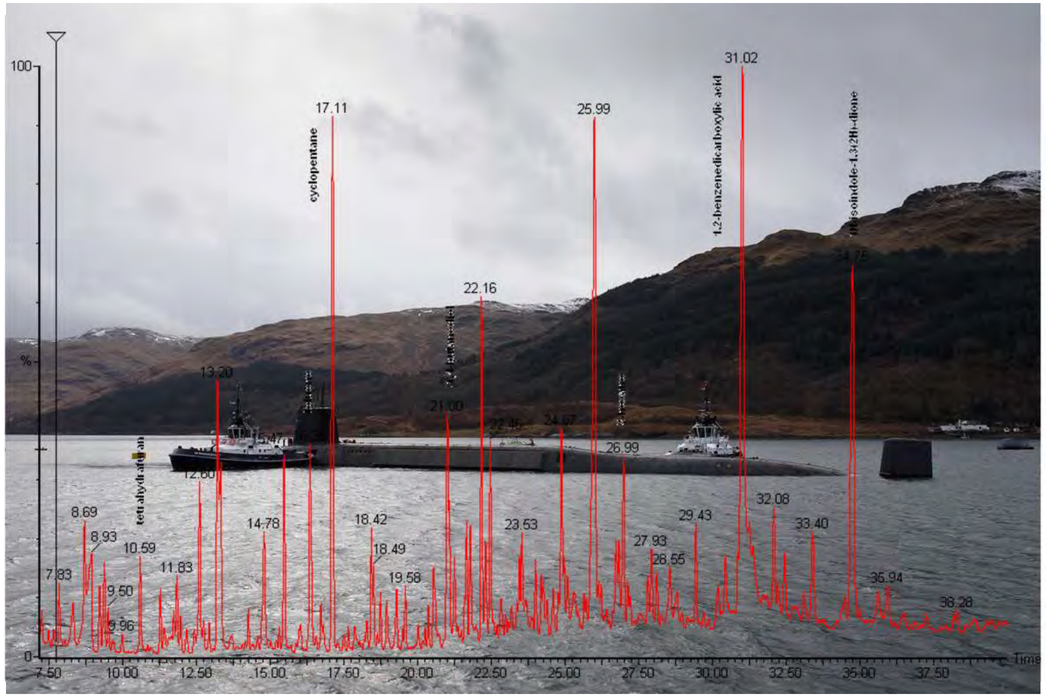
Charles Cummings, Tim Taylor
Chemistry (Atmospheres) Team
QinetiQ Haslar

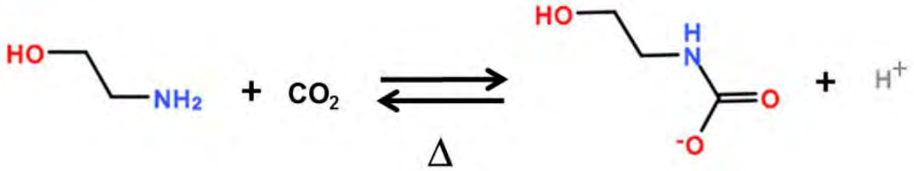
Introduction

- Atmosphere contaminants
  - Duty of care
  - Control

- Carbon dioxide (CO_2)
  - Consumable vs. regenerable
  - Amine based regenerable system
    - Monoethanolamine (MEA)

- NH_3 produced from MEA degradation





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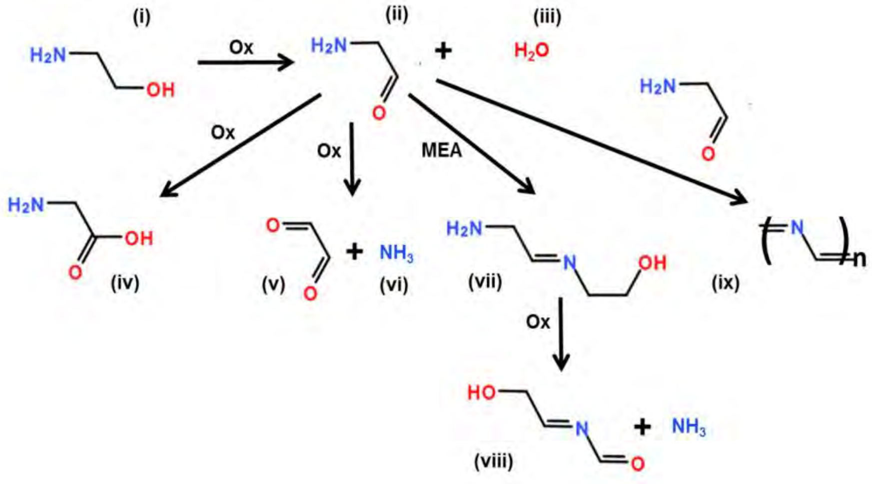
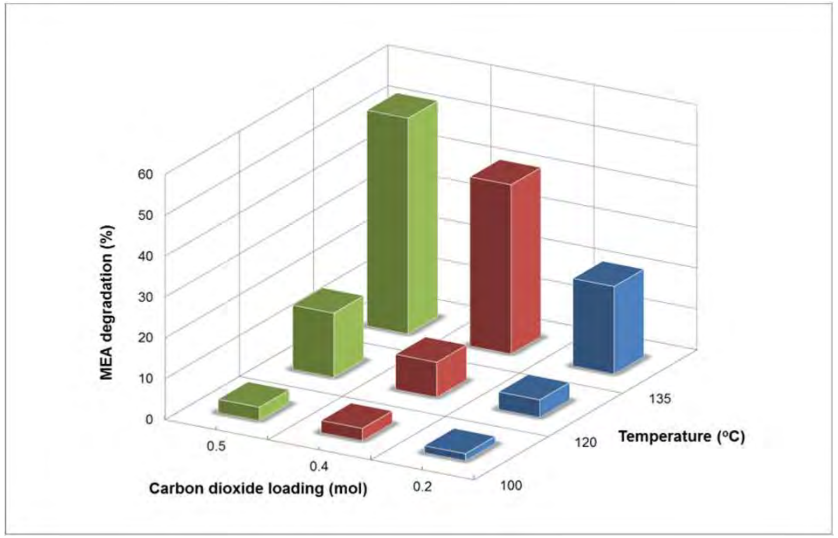
Introduction

- Degradation propagates further degradation
  - Auto-oxidation
  - Free-radical – metal ions
- Factors
  - Temperature
  - Impurities
  - CO_2 loading
- Mitigation
  - Inhibitor
    - Bind to impurities, potentially act as a passivator
  - Filtration
    - Removal of impurities and decomposition by-products
- Can we do better?

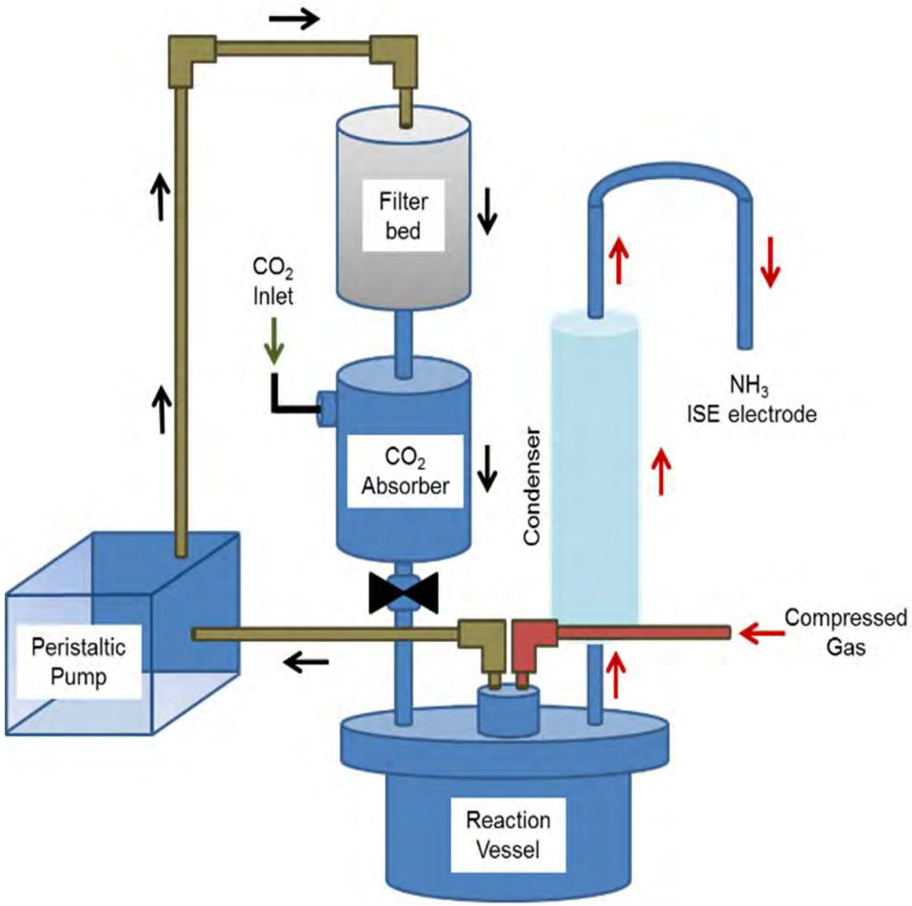


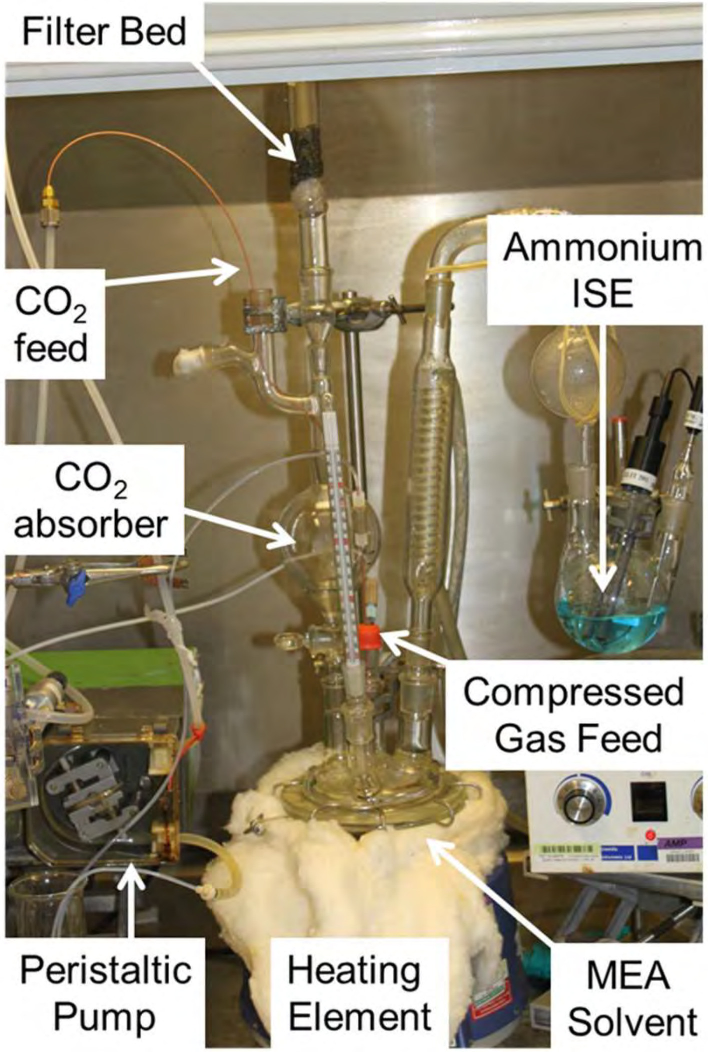


The effect of CO_2 loading and temperature on MEA degradation[1]

[1] Davis J. and Rochelle G., *Thermal degradation of monoethanolamine at stripper conditions*, Energy Procedia, 1, pp. 327-333, 2009

Experimental





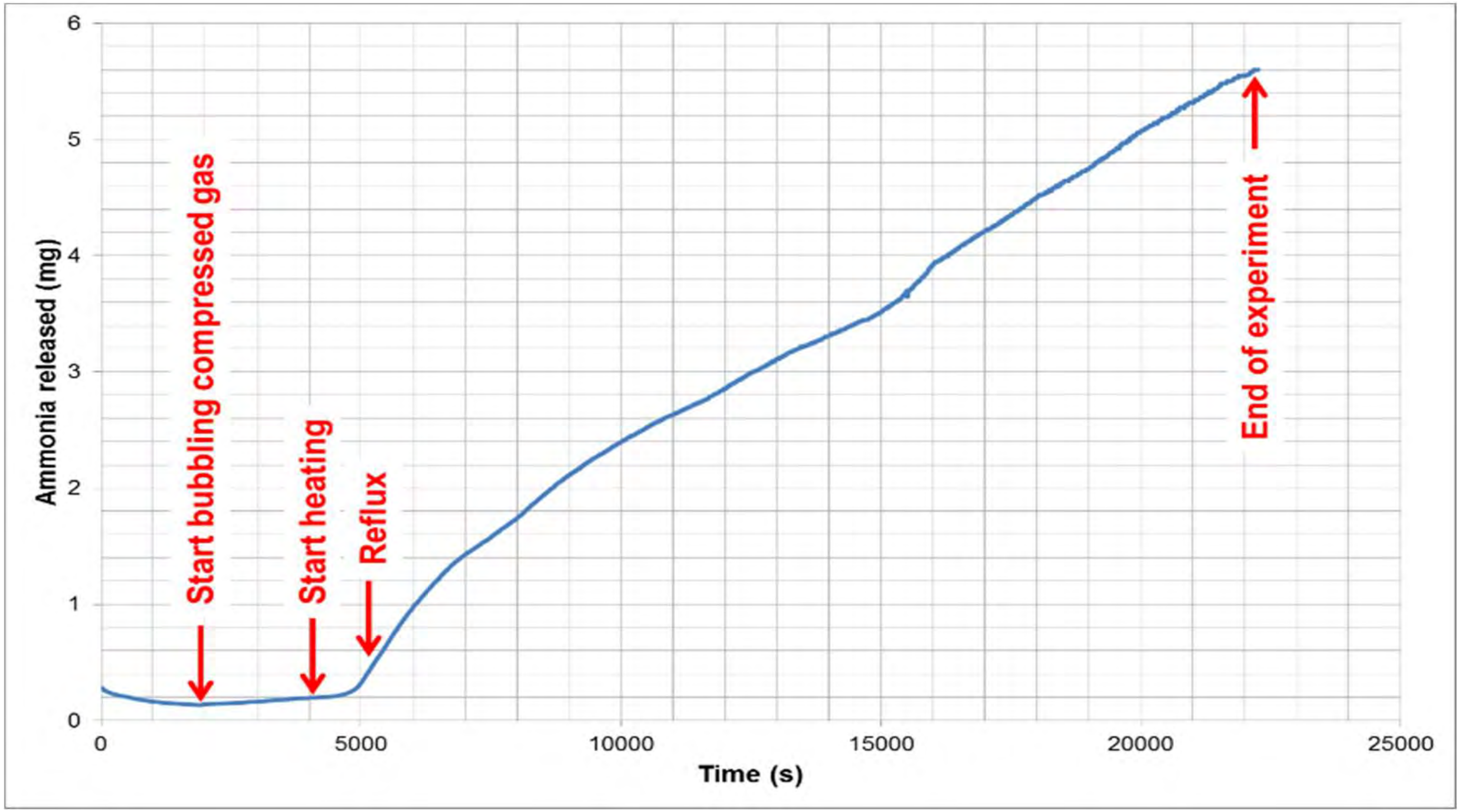
Experimental

Inhibitor	Chemical functionality
1	Alcohol, carboxylic acid
2	Sulfoxide, amide, aromatic
3	Alcohol, pyridine-like
4	Pyridine-like, thioether
5	Azo, secondary amine, aromatic
6	Secondary amine, sulfoxide
7	Alcohol, ester

Sorbent	Description
1	Activated carbon (Granular)
2	Activated carbon (Pellet)
3	NH_3 enhanced functionalised activated carbon (Pellet)
4	Zeolite
5	Porous resin for cation & anion ion exchange
6	Cation ion exchange resin (strong)
7	Cation ion exchange resin (weak)

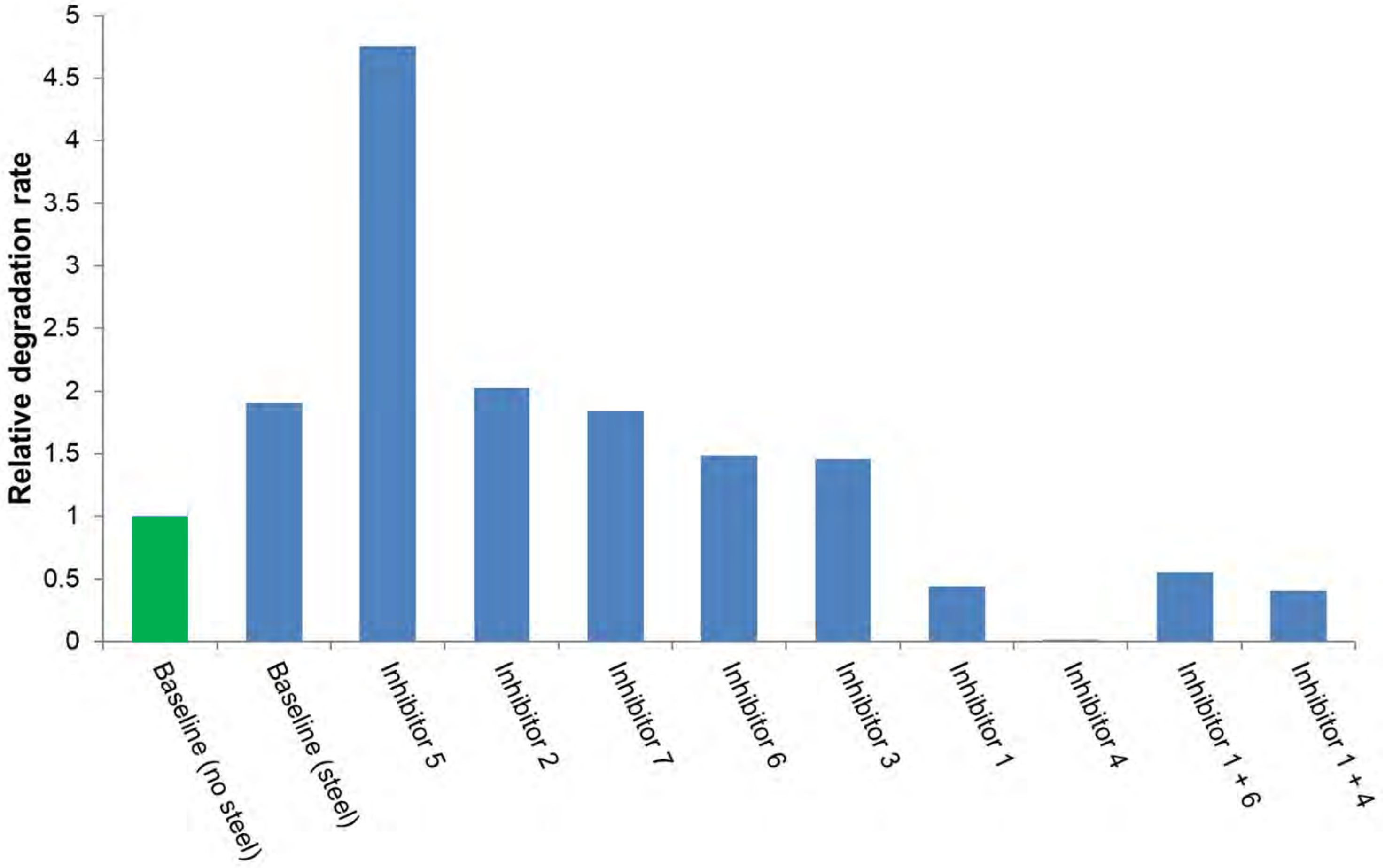
Results - Baseline

- No inhibitor or filtration
  - Degradation rate constant 1.64 x 10^{-8} s^{-1}



NH_3 release from 4.5 M MEA solution during an experiment

Results - Inhibitors



Prospective inhibitor degradation rates

Results - Inhibitor 1 & 4

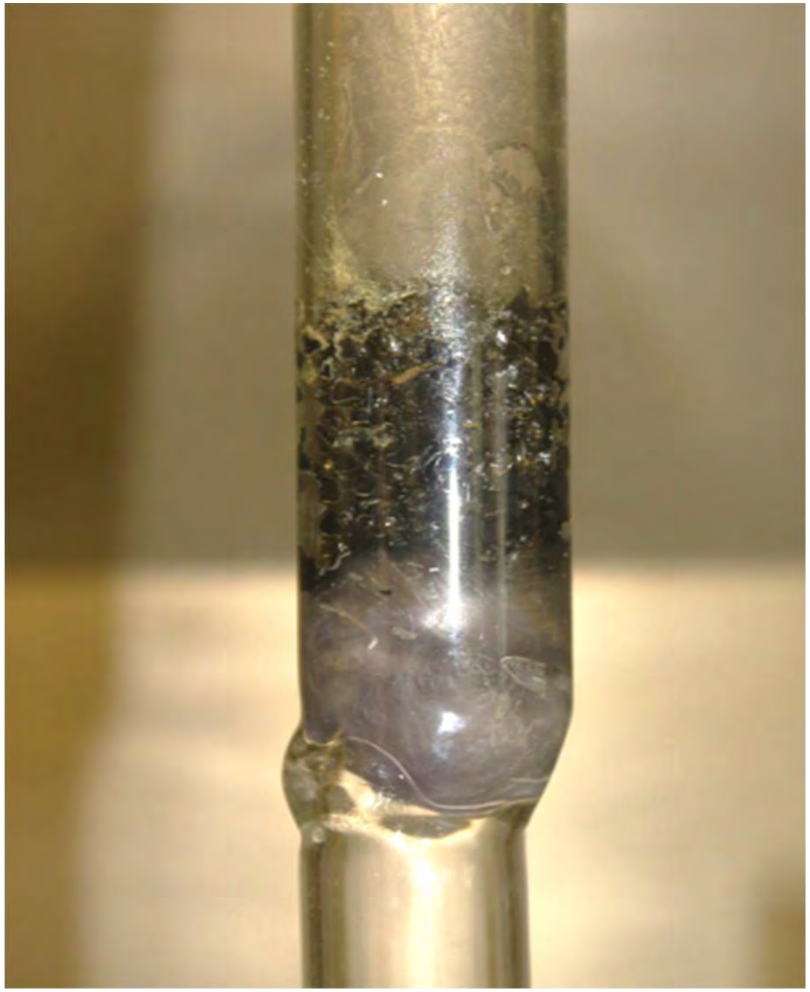
Experiment	Inhibitor	Test solution composition		k'
		MEA (M)	Inhibitor Concentration (mM)	($\times 10^{-8}$ s^{-1})
Test 12	None	4.5	0	4.74
Test 13a	Inhibitor 1		2	4.08
Test 13b			20	2.15
Test 13c			200	0.13
Test 14a	Inhibitor 4		2	0.65
Test 14b			20	0.15

Inhibitor 1 & 4

Experiment	Inhibitor	Test solution composition		k' ($\times 10^{-8}$ s^{-1})
		MEA (M)	Inhibitor Concentration (mM)	
Test 12	None	4.5	0	4.74
Test 13a	Inhibitor 1		2	4.08
Test 13b			20	2.15
Test 13c			200	0.13
Test 14a	Inhibitor 4		2	0.65
Test 14b			20	0.15

Results - Filter media - recirculation

- Sorbent 1 with Inhibitor 1
  - Initially showed no clear improvement
- Sorbent 1 with Inhibitor 4
  - Precipitated out



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Results - Filter media - recirculation

- Reduced inhibitor concentration
- Sorbent 4 caking

Experiment	Test solution composition		Filter bed		k'
	MEA (M)	Inhibitor 1 (mM)	Sorbent	Mass (g)	x 10^{-8}(s^{-1})
Test 17	4.5	20	-	-	0.89
Test 18a		20	Sorbent 1	10	1.23
Test 18b		200			1.16
Test 19a		20	Sorbent 2		2.51
Test 19b		200			0.91
Test 20a		20	Sorbent 3		2.15
Test 20b		200			1.52
Test 21a		20	Sorbent 5		0.60
Test 21b		200			0.74
Test 22a		20	Sorbent 6		1.15
Test 22b		200			0.42
Test 23a		20	Sorbent 7		0.78
Test 23b		20		2	1.35

Results - Dual sorbent beds

- Pelletised sorbent 2 plus
  - Sorbent 4
  - Sorbent 5
  - Sorbent 6
  - Sorbent 7

- All dual beds underperformed with 20 mM inhibitor
- At 200 mM all dual beds outperformed sorbent 1 alone, with the exception of sorbent 2 | 5
- Sorbent 2 | 7 best performing 0.27 x 10^{-8} s^{-1}

Conclusions

- Inherently MEA will degrade over time and this is exacerbated by temperature and the presence of impurities
- Impact on degradation: Inhibitor >> sorbent = CO_2 loading
- Inhibitor 1 was the most appropriate for the application in the system. Inhibitor 4 performed better but raised toxicity concerns and precipitated out of solution
- Sorbent 1 was outperformed by several alternative sorbent medias
- Dual sorbent beds, with synergistic functionalities, yielded the best performance

Acknowledgements

Charles Cummings

UK MOD atmosphere control stakeholders

Chemistry (Atmospheres) Team

Submarine
Delivery Agency

This work was undertaken as part of the Maritime Strategic Capability Agreement between the Naval Authority Group and QinetiQ

Any questions

?

Volatile Organic Compounds (VOC) interaction with high and low temperature carbon monoxide/hydrogen oxidation catalysts

Gareth Toft and Charles Cummings

Chemistry (Atmospheres) Team, QinetiQ Haslar

Tina Goodall

Submarine Delivery Agency

November 2019

Contents

PROCEEDINGS

Introduction

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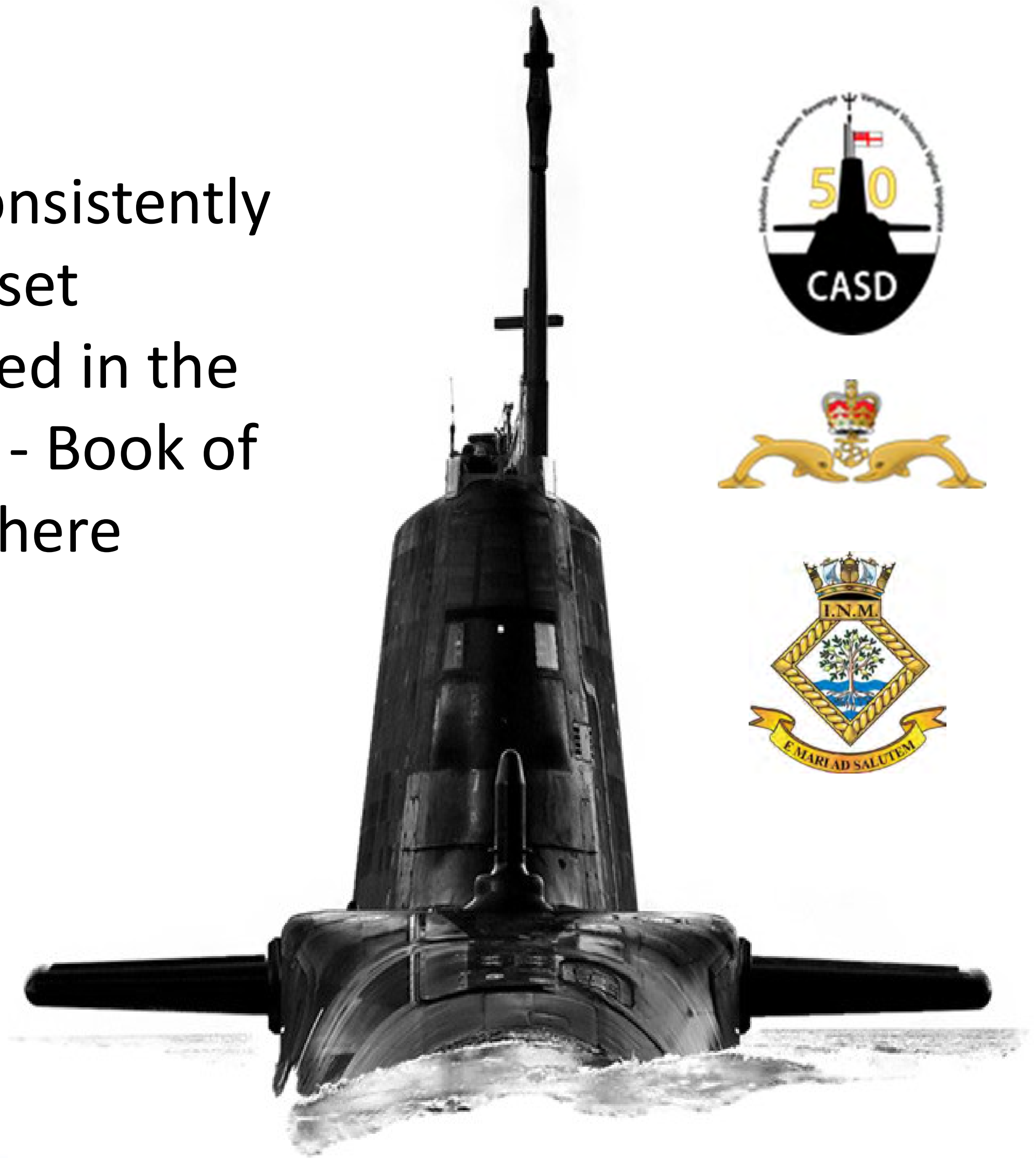
Under its duty of care, the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere.

The submarines atmosphere is consistently monitored and controlled within set exposure reference values (detailed in the UK restricted publication BR1326 - Book of Reference for Submarine Atmosphere Control)



PROCEEDINGS

The UK have (for the last twelve years, run a contract with QinetiQ (QQ) to provide scientific support to atmosphere control under the Maritime Strategic Capability Agreement (MSCA)

The MoD tasked QinetiQ under this contract to evaluate the potential use of preidentified precious metal catalysts for low temperature CO / H_2 removal and subsequent VOC removal This work is reported further in this paper

PROCEEDINGS

VOC removal by high temperature catalysts

Submarine
Delivery Agency

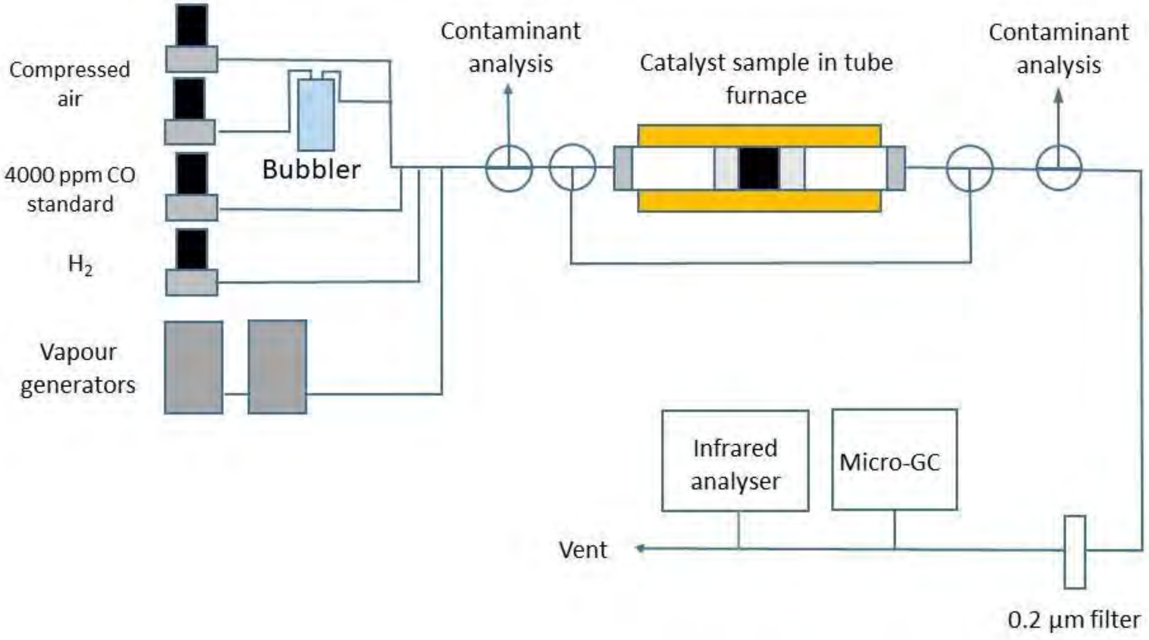
QINETIQ

High temperature catalyst - Experimental

- Burners use Moleculite catalyst
  - Copper oxide/manganese dioxide at >200 °C
- Contribution of high temperature CO/H_2 burner VOC removal
- VOC drawn from literature

– 2-Butanone	2.1 ppm
– Benzene	2.5 ppm
– Decane	1.4 ppm
– 1,2,3-trimethylbenzene	4.2 ppm
– Acetophenone	3.0 ppm
– Naphthalene	1.3 ppm

- Test gas contained 6 ppm CO and 0.5 % H_2
- Tedlar bag samples analysed by TD/GC/MS



Experimental apparatus

High temperature catalyst – VOC removal results

VOC	Inlet concentration (ppm)	Outlet concentration (ppm)	Percentage removal (%)
2-Butanone	1.148	0.023	98
Benzene	0.895	0.474	47
Decane	0.251	0.073	71
1,2,3-trimethylbenzne	0.081	0.015	82
Acetophenone	0.031	0.006	81
Naphthalene	0.012	0.003	75
		Average VOC removal	76

- Measured concentrations lower than that calculated from diffusion tube weight loss
  - Possible loss to apparatus
- Overall removal efficiency in close agreement to 70-80 % removal results of minor trial

High temperature catalyst – Effect of hydrogen

VOC	Percentage removal (%)		
	0.0 % H_2	0.5 % H_2	1.8 % H_2
2-Butanone	79	80	76
Benzene	46	26	25
Decane	66	65	55
1,2,3-trimethylbenzne	71	77	72
Acetophenone	72	79	79
Naphthalene	68	71	-
Average VOC removal	67	66	61

- VOC not affected by presence of hydrogen
- No partial breakdown products found by TD/GC/MS analysis

PROCEEDINGS

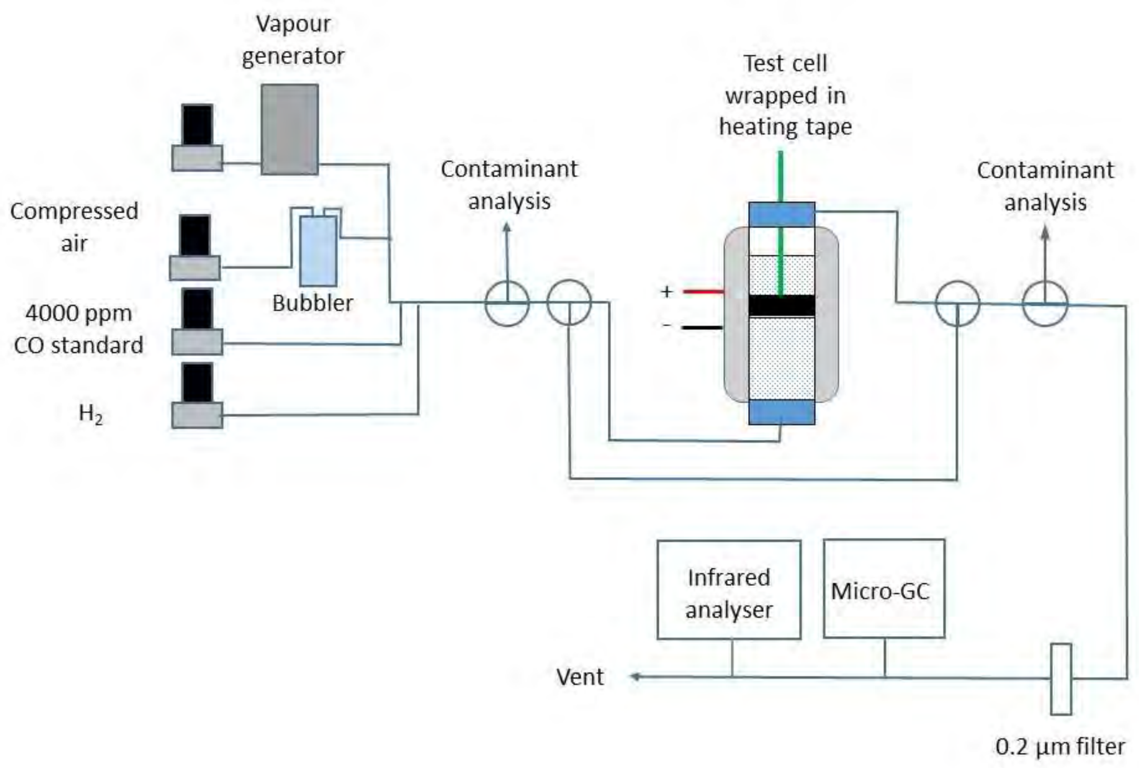
VOC exposure to low temperature catalysts

Submarine
Delivery Agency

QINETIQ

Low temperature catalyst - Experimental

- Johnson-Matthey catalysts – dual bed
  - Q1 palladium on iron oxide
  - Q3 platinum on titanium dioxide
  - Catalysts operated at 100 °C
- Effect of VOC on CO and H_2 oxidation
- Classes of VOC drawn from literature
  - Alcohols
  - Alkanes
  - Aromatics
  - Aldehydes and ketones
  - Chlorinated compounds
  - Siloxanes
  - Hydrogen sulfide
  - Ammonia
- Exposed for up to 7 days
- Analysis using FTIR and TD/GC/MS



Experimental apparatus

Low temperature catalyst - VOC

VOC Group	VOC	Exposure duration (h)	Inlet concentration (ppm)	
Alcohols	Methanol	168	1.90	
	Ethanol		0.99	
	Butanol		1.56	
Alkanes	Decane	168	0.36	
	Nonane		0.82	
Aromatics	Toluene	168	2.25	
	Ethyl-benzene		0.55	
	P-xylene		0.78	
Aldehydes and ketones			Low temp.	High temp.
	Butan-2-one	96	33.2	-
	Benzaldehyde		0.43	0.65
	Acetophenone		0.14	0.36
Chlorinated compounds	1,1,1-Tricholorethane	168	0.25	
	1,1,1-Trichloroethylene		0.11	
	Tetrachloroethane		0.07	
Siloxanes	Hexamethylcyclotrisiloxane	168	0.25	
	Octamethylcyclotetrasiloxane		0.11	
	Decamethylcyclopentasiloxane		0.07	
Hydrogen sulfide		21	0.05	
Ammonia	Test 1	7	1.80	
	Test 2	14	3.10	

Low temperature catalyst – Effect on oxidation performance

VOC	Average removal (%)			
	Pre-exposure		Post-exposure	
	CO (%)	H_2 (%)	CO (%)	H_2 (%)
Alcohols	98.4	100.0	100.0	100.0
Alkanes	100.0	100.0	100.0	100.0
Aromatics	100.0	99.3	99.9	100.0
Aldehydes and ketones	99.4	97.3	99.5	98.1
Chlorinated compounds	100.0	96.0	100.0	100.0
Siloxanes	98.3	95.0	100.0	88.4
Hydrogen sulfide	99.3	95.5	100.0	100.0
Ammonia (Test 1)	100.0	100.0	100.0	43.9
Ammonia (Test 2)	100.0	100.0	100.0	100.0

- Catalysts affected by siloxanes and, in one case, ammonia

Low temperature catalyst – VOC removal

VOC	Outlet (ppm)	Removal (%)
Methanol	0.00	100.0
Ethanol	0.00	100.0
Butanol	0.00	100.0
Decane	<0.01	97.2
Nonane	<0.01	98.8
Toluene	0.24	89.3
Ethyl-benzene	0.04	92.7
p-Xylene	0.12	84.6
Butan-2-one	0.40	98.8
Benzaldehyde	<0.01	98.5
Acetophenone	<0.01	97.4
1,1,1-Tricholorethane	1.84	62.7
1,1,1-Trichloroethylene	0.03	97.4
Tetrachloroethane	<0.01	93.8
Hexamethyltricyclosiloxane	0.13	48.0
Octamethylcyclotetrasiloxane	0.08	27.3
Decamethylcyclopentasiloxane	<0.01	85.7
Hydrogen sulfide	0.00	100.0
Ammonia	0.57	81.6
Average VOC removal		78.5

- No partial breakdown products found in TD/GC/MS samples

Conclusions

High temperature catalyst

- The high-temperature catalyst oxidised most VOC.
- Average total VOC removal of the six test compounds was 61 – 76 %.
- CO/H_2 burner does make a measurable contribution to controlling VOC in the atmosphere on RN submarines.

Low temperature catalyst

- Low temperature catalysts unaffected by the majority of submarine atmosphere contaminants.
- Siloxanes had the largest effect, but the effect was reversible over time.
- The catalysts had an average VOC removal of 78.5 %
- This secondary function of VOC removal would not be lost in a low-temperature precious metal burner.

Acknowledgements

Charles Cummings and Tim Taylor

UK MOD atmosphere control stakeholders

Chemistry (Atmospheres) Team

Submarine Delivery Agency

This work was undertaken as part of the Maritime Strategic Capability Agreement between the Naval Authority Group and QinetiQ

Any questions

?

Submarine
Delivery Agency

QINETIQ

DESIGN IMPROVEMENTS TO THE MPOG OXYGEN GENERATOR

MOLECULAR PRODUCTS GROUP

ABOUT US

ESTABLISHED
1973

150
employees

US DoD Title III Program worth
$12M

$50m
annual sales

Global exports to 90 countries

5
businesses worldwide

Over
8,000
surgeries each day

Healthcare, defense, safety, high end industrial

50% USA
30% EMEA
20% ASIA

2M
medical devices each year

GLOBAL LEADER

Molecular Products is a world leading Pure Air Technologies company. Our products purify air in life critical applications and we are preeminent in the market for:

- CO_2 and toxic gas filtration
- Chemically generated oxygen systems

Commercial in confidence

O_2 FAMILY OF PRODUCTS

Oxygen generator	Oxygen (litres)	Size (mm) H x D x W	Weight (kg)	Duration (mins)
CAN33	3341	295 x 165	12.7	40-60
MPOG	2600	400 x 133 x 133	12.2	60-90
EO2-30	3000	420 x 142 x 140	15.0	25-45
ROG	90	270 x 115 x 115	2.3	15

CHLORATE CHEMISTRY APPLICATIONS

- Chlorate O2 solutions used globally in applications including submarines, aircraft, battlefield and mine refuge chambers
- Supply oxygen generators to NATO and allied force navies throughout Europe, Americas, Asia and Australia
- The chemistry is commercially proven and well understood by Molecular Products

Image courtesy of Rio Tinto

THE BEST SOLUTIONS COME THROUGH COLLABORATION AND PARTNERSHIP

molecular

- Close collaboration between the Royal Navy and Molecular Products that led to the development of the MPOG
- When launched in 2011, the MPOG was a new evolution of oxygen generator
- Offers improved user experience and better protection
- MilSpec and MineSpec oxygen generators are used globally to provide breathable oxygen in closed environments; primarily submarines, mines and safe havens
- These life support devices used in some of the world's most inhospitable environments, so we rely on close working relationships with our customers and honest feedback to make our products better
- This is what has happened with the MPOG and led to the Mk2

SWOLLEN OUTER TIN

- Royal Navy reported to Molecular Products that swollen MPOGs had been identified onboard a submarine
- Molecular Products visited Faslane to inspect the units
- MPOG shipped back to Molecular Products' facility in UK to be opened in a controlled manner and tested
- No recorded history of swollen tins throughout the years of oxygen manufacturing at Molecular Products

Standard outer tin

Swollen outer tin

THE CONCLUSION - SWOLLEN OUTER TIN

molecular

- Inner chemical block produces a small amount of oxygen rich gas over a number of years
- This oxygen produces a slight over pressure in the inner tin and can, on occasion, produce bulging of the outer thinner walled canister
- Present in all generators, but finds an escape route. Improved sealing of MPOG results in this gas being trapped
- Heating the generators in storage may slightly increase the rate of the gas build up
- No evidence to suggest that the slight pressurisation leads to a reduction in performance or a hazardous or unsafe condition

THE PROBLEM – PARTICULATE MATTER

- MoD reported a small amount of particulate being discharged with the gas release of an MPOG onboard a Royal Navy submarine
- Concern that part of the chemical block being discharged and that MPOG would not perform as expected
- Molecular Products visited Faslane to inspect the units
- Representative sample of MPOGs across a range of LOT numbers and in-use/in-stores product shipped back to Molecular Products' facility in UK for testing

THE INVESTIGATION – PARTICULATE MATTER

- Outer tins opened using the normal key and inner tins removed for inspection
- Bag taped to top of a selection of the tins and the MPOGs opened, capturing any gas/particulates within the bag
- MPOGs then tested following normal test procedures for this product
- MPOGs performed to specification
- When analysed, particulate ejected from filter section not part of chemical block

THE INVESTIGATION – PARTICULATE MATTER

molecular

Batch	Gas release	Particles with the gas release	Duration (mins) (spec 60-90)	O_2 output (spec 2600 +/- 100)	Max surface temp °C (spec 500°C)	CO (ppm) (spec 50 ppm)	CO_2 (ppm) (spec 1000 ppm)
O50-116	Yes	No	90	2671	275	10	23
N50-044	No	No	75	2619	312	12	42
L50-128	Yes	No	77	2655	305	8	25
B50-060	Yes	Yes	80	2687	337	18	104
J50-005	Yes	Yes (8g)	74	2621		18	51
J50-032	Yes	No	84	2627	322	14	40
H50-078	Yes	No	71	2635	339	19	118
H50-141	Yes	No	68	2623	348	13	79
B50-070	Yes	Yes	72	2684	341	11	135

MPOGs tested performed to specification

THE SOLUTION – PARTICULATE MATTER

- Prevent discharge and update the filter material
- Escape route for particles is through the centre of the lid/filter plate. This hole is required for insertion of brass starter and so open (within a sealed unit) until initiation is required
- Further testing proved the effectiveness of:
  - Addition of a brass plug to block hole in centre of filter plate
  - Change filter assembly during manufacturing process from outside to within MPOG

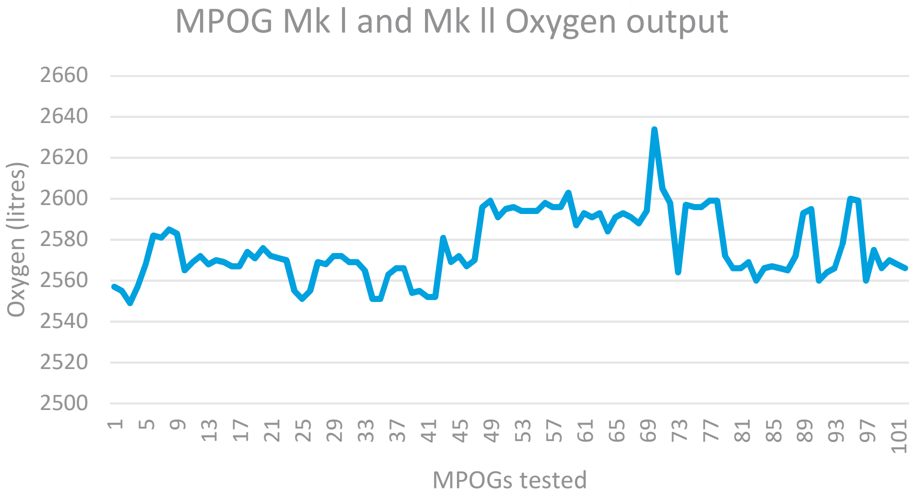
THE SOLUTION – PARTICULATE MATTER

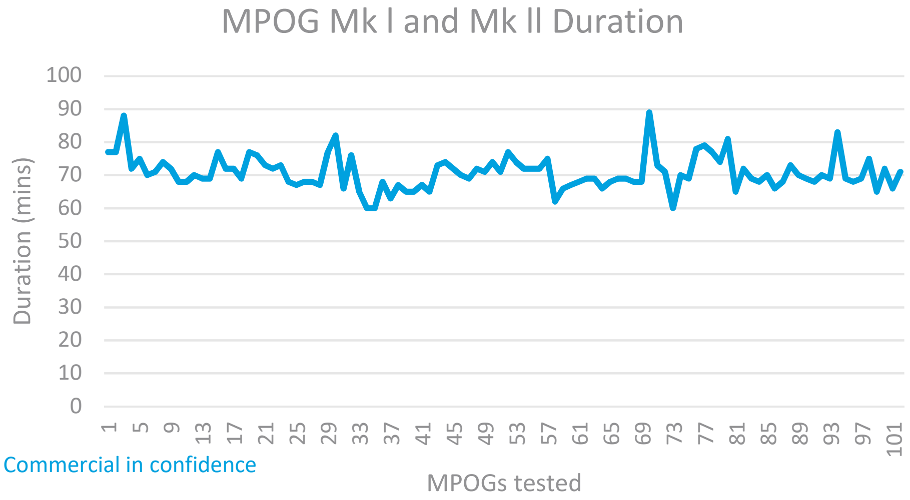
molecular

Difference between MPOG with a brass plug and without after opening pressurised units

Shows the filter plate and underside of the lid of both the new including brass plug (right) and old design (left)

THE SOLUTION


MPOG Mk I and Mk II Oxygen output


MPOG Mk I and Mk II Duration

- Results of testing demonstrate that there is no concern regarding performance of MPOG Mk2

MPOG MK2

- Introduction of the MPOG Mk2 is the result of collaboration between Molecular Products and MoD following period of feedback and review
- For end user, the changes from Mk1 to Mk2 are only in the initiation. Once tear off cap is pulled off, the brass plug needs removing to enable initiation

- Testing carried out by both Molecular Products and an independent test house on the MPOG Mk2 demonstrate that the changes have removed the likelihood of particulates escaping from MPOG Mk2 molecular

THANK YOU

CO2 Scrubber Instrumentation

GAS DETECTION
SOLUTIONS
FOR HOSTILE
ENVIRONMENTS

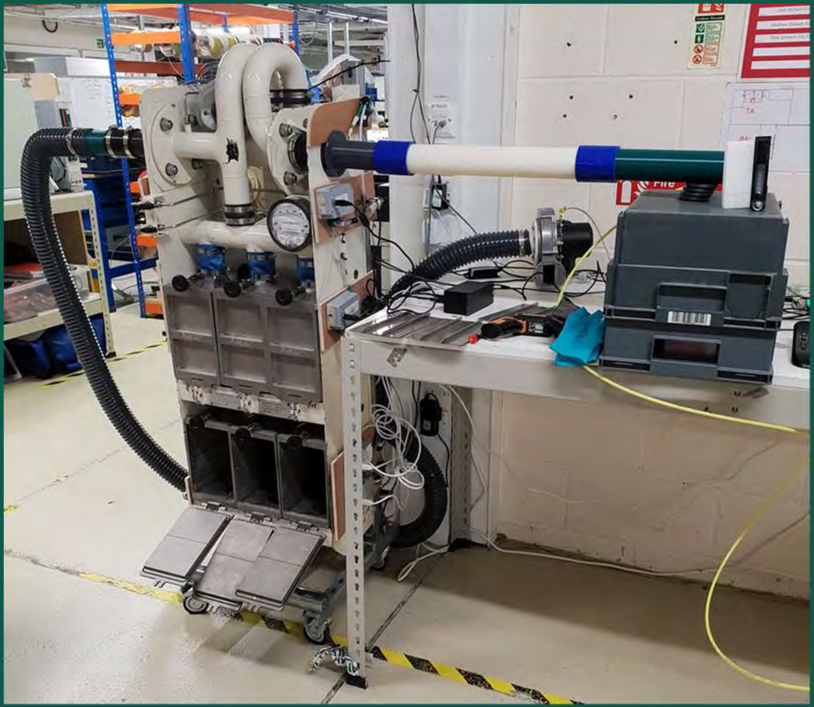
ANALOX
Military Systems

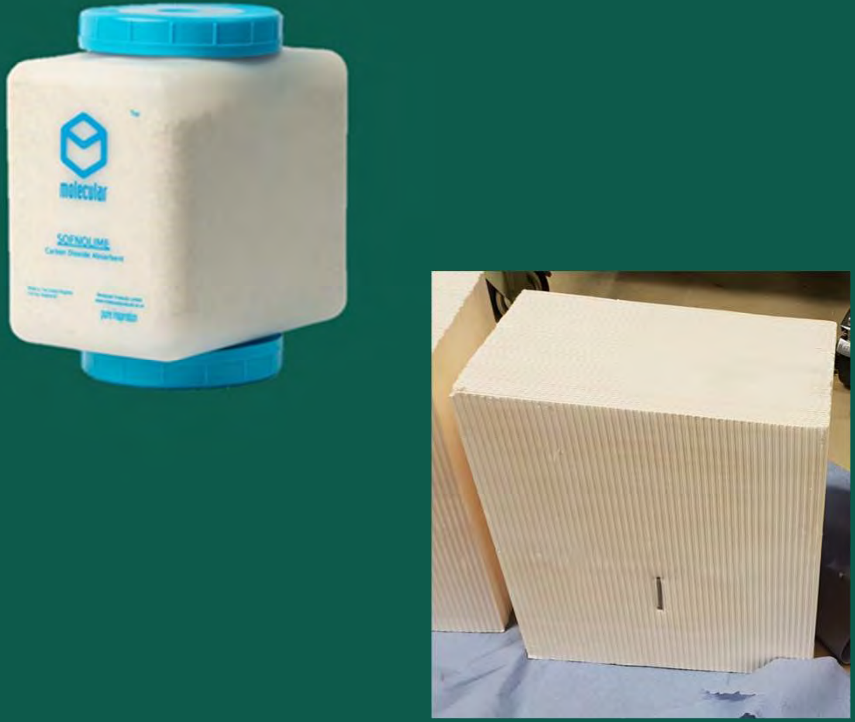
✉ info@analox-military.net

☎ +44 (0) 1642 711400

www.analoxmilitarysystems.co.uk

Introduction


Experimental setup of the system



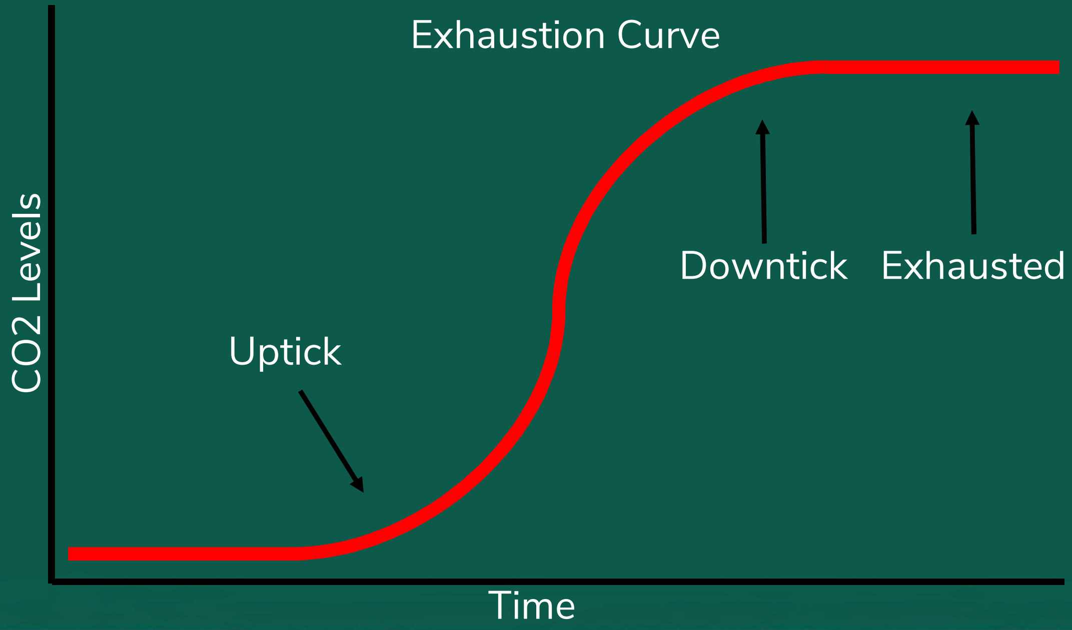
Examples of scrubber media

Why monitor the Inlet and Outlet CO2

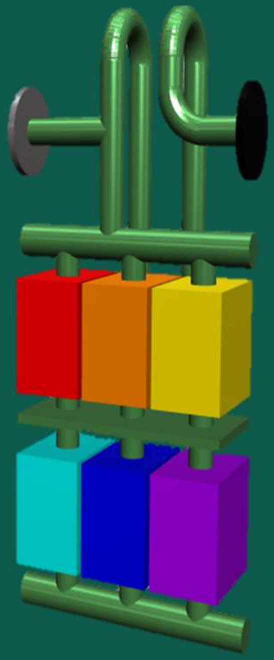
- Several factors affect Scrubbing capability
- Learn their system better
- Determine efficient meida switch out times
- Faster indication if scrubber isn’t working as expected

Terminology

- Scrubber Medium - CO2 Reactant
- Scrubber Canister - Container for Medium



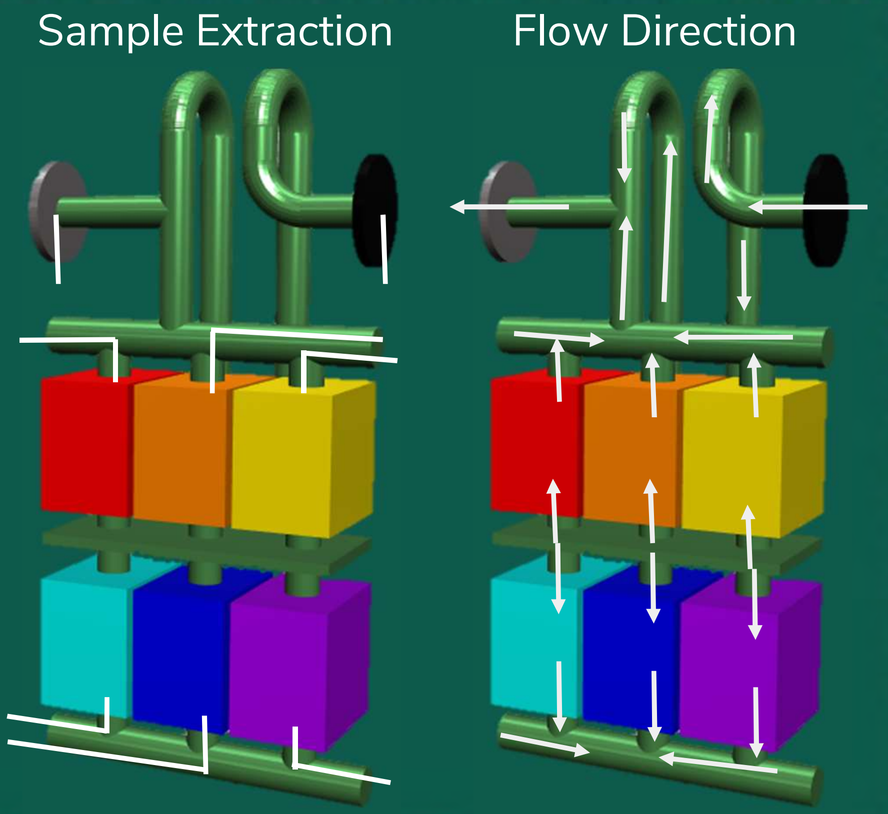
Exhaustion Curve



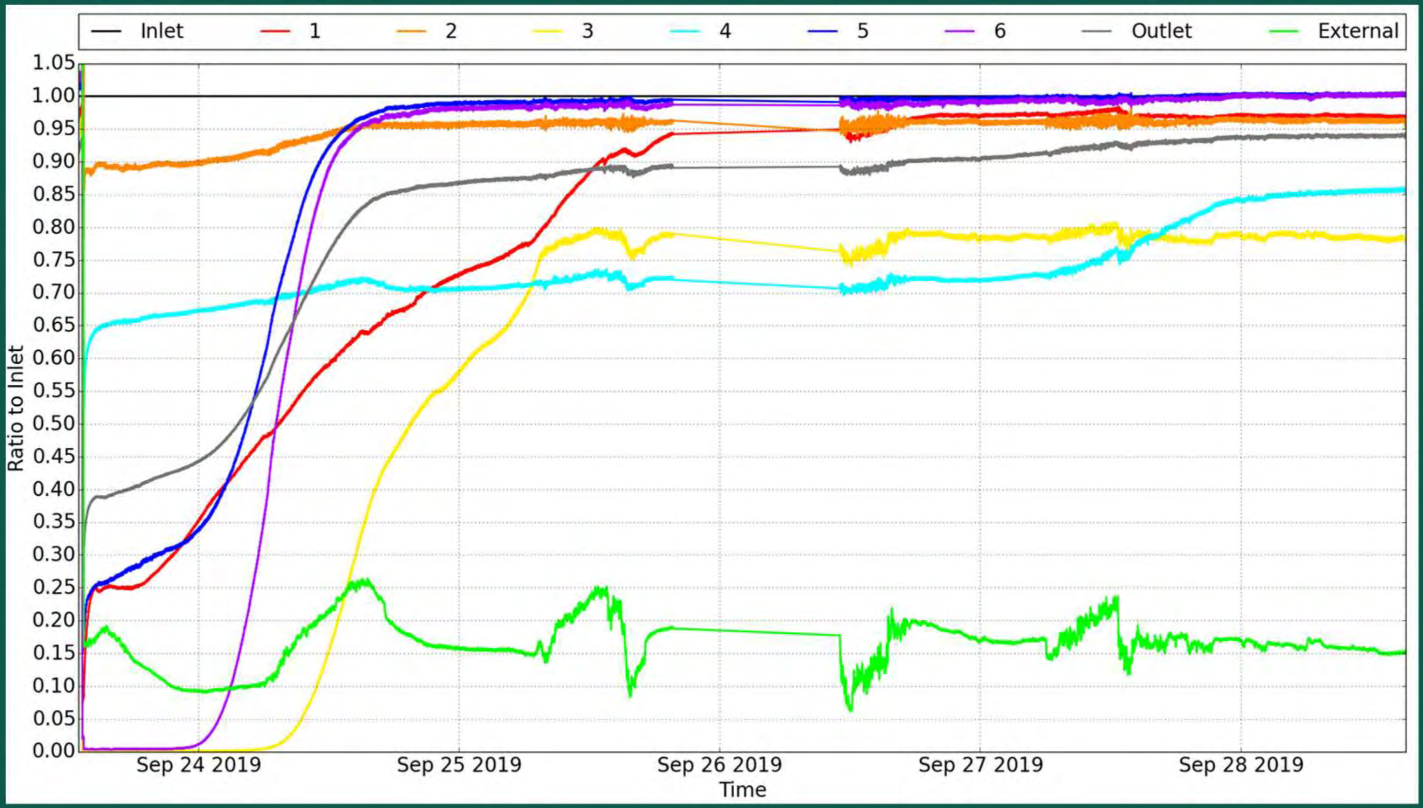
Scrubber System

Experiment Basics

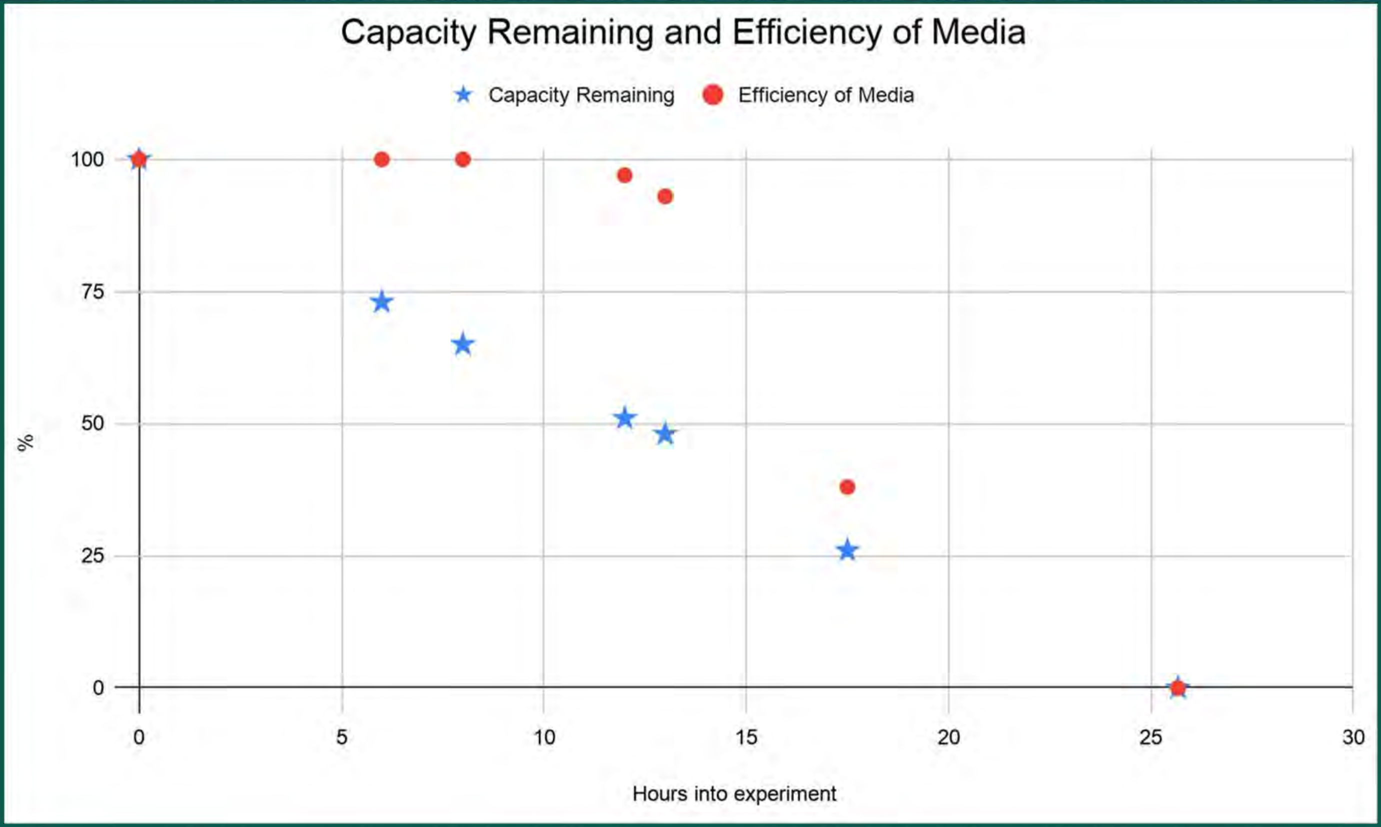
- Flow rate of 90m3/hr was used through the system
- CO2 level at inlet was set to about 0.7% (which was used as it is the worst case scenario on some submarines)
- Experiments were done when atmosphere was around 50% Humidity



Establishing feasibility

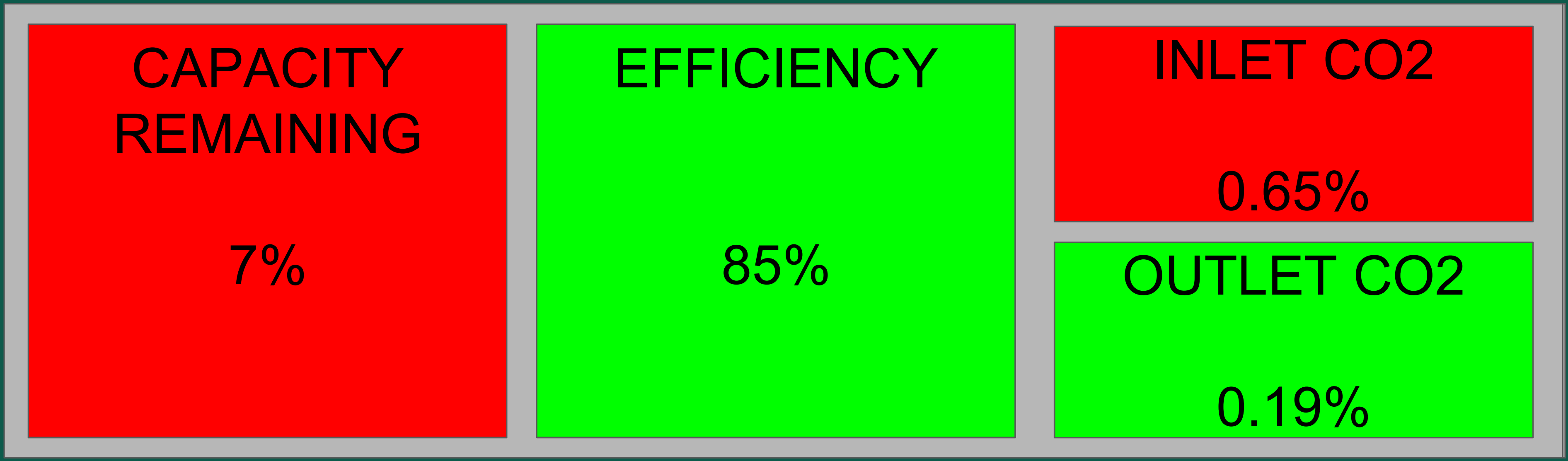


6’s Efficiency and Capacity



What this means...

- Able to show real time Scrubber Media Capacity remaining
- Also able to show Scrubber Media Efficiency



CAPACITY REMAINING

7%

EFFICIENCY

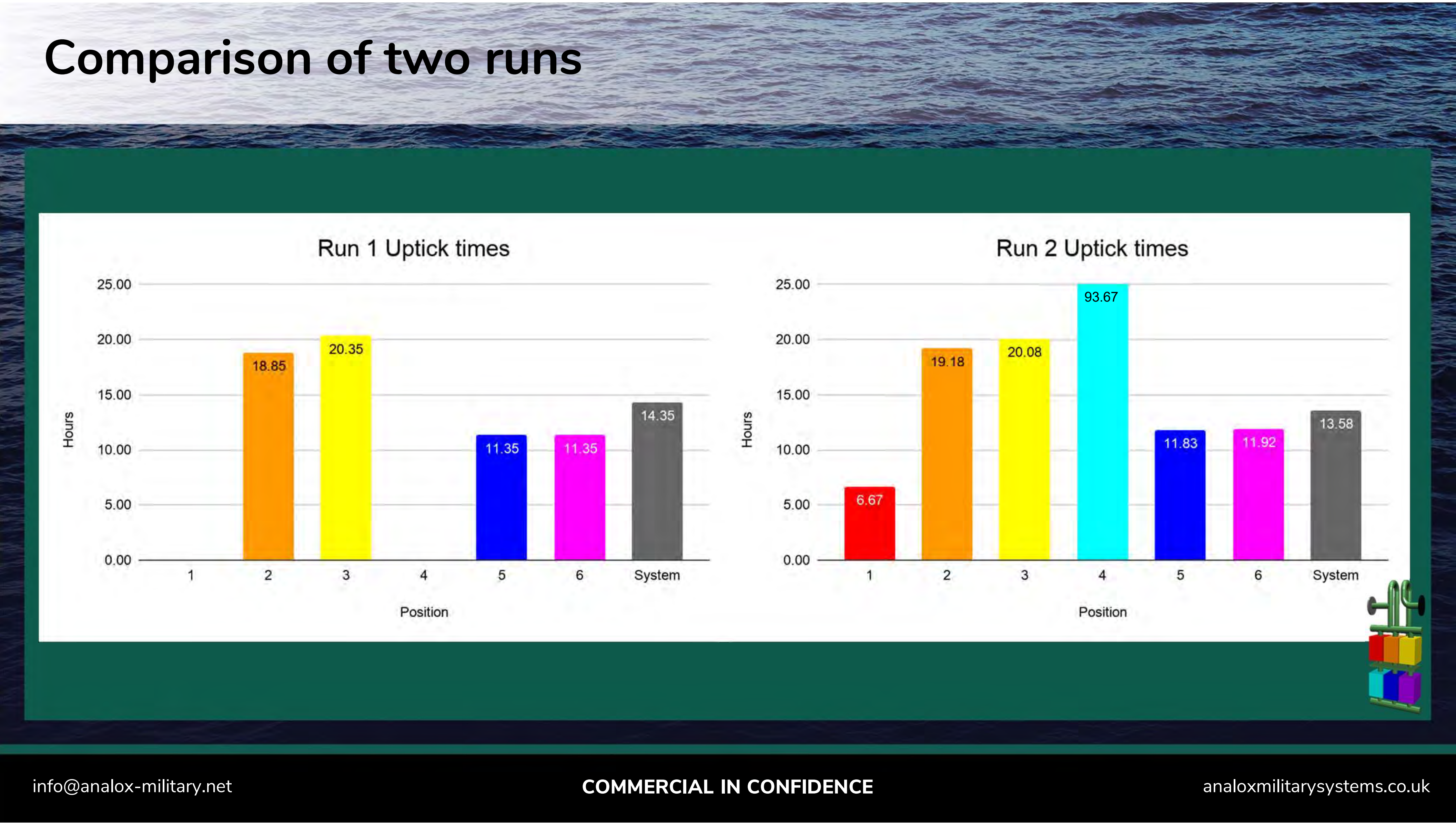
85%

INLET CO2

0.65%

OUTLET CO2

0.19%



Comparison of two runs

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COMMERCIAL IN CONFIDENCE

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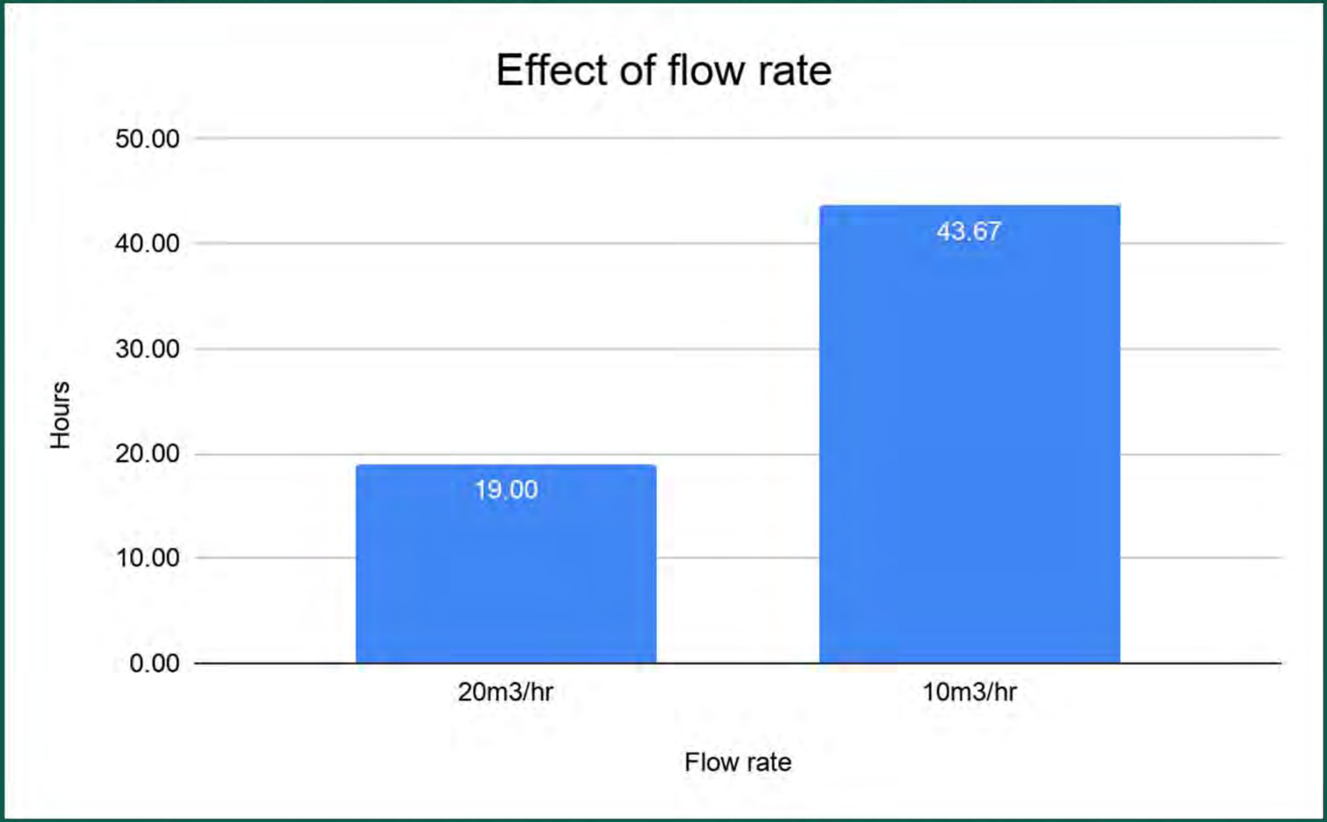
Effect of flow rate



Basic Model Assumptions

- 1 kg of CO2 produced per person per day
- 65 People in a Submarine
- 18 Media are used (or 3 Systems)
- Submarine has a volume of 1,000,000 litres
- System is balanced
- Flow rate 90m3/hr

Switch out time	6 hr	
Media used per day	72	Media x 24hrs/(Switch out)
CO2 Production kg	65	People x CO2 per person
CO2 Removed kg	53.136	CO2 Removed per Media in switch out time x Media used per day
CO2 Net kg	11.864	CO2 Production - CO2 Removed
% CO2 rise per day	0.65%	CO2 Net kg / CO2 Density

Effect of changing switch out times 6hr/8hr

Switch out time	6 hr	8 hr
Media used per day	72	54
% CO2 rise per day	0.65%	0.72%

Changing number of Media used at once so % CO2 rise per day is less than 0

Switch out time	6 hr	8 hr
New number of Media used at once	23	23
New number of Media used per day	92	69

Effect of changing switch out times 6hr/13hr/14hr

Switch out time	6 hr	13 hr	14 hr
Media used per day	72	33	31
% CO2 rise per day	0.65%	0.94%	0.99%

Changing number of Media used at once so % CO2 rise per day is less than 0

Switch out time	6 hr	13 hr	14 hr
New number of Media used at once	23	25	25
New number of Media used per day	92	46	43

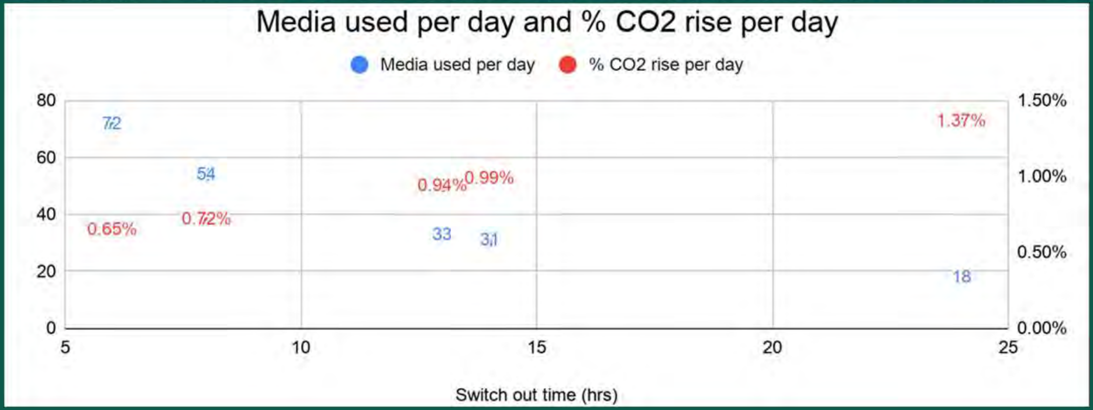
Effect of changing switch out times 6hr/24hr

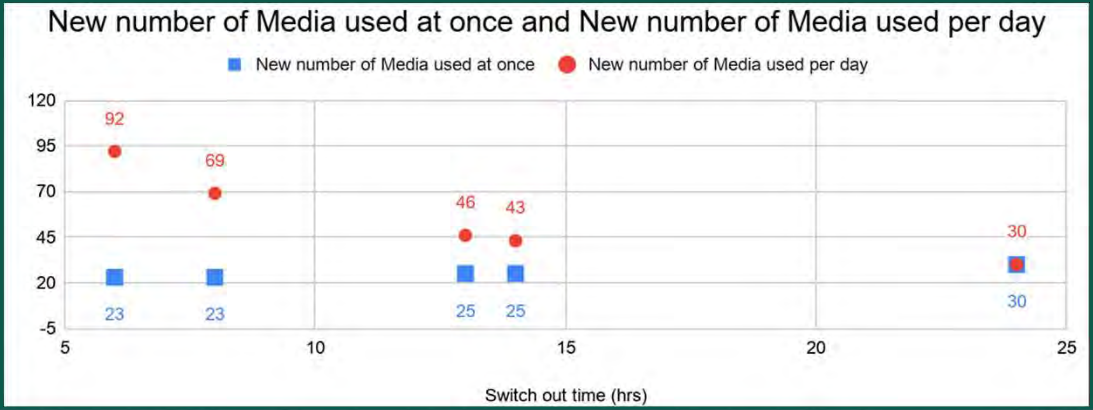
Switch out time	6 hr	24 hrs
Media used per day	72	18
% CO2 rise per day	0.65%	1.37%

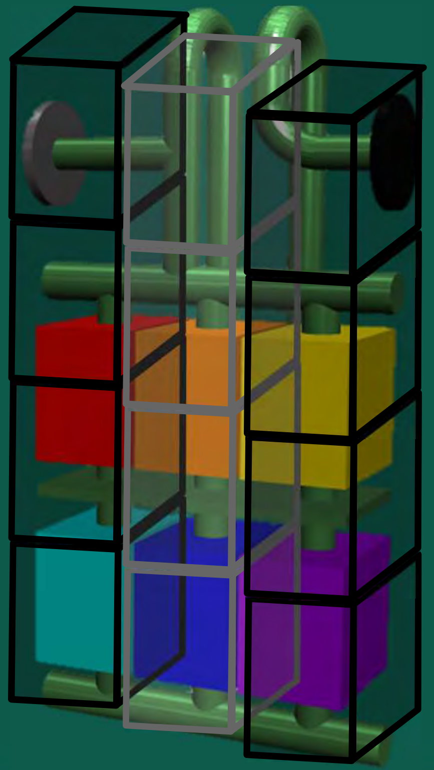
Changing number of Media used at once so % CO2 rise per day is less than 0

Switch out time	6 hr	24 hrs
New number of Media used at once	23	30
New number of Media used per day	92	30

Effect of changing switch out times





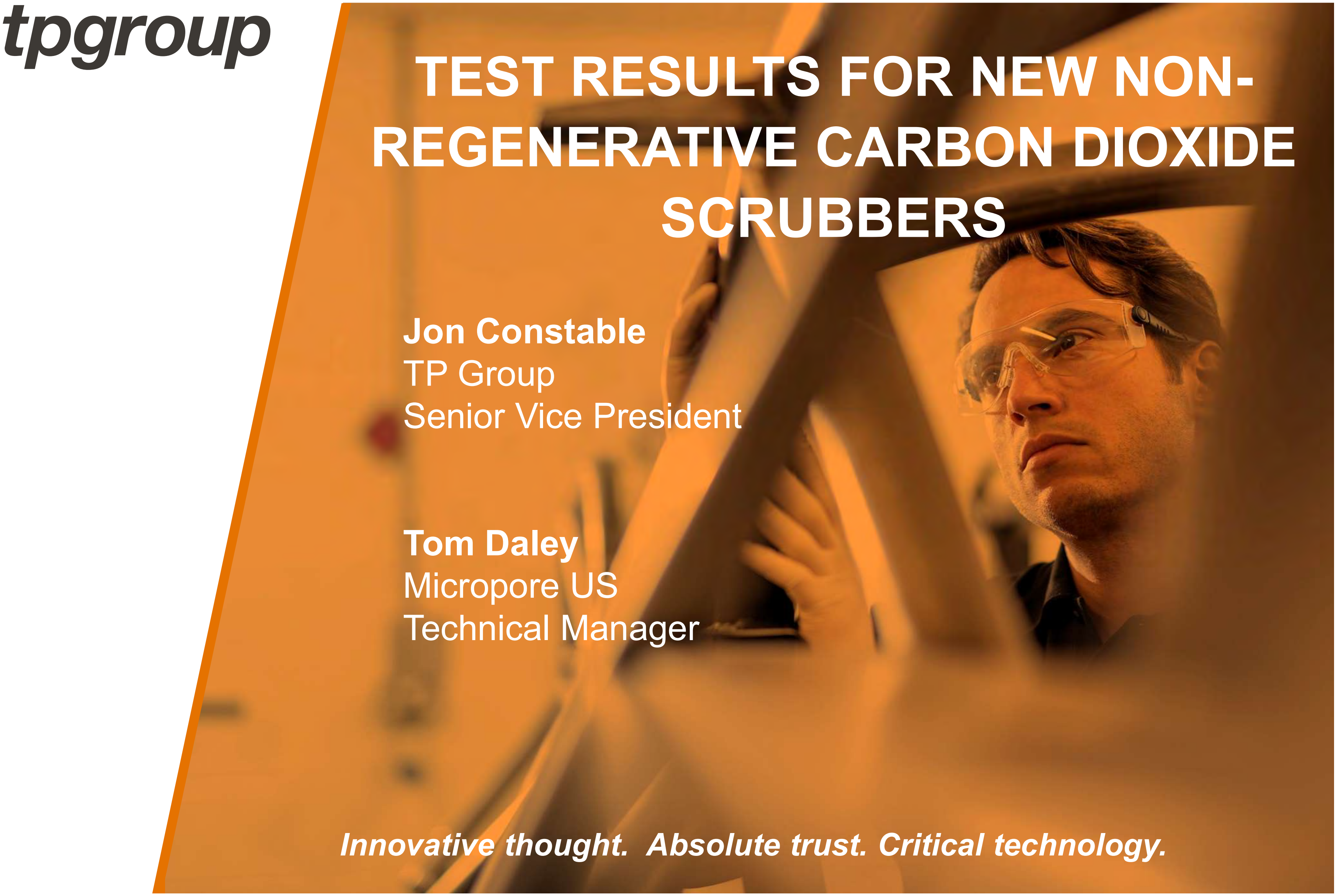


Conclusions

- By monitoring CO2 scrubbing media efficiency we can alert crew within a reasonable time for media change out
- Differing CO2 levels onboard and scrubbing capacity (or the number of media) will lead to changing ideal scrubber media changeover times
- Instrumenting scrubbers may be able to reduce the amount of media used

ANY QUESTIONS

?



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TEST RESULTS FOR NEW NON-REGENERATIVE CARBON DIOXIDE SCRUBBERS

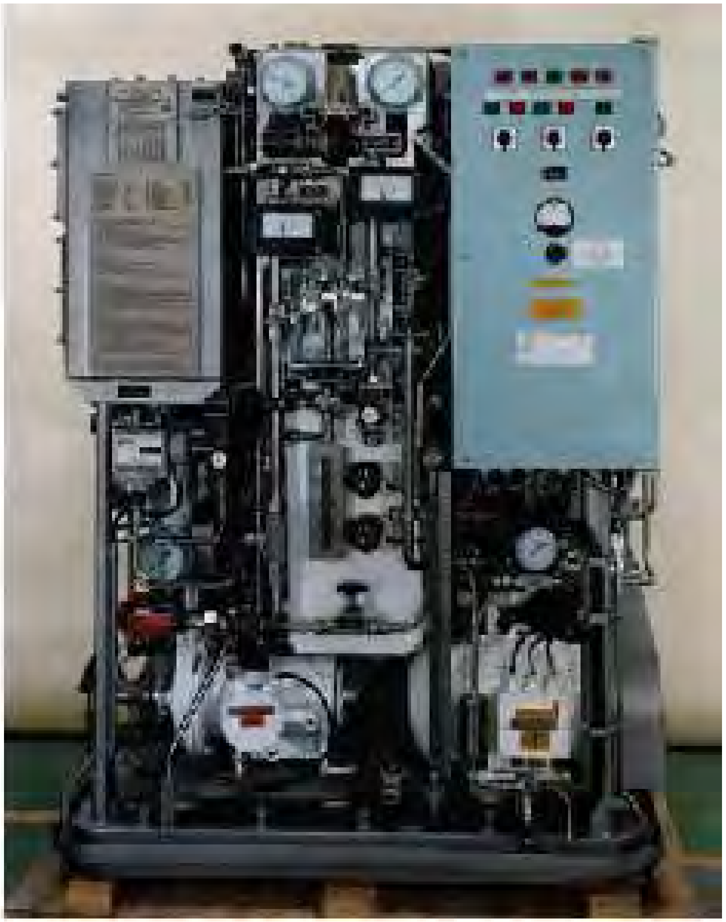
Jon Constable
TP Group
Senior Vice President

Tom Daley
Micropore US
Technical Manager

Innovative thought. Absolute trust. Critical technology.

/ Innovation in CO_2 removal systems

- Long history of providing CO_2 scrubbers to global navies
- Traditionally providing regenerative MEA based systems
- Partnered with Micropore USA to develop new technologies



Background

Current trends in submarine carbon dioxide control are driven by:

1. Manning levels above submarine baseline design due to additional riders, especially special forces or training compliment
2. Decreasing CO_2 levels to comply with national worker's safety requirements or risk of cognitive decline at elevated CO_2 concentration
3. The need to minimize hardware and consumable volume within the pressure hull.
4. The need for safe-3 and non-toxic adsorbents

CO_2RE Single Cube Scrubber

/ A new range of systems

Non-regenerative CO2 removal systems using Micropore PowerCube®

Modular and can be scaled to suit application

Designed with AIP / Diesel Electric submarines in mind

Good for spot CO_2 removal e.g. single compartments

/ TP Group CO$_2$RE range of CO$_2$ scrubbers

CO$_2$RE
Single cube & sensors

CO$_2$RE
3 + 3 scrubber

CO$_2$RE 6XK
6 Cube with sensors

Straight 6 and V6 configurations

- A 6 cube arrangement badged as the STRAIGHT-6 CO_2RE
- This scrubber is intended for back-fit or new construction diesel electric submarines
- These scrubbers offer 6 cubes in either two banks with parallel flow or all 6 cubes in parallel
- Due to the low pressure drop, airflow can be provided by existing ventilation system or by a dedicated fan
- Very Good Performance test results

CO_2RE Straight 6

CO_2RE V6

tpgroup

Micropore USA

- Micropore is a 21 year old USA Corporation founded to exploit patented technology
- Micropore is uniquely qualified to encapsulate fine powders into solid sheet adsorbents
- Micropore technology produces solid sheet adsorbent with greater than 95% purity.

/ MICROPORE PRODUCTS

Military Diving:

- Diver Safety: 70% less caustic even after 5 minute flood
- Absorbent can be stored with rebreather instead of separately in bulk containers
- Platform Friendly- no caustic dust on metal surfaces
- Diver's breathing workload is reduced up to 15%
- Canister loads 5 times faster
- Reduces performance variability

/ MICROPORE PRODUCTS

Medical Anesthesia Adsorbents:

- Portable Patient Transport Life Support System (PPTLSS)
- Operating Room Anesthesia Machines

/ MICROPORE PRODUCTS

Submarine/Space Products:

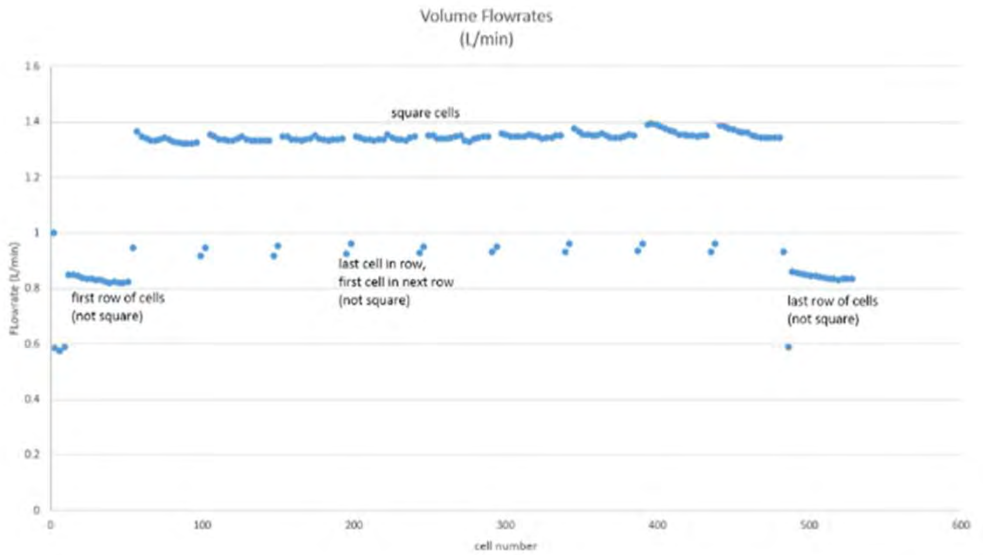
- Emergency Life Support Curtains
- PowerCube® adsorbent blocks

Single Cube Scrubber CfD analysis

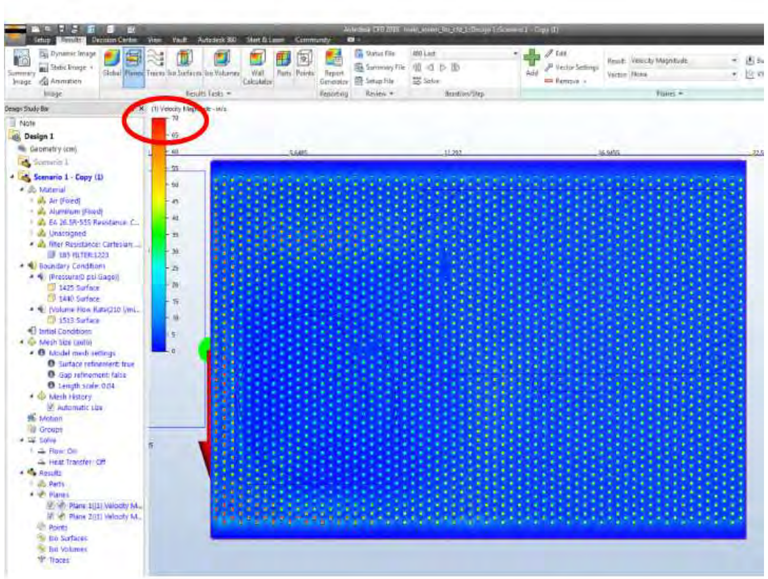
- In addition to the test work carried out, flow modelling was completed to assure air distribution across the cube and optimal utilization of the cube

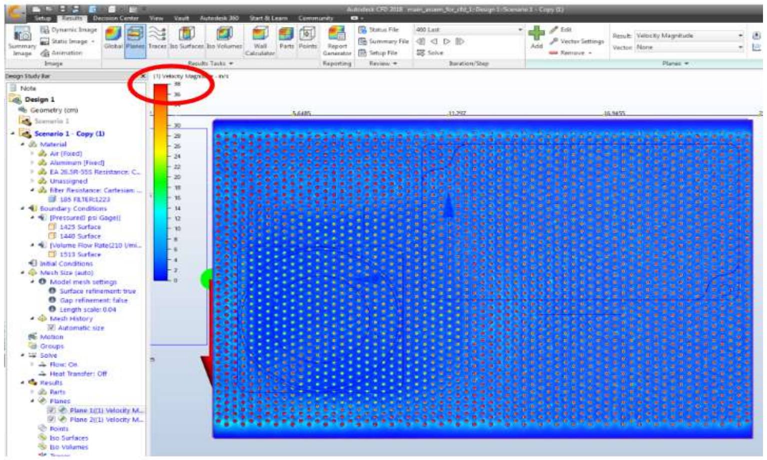
- Whilst for physical reasons the fan was offset, baffle plates and a plenum chamber allowed air distribution across the face of the cube

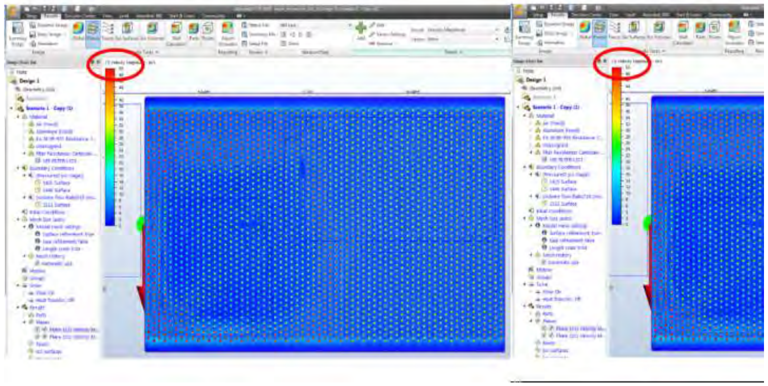
- Looking end on to the individual channels through the cube the colour is fairly consistent indicating even flow distribution

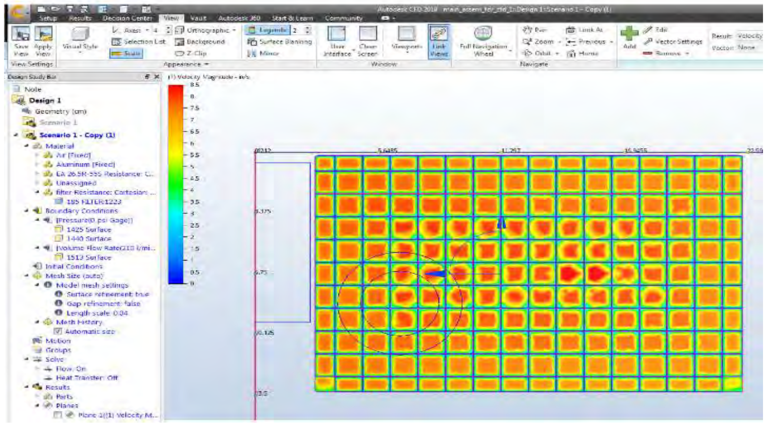


CO$_2$RE Scrubber Computational Fluid Dynamics





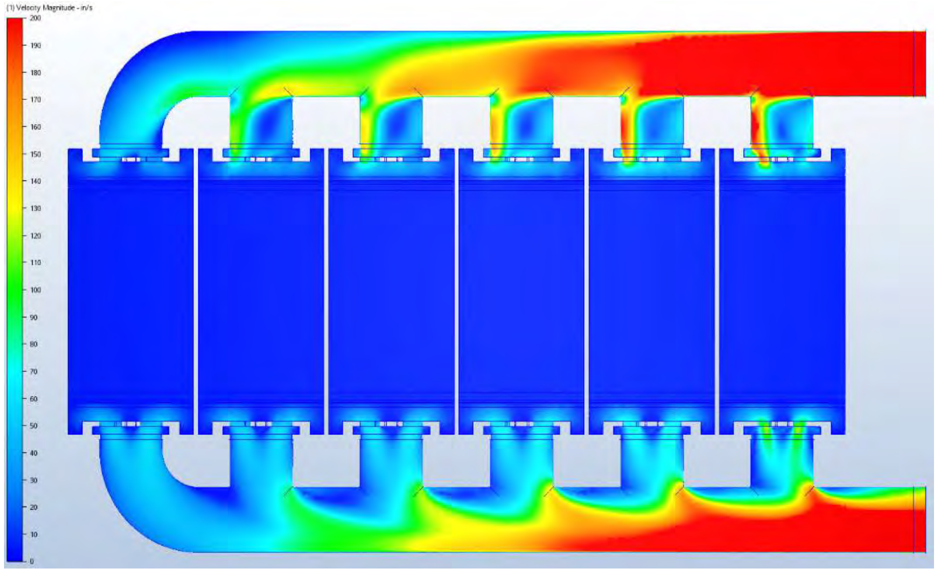


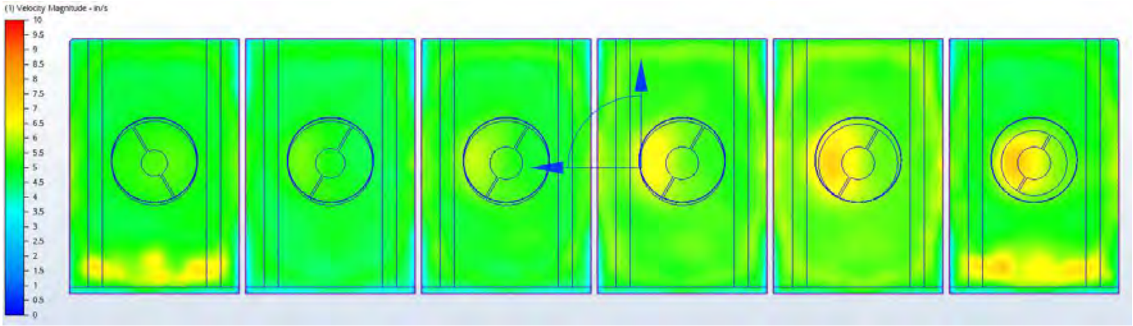


Straight 6 Computational Fluid Dynamics

- Optimisation of baffles to assure even flow distribution and performance

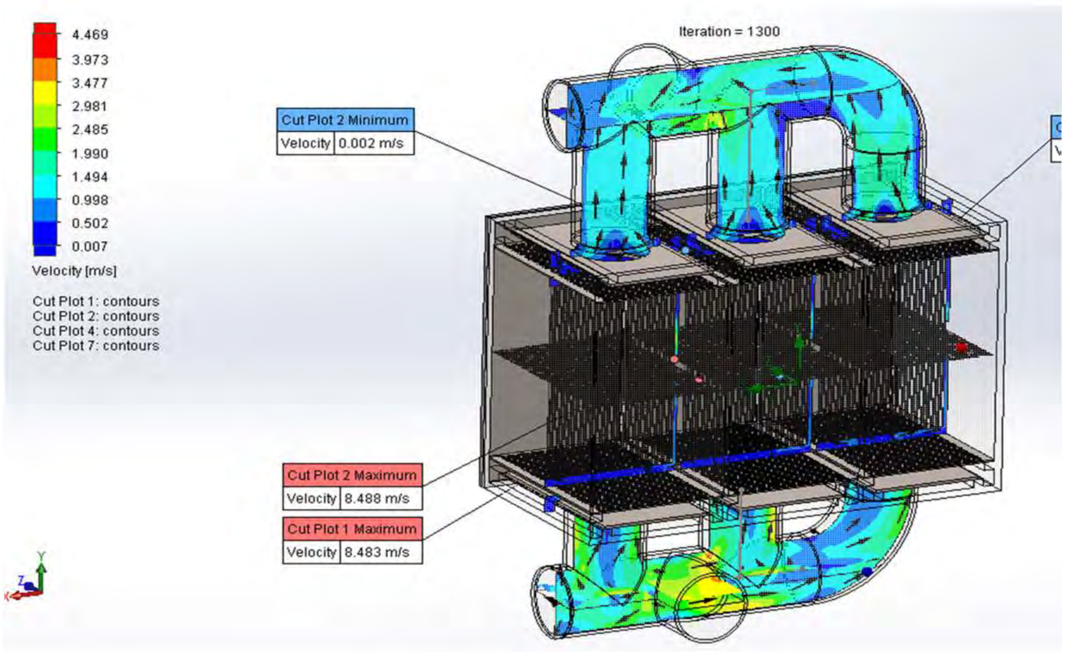
- As it can be seen whilst the flow in the feet pipes reduces from red to blue as it distributes to the 6 cubes, the flow colour through all the cube areas is an even shade of dark blue indicating even flow distribution





- A section view through the manifold on the end of the cubes showing the different flow balancing plates in each segment. Again the colours are even indicating even flow

3 Block Scrubber

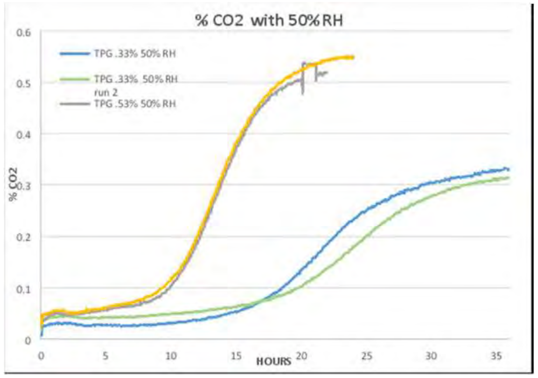


- An early flow analysis on the 3 block scrubber unit
- This shows slight variation in the flow which will be optimized

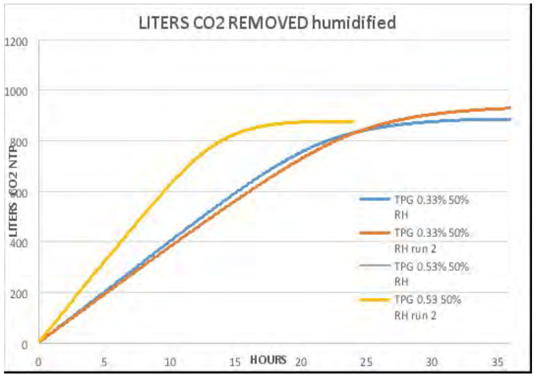
Performance Data Single Cube Core Scrubber

- The single cube CO_2RE scrubber was test in the laboratory at varying CO_2 inlet concentrations
- The humidity was controlled to 50% RH
- The testing was conducted with calcium hydroxide cubes
- Note that calcium hydroxide adsorbents are sensitive to relative humidity of the feed gas
- For controlled/air conditioned environments such as submarines the adsorbent becomes exhausted due to removal of water from the granule or Micropore block 5
- Note that lithium hydroxide adsorbent is not sensitive to feed stream humidity
- The inlet gas temperature was controlled to 70OF and the pressure was ambient. The test rig was detailed previously 6
- The test apparatus is calibrated in accordance with Micropore's quality procedures
- The **following illustrations** show performance of the CO_2RE Scrubber when operated at low inlet CO_2 concentrations

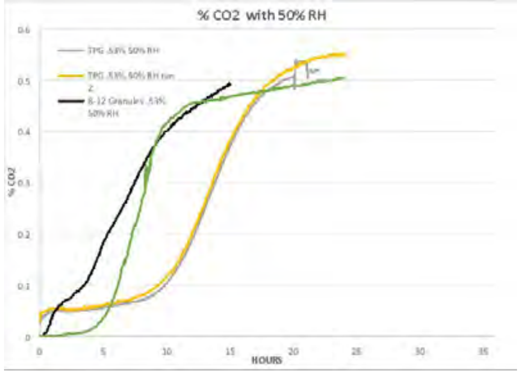
CO$_2$RE Scrubber performance operated at low inlet CO$_2$ concentrations



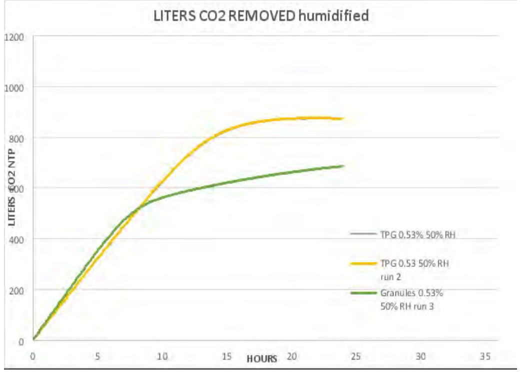
CO$_2$RE Scrubber CO$_2$ vs time



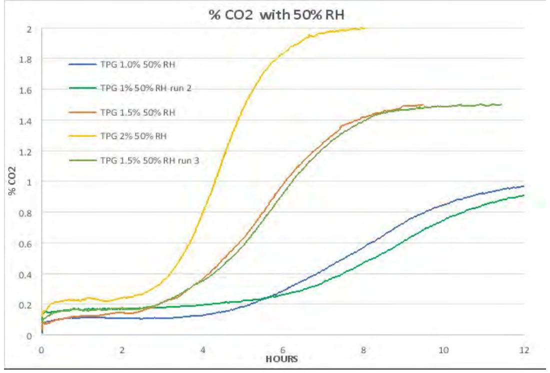
CO$_2$RE Scrubber litres CO$_2$ Removed vs time



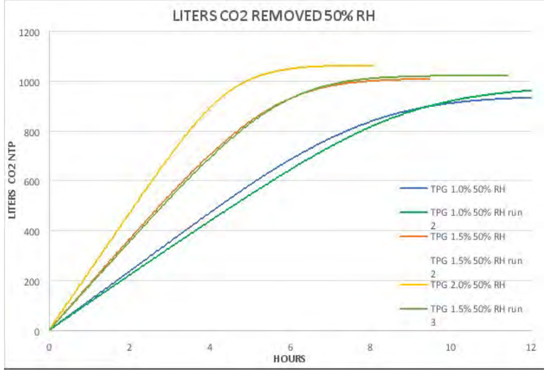
CO$_2$RE Scrubber and Granules - % CO$_2$ vs time



CO$_2$RE Scrubber and Granules – Litres CO$_2$ Removed vs time



CO$_2$RE Scrubber with High CO$_2$ Inlet % CO$_2$ vs time



CO$_2$RE Scrubber with High CO$_2$ Inlet Litres vs time

Future Testing and Performance outcomes

- In the next few months TP Group have test bay work planned to confirm the CFD performance predictions

- The following will be measured:-
    - Inlet CO_2 concentration
    - Flow rate bulk
    - Pressure drop across each cube
    - Temperature of the room
    - Humidity

- In order to do this in broad outline the following will be completed:-
    - Test plan generated
    - Fixtures and EUT setup
    - Testing in both LiOH and Calcium Hydroxide
    - Test report generated

- CO_2RE scrubbers both single cube and STRAIGHT-6 have the PowerCube® adsorbent advantages:
    - No dusting
    - No settling
    - Increased CO_2 removal at same storage volume
    - Designed to operate at submarine humidity levels
- Working with TP GROUP for submarine CO_2 control has numerous advantages:
    - 50 years experience with SM atmosphere control systems
    - System/component design for crew sizes of 30 to 150
    - Manufacturing expertise for submarine hardware
    - Compact designs that can be back fit into existing spaces
    - Through life support capability

Conclusions and References

- The next step in the CO_2RE new product launch is shipboard testing
- The CO_2RE single cube scrubber can easily installed for localized CO_2 control to supplement existing scrubbers
- The CO_2RE can also be used for CO_2 control in submarine rescue vehicles although hyperbaric testing is required
- The STRAIGHT-6 or multiple 3 UP scrubbers require some engineering for installation and operator access

1. In USA NIOSH has set CO_2 concentration at 0.5% TWA
2. Add citation
3. For example super-oxides react violently with water
4. Non-toxic materials are easy to transport and dispose of
5. SAMAP 2011, Taranto, Water is the Key;
6. Dr. Michael Clarke and Dr. Mandy Crudace
7. SAMAP 2011, Taranto, Further Developments and Full Scale Testing Of Micropore’s Calcium Hydroxide and Lithium Hydroxide Powercubes®

tpgroup

Thank you.

WWW.TPGROUP.UK.COM
WWW.MICROPOREUSA.COM

Single cube option

- The first available scrubber was the single cube CO_2RE (Carbon Dioxide Removal Equipment) scrubber.
- This has an installed fan (AC or DC powered)
- option of inlet and outlet infrared CO_2 analyzers for automated operation and indication on when to change the adsorbent cube.
- The power requirement is low (7 watts) due to low airflow resistance through the scrubber and adsorbent

CO_2RE Single Cube Scrubber

3 Block scrubber option

- A third TP Group scrubber option for Micropore PowerCube® adsorbent is the 3 block scrubber
- This unit is powered by an external fan and can be ganged together as 3, 6, 9 or 12 cubes
- Flow is either parallel or parallel/series. This style scrubber is intended to fit into the frame bay of a submarine
- A small fan can be supplied with the scrubber if needed

CO2RE 3+3 Scrubber

tpgroup

CO_2 Scrubbing onboard Walrus Class an overview

By Toon Mariën
RNLNAVMAINEST

Topics

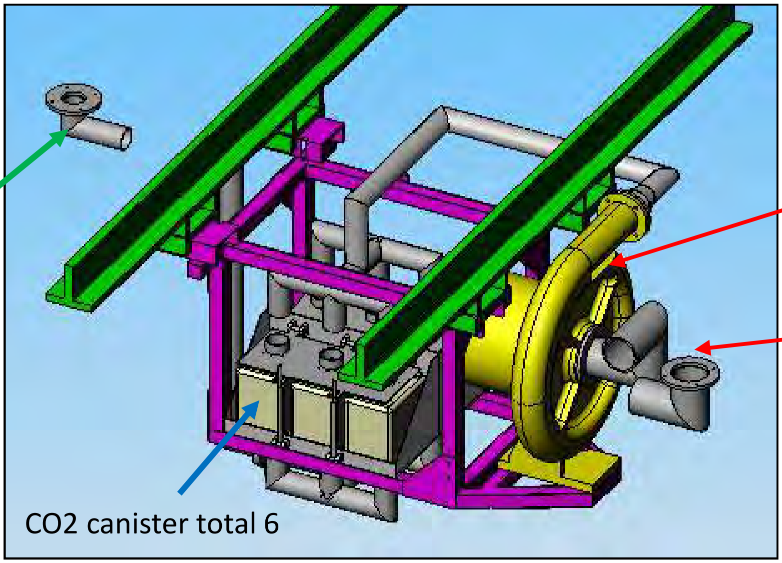
- Introduction
- History
  - Scubbers 1 and 2 (original view)
  - Prototype 3rd scrubber
  - WCA (Working Conditions Act)
  - Powercube and powercube adapter (first test)
  - Nesquick test
  - Overview of all three scrubbers after build and implementation of 2nd generation third scrubber
- Combined conclusions
- Improving airflow
- What now
  - Trials
- Q&A

Scrubber original view

- During the build of the Walrus class, 8 scrubbers for scrubbing CO2 were build and implemented
- 2 scrubbers were installed on each Submarine
- Positioned in Wardroom and Torpedo storage room
- The scrubber made use of canisters filled with Sodalime Granuals

Prototype 3rd scrubber

- Already during the first few years it became clear that the scrubbers were not performing as expected.
- So throughout the years RNLN made small changes, as air flow rate and internal cannister changes by OEM.
- In 2007 there was a study upon improving CO2 scrubbing, one of the conclusions was that more volume of adsorbing material was needed , even with 100% use of the canisters in the two existing scrubbers. **This resulted in a 3rd scrubber**



PROTOTYPE AND FIRST SCRUBBER

drawing

Connection to mechanical vent exhaust ducting of SUB

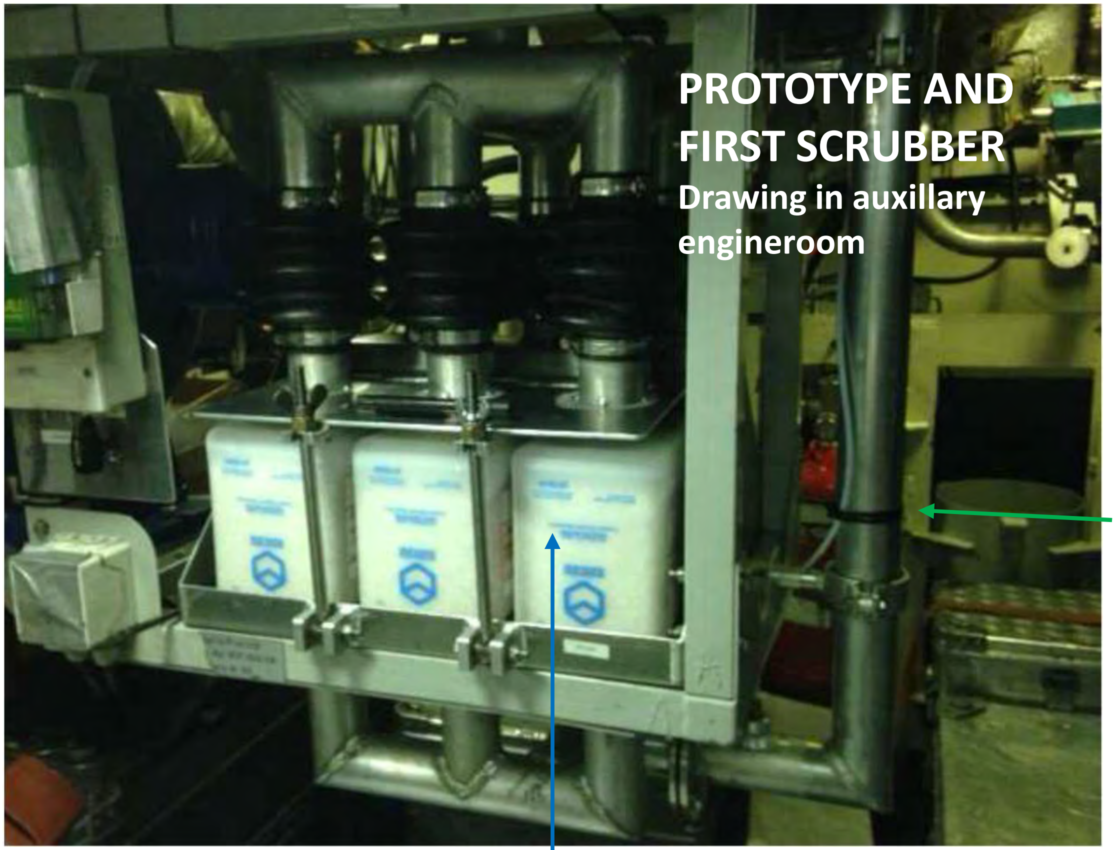
Vent

Connection to mechanical vent inlet ducting of SUB

CO2 canister total 6

There was a slight but not sufficient improvement so further research was done

PROCEEDINGS



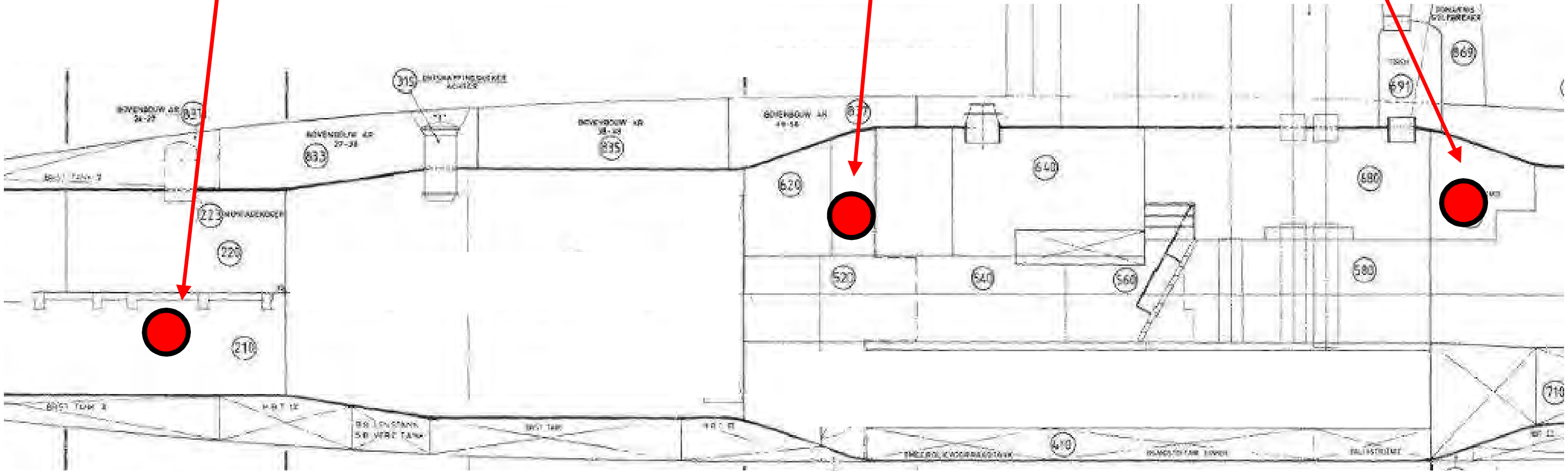
PROTOTYPE AND FIRST SCRUBBER

Drawing in auxillary engineroom

Connection to mechanical vent exhaust ducting of SUB

CO2 canister, 6 in total

Positions of the three scrubbers



Proto type - and now 2nd generation scrubber Auxiliary Engineroom

Original type scrubber Wardroom

Original type scrubber Torpedoroom

PROCEEDINGS

- From start of operating Walrus class untill 2013/2014, the MAC values of CO2, were a maximum level of 1.5% (no designated time limit), and a 24 hours maximum level of 2%.
- The third (prototype) scrubber brought some improvements.

- With a new POR for new canisters the responsible department of the Defense Material Organization was triggered on the MAC levels
- At the end of 2013 a research was initiated on admissible CO2 levels, this resulted in new MAC levels for CO2 on Netherlands submarines

Changes in WCA

- After a study on values to be in forced on submarines RNLN decided that we had to go down with .5% on our values now resulting in a CO2 operational maximum for 1%, and a 24 hours maximum level of 1,5%.

- During 2014 and 2015 RNLN did several tests, first test (Power cube test)was presented at SAMAP 2015. This made RNLN switch from granual canisters to the Powercube adapter and the CaOH power cubes. (next slide)
- A other test was ("The Nesquick" test) on the internal airflow on the original two scrubbers. Also presented at SAMAP 2015 (by Barend van der Giesen)

"The Nesquick" test

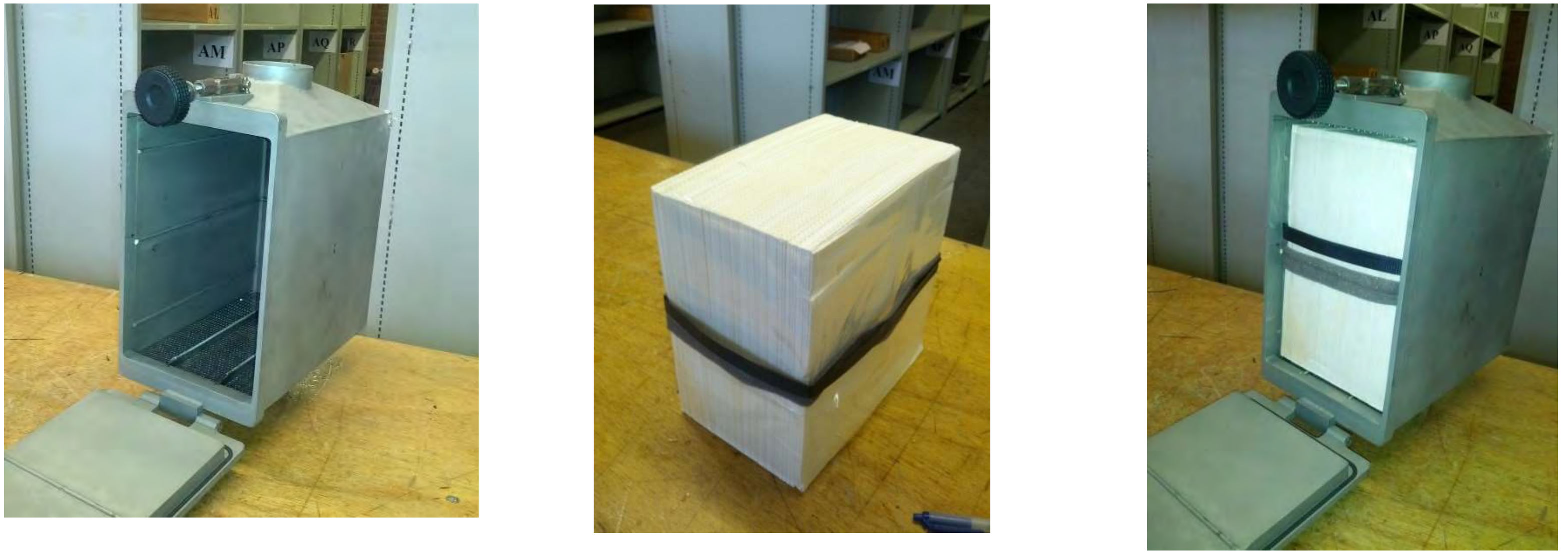
Internal airflow or the a first test of
performance of the seperate canisters
and the airflow through the seperate canister.

Powercube test

- RNLN, together with manufacturer of the Powercube adapter and the 2 different Powercube blocks wanted to perform an on board test. So in 2014 RNLN performed a test on board submarine Dolfijn.

- The Power cube adapter
- 2 different kinds of scrubbing material blocks (CaOH- and LiOHPowerCube)
- This was presented at SAMAP 2015

Powercube adapter with Calcium Hydroxide block, VM-1050P(Micropore)

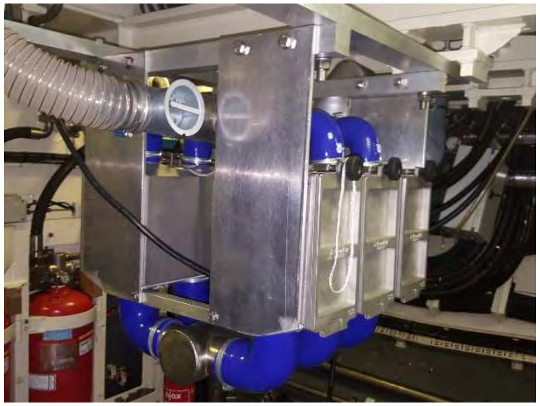


Overview of all three scrubbers

(current situation)

Torpedo storageroom

Third scrubber final design



Auxiliary Engineroom

Wardroom

combined conclusions

The combined conclusions of these test were:

- Install a third scrubber
- Use the Micropore powercube adapters in combination with the Micropore calcium hydroxide blocks (Powercube)
- Improve airflow through the two existing scrubbers

After implementing the first two conclusions the CO2 levels on board submarines improved and even became lower than expected. Although RNLN did not perform an endurance test up to this moment

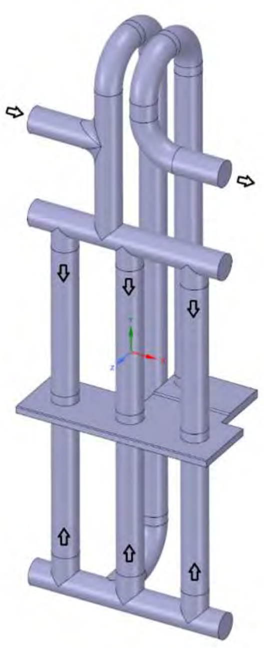
The third conclusion is work in progress. In 2018 a company performed CFD analysis on both old scrubbers and were asked for suggestions on improving the internal airflow

With a small change on a part of the scrubber the airflow can be improved to get an almost evenly airflow through all powercubes.

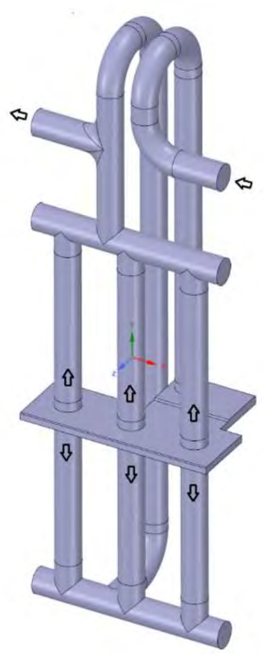
RNLN implemented this improvement on one of the submarines and is looking for an opportunity for testing

Improving airflow

- To improve the airflow thoughout the two existing scrubbers van asked DECOM bunova to do some research on our scrubbes (Wardroom and Torpedo storageroom)

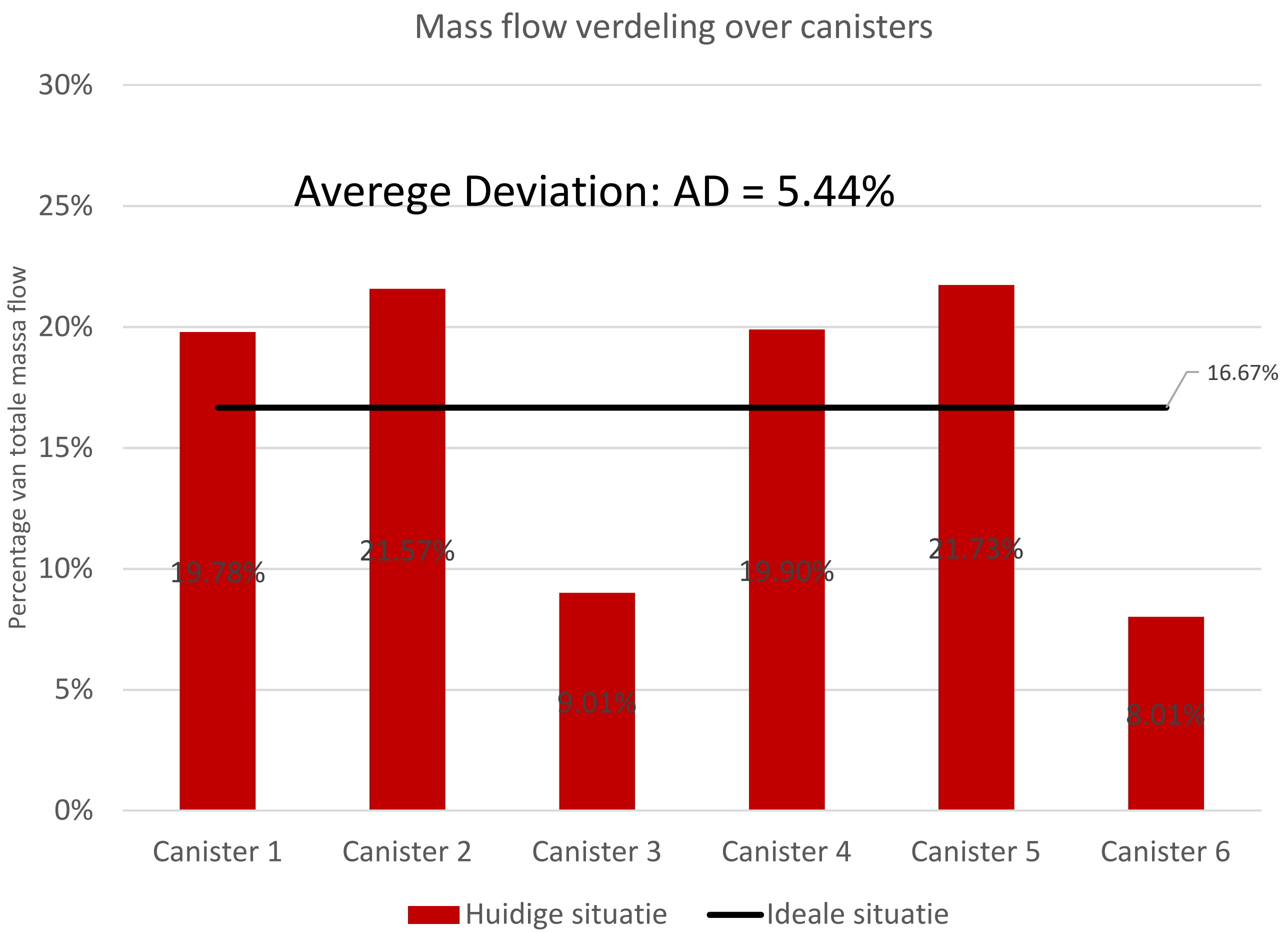


Wardroom

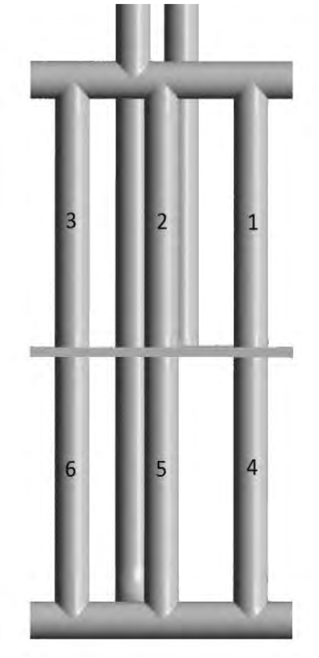


Torpedo storageroom

Mass flow distribution CO_2 unit Torpedo storageroom



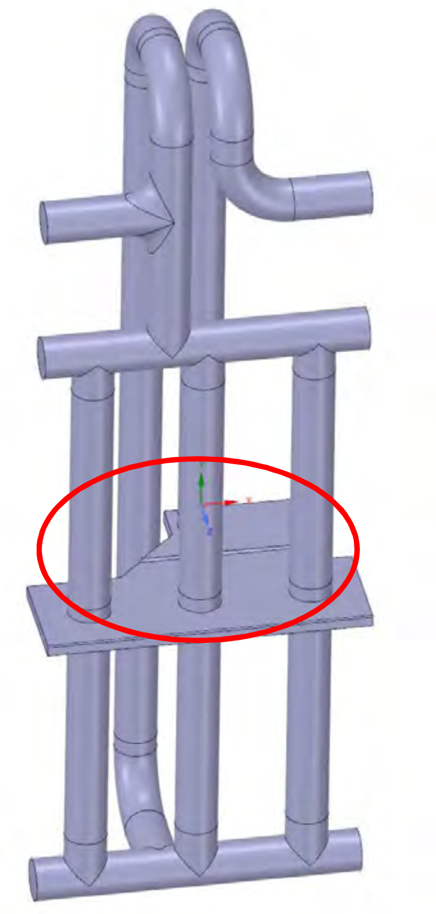
Averege Deviation: AD = 5.44%

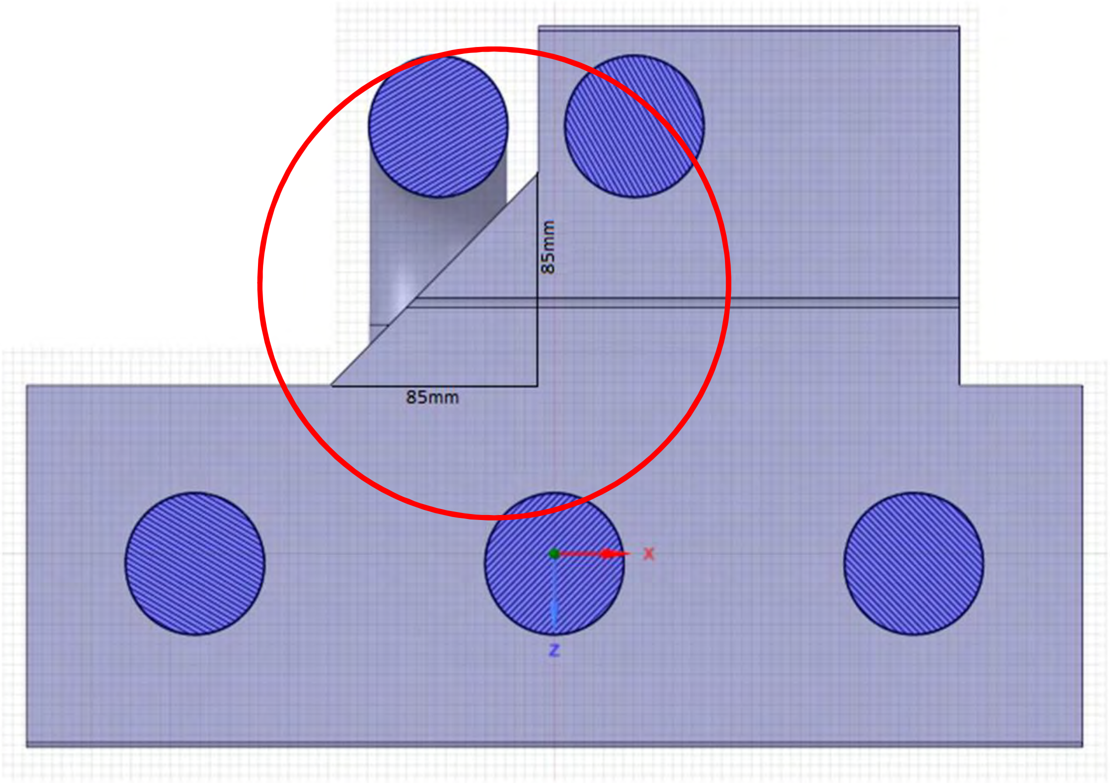


- Two left canisters (3 en 6) have little mass flow

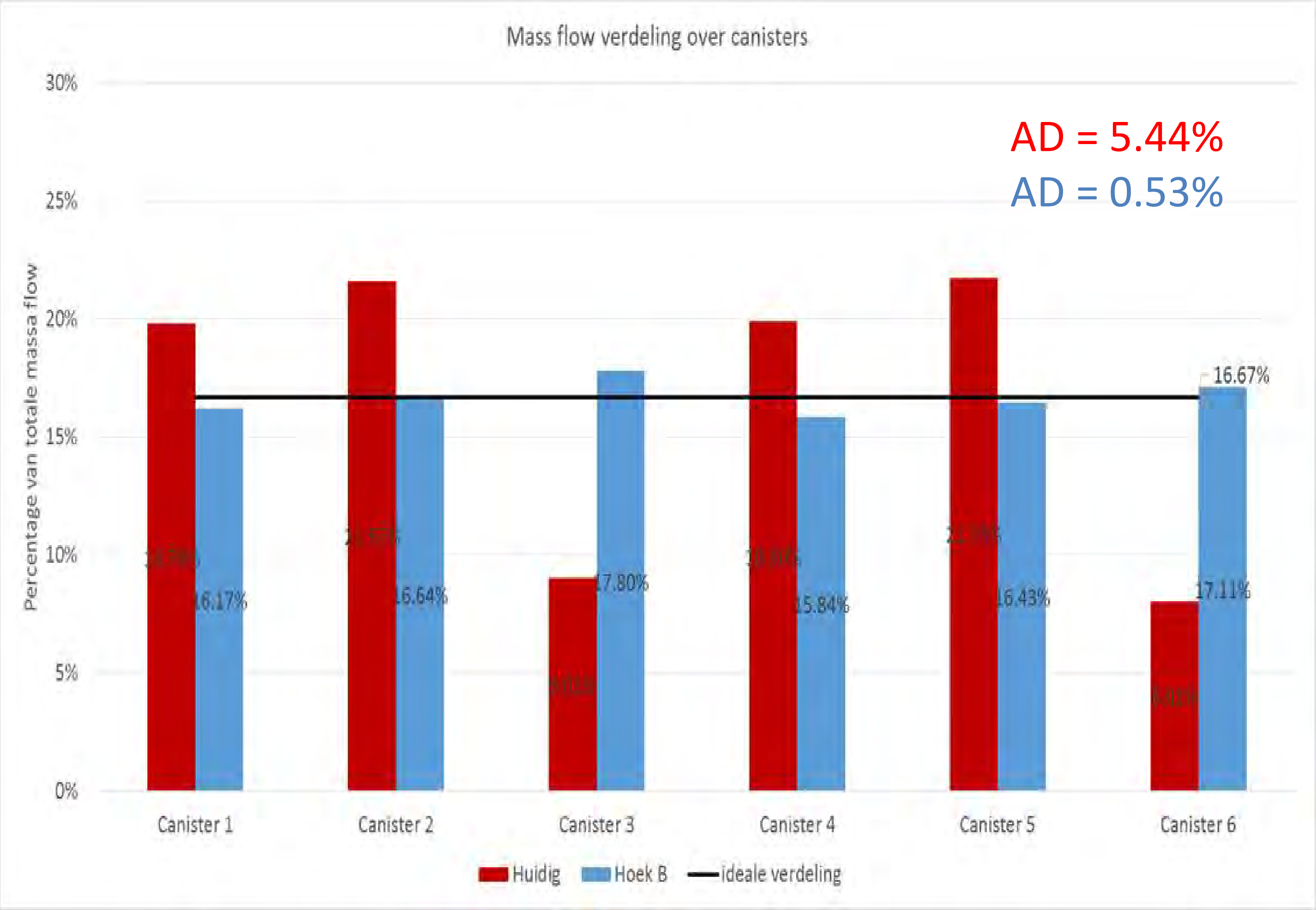
PROCEEDINGS

- After some modelling and calculations the conclusion was that the change as suggested with line B was the best solution for both scrubbers



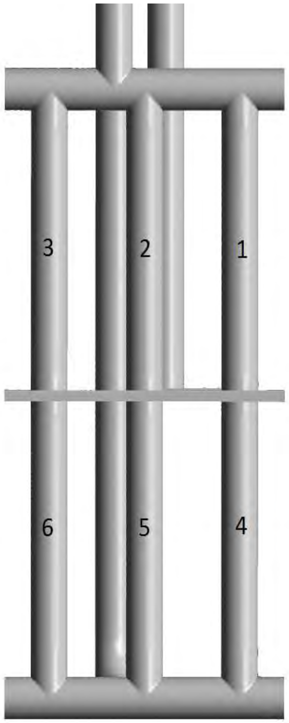


Mass flow distribution CO_2 unit Torpedo storageroom after implementing change B



AD = 5.44%

AD = 0.53%

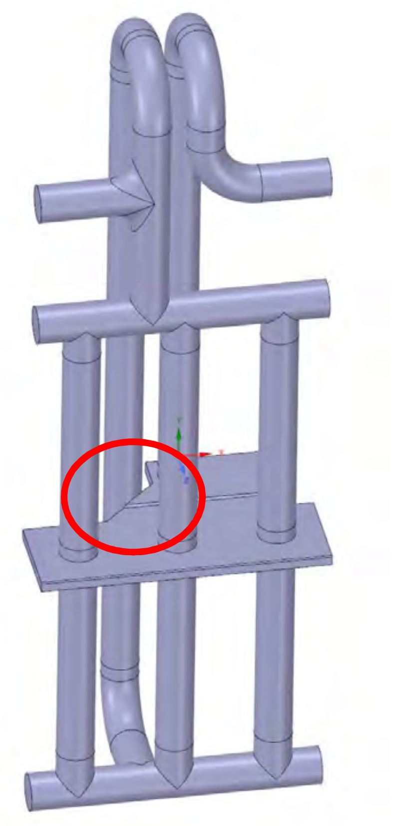


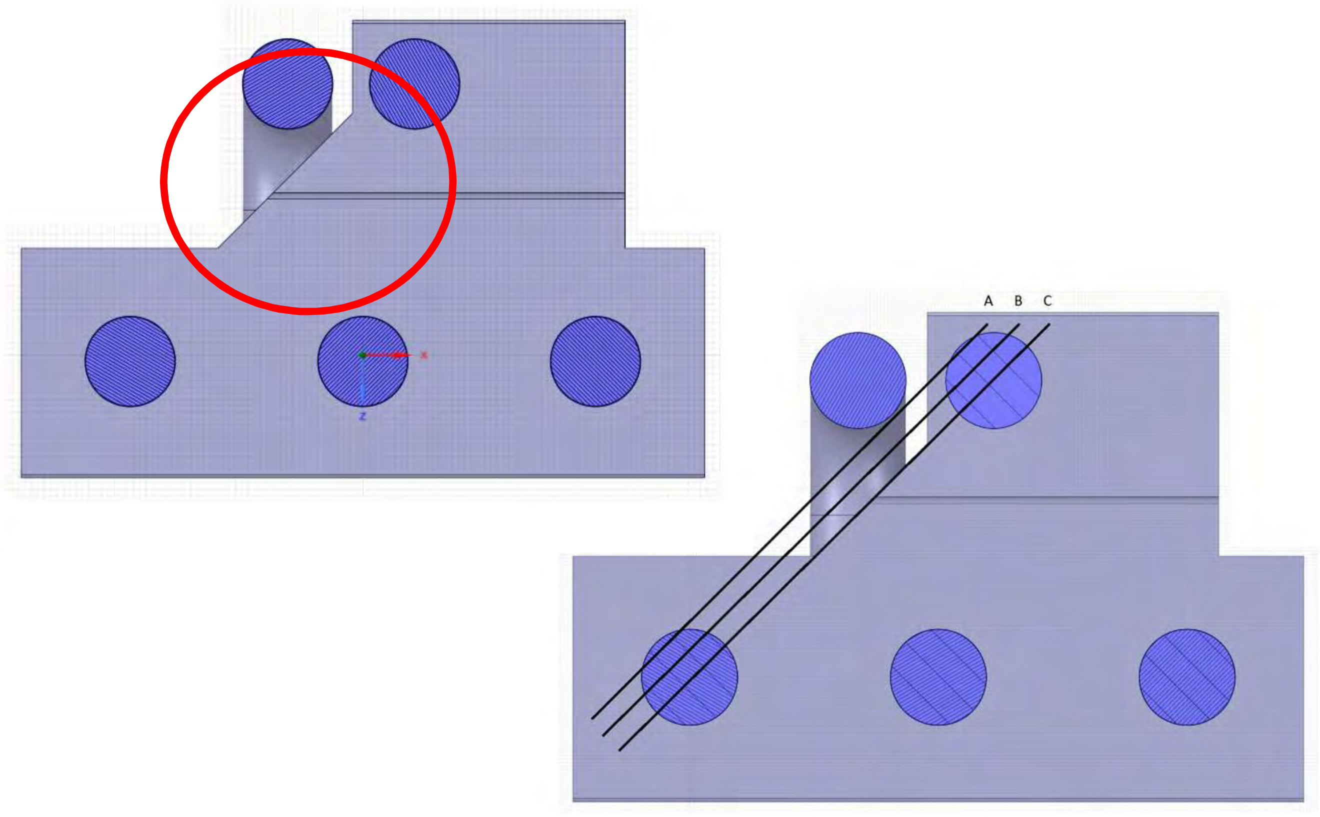
- Mass flow distibution improved approaching the Ideal line of 16.67%

PROCEEDINGS

- The improvement on the Wardroom scubber was significant less than the improvement on the Torpedo storageroom scrubber. Never the less RNLN made the change on the scrubber.
- The Average Deviation on the wordroom scrubber is under 1%
- No graphs or pictures on the Wardroom scrubber about air flow are available in this presentation

Adjustment for improving mass flow distibution





What now?

- RNLN has mounted a third scrubber (final design) and made the changes to the two existing scrubbers on one of our submarines .
- This coming fall RNLN will implement the changes to the two scrubbers on the second submarine
- Perform a quayside- and sea trial

Trials

How to trial CO2 scrubbing on board a Walrusclass submarine?

PLAN:

- 1st, Perform a static quayside trial, like RNLN did before, find a few a bit crazy guys, Put these guys in a closed down submarine, give them fire extinguishers, have them discharge aprox 2,8 kg CO_2 /hour into the submarine for simulating a crew of 62 and let them measure:
  - CO_2 ;
  - O_2 ;
  - temperature ;
  - humidity

- 2nd Perform sea trial to look at the performance under real life submarine conditions,

PROCEEDINGS

Questions

maybe answers !!!!

Distressed Submarine Ventilation and Decompression System

Jos Bogaert
Smeras Consultant

Agenda

- What Is DSVDS
- Why DSVDS
- DSVDS Exercises
- Questions

The Problem

Le Petit Journal

SUPPLEMENT ILLUSTRÉ

ABONNEMENTS

DIMANCHE 23 JUILLET 1905

LA CATASTROPHE DU « FARFADET »

Les scaphandriers travaillant au renflouement du sous-marin

Every scenario of distressed submarine is different, but critical parameters that may limit survivability of the crew are always the same:

- Pressure rise
- Toxic atmosphere
- Loss of life support capability
- **Time**

➔ How can these vital parameters can be managed?

The Ideal Case

In an ideal world, it should be possible to undertake:

- **Fast mobilization of rescue elements**
- **Fast localisation and environment assessment**
- **Safe & fast rescue intervention**
- **Immediate medical treatment for sub's crew**

***NATO NSRS** (or equiv.):*

- Transportable full rescue system
- TUP facilities
- On-board decompression chambers & medical experts

Rescue Systems

- A lot of rescue systems like NATO NSRS (or equiv.)are available.
- Most of these systems have the following functions :
- • Transportable full rescuesystem
- • TUP facilities
- • On-board decompression chambers & medical experts

Time Limit

- In some cases, SRS intervention may be difficult, or even impossible:
- • System not available (maintenance…)
- • Longer mobilization of system
- • Technical failure before or during operation
- • Bad sea conditions
- • Sub/SRS interface unreachable by SRS or damaged
- • Sub/SRS interface unreachable by sub’s crew
- In such situations ADDITIONAL TIME is needed

The Challenge of Additional Time

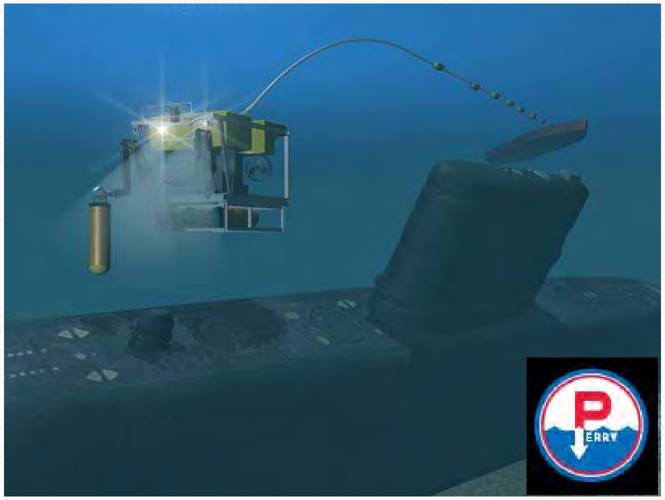
To increase significantly preparation and intervention time, the following problems must be addressed :

- **Avoid toxic atmosphere inside Sub by regeneration/ventilation**
- **Continuous monitoring and control of inside pressure**

➔ ***Ventilation and Depressurization System (DSVDS)***

- **Ensure life support for the sub's crew**

➔ ***ELSS Pod posting***



DSVDS Main Requirements

DSVDS main functions :

- **Assessment of inside air composition and pressure**
- **Ventilation of Sub with a suitable fresh air flow**
- **Simultaneous fine control of inside pressure**
- **Continuous monitoring and adjustment of vital parameters**

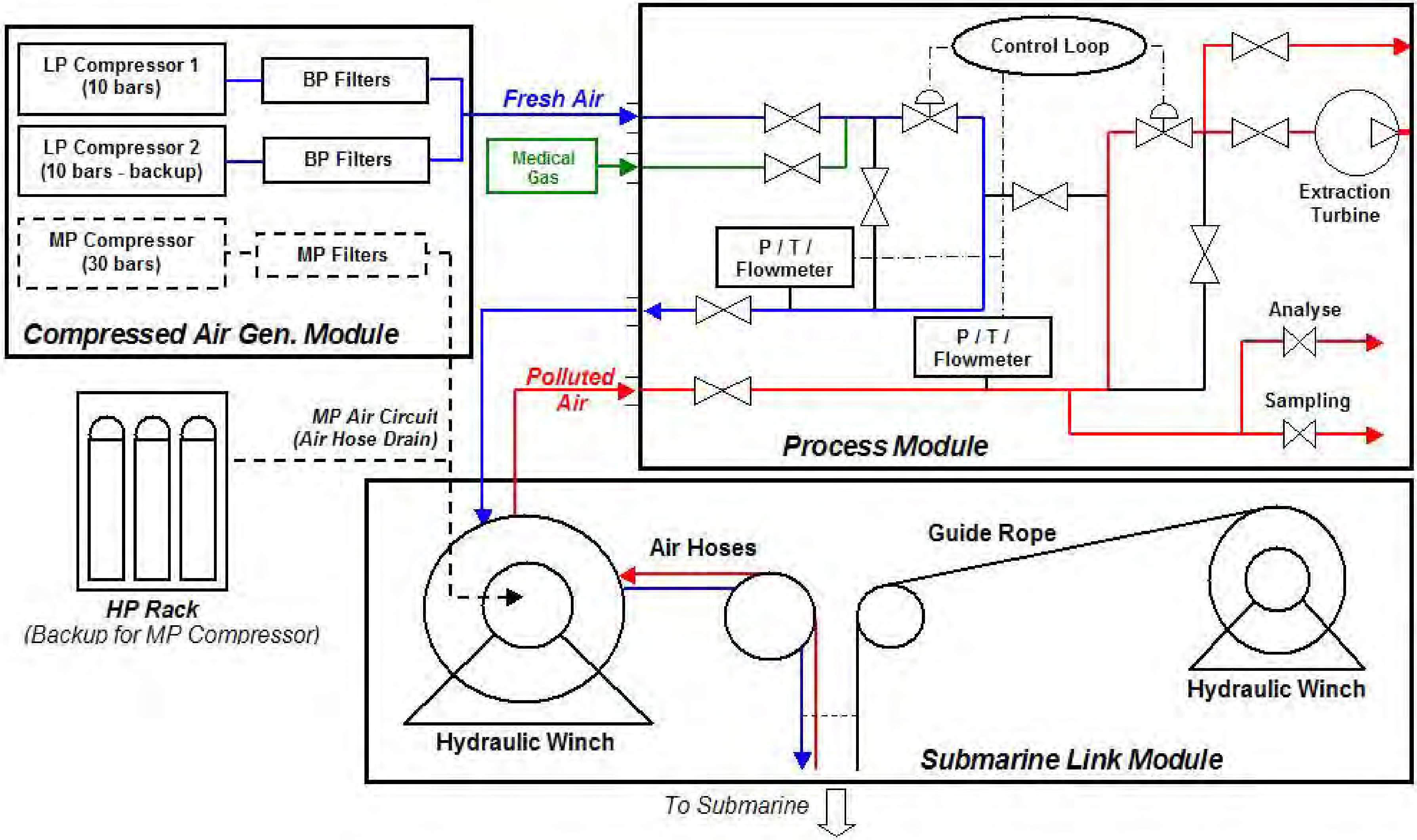
DSVDS main operational requirements :

- **Easy mobilization/Operation with limited personnel**
  ➔ DSVDS must be deployed as fast as possible
- **« Independance » from sub: DSVDS must not rely on crew nor on sub's onboard systems to be operated**
- **Adapted for harsh conditions**
- **Safety**

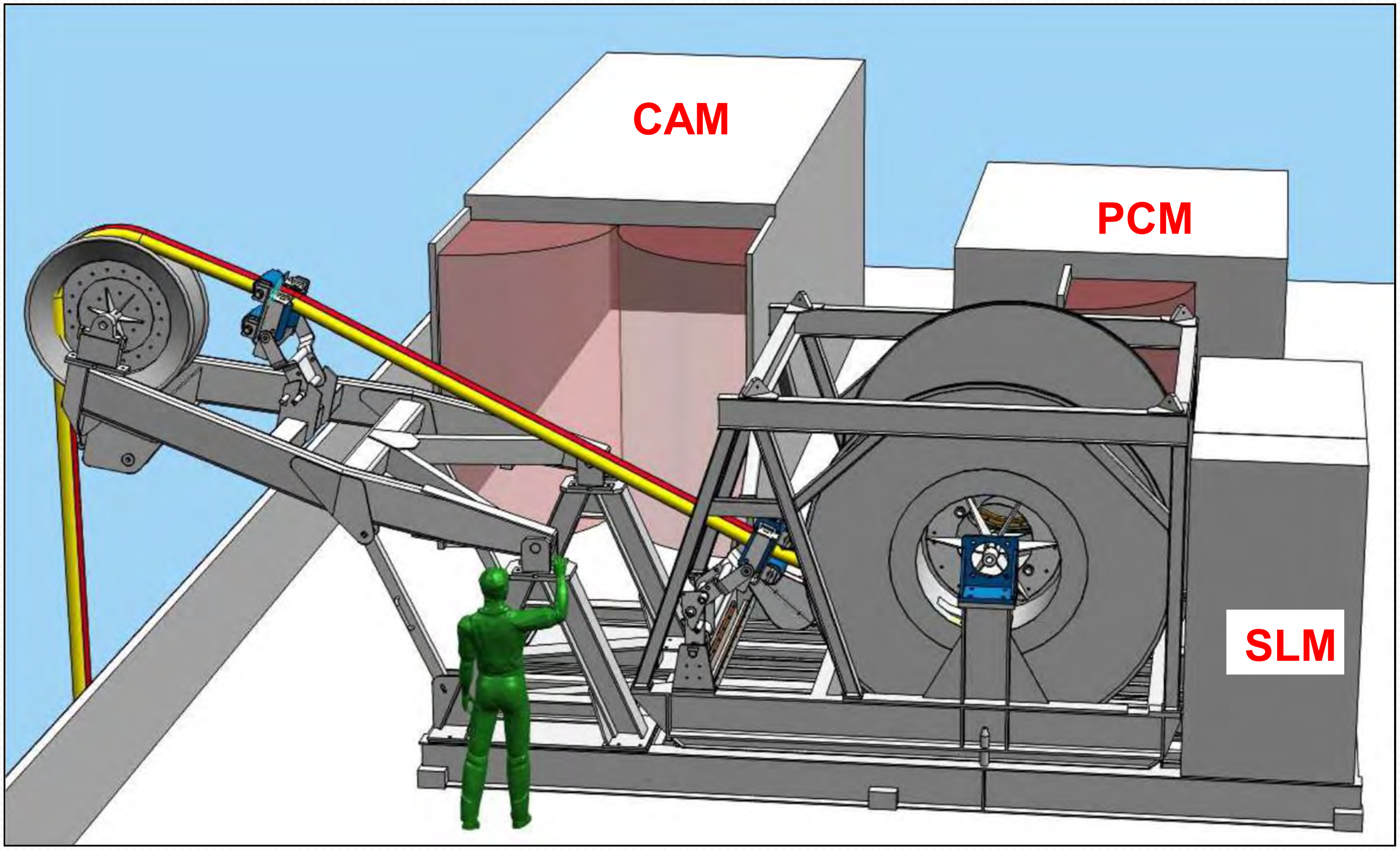
Background

- A DSDVS provides the means of remotely depressurising and / or ventilating a DISSUB compartment that is subject to elevated internal pressure, or has an atmospheric specification beyond breathable limits.
- A DSDVS therefore has two purposes; firstly to control pressure /de-pressurise, and secondly to ventilate.
- The former would either be able to maintain pressure within survivable limits(against for example a rising pressure gradient) or to lower the pressure to reduce the surface decompression obligation.
- The latter would supply air and remove waste gases.

Synoptic Diagram



Hi-Level System Description



Dissub Internal Pressure

- Of all the factors influencing the system capabilities, the target pressure (and airflow) in the DISSUB is arguably the most critical. It is from this point that the rest of the system must be matched and sized
- When looking at a system that supplies breathing air, too high a DISSUB internal pressure demands a high flow to provide sufficient refreshing of the atmosphere to accommodate the submariner's life support consumption rates – whilst the higher internal pressure aids recovery of the exhaust gasses, the size of the recovery hose this may entail on the recovery side could hamper system mobilisation.

DISSUB Internal Pressure

- The consequent increase in supporting equipment quickly adds to the overall size of the rescue spread.
- Too low a target pressure reduces the differential available to exhaust spoiled air at the surface.

Flow Rate Limitations

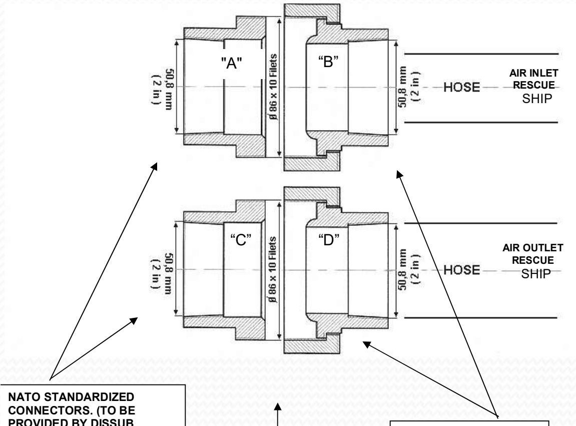
- The flow rates required to maintain the atmosphere within habitable bounds are a function of:
- - the consumption rates of the submariners
- - the pressure of the chamber
- - the size of the chamber
- - any contaminated air to be removed and production sources of contamination
- - the smallest restriction in the line

Flow Rate Limitations

- It is also worth noting that the flow rates may produce problems at entry to the DISSUB –there is a physical limit to the velocity with which air may enter and exhaust through a salvage point. A restriction at this point, should be investigated with respect of orifice size and internal layout. This will then have an impact on the system. Although it is possible to increase mass flow rate with pressure, the velocity shall remain constant, the point at which this occurs on a submarine requires understanding ahead of purchasing a system as it may affect internal pressures
-

DISSUB Ventilation

- ANEP-85 couplings & hoses: ø50mm
- ATP 57.1 outlet hose dia. ≥ 50mm
- ATP 57.1 minimum flow rate: 30 liters/min/surv



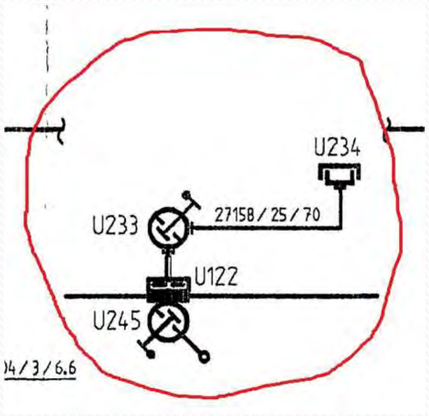
NATO STANDARDIZED CONNECTORS. (TO BE PROVIDED BY DISSUB NATION) FITTED,ON THE OPPOSITE END, EITHER WITH A NATIONAL CONNECTOR OR WITH A PIECE OF HOSE TERMINATING WITH THE NATIONAL CONNECTOR

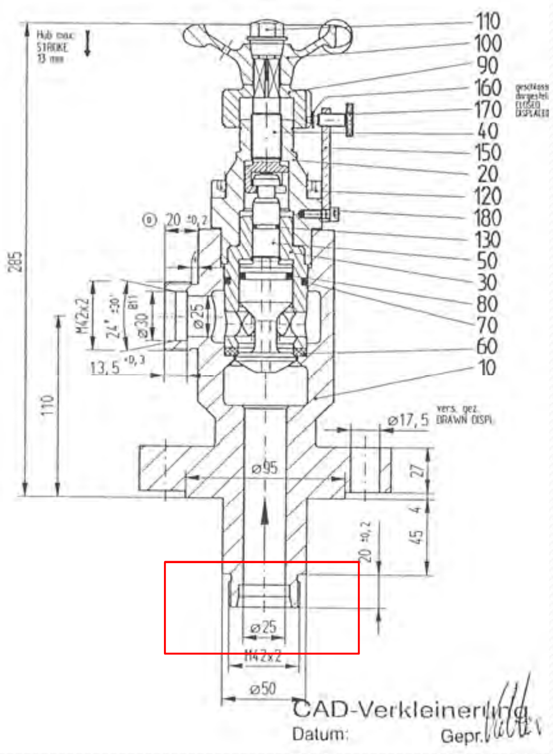
ASSEMBLY POINT

NATO STANDARDIZED CONNECTORS (TO BE AVAILABLE ABOARD OF RESCUE SHIPS/ ASSETS), FITTED TO DELIVERING AIRHOSE/ UMBILICAL.

DISSUB Ventilation

- SM valves for PH blow-off not designed for ventilation
- valves & pipes are ø25





DISSUB Ventilation

- conversion study underway for U214

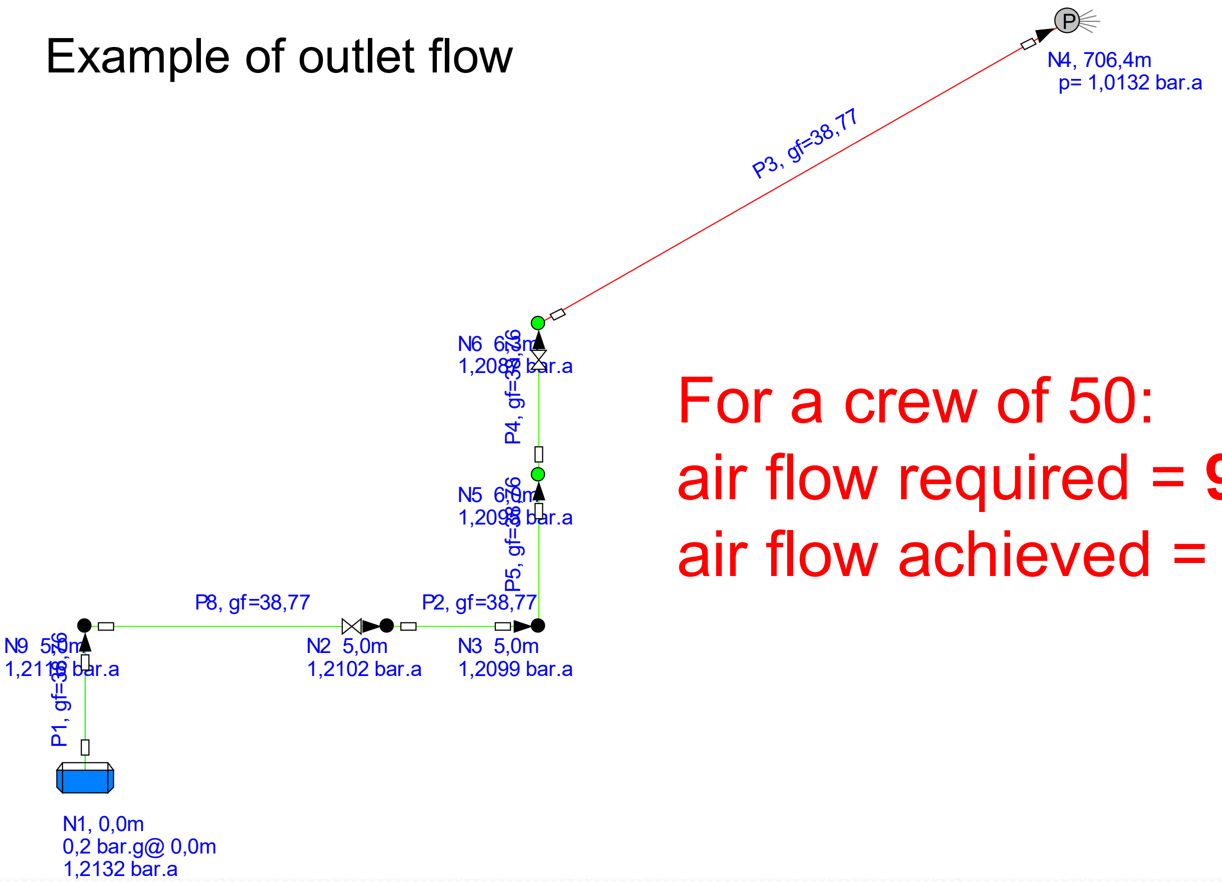
- early findings from compressed-air flow model:

1. air outlet without vacuum suction may prove insufficient, even with full diameter fittings and hoses

2. pressure drop sensitive to DISSUB depth (at deep depths pressure loss due to friction comparable to static head loss)

DISSUB Ventilation

Example of outlet flow



For a crew of 50:

air flow required = **90** m^3/hour

air flow achieved = **38.77** m^3/ho

Transportation

- The system has to be air transportable, and the items specified comply with JADTEU guidelines.
- It is worth noting however that standard 20ft ISO specified size of shipping container disqualifies use of certain common 747 transport planes. These planes have historically been the most readily available means of air mobilisation and form the basis of many designs.
- If a specific set of air transport guidelines or the details of the most readily available air transporter were available, the design may be specifically tailored to this.

Medical Air / Oxygen

- A system capable of introducing oxygen, coupled with ELSS pod posting of LIOH Curtains or similar would offer additional system flexibility at extremes of operation.
- Integration of such facility is a relatively small cost when considering the purchase of a system but adds an additional layer of capability and the ability to extend the habitable environment in certain scenarios.
- A system capable of supplying oxygen must be designed with this in mind at the outset and material and safety considerations applied throughout as standard

Umbilical System Deployment

- The means of deploying the umbilical, requires thoroughly integrated and must be considered as the system develops. Historically this is one of the most challenging aspects when providing a rescue ready DSDVS.
- Regard for factors such as deck handling, splash zone transition, submarine interface, ROV and diver interface and surface ship stability are critical. Whilst a large diameter umbilical facilitates the flow rates, were it also load rated, its stiffness would demand a winch of such dimensions that it would severely limit deployment and mobilisation

Umbilical System Deployment

- Similar systems are deployed utilising a clump weight arrangement. The clump weight is deployed from a dedicated winch using a dedicated line – thereby eliminating the umbilical from the deployment loads. The design of the deployment method and the winch will require careful consideration to isolate elements from the load path. That said, the design of winch system would lend itself to neat integration with a weight deployment winch.
- Over boarding of the umbilical, flying leads and any clump weight can be simplified using dedicated lifting equipment. LARS's used by similar air mobile rescue assets routinely incorporate deployable cranes. This gives the system autonomy and independence from MOSHIP facilities and increases the number of VOOs available for mobilisation

DSVDS Exercises

- Although their are several systems in use with different Navies, knowledge of the working of the systems is minimal
- Every exercise a succesfull coupling of the hoses is performed and when air is flowing the exercise stops
- All these exercises take place at limitted depths while the real challeng is to do it deep
- Also not much thought is given how to deal with partial pressure of oxygen / CO2 and what mixture to supply to the submarine

New Solutions

- An Italian Company , Drass, is busy with a new and revolutionary idea.
- They will bring a pressure tight container to the dissub
- In that container they install two compressors who will take the foul air out of the submarine.
- This way a return hose to the surface is not necessarry
- The system is at the moment being develloped.

Questions ?????

FULL PAPERS

Atmosphere Monitoring – Assessing functional limits of detection

Mr Alan Chapman

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Gosport, Hampshire, PO12 2AG, UK.

Abstract

The UK Ministry of Defence has developed its own regulations for atmosphere control in submarines (BR1326). The UK Health & Safety Executive, and the European Union, continues to drive down chemical exposure limits for Industry and these are published in The Health & Safety Executive UK EH40 guidance document. Submarine Maximum Permissible Concentration (MPC) action levels for atmosphere contaminants must be reviewed when revised evidence of the risk to health of exposure becomes available.

Understanding the Limit of Detection (LoD) and Limit of Quantification (LoQ) achievable by on-board monitoring techniques is particularly important for Royal Navy submarines because continuous MPC action levels are typically lower than Workplace Exposure Limits and consequently are more challenging for monitoring techniques to achieve. Typically the upper limits of detection and quantification are less critical in the submarine environment and these are not addressed in this paper.

A number of alternative methods of assessing the lower operation limit of analytical techniques are routinely used. For direct reading toxic gas monitors sold in Europe this is most commonly performed to EN 45544:2015 [1] whilst retrospective analysis techniques are typically based on the in-house quality requirements of the individual laboratories. Eurachem Method Validation Working Group give guidance on how to determine LoDs and LoQs in their guide, The Fitness for Purpose of Analytical Methods [2]. This paper looks at the process used in both the EN 45544 and Eurachem methodologies and how this affects the confidence in the lower operating limit. It is especially important to use a single methodology for assessing the functional limits of methods when comparing real-time monitoring techniques against retrospective methods to allow a fair unbiased assessment.

1 Introduction

Under its duty of care, the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere. To achieve this, the MoD adopts a rigorous Passive and Active atmosphere control programme which has been discussed in previous SAMAP papers.

The submarine's atmosphere is consistently monitored and controlled within set exposure reference values (detailed in the UK restricted publication BR1326 - Book of Reference for Submarine Atmosphere Control) [3]. These levels are set to ensure that submariner health is not compromised, and so operational capability of the platform is maintained

The UK MoD has for the last twelve years, run a contract with QinetiQ to provide scientific support to atmosphere control under the Maritime Strategic Capability Agreement (MSCA). The contract objective is to assist the UK MoD in providing assured support to critical capabilities. The life support section for Submarine Atmosphere Control, consists of six specialist scientists which assist the MoD in providing scientific support / evaluation, and targeted and underpinning research on atmosphere management techniques. This paper focuses on work on addressing the minimum operational limits of monitoring techniques performed under this contract.

2 Definitions

For the purpose of this paper the Lower Limit of Measurement (U_{zero}) is defined in accordance with EN 45544-1:2015 as *'smallest value of the measured quantity within the measuring range'*. The LoD is defined as the lowest level of an analyte that can be detected, with sufficient confidence, within the sample matrix and LoQ are defined as lowest level of an analyte that can be quantified, with sufficient confidence, within the sample matrix.

3 EN 45544:2015

Most manufacturers of direct reading gas concentration instruments selling instrumentation within Europe validate their equipment to EN 45544-1:2015. As part of this validation process the standard requires the manufacturer to calculate the U_{zero}. This is determined using Equations 1 to 4 from 10 measurements of clean air that is free of the target analyte and any other matrix contaminants.

$$ur_{zero} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})}{n-1}}$$

$Where$
$ur_{zero} = Random\ element\ of\ zero\ uncertainty$
$x_i = Zero\ measurement$
$\bar{x} = Mean\ of\ repeated\ zero\ measurements$

Equation 1

$$unr_{zero} = \sqrt{\left(\frac{\bar{x}}{\sqrt{3}}\right)^2 + \left(\frac{x_{res}}{2 \times \sqrt{3}}\right)^2}$$

$Where$
$unr_{zero} = Non - random\ element\ of\ zero\ uncertainty$
$x_{res} = Resolution\ of\ the\ indicating\ device$

Equation 2

$$u_{zero} = \sqrt{(ur_{zero}{}^2 + unr_{zero}{}^2)}$$

$Where$
$u_{zero} = Total\ zero\ uncertainty$

Equation 3

$$U_{zero} = 2 \times u_{zero}$$

$Where$
$U_{zero} = Lower\ limit\ of\ measurement$

Equation 4

4 Eurachem guidance

The methods for determining the minimum concentrations of a gas contaminant that can be reliably measured by retrospective techniques are more varied. Where the laboratory is working to a national or international standard the process for determining these may be defined within the standard, although the inclusion of this requirement is not uniformly adopted by all standards committees. If the process is not defined in the standard then the test laboratory should be using a documented in-house procedures for calculating the LoD and LoQ as part of their quality system. The Eurachem Guide, The Fitness for Purpose of Analytical Methods [2], is often used as a basis of these in-house procedures and gives clear guidance on assessing a broad range method performance characteristics including techniques for determining the LoD and LoQ. The Eurachem approach requires the repeated measurement of samples that are either analyte free or with an analyte concentration close to the expected limit of determination. These samples are prepared using the normal sample matrix and therefore should contain other contaminants that are routinely present. The Eurachem method recommends the use of 10 replicate readings to calculate an estimated standard deviation s_0' using the formula given in Equations 5 to 9. Once s_0' is determined a coverage factor of 3 is applied to estimate the LoD and a coverage factor of 10 to estimate the LoQ.

$$s_0 = \sqrt{\sum_{i=1}^{m} \frac{(z_i - \bar{z})}{m-1}}$$

Where
s_0 = *Estimated standard deviation of a reading at or near zero concentration*
z_i = *Near zero measurements*
$\bar{z}$ = *Mean of the repeated near zero measurement*
m = *Number of readings taken*

Equation 5

$$s_o' = \frac{s_0}{\sqrt{r}} \text{ when readings are not retrospectively blank corrected during use}$$

$$\left(\text{or } s_o' = \frac{s_0}{\sqrt{\frac{1}{r} + \frac{1}{r_b}}} \text{ when readings are retrospectively blank corrected during use} \right)$$

Where
r = *Number of replicate readings averaged to produce a final result*
r_b = *Number of blank replicate readings averaged to produce a final result*
s_0' = *Standard deviation used for calculating LoD and LoQ*

Equation 6

For instruments where each reading is considered to be independent and no blank correction is applied Equation 6 simplifies to:

$$s_0' = \frac{s_0}{\sqrt{1}} = s_0$$

Equation 7

$$LoD = 3 * s_0'$$

Equation 8

$$LoQ = 10 * s_o'$$

Equation 9

5 Coverage factors

The Eurachem Guide gives a clear explanation of the statistical basis for setting the LoD coverage factor which estimates the point at which there is 95 % confidence that false positive and false negative readings are avoided. These are derived from assigning the critical value where the there is only a 5 % probability of obtaining false positive readings. One tailed, student t test tables give a coverage factor of 1.65. However, as false negative readings are also important an additional coverage factor of 1.65 is required giving a total factor of 3.3 which is normally rounded down to 3 for the LoD. A more rigorous statistical treatment that includes degrees of freedom gives an overall coverage factor of 3.7. There is no equivalent justification given in EN 45544 for the setting of the coverage factor used in determining the U_{zero} value, however, as this uses a smaller coverage factor on the same number of data points the confidence interval will be lower and hence there is a lower certainly that false positive or negative readings are avoided.

6 Portable oxides of nitrogen monitor

QinetiQ was recently tasked by the UK MoD, under the Maritime Strategic Capability Agreement, to perform an in depth assessment of the LoD and LoQ for oxides of nitrogen (NO_x) on a portable Fourier Transform infrared (FTIR) analyser. Some of the nitric oxide (NO) data from this study will be used in the remainder of this paper to highlight the differences in the estimated lower operational limits predicted by the two methods previously discussed and highlight why caution is required with either approach.

This study involved the exposure of the instrument to a series of both in-house and certified NO and (NO_2) gas standards over the 0 – 5 ppm range. Initially exposure standards contained the analyte in nitrogen (N_2) and then sequentially adding water vapour (H_2O), carbon dioxide (CO_2) and 1,1,1,2-tetrafluoroethane (R134a). During each exposure 10 readings were taken to allow the calculation of, U_{zero}, LoD and LoQ under each condition.

Figure 1 show a plot of the calculated s_o results for exposures to NO standards in humidified N_2. The software for the FTIR under evaluation does not permit the reporting of negative readings and therefore towards the lower operation limit the instrument becomes prone to reporting zero. In this figure points coloured blue are the s_o values for datasets that only contained readings >0. Points coloured red are s_o values which have been artificially lowered by the inclusion of zero reading in the data set. Instruments that record both positive and negative results do not show this affect. It is therefore important, when determining the lower operation limit, to understand how the instrument reports results in this region to avoid artificially lowering the predicted detection limits.

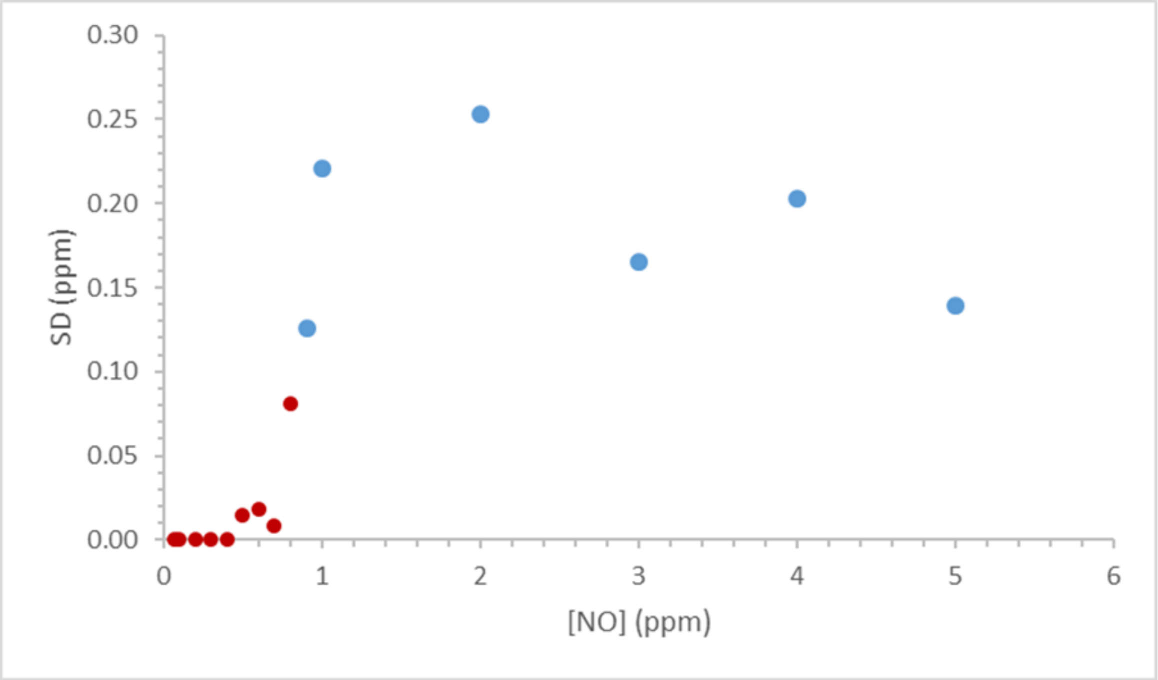

Figure 1: s_o results for NO in N_2 at 50 % relative humidity

Table 1 shows the calculated U_{zero}, LoD and LoQ values. The s_o value produced by exposure to contaminant free N_2 returned 0.00 ppm readings although based on results in Figure 1 it is probable that these results do not reflect the actual variance in the data that would have been observed had the software also reported negative results and therefore the U_{zero}, LoD and LoQ values are probably artificially low. Since the EN 45544:2015 method is only applicable to analyte free measurements there is no data for U_{zero} for the NO test mixtures. The results shown in Table 1 are for the minimum concentration of NO which did not report zero readings to avoid skewing the estimation of LoD and LoQ. It was unclear why the variance in the exposures with humidified N_2 were higher than when additional contaminants were present. This was consistently seen throughout all the humidified NO concentrations challenge gases and may relate to the water correction process used in the instrument processing software. Measuring NO at trace concentrations in humidified gas is always challenging using mid infrared spectroscopy as the NO absorption bands predominantly lie under the water absorption bands. The relative intensity of 50 % relative humidity N_2 and 31 ppm NO are shown in Figure 2.

Challenge gas composition	**s_0 (ppm)**	**U_{zero} (ppm)**	**LoD (ppm)**	**LoQ (ppm)**
N_2	0.00	0.00	0.00	0.00
1 ppm NO in N_2	0.09	N/A	0.27	0.90
1 ppm NO, 50 % RH in N_2	0.22	N/A	0.66	2.20
1 ppm NO & 0.5 % CO_2 in 50 % RH N_2	0.13	N/A	0.39	1.30
2 ppm NO, 0.5 % CO_2 & 25 ppm R134a in 50 % RH N_2	0.08	N/A	0.24	2.40

Table 1 Calculated U_{zero}, LoD and LoQ results for NO

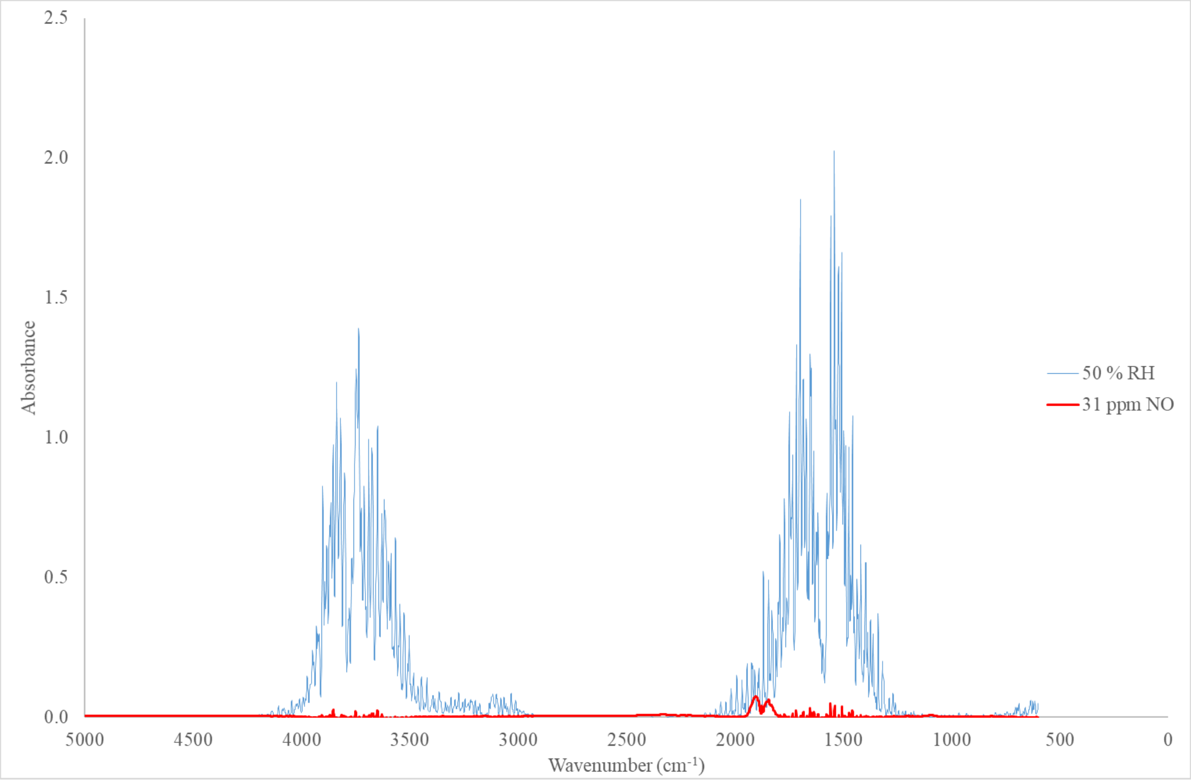

Figure 2 Mid-infrared spectra 31 ppm NO in dry air and 50 % RH N_2

7 Conclusion

Most direct reading toxic gas monitoring equipment sold in Europe state their Lower Limit of Measurements based on EN 45544:2015. This methodology uses the same number of replicates in determining this lower operating limit as the Eurachem methodology but uses a small coverage factor and therefore has a lower degree of confidence for the U_{zero} limit than a Eurachem LoD. This results in lower quoted operating limits which may not reflect the performance of the instrumentation in real world applications.

When performing assessments of the operating limits of a monitoring technique the assessor must be aware of how the instrument processes readings which would be negative values as systems that report these readings as zero artificially lower the calculated operating limits.

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[2] B. Magnusson and U. Örnemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics (2nd Ed. 2014).
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An Evaluation of Monoethanolamine (MEA) degradation and mitigation under the conditions used in submarine carbon dioxide removal plants

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Abstract

The current carbon dioxide (CO_2) removal system on Royal Navy (RN) submarines is based on the amine, monoethanolamine (MEA). This reversibly binds CO_2 under ambient conditions and releases it when heated. However, this amine degrades within the plant yielding hazardous compounds including ammonia (NH_3). In this study laboratory test apparatus was used to evaluate MEA solutions containing a range of inhibitor additives to determine which best suppressed degradation. A series of additional experiments were carried out to optimise the sorbent used to remove reaction adducts and metal impurities from the MEA within the system. These investigations concluded that the existing inhibitor additive was the most appropriate based on performance, cost, and exposure hazard but reduced rates of MEA degradation could be achieved by using alternative sorbent media. The kinetic methodology presented can also be applied to new CO_2 removal technologies including solid amines which also degrade and release NH_3.

1 Introduction

The RN has a duty of care to provide a safe environment for submariners and this includes maintaining a breathable atmosphere with contaminants kept as low as reasonably practicable (ALARP). A key requirement is a removal system that removes CO_2 produced by respiration of the personnel on-board and other activities such as food preparation. The current system achieves this using the reversible absorption and de-absorption of CO_2 from MEA. Like all amine based CO_2 removal technologies this relies on the formation of a stable carbamate. Although CO_2 levels are maintained within acceptable limits the breakdown of MEA within the removal plant results in some NH_3 release to the atmosphere. NH_3 is a hazard to health and its atmospheric concentration is monitored and controlled within action levels.

MEA degrades into organic decomposition products and NH_3. The rate of MEA degradation is dependent on several factors such as temperature, impurities present and CO_2 loading. Figure 1-1 shows the effect of CO_2 loading and temperature on the degradation of MEA that had been stored in a sealed steel container[i].

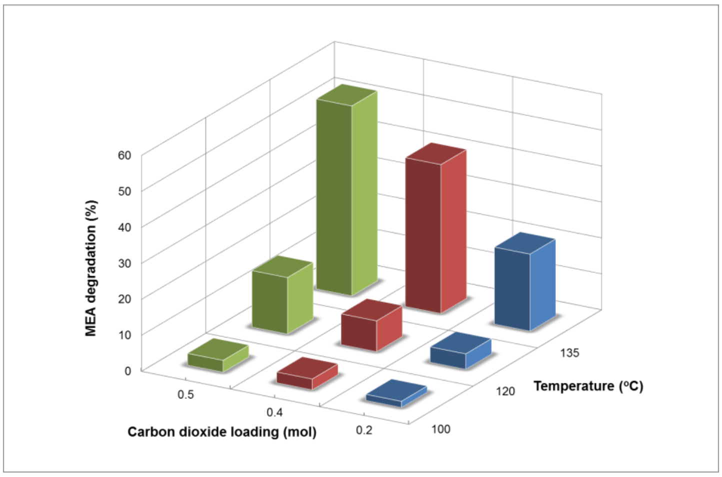

Figure 1-1: The effect of CO_2 loading and temperature on MEA degradation[i]

Previous work conducted by the Admiralty Research Establishment (ARE) suggested that MEA auto-oxidation occurred *via* two routes: air oxidation and irreversible condensation brought about *via* CO_2 adsorption. Numerous complex reaction pathways have been documented that indicate NH_3 can be produced from both the direct breakdown of MEA and the breakdown of other organic reaction products[i,ii,iii].

The use of deionised water to prepare low-ion MEA solution (LIMEA) and the addition of an inhibitor improves the stability of the MEA within the CO_2 removal plants. Additional stability is provided by a filtration systems that removes formed reaction adducts (by-products) from the MEA solution. Periodic replacement of the inhibited MEA solution will maintain as low a rate of MEA breakdown as possible.

MEA degradation is also promoted by metal impurities and formed peroxide species. These react with MEA to produce free radicals which then result in MEA decomposition to organic by-products and NH_3. Peroxides can be produced from organic and inorganic contamination of the LIMEA from the atmosphere. Metal impurities derive from corrosion of the steel used in the construction of the plant. Due to the elevated operating temperature of the CO_2 stripper, corrosion is greatest in this location. Inhibitor additives in the LIMEA mitigate the effect of impurities. Inhibitors suppress degradation by either chelation or reaction to produce non-reactive compounds. Inhibitors can also act as surface passivators which bind to the surface of the steel and retard corrosion.

Some MEA breakdown is inevitable and once formed organic by-products further accelerate the rate of decomposition. An activated charcoal filter is used within the CO_2 removal plant to remove these organic by-products. Alternative filter materials, such as zeolites and ion exchange resins, could remove more reactive by-products and reduce the rate of MEA breakdown.

The aim of the studies presented was to investigate the degradation of MEA under the conditions present within the CO_2 removal plant and assess the ability of both the existing and potential alternative inhibitor additives and filtration sorbents to reduce the rate of MEA breakdown.

2 Experimental

2.1 MEA degradation test apparatus

2.1.1 MEA degradation in the stripper only (static system)

LIMEA solution, either 250 ml or 500 ml of 30 w/w% MEA (4.5 M) was prepared and placed into either a 0.5 dm^3 round bottom flask or a 1 dm^3 flanged flask. The reaction vessel was fitted with a PEEK tubing which sparged the solution with air, a thermometer and a refluxing condenser. Test solutions were prepared using newly purchased MEA and deionised water. As required, pieces of 304 grade stainless steel (Advent Materials), with an exposed surface area of 8 cm^2 for 250 ml experiments or 16 cm^2 for 500 ml experiments, were added to the solution. The ammonia contaminated head-space of the sparged and heated reaction vessel flowed through gas-tight glassware to a round bottom flask containing an ion selective electrode (ISE) and acidified electrolyte (0.1 M copper sulfate and 0.1 M phosphoric acid). The ISE (ELIT 8051) measured the concentration of ammonium ion (NH_4^+) in solution using a NICO 2000 monitor (ELIT 9801), and a lithium acetate reference electrode (ELIT 003). The ISE was calibrated daily using prepared standards containing 1000, 100, 10, 1 and 0.1 ppm of ammonium chloride (NH_4Cl).

2.1.2 MEA degradation in a recirculating simulated CO_2 removal system

Recirculation of the solution allowed MEA filtration, CO_2 absorption and CO_2 de-absorption to occur simultaneously in separate sections of the apparatus (MEA flow shown as black arrows, Figure 2-1). Hot CO_2-lean MEA was extracted from the reaction vessel cooled to 60-80 °C using an external room temperature water bath (not shown), and transferred to the sorbent filter bed. A peristaltic pump circulated the MEA around the apparatus. MEA percolated through the filter and was collected in a dropping funnel. Either 0.5 or 1.0 % CO_2 was bubbled through the absorber at ~1 $dm^3.min^{-1}$. The MEA solution (now CO_2-rich) was returned to the reaction vessel at a rate of 10 - 20 $ml.min^{-1}$.

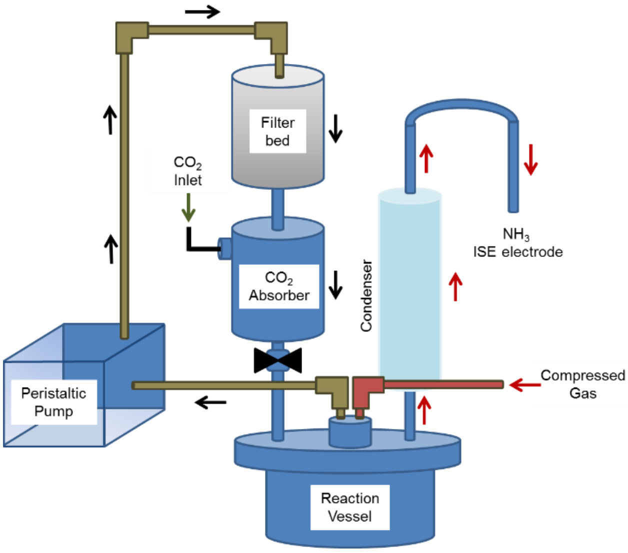

Figure 2-1: Schematic of the laboratory apparatus

2.2 Experimental method, data acquisition and interpretation

At the start of each experiment the ISE was calibrated and allowed to equilibrate for ~10 minutes in the electrolyte. Compressed air (~0.5 $dm^3.min^{-1}$) was used to sparge dissolved NH_3 from the reaction vessel for a further 10 min. In the static experiments, the MEA solution was heated at 5 $^oC.min^{-1}$ until the vapour above the solution reached 94 ±1 ^oC. In recirculating CO_2 removal experiments the peristaltic pump was operated until the reaction vessel contained 350 ml of MEA solution. The reaction vessel was then heated as above. The experiment was run at this temperature for a minimum of 5 h.

Throughout the experiment the ISE recorded the NH_3 concentration in the electrolyte every 10 s. The steady state degradation rate was taken as the average rate of NH_3 release after 10,000 s.

The rate of degradation of MEA is dependent upon the MEA concentration and can be approximated to:

$$Rate\ of\ degradation = k'[MEA]$$

The pseudo rate constant of degradation (k') includes all degradation pathways. Assuming a stoichiometric relationship between MEA breakdown and ammonia release the following equation can be used.

$$[MEA]_t = [MEA]_0 - [NH_3]_t$$

The concentration of MEA at time t ($[MEA]_t$) is given by the initial concentration MEA ($[MEA]_0$) and the emission of ammonia at time t, $[NH_3]_t$. The degradation rate constant k' was obtained from the gradient of a plot of In($[MEA]_0$-$[NH_3]_t$) vs. time.

2.3 Inhibitor tests

Performance testing of seven inhibitor additives was carried out. Inhibitors were added to the prepared LIMEA solution prior to heating. All were purchased from Sigma-Aldrich and were analytical grade. The chemical functionality of each additive tested is shown in Table 2-1.

Inhibitor	Chemical functionality
1	Alcohol, carboxylic acid
2	Sulfoxide, amide, aromatic
3	Alcohol, pyridine-like
4	Pyridine-like, thioether
5	Azo, secondary amine, aromatic
6	Secondary amine, sulfoxide
7	Alcohol, ester

Table 2-1: Inhibitor functionality

2.4 Sorbent filter material tests

Seven commercially available sorbent materials were purchased and evaluated (Table 2-2). Each sorbent was weighed and made into a packed-bed retained by glass wool in a condensing tube. Sorbent 1, was the activated charcoal used currently in RN CO_2 removal plants and provided a baseline against which to compare the alternative materials.

The MEA test solutions contained either 20 mM or 200 mM of Inhibitor 1. The lower inhibitor concentration reduced MEA degradation suppression and enabled the relative effectiveness of the filter to be determined.

Sorbent	Description
Sorbent 1	Activated carbon (Granular)
Sorbent 2	Activated carbon (Pellet)
Sorbent 3	NH_3 enhanced functionalised activated carbon (Pellet)
Sorbent 4	Zeolite
Sorbent 5	Porous resin for cation & anion ion exchange
Sorbent 6	Cation ion exchange resin (strong)
Sorbent 7	Cation ion exchange resin (weak)

Table 2-2: Sorbent material functionality

3 Results & Discussion

3.1 MEA degradation – 250 ml sample

Initial experiments were conducted with 250 ml of LIMEA in a static system. The degradation of 4.5 M MEA without an inhibitor was determined as a baseline experiment. Degradation is likely to be Arrhenius dependant and therefore temperature would have an exponential effect on the reaction rate[iv]. Degradation of MEA primarily occurred at elevated temperature under CO_2 stripping conditions (> 100 °C).

Throughout the experiment NH_3 produced by MEA breakdown was captured by the acid scrubber in real-time. The acidified scrubbing solution protonates the NH_3 converting it to the ammonium ion, which was then measured by the ISE.

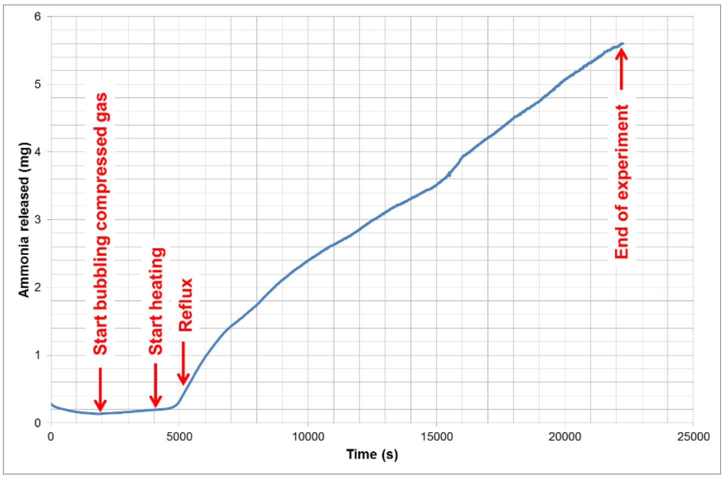

Figure 3-1: NH_3 release from 4.5 M MEA solution during an experiment

Figure 3-1 shows a typical plot of the NH_3 released during an experiment. At time = 0 s the apparatus was charged with the MEA solution and the ISE was switched on. The system was allowed to stabilise, then the bubbler was started. The introduction of compressed gas caused a small rise in the ISE reading as dissolved NH_3 from the auto-oxidation of MEA during storage volatised. The MEA solution was heated until the system was refluxing, causing an increase in release of NH_3. This experiment was repeated and the overall average rate of NH_3 release was 3.47 x 10^{-4} mg.s^{-1}. This corresponds to a rate constant of degradation of 1.64 x 10^{-8} s^{-1} which was comparable with literature values (ca. 10^{-8}–10^{-6} s^{-1})[v].

3.2 Inhibitor additives

A range of degradation inhibitor additives were tested. These included aromatic compounds that are efficient radical quenchers and compounds with hydroxyl and amine functional groups which bond with metal surfaces and dissolved metal ions. The results of inhibitor evaluation experiments are shown in Figure 3-2 and Table 3-1. The best performing additives were Inhibitor 1 and Inhibitor 4 which had the lowest calculated rate constants of degradation ca. < 6.5 x 10^{-9} s^{-1}.

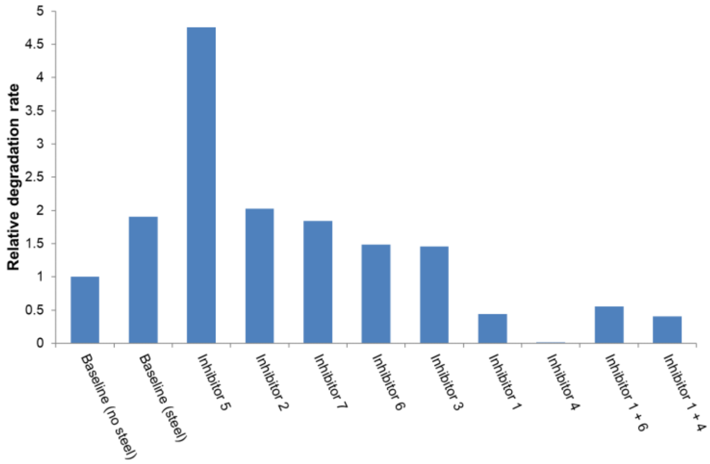

Figure 3-2: Relative degradation rates in the presence of steel and inhibitors

Experiment	Inhibitor	Test solution composition		k' ($x10^{-8}$ s^{-1})
		MEA (M)	Inhibitor Concentration (mM)	
Test 1 – Baseline (no steel)	None	4.5	0	1.64
Test 2 – Baseline (steel)	None		0	3.85
Test 3	Inhibitor 5		200	7.76
Test 4	Inhibitor 2		200	3.42
Test 5	Inhibitor 7		200	2.95
Test 6	Inhibitor 6		200	2.51
Test 7	Inhibitor 3		100	2.48
Test 8	Inhibitor 1		200	0.65
Test 9	Inhibitor 4		100	0.02
Test 10	Inhibitor 1 + 6		200 (Inhibitor 1) 200 (Inhibitor 6)	0.89
Test 11	Inhibitor 1 + 4		200 (Inhibitor 1) 0.02 (Inhibitor 4)	0.61

Table 3-1: Inhibitor experiment test matrix

3.3 MEA with inhibitor additives degradation – 500 ml samples

Additional dynamic testing was carried out using larger volume samples (ca. 500 ml), containing Inhibitor 1 and Inhibitor 4. The results of these experiments are shown in the Table 3-2.

Experiment	Inhibitor	Test solution composition		k' ($x10^{-8}$ s^{-1})
		MEA (M)	Inhibitor Concentration (mM)	
Test 12	None	4.5	0	4.74
Test 13a	Inhibitor 1		2	4.08
Test 13b			20	2.15
Test 13c			200	0.13
Test 14a	Inhibitor 4		2	0.65
Test 14b			20	0.15

Table 3-2: Effect of Inhibitor 1 and Inhibitor 4 on MEA degradation rate constant (k')

In Test 12(no inhibitor) a degradation rate constant of 4.74 x 10^{-8} s^{-1} was found. In Tests 13a-13c the degradation rate constant decreased as the concentration of Inhibitor 1 was increased. The rate constant of degradation with 20 mM Inhibitor 4 (Test 14b) was comparable to that with 200 mM Inhibitor 1 (Test 13c), indicating Inhibitor 4 was approximately ten times more effective at reducing MEA degradation. Unfortunately exposure to Inhibitor 4 is more hazardous to health than exposure to Inhibitor 1.

3.4 The effect of CO_2

The effect of CO_2 on MEA breakdown rates was investigated in the absence of filtration or added steel pieces. In Test 15a, no CO_2 was introduced, Test 15c had an inlet CO_2 concentration of 0.5 % and Test 9 had a CO_2 concentration of 1.0 %. The results in Table 3-3 show a small decrease in k' as the inlet CO_2 concentration increased. Over the short duration of these tests the effect of CO_2 on degradation was not significant.

Experiment	Test solution composition		CO_2 (%)	k' ($x10^{-8}$ s^{-1})
	MEA (M)	Inhibitor 1 (mM)		
Test 15a	4.5	200	0	0.06
Test 15b			0.5	0.04
Test 15c			1.0	0.02

Table 3-3: Effect of CO_2 on the MEA degradation rate constant (k')

3.5 Effect of filter media on MEA degradation

3.5.1 Different amounts of Sorbent 1 and Inhibitor 1

Experiments were carried out with both CO_2 and steel pieces (ca. 16 cm^2) present in the recirculation system. Test 16a (without filtration) had a k' of 0.96 x 10^{-8} s^{-1} and this increased to 1.01 x 10^{-8} s^{-1} in Test 16b when 0.5 % CO_2 was bubbled into the absorber. Both degradation rates were more than ten times greater than in equivalent experiments not containing steel pieces. Tests 16c-16f were carried out using increasing amounts of Sorbent 1 (0.2-10 g), with Test 16f using the MEA used in previous tests therefore showing the increase in degradation with aged MEA. During these experiments filtration of the MEA solution had no beneficial impact on degradation rates which increased from 3.16 to 6.55 x 10^{-8} s^{-1}.

Experiment	Test solution composition		CO_2 (%)	Sorbent 1 (g)	k' (x 10^{-8} s^{-1})
	MEA (M)	Inhibitor 1 (mM)			
Test 16a	4.5	200	0	0	0.96
Test 16b			0.5	0	1.01
Test 16c			0.5	0.2	3.16
Test 16d			0.5	2	4.31
Test 16e			0.5	10	6.55
Test 16f			0.5	0	6.67

Table 3-4: Effect of carbon filter

3.5.2 Sorbent 1 and Inhibitor 4

During recirculation experiments with Inhibitor 4 this additive precipitated in the colder parts of the test apparatus, *i.e.* the peristaltic pump and sorbent filter, causing flow problems. A sulfurous odour also was produced during this experiment which could indicate breakdown of the inhibitor. Due to these difficulties and the greater toxicity of this additive it is not considered suitable for use in submarine CO_2 removal plants.

3.5.3 Sorbent screening experiments using MEA containing Inhibitor 1

Several filtration sorbents were tested, Table 3-5 shows the experimental conditions used and the calculated MEA degradation rate constants (k'). Apart from Sorbent 2 and Sorbent 3 all sorbents had a lower k' than Sorbent 1 with 20 mM of Inhibitor 1. During Test 22 flow problems were encountered as the polymer sorbent expanded upon contact with the MEA solution. This experiment was repeated using less mass of Sorbent 7 to mitigate this problem. However at the end of this experiment the MEA solution had become turbid probably due to resin dissolution.

At 200 mM Inhibitor 1 experiments; Sorbent 2, Sorbent 5 and Sorbent 6 suppressed degradation and gave rise to lower k' than Sorbent 1. Sorbent 6 was the best at suppressing degradation with a measured rate constant of degradation of 4.2 x 10^{-9} s^{-1} (Test 22b).

Experiment	Test solution composition		Filter bed		k' $\times 10^{-8}(s^{-1})$
	MEA (M)	Inhibitor 1 (mM)	Sorbent	Mass (g)	
Test 17	4.5	20	-	-	0.89
Test 18a		20	Sorbent 1	10	1.23
Test 18b		200			1.16
Test 19a		20	Sorbent 2		2.51
Test 19b		200			0.91
Test 20a		20	Sorbent 3		2.15
Test 20b		200			1.52
Test 21a		20	Sorbent 5		0.60
Test 21b		200			0.74
Test 22a		20	Sorbent 6		1.15
Test 22b		200			0.42
Test 23a		20	Sorbent 7		0.78
Test 23b		20		2	1.35

Table 3-5: Single sorbent tests

Additional experiments were undertaken using combinations of activated charcoal and a second sorbent. The purpose of these experiments was to determine whether it was possible to achieve a synergistic effect with two materials. Carbonaceous adsorbents predominantly adsorb organic compounds, ion exchange resins mainly retain ionic species and zeolites are general adsorbents. Each experiment was carried out with Inhibitor 1, CO_2 and steel present. Dual adsorbent filter beds contained Sorbent 2 plus either Sorbent 5, Sorbent 6, Sorbent 7 or Sorbent 4. Due to its pelletised physical form, Sorbent 2 packed inefficiently creating voids that were filled with the second sorbent. This was particularly advantageous for Sorbent 7 which swelled and Sorbent 4 which was prone to caking. Table 3-6 gives the degradation rate constants for each of the five dual adsorbent filter beds tested.

Experiment	Test solution composition		Filter bed		k' $(\times 10^{-8}\ s^{-1})$
	MEA (M)	Inhibitor 1 (mM)	Sorbents	Mass (g)	
Test 24a	4.5	20	Sorbent 2 |Sorbent 5	5 | 5	1.88
Test 24b		200			4.78
Test 25a	4.5	20	Sorbent 2 |Sorbent 5	10 | 10	3.23
Test 25b		200			2.04
Test 26a	4.5	20	Sorbent 2 |Sorbent 6	5 | 5	3.50
Test 26b		200			0.45
Test 27a	4.5	20	Sorbent 2 |Sorbent 7	5 | 2	1.41
Test27b		200			0.27
Test 28a	4.5	20	Sorbent 2 |Sorbent 4	5 | 2	1.91
Test 28b		200			0.52

Table 3-6: Dual-bed sorbent tests

The worst performing dual adsorbent filter was sorbent 2 | sorbent 5 with a maximum degradation of $4.78 \times 10^{-8}\ s^{-1}$ in test 24b. With 20 mM of Inhibitor 1 all dual adsorbent beds had greater degradation than Sorbent 1 alone. However, with 200 mM of Inhibitor, Sorbent 2 |Sorbent 6, Sorbent 2 |Sorbent 7 and Sorbent 2 |Sorbent 4 suppressed degradation and performed better than Sorbent 1 alone. The best sorbent filter was Sorbent 2 |Sorbent 7 which suppressed the degradation of MEA to $2.7 \times 10^{-9}\ s^{-1}$ (Test 27b).

4 Conclusions

Investigations found that the currently used additive, Inhibitor 1, was the most appropriate of those tested when both performance and toxicity were considered. Some alternative sorbents outperformed the current used sorbent (sorbent 1) in a single-bed system. A dual-bed MEA filter containing two complimentary functionalities and forms, *i.e.* activated charcoal and ion exchange resin, had the lowest degradation rates measured.

Degradation of MEA was found to be dependent on all factors investigated. The concentration of the inhibitor additive had the greatest impact on MEA degradation with the sorbent filter media and CO_2 presence having an approximately equal but lesser effect.

Future investigations will focus on alternative dual-bed filters and identifying factors that affect longer-term degradation rates.

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EXPOSURE TO DIESEL EXHAUST EMISSIONS: IRRITANTS

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Introduction

Engine exhaust emissions are amongst the most complex and most extensively studied air pollutants. They are the most problematic air contaminants in diesel-powered submarines. The two major sources being fugitive engine emissions and re-entrainment of the engine exhaust through the snorkel, commonly referred to by submariners as “getting your own back”. Other military platforms such as tanks, armoured personnel carriers, transport vehicles, fixed wing aircraft and helicopters also operate under conditions where personnel may be routinely and directly exposed to engine exhaust emissions.

Over the years various components of diesel exhaust have been singled out for their toxicity. Carbon monoxide was initially identified as the most toxic component and first subject to monitoring on a RN submarine in 1947 (Ellis) with the exclusion of the other exhaust components of lesser known toxicity at the time. With the growing use in commercial and private road vehicles in the post-war period, other exhaust components were targeted for their toxicity.

In 1974 the US Environment Protection Agency (EPA) introduced emission standards for heavy-duty diesel engines which included carbon monoxide and nitrogen oxides in combination with hydrocarbons under the Clean Air Act of 1970. Subsequently, in 1985, separate emission limits were introduced for nitrogen oxides and hydrocarbons and in 1988 diesel particulate emission limits were added (EPA, 2002).

During the same period, diesel exhaust emissions of aldehydes were reported causing acute lachrymatory health effects at low concentration such as 1 -3 ppm (Cernansky 1983, Nightingale et al. 2000). In `1991 the Californian Low Emission Vehicle (LEV) standards, were introduced through the Clean Air Act Amendments (CAAA) of 1990, which addressed emissions of formaldehyde in addition to the above emissions for both petrol and diesel-powered vehicles (CARB, 2016). Although the LEV controls on formaldehyde exhaust emissions for vehicles have been maintained (CARB, 2016), aldehyde exhaust emissions have been consistently omitted from the European Union (EU) vehicle exhaust emission regulations (DieselNet 2019a).

The aim of this paper is to review aldehyde emissions from internal combustion engines and their potential acute health effects within a military occupational environment and in the context of commonly regulated emissions such as particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbon emissions and to suggest a strategy for monitoring aldehydes.

Current Combustion Engine Exhaust Emission Controls

US Federal and US EPA emission standards for passenger cars and light duty trucks, Tier 1 standards were introduced from 1991 to 1994 and covered PM (diesel engines only), CO, NO_x, total hydrocarbons (THC) and non-methane hydrocarbons (NMHC) (DieselNet 2019b). These were replaced by Tier 2 regulations over the period 2004 to 2009 and later by Tier 3, standards which were signed in law in 2014. Tier 3 regulations are closely aligned with Californian LEV III standards and include emission controls on formaldehyde (DieselNet 2019c).

EU diesel and petrol engine emission standards for passenger cars, Euro 6, apply to CO, HCs, NO_x and PM but do not include aldehydes (DieselNet 2019c). Similarly, for locomotive engines, EU Stage V, which bear the closest resemblance to submarine engines.

Diesel Exhaust Emissions Monitoring for Occupational Exposure

Many of the new regulations for occupational exposure to diesel exhaust have been prompted by exposures in underground mining where diesel-powered equipment is operated in confined spaces. Here the recent focus has been largely on diesel particulate matter (DPM) in addition to the long-standing hazards of CO_2, CO, NO_x and SO_2 as well as the recognition of hydrocarbon and aldehyde emissions (DMP 2013, MSHA 2016, Maximilien et al. 2017). In addition to US Federal regulations, some US state authorities have also regulated CO, NO_x and DPM exposures from diesel engine exhaust in underground coal mines (MSHA 2016) following exposure surveys of miners (Stewart et al. 2010, Coble et al. 2010). Likewise, vehicular exhaust exposure monitoring has concentrated on PM, CO and NO_x (Maximilien et al. 2016).

The UK, Health and safety Executive (HSE 2012) has recognised the hazardous nature of formaldehyde in engine exhaust emissions and has recommended avoidance of exposure to engine exhaust where possible, or at least, has advocated the control of such exposures. To this end carbon dioxide has been proposed as a conveniently monitored surrogate for diesel exhaust exposure and risk assessment in the work place in addition to visual assessment of smoke and soot together with a subjective assessment of irritancy.

The need to monitor aldehydes may have been reduced in priority over time, since it has been claimed that significant progress has been made in reducing the exhaust emissions of aldehydes (formaldehyde and acetaldehyde). This has been supported by comparing emission data from heavy diesel engines using 2004 and 2007 technologies (Liu et al. 2010, Khalek et al. 2011). A study published in 2001 (Lloyd and Cackette) showed that low volatile carbonyls had, at the time, constituted the largest fraction of gas-phase organic compounds emitted from a medium-duty diesel truck engine with acetaldehyde and formaldehyde predominating.

Aldehyde Emissions from Engine Exhausts

While aldehyde emissions from engine exhausts may have declined with advanced engine management technology in modern, well-maintained engines, because of the nature of the combustion process, the operating conditions of the engines and engine wear, aldehyde emissions can still be problematic. For example, controlled human exposure chamber studies of diluted exhaust emissions from a Volkswagen Passat diesel car engine, 81 kW in idle mode, measured formaldehyde at 0.40 mg m^{-3} (0.33 ppm) and acetaldehyde at 0.20 $mg.m^{-3}$ (0.1 ppm) (Xu et al. 2013, Wierbicka et al. 2014). By comparison the NO_x concentration was 1.3 ppm (8h avg.) and DPM (< 1 µm dia.) averaged ~300 $\mu g.m^{-3}$. The authors concluded that throat and eye irritations were primarily due to aldehydes, consistent with previous findings (Ceransky 1983, Rudell et al. 1996).

Formaldehyde has been previously shown to produce these symptoms at concentrations in the range 0.16 – 0.54 m gm^{-3} (0.13 – 0.44 ppm) both from exhaust exposure studies (Rudell et al. 1994; Wilhelmsson et al. 1992); and as formaldehyde alone, where the minimal eye irritation was reported at 0.4 - 0.6 mg m^{-3} (0.3 - 0.5 ppm) for daily 4 h exposures (Lang 2008). In addition to formaldehyde and acetaldehyde, acrolein is also known to be present in diesel engine exhaust (Ceransky 1983) and has been reported to cause eye irritation at a concentration of 0.2 mg m^{-3} (0.1 ppm) (Dwivedi et al. 2015).

Sawant et al. (2008) carried out controlled human exposure trials where the concentration of diesel exhaust was adjusted to 100 µg.m^{-3} DPM, using an International 444E, 7.27 L turbo-charged V-8 diesel engine. At this dilution formaldehyde, acetaldehyde and acrolein were measured at 0.053 – 0.074 mg.m^{-3} (0.043 – 0.060 ppm), 0.020 – 0.028 mg.m^{-3} (0.011 – 0.016 ppm) and 0.0009 – 0.0043 mg.m^{-3} (0.0004 – 0.002 ppm) respectively. After exposure for 2 h, no adverse effects were observed in terms of loss of lung function for the 11 subjects including 7 asthmatics however, symptoms of nasal and eye irritation was not investigated.

In terms of exposure limits, the American Conference of Occupational Hygienists (ACGIH 2017) has established a Short-Term Exposure Limit (STEL) of 0.36 mg.m^{-3} (0.3 ppm) and an 8 h Threshold Limit Value – Time-Weighted Average (TLV-TWA) of 0.12 mg.m^{-3} (0.1 ppm) for formaldehyde which are consistent with earlier sensory response findings (*vide supra*). Currently the ACGIH maximum occupational exposure limit (TLV-ceiling) for acetaldehyde is 45 mg.m^{-3} (25 ppm) and for acrolein it is 0.23 mg.m^{-3} (0.1 ppm). Hence on the basis of the exhaust exposure concentrations reported above, formaldehyde and acrolein are most likely to be major gaseous irritants in engine exhaust emissions.

In addition to the acute sensory effects, the three aldehydes also exhibit chronic health effects. Formaldehyde was initially classified as a probable carcinogen by the US EPA (1987) under conditions of prolonged exposure or high concentrations. In 2004, the International Agency for Cancer (IARC) classified formaldehyde as a carcinogen to humans (IARC 2004). The National Institute for Occupational Safety and Health (NIOSH) has recommended that acetaldehyde be considered as a potential carcinogen while the evidence for the carcinogenicity of acrolein is incomplete (NIOSH 2020) although it has been reported that acrolein causes DNA damage and inhibits DNA repair (Wang et al. 2012).

As for the other gaseous emissions from engine exhaust, human sensitivity to nitrogen dioxide is considerably greater that of carbon monoxide and comparable to formaldehyde and acrolein, for example, the CO TLV-TWA (ACGIH 2019) is 25 ppm (29 mg m^{-3}) while the NO_2 TLV-TWA (ACGIH 2019) is 0.4 mg m^{-3} (0.2 ppm). Carbon monoxide is odourless but humans can detect the odour of NO_2 at low concentrations. Earlier studies found that at a NO_2 concentration of 0.23 mg. m^{-3} (0.12 ppm), 3 of 9 subjects perceived the odour immediately, and 8 of 13 detected a threshold concentration of 0.41 mg.m^{-3} (0.22 ppm) (Henschler et al. 1960). At a higher concentration, 0.79 mg. m^{-3} (0.42 ppm), 8 of 8 subjects recognized the odour (Henschler et al. 1960). Feldman (1974) reported that 26 of 28 subjects perceived NO_2 odour at concentrations of 0.2 mg.m^{-3} (0.11 ppm). At slightly higher concentrations, 0.9 to 8 mg.m^{-3} (0.5 to 4 ppm), a study by Kerr et al (1978, 1979) found that some asthmatics experienced slight burning of the eyes sensation, slight headache and tightness of the chest after exposure for 2 h. Thus the no-adverse-effect level (NOEL) for short-term exposure is considered to be 0.94 mg.m^{-3} (0.5 ppm) (NRC 2012) while the occupational TLV-TWA has been set at 0.37 mg.m^{-3} (0.2 ppm) (ACGIH 2019).

Although a plethora of hydrocarbons have been reported in diesel exhaust emissions, the health effects of these compounds are not immediate, at the concentrations found in the exhaust emissions, but are mostly chronic particularly in the case of aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs), although the more volatile hydrocarbons may contribute to the exhaust odour (Khalek et al. 2011).

Conditions for the Generation of Aldehyde Emissions.

Studies of carbonyl exhaust emissions from diesel engines published in 1962 (Linell and Scott) indicate that peak concentrations of formaldehyde and acrolein are generated at high engine loads and high engine speeds and also at high loads and low engine speeds (Figs. 1a, 1b). To a lesser extent, idling speeds, with no load, are also likely to generate elevated formaldehyde and acrolein concentrations compared to average operating conditions. Understandably, engine combustion appears to be optimised for mid-range engine speeds and loads representing typical operating conditions.

Carbonyl emissions from a more modern engine (Pang et al. 2006) also show elevated carbonyl concentrations at both low and high engine loads but the effects are less pronounced compared with the older engine (Fig.2). Thus there is considerable variability in the data, for example Figure 2b shows an anomalous behaviour in formaldehyde concentrations compared with the other carbonyl compounds. In this case, formaldehyde concentrations decline at engine speeds >1600 rpm whereas the other carbonyl concentrations have increased in concentration. Variations in exhaust emissions, including formaldehyde, have been observed from engine to engine with respect to engine load and speed (Chin et al. 2012) making it difficult to predict conditions for maximum aldehyde emissions with certainty.

In terms of occupational exposure, engine idling conditions are more likely to be problematic when the vehicle is stationary and there is little exhaust dilution from airflow compared with high engine loads when the vehicle is in motion. In the case of submarine and generator engines however, the diesel engines are operated at constant speed and constant load. Here, engine starts are most likely to generate emissions due to partially combusted fuel before stable operating conditions are achieved. The submarine situation is unique in that engines cause two problems, fugitive emissions into the engine room and exhaust entrainment through the snorkel into the submarine ventilation system.

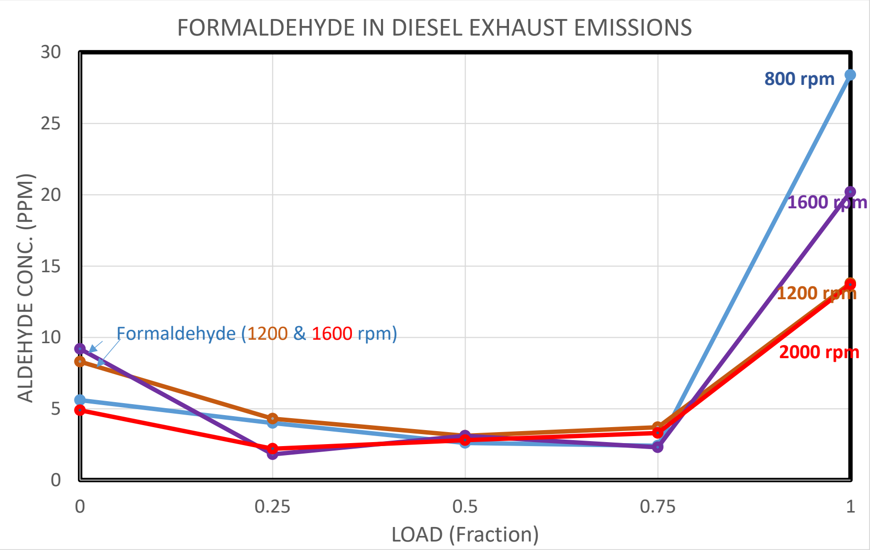

Figure 1a. Formaldehyde emissions from diesel exhaust dependence on engine speed and engine load (Linell and Scott 1962), 7 L, 6 cylinder engine.

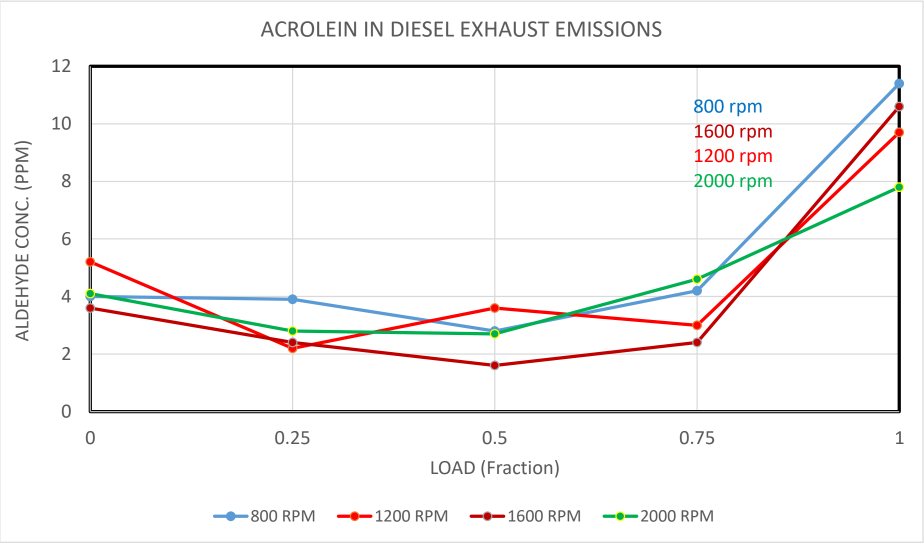

Figure 1b. Acrolein emissions from diesel exhaust dependence on engine speed and engine load (Linell and Scott 1962), 7 L, 6 cylinder engine.

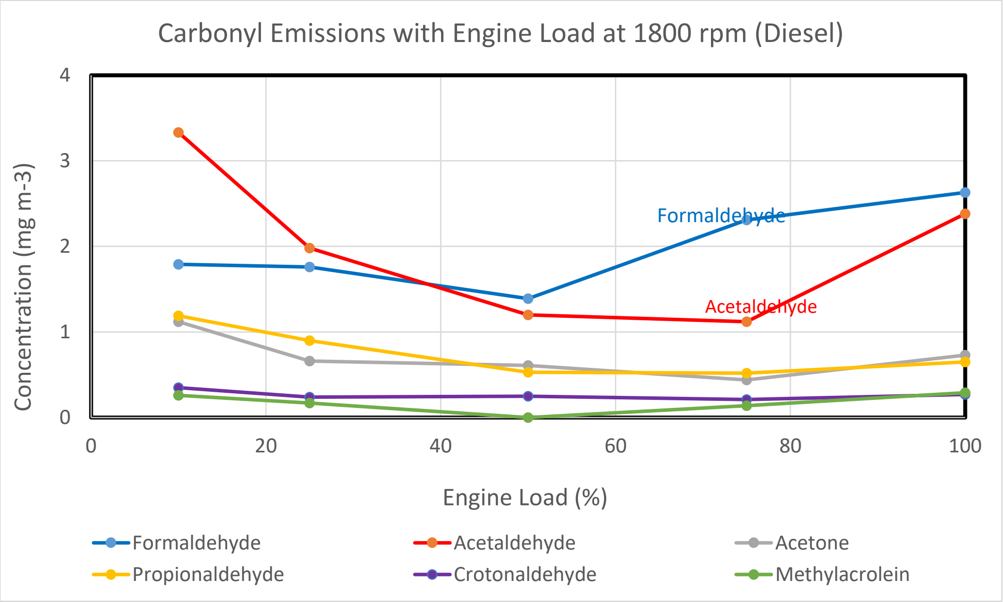

Figure 2a. Diesel exhaust carbonyl emissions at various loads and constant engine speed of 1800 rpm for a Commins-4B diesel engine 4 cyl, 3.9 L, 105 – 140 hp (Pang et al 2006).

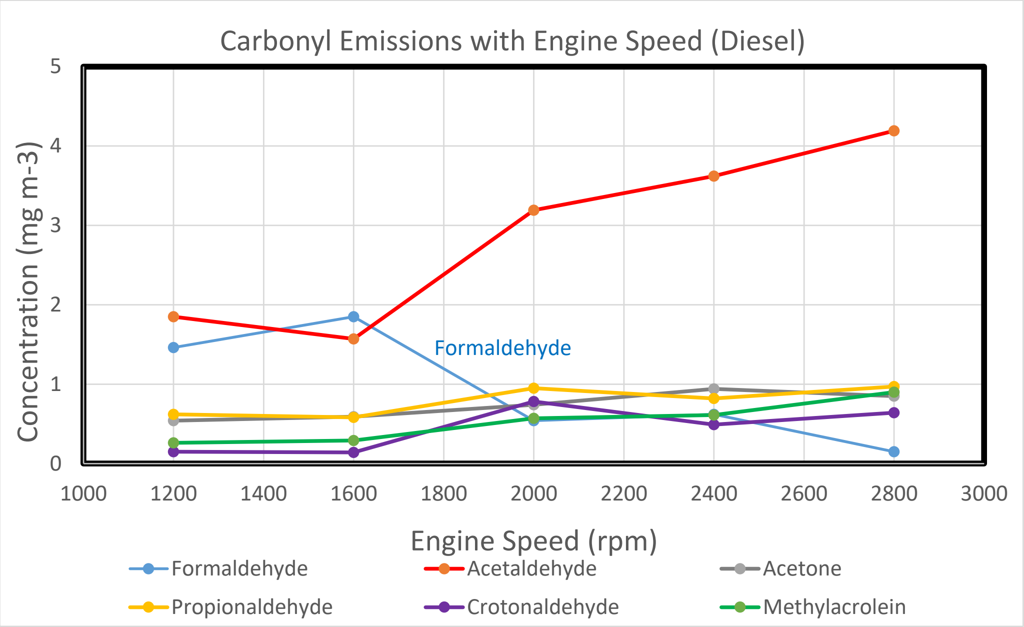

Figure 2b. Diesel exhaust carbonyl emissions at a constant full load and varying engine speeds for a Commins-4B diesel engine 4 cyl, 3.9 L, 105 – 140 hp (Pang et al 2006).

In addition, some studies have claimed that gasoline bio-fuels tend to produce higher acetaldehyde emissions than hydrocarbon based fuels but only when they contain ethanol whereas formaldehyde emissions tend to be lower for bio-diesel, which do not contain ethanol (Pang et al. 2006, Chin et al. 2012). It has been widely accepted that ethanol contributes to acetaldehyde formation while aliphatic hydrocarbons contribute to formaldehyde formation. (Pang et al. 2006, Chin et al. 2012). Zarante et al. (2010) found no difference in formaldehyde and acetaldehyde emissions between hydrocarbon and bio-diesel containing up to 35 percent castor oil fatty acid methyl esters[#] in hydrocarbon diesel fuel while Liu et al. (2009) found 3-6 fold increases in formaldehyde and acrolein with increasing palm oil fatty acid methyl ester content from 0 – 100 percent. However, there was no consistent increase in acetaldehyde emissions with increasing methyl ester content.

Monitoring and analysis of aldehyde emissions from engine exhausts.

Due to the reactive nature of low molecular weight aldehydes (eg. formaldehyde, acetaldehyde and acrolein), traditional gas sampling techniques such as sorbent tubes, polyester (Tedlar®) bags and stainless steel passivated (SUMA) canisters are not ideally suited. The gold standard for this appears to be derivatisation with 2,4-dinitrophenyl hydrazine (DNPH) in the form of a solution (eg. 20 ml) added to a Tedlar bag containing a sample of exhaust gas (eg.10 l) (Roy 2007) or on a substrate in pre-prepared cartridges eg. Waters DNPH coated cartridges, Sep-Pak® DNPH-Silica (WAT 037500) (Benvenuti 2007, CPCB 2010). The DNPH forms a stable, non-volatile hydrazone with the aldehydes, in a quantitative reaction, which can later be extracted with acetonitrile and analysed by high performance liquid chromatography (HPLC) using an ultraviolet detector (CPCB 2010).

[#] *Vegetable oil based bio-fuels are derive from the transesterification of the vegetable oil producing a more volatile product in the form of fatty acid methyl (or ethyl) esters (Keera et al. 2011).*

Strategy for monitoring aldehyde emissions.

Many of the significant engine exhaust emissions can be monitored in real-time, for example DPM, hydrocarbons, CO_2, CO and NO_x. Aldehydes, such as formaldehyde, acetaldehyde and acrolein require a more complex sampling and retrospective analytical procedure. Hence, if NO_x concentrations appear to be below the NOEL and exposed personnel are reporting nasal and eye irritations, the presence of the above 3 aldehydes should be investigated, particularly if old engines are involved and these effects are experienced at idling speeds or under high load conditions.

Conclusions

The first indication of occupational exposure to aldehydes from engine exhaust emissions are manifested as irritation to the eyes. It is most likely to occur with an old engine at idling speed and higher speeds under heavy load conditions. Under these circumstances it may be prudent to monitor formaldehyde, acetaldehyde and acrolein in addition to the usual emissions such as hydrocarbons, CO, NO_x and DPM. Addressing such acute effects is of paramount importance as these symptoms may impact on the performance and safety of personnel.

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Volatile Organic Compounds (VOC) interaction with high and low temperature carbon monoxide/hydrogen oxidation catalysts

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Abstract

Under its duty of care the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere. A key component in this is the high-temperature carbon monoxide (CO)/hydrogen (H_2) burner. This employs a bed of Moleculite®, a copper oxide/manganese dioxide oxidation catalyst at elevated temperature. Although the primary function of the burner is the removal of H_2 and CO an important secondary role is the removal of Volatile Organic Compounds (VOC). This paper presents the finding of an investigation to determine the removal performance of Moleculite® for several submarine atmosphere VOC. Removal of between 61 and 76 % total VOC content was found, suggesting that the CO/H_2 burner has a significant impact on the level of atmospheric VOC. Whilst Moleculite® has been the catalyst of choice for many years, other materials which operate at lower temperatures are of growing interest. Use of these alternatives would provide significant power savings. Low-temperature catalysts have the potential to be poisoned by submarine atmosphere contaminants. The laboratory evaluation of two Johnson-Matthey precious metal catalysts is reported. Results showed that VOC had only a minimal effect on CO and H_2 oxidation performance and that these catalysts had an average VOC removal of 78.5 %. Low-temperature catalysts have potential to replace the currently used high-temperature catalyst with no adverse effect on either CO/H_2 or VOC removal performance.

Introduction

Under its duty of care, the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere. To achieve this, the MoD adopts a rigorous Passive and Active atmosphere control programme which has been discussed in previous SAMAP papers.

The submarine's atmosphere is consistently monitored and controlled within set exposure reference values (detailed in the UK restricted publication BR1326 - Book of Reference for Submarine Atmosphere Control) [1]. These levels are set to ensure that submariner health is not compromised, and so operational capability of the platform is maintained.

The UK has for the last twelve years, run a contract with QinetiQ to provide scientific support to atmosphere control under the Maritime Strategic Capability Agreement (MSCA). The contract objective is to assist the UK MoD in providing assured support to critical capabilities. The life support section for Submarine Atmosphere Control, consists of six specialist scientists which assist the MoD in providing scientific support / evaluation, and targeted and underpinning research on atmosphere management techniques.

Every year the MoD and QinetiQ evaluate areas of interest and potential development opportunities to support submarine atmosphere control. A full scientific programme is developed and contractually agreed, and progress evaluated at quarterly intervals.

The MoD tasked QinetiQ under this contract to evaluate the potential use of preidentified precious metal catalysts for low temperature carbon monoxide (CO) / hydrogen (H_2) removal and subsequent Volatile Organic Contaminants (VOC) removal. This work is reported further in this paper

On RN submarine's, CO and H_2 are removed by a high-temperature catalytic burner. The burner employs a bed of Molecular Products' Moleculite®, a copper oxide/manganese dioxide oxidation catalyst that operates at an elevated temperature.

While the primary function of the burner is the removal of CO and H_2, anecdotally, it has a number of secondary benefits that include the removal of VOC, microbiological contamination, and aerosols. Although there has been some work [2] to measure the contribution made by the burner to the removal of submarine VOC, it is still not fully quantified. Complete thermal oxidation of VOC would normally require temperatures in excess of 1000 °C. Catalytic oxidation can occur at far lower temperatures [3, 4, 5, 6, 7, 8, 9, 10, and 11], however this does not always result in complete VOC degradation. Partial breakdown products can be formed, which contribute to a submarine's VOC load and may be more hazardous to health. This paper details some of the work carried out to quantify VOC breakdown over the Moleculite®.

Moleculite® has been used for many years, however, there has been increasing interest in alternative low-temperature catalysts. The advantage of these catalysts would be a significant reduction in power consumption. Under contract to the MoD, QinetiQ has evaluated several potential alternative low-temperature catalysts for CO and H_2 removal. This work identified a dual-bed catalyst consisting of Johnson-Matthey's (JM) Q1 (palladium on iron oxide) and Q3 (platinum on titanium dioxide) that can oxidise CO and H_2 at 100 °C.

One obstacle to the introduction of low-temperature catalysts is their potential poisoning by contaminants in the submarine atmosphere. QinetiQ has exposed the JM catalysts to a range of VOC in laboratory tests. Although it is impossible to completely replicate the complex VOC mix present on-board a submarine, this study exposed the catalysts to several different classes of contaminant, such as, alkanes, aldehydes, and alcohols.

Experimental

High-temperature Moleculite® tests

The laboratory test apparatus is shown in Figure 1. A compressor supplied diluent air which was then divided into a 'dry' flow and a 'wet' flow that had passed through a wash bottle. The required relative humidity (RH) of the challenge air was obtained by controlling the proportion of 'wet' and 'dry' air using flow controllers. The humidity of the challenge air was maintained at around 50 % RH measured at room temperature. The air flow was set to a gas hourly space velocity (GHSV) of 60000 h^{-1} through the catalyst to match that of the high-temperature CO/H_2 burner.

The catalyst was fresh Moleculite® packed to a depth of 0.5 cm in a glass furnace tube. The tube furnace temperature was operated at 280 °C which is the standard operating temperature of the CO/H_2 Burner.

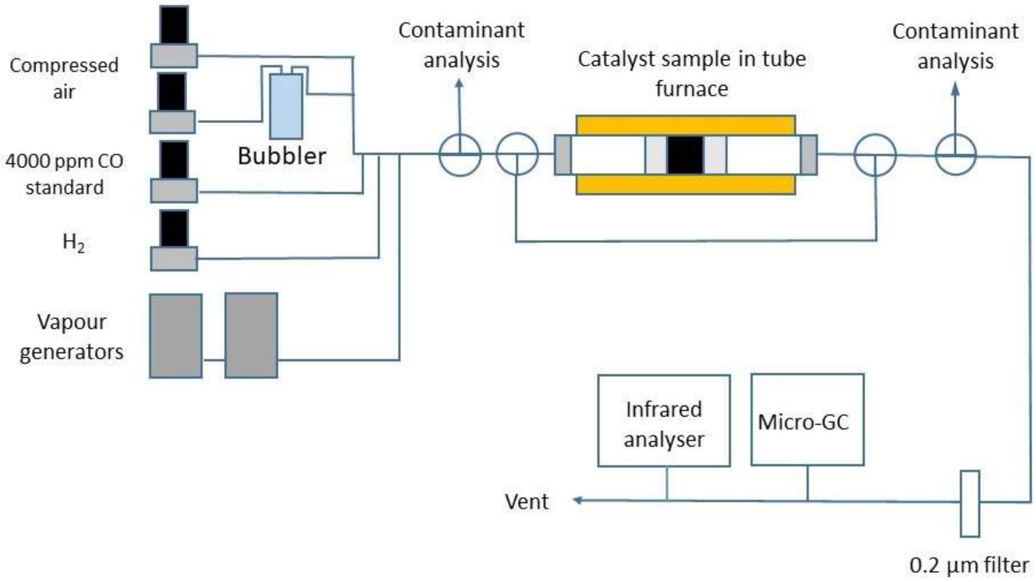

Figure 1: Schematic experimental arrangement for the high-temperature catalyst study

A test gas of 6 ppm CO concentration was produced in the challenge gas by blending a 4000 ppm standard with diluent air. CO was monitored by infrared using either a Thermo Environmental Instruments 48 °C analyser, or a Gasmet DX4040. Test H_2 concentrations were produced by blending the pure gas with diluent air and measured using a micro-GC fitted with a molecular sieve column and thermal conductivity detector.

The test VOC were selected from the list of target contaminants in BR1326 [1]. VOC were produced using two Graseby standard generators, operated at different temperatures to account for the difference in volatility of target compounds. The first generator contained: 2-butanone, benzene and decane and operated at 33 °C, and the second contained: 1, 2, 3-trimethylbenzene, acetophenone and naphthalene and operated at 70 °C. Details of the dimensions of the diffusion devices and the test concentration are shown in Table 1.

VOC	**Diffusion tube capillary**		**Diffusion chamber temperature (°C)**	**Concentration (ppm)**
	Length (mm)	**Diameter (mm)**		
2-Butanone	75	1	33	2.1
Benzene	75	1	33	2.5
Decane	15	3	33	1.4
1,2,3-Trimethylbenzene	21	2	70	4.2
Acetophenone	75	5	70	3.0
Naphthalene	75	5	70	1.3

Table 1: Standards generator conditions for the high-temperature Moleculite® tests

Inlet and outlet samples were collected using Tedlar gas bags. A 400ml aliquot of this gas was then sampled onto Carbograph 1-TD sorbent tubes (Markes International) and analysed using thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) - Markes International Unity/Ultra, Thermo Scientific Trace GC Ultra and DSQ II MS. The GC was fitted with a BPX5 capillary column (SGE, 50 m x 0.2 mm x 1.0 µm film thickness). Stock VOC solutions were produced gravimetrically in methanol (HPLC grade Fisher). Calibration standards were prepared by serial dilutions of these solutions. The analysis of Carbograph tubes spiked with 4 µl of liquid standard was used to produce VOC calibration graphs.

Moleculite® was exposed to the CO, H_2 and the VOC mix for 6 h. As H_2 oxidation is highly exothermic, tests were repeated, using a fresh catalyst bed, for a challenge concentrations of 0.0, 0.5 and 2.0 % H_2.

Low-temperature catalyst tests.

Figure 2 shows the modified experimental arrangement used for the low-temperature catalyst tests. Packed dual-beds of Q1 and Q3 catalyst (5 mm each) were held in place using glass beads in the 18mm diameter test cell. Heating tape was used to maintain the required temperature of the catalyst bed. The voltage across the heating tape was reduced during tests with H_2 in the challenge gas to maintain the temperature constant at 100 °C.

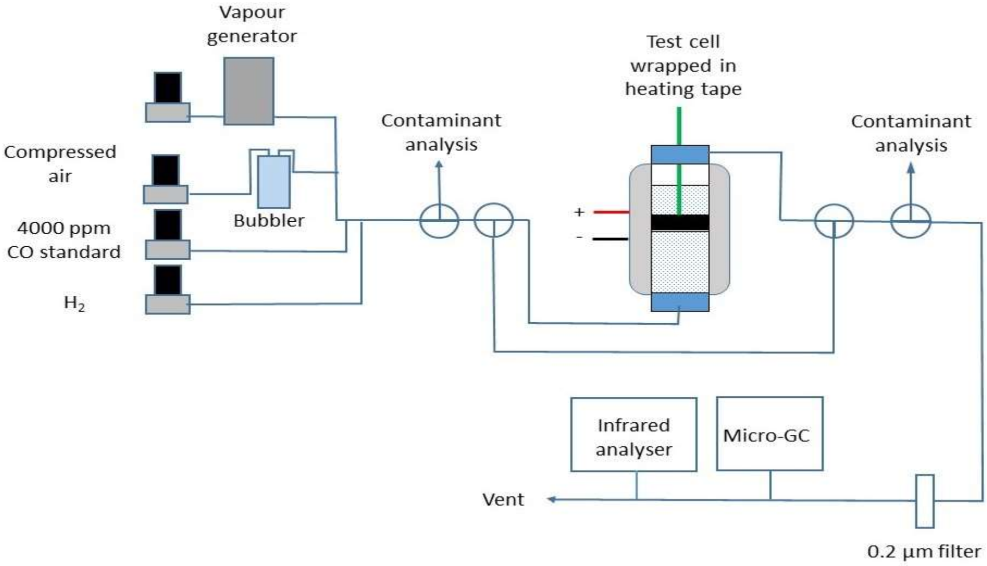

Figure 2: Schematic experimental arrangement for the high-temperature catalyst study

Test VOC were again selected from the BR1326 [2] list of target contaminants. The intent was to expose the catalysts to the low concentration of VOC typically present in a submarine atmosphere rather than the higher submarine action limits. Vapour phase VOC were supplied by the Standards Generator and gases by an additional flow controller. A GHSV of 60000 h^{-1} was used and the challenge gas contained 6 ppm CO and 0.5 % H_2.

VOC measurement, apart from methanol, ethanol and butanol, used the same sampling method as the high temperature catalyst work. A smaller 100 ml sample was transferred to the Carbograph TD1 tube for TD/GC/MS analysis. The other contaminants were measured using either Draeger gas detection tubes or the Gasmet DX4040 analyser.

Table 2 lists the contaminants, their measured concentrations, and the exposure times. A miscalculation of the required standard generator conditions resulted in a higher than planned concentration of butan-2-one. After the first aldehyde and ketones test, the butan-2-one diffusion vial was removed from the generator and oven temperature raised to increase the concentration of benzaldehyde and acetophenone.

VOC		Exposure duration (h)	Concentration (ppm)	
Alcohols:				
Methanol		168	1.90	
Ethanol			0.99	
Butanol			1.56	
Alkanes:				
Decane		168	0.36	
Nonane			0.82	
Aromatics:				
Toluene		168	2.25	
Ethyl-benzene			0.55	
Para-xylene			0.78	
Aldehyde and ketones:			Low Temp.	High Temp.
Butan-2-one		96	33.2	-
Benzaldehyde			0.43	0.65
Acetophenone			0.14	0.39
Chlorinated:				
1,1,1-Tricholorethane		168	4.93	
1,1,1-Trichloroethylene			1.16	
Tetrachloroethane			0.16	
Siloxanes:				
Hexamethylcyclotrisiloxane		168	0.25	
Octamethylcyclotetrasiloxane			0.11	
Decamethylcyclopentasiloxane			0.07	
Hydrogen sulfide		21	0.05	
Ammonia	Test 1	7	1.80	
	Test 2	14	3.10	

Table 2: Experimental conditions for the low-temperature catalyst tests

Results

High temperature Moleculite® tests

The percentage removal of analytes was calculated using the equation below.

$$Removal = \frac{[analyte]_{inlet} - [analyte]_{outlet}}{[analyte]_{inlet}} \times 100$$

The average percentage removal of the six test VOC during the 6 h experiment are shown in Table 3.

VOC	Inlet concentration (ppm)	Outlet concentration (ppm)	Average removal (%)
2-Butanone	1.148	0.023	98
Benzene	0.895	0.474	47
Decane	0.251	0.073	71
1,2,3-Trimethylbenzene	0.081	0.015	82
Acetophenone	0.031	0.006	81
Naphthalene	0.012	0.003	75
		Average VOC percentage removal	76

Table 3: High-temperature Moleculite® results

The results in Table 3 show that the measured inlet VOC concentrations was less than that expected from the reduction in weight of the diffusion tubes (Table 1). This may indicate VOC adsorption within the test apparatus. The total VOC challenge concentration was about 2.4 ppm. Benzene had the lowest removal of 47 % probably due to the inherent stability of the aromatic ring structure.

The results of this study were in agreement with those of the sole submarine Minor Trial from 1984. During this trial the VOC removal efficiency of the high-temperature burner was 70 – 80 % [2].

Table 4 contains the results of experiments to determine the effect of H_2 in the inlet air.

VOC	**0.0 % H_2**	**0.5 % H_2**	**1.8 % H_2**
	Average removal (%)		
2-butanone	79	80	76
benzene	46	26	25
decane	66	65	55
1,2,3-trimethylbenzene	71	77	72
acetophenone	72	79	79
naphthalene	68	71	-
Average VOC removal	67	66	61

Table 4: Effect of H_2 concentration on VOC removal by Moleculite®

The results in Table 4 show that, apart from benzene, H_2 had little effect on the removal of the VOC. It is unclear why the breakdown of benzene was so much less. The fresh catalyst bed in the 0.0 % H_2 experiment had a lower VOC removal efficiency than that used for the earlier experiment (Table 3). It is possible that this was due to differences in the packing density of the catalyst bed.

In addition to measuring the reduction of target VOC, outlet samples were analysed for partial breakdown products. These results indicated that none of the target VOC were incompletely oxidised. Given the very low challenge concentration, it is possible that the concentration of partial breakdown products was below the limit of detection of the analytical procedure.

Low-temperature catalyst tests

Table 5 shows the CO and H_2 oxidation performance of the low-temperature dual catalysts prior to and after exposure to atmosphere contaminant compounds.

Contaminants		**Exposure duration (h)**	**Average removal (%)**			
			Pre-exposure		**Post-exposure**	
			CO	**H_2**	**CO**	**H_2**
Alcohols		168	98.4	100.0	100.0	100.0
Alkanes		168	100.0	100.0	100.0	100.0
Aromatics		168	100.0	99.3	99.9	100.0
Aldehydes and ketones		192	99.4	97.3	99.5	98.1
Chlorinated		168	100.0	96.0	100.0	100.0
Siloxanes		168	98.3	95.0	100.0	88.4
Hydrogen sulfide		7	99.3	98.5	100.0	100.0
		14			100.0	100.0
		21			100.0	100.0
Ammonia	Test 1	7	100.0	100.0	100.0	43.9*

Contaminants		**Exposure duration (h)**	**Average removal (%)**			
			Pre-exposure		**Post-exposure**	
			CO	**H_2**	**CO**	**H_2**
	Test 2	14	100.0	100.0	100.0	100.0

*Averaged result

Table 5: Effect of atmosphere contaminants on low-temperature CO and H_2 oxidation

These results show that exposure of the catalysts to most contaminants did not adversely affect CO and H_2 oxidation. The only exceptions to this were found during the ammonia and siloxanes exposure experiments.

In the first ammonia exposure experiment H_2 oxidation initially dropped to 67.8 % then declined over time to 16.5 % (averaged oxidation 43.9 %). Heating the catalyst in contaminant-free air at 100 °C restored the H_2 removal to 69.0 %. The second ammonia exposure experiment was conducted using fresh catalyst and this maintained 100 % H_2 for 14 h. The catalysts used in these experiments came from the same batches and it is unclear why results were so variable.

After the siloxane experiments, a baseline performance test using fresh catalyst had degraded H_2 removal. This was attributed to residual siloxane within the test apparatus. After thorough cleaning of the apparatus, H_2 removal using a second sample of fresh catalyst beds remained lower (67 %) than expected (100 %). An and extended purge of the catalyst at 100 °C with contaminant free air removed all remaining siloxane from the system and restored the H_2 removal efficiency to 100 %.

The percentage removal of the target atmosphere contaminants during the low-temperature catalyst experiments are shown in Table 6.

Contaminant		**Outlet concentration (ppm)**	**Percentage removal (%)**
Methanol		0.00	100.0
Ethanol		0.00	100.0
Butanol		0.00	100.0
Decane		<0.01	97.2
Nonane		<0.01	98.8
Toluene		0.24	89.3
Ethyl-benzene		0.04	92.7
p-Xylene		0.12	84.6
Butan-2-one		0.40	98.8
Benzaldehyde		<0.01	98.5*
Acetophenone		<0.01	97.4*
1,1,1-Tricholorethane		1.84	62.7
1,1,1-Trichloroethylene		0.03	97.4
Tetrachloroethane		<0.01	93.8
Hexamethyltricyclosiloxane		0.13	48.0
Octamethylcyclotetrasiloxane		0.08	27.3
Decamethylcyclopentasiloxane		<0.01	85.7
Hydrogen sulfide		0.00	100.0
Ammonia	Test 2	0.57	81.6
Average contaminant removal			78.5

* High temperature experiment

Table6: Test cell outlet concentration of contaminants and breakdown products

These results show >80% removal of most contaminants and an overall average removal of 78.5%. The exceptions were 1,1,1-tricholorethane, hexamethyltricyclosiloxane and octamethylcyclotetrasiloxane. Analysis of samples of the outlet air found no partial breakdown products.

During the second ammonia experiment the outlet air was monitored for oxides of nitrogen (NO_x). Table 7 shows the concentration of nitric oxide, nitrogen dioxide and nitrous oxide in catalyst inlet and outlet air.

	Ammonia (ppm)	**Nitric oxide (ppm)**	**Nitrogen dioxide (ppm)**	**Nitrous oxide (ppm)**
Inlet	3.08	0.23	0.13	0.36
Outlet	0.57	0.00	0.05	0.25

Table 7: Ammonia and NO_x concentrations during second ammonia test

These results shows that although the catalysts removed 81 % of the ammonia in the inlet air, there not a proportionate increase in the NO_x concentrations of outlet air. Further work has been recommended using a more sensitive NO_x chemiluminescent analyser to determine the fate of ammonia on these catalysts.

Conclusions

The high-temperature catalyst Moleculite® oxidised most VOC. Laboratory experiments showed average total VOC removal of the six test compounds was 61 – 76 %. These finding indicate that the CO/H_2 burner makes a significant contribution to controlling VOC in the atmosphere on RN submarines.

The low-temperature catalyst study showed that the CO and H_2 removal performance of a dual-bed of JM Q1 and Q3 catalysts was unaffected by the majority of submarine atmosphere contaminants. This system could potentially form the basis of a future low-temperature CO/H_2 burner. The catalysts had an average contaminant removal of 78.5 % suggesting that this important secondary function would not be lost in a low-temperature precious metal burner.

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PROCEEDINGS

The Future of Submarines

FACILITATED BY
ANALOX

SAMAP

A USER PERSPECTIVE

- Walrus class replacement NL → AIP;
- TNO research -> aim is to provide a ‘banned materials’ list and set requirements for substances we’re not monitoring yet;
- What are the best AMAP system characteristics for me as a user?
- Improvements I’ve seen for the past 2 days
- Next SAMAP → Das boost and TNO?

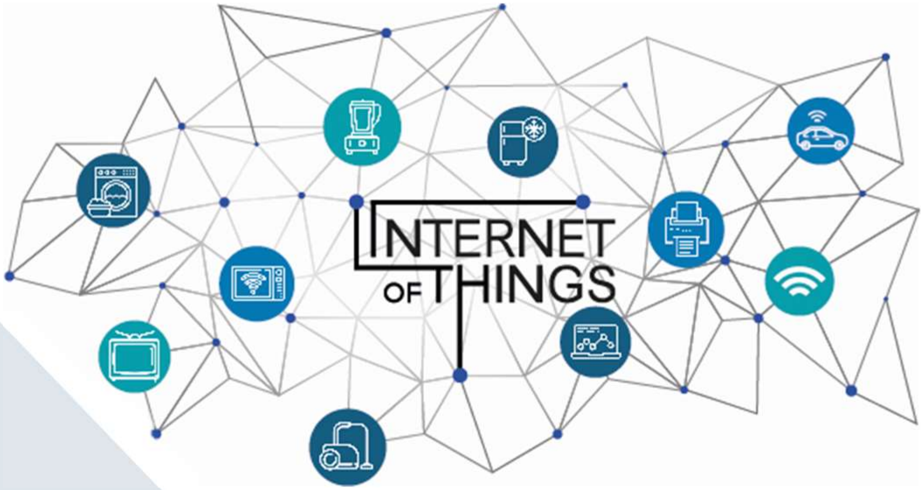
FUTURE SUBMARINES

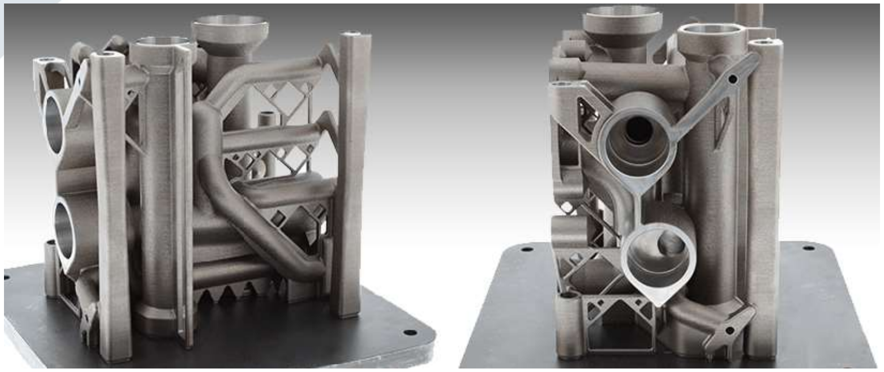
Huge changes to submarine warfare in the next decades

- Capability delivered across multiple platforms
- Modularity/ adaptability
- Unmanned systems
- Different forms
- Anti-submarine warfare

Technologies

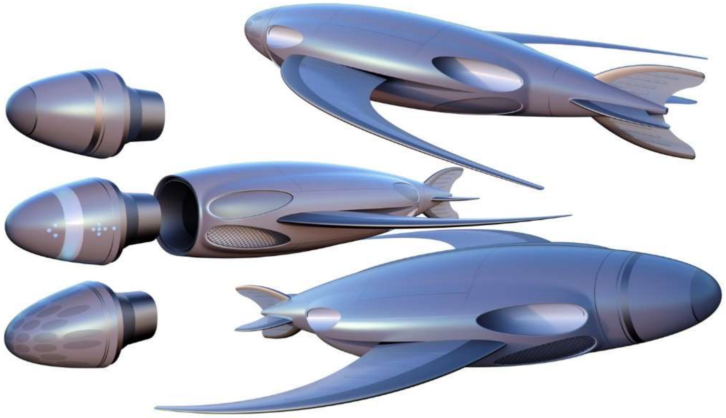
- Processing power
- Internet of things
- Reducing transducer prices
- Big data
- Artificial intelligence
- Communications
- Materials – e.g. graphene
- Manufacturing e.g. 3D printing
- New battery technologies





TECHNOLOGY IMPLICATIONS

- Increased automation and decision support
  - Improved HMIs
  - Condition monitoring
  - Automated diagnostics
- Increased integration
  - Ability to connect systems for improved control
  - Improved interoperability
- Improved techniques
  - Sensing on board
  - Threat detection



HUMAN ASPECTS

- Crew costs are very high – wages, training, food, accommodation, pensions etc.
- Pressure to reduce manning levels
- Less people will do more, supported by technology
- Need to be highly capable
- Selection, training and retention will change
- Health and safety and environmental legislation increasing

PROCUREMENT

Ministry of Defence faces fury over cost of Dreadnought subs

There are growing fears that the Dreadnought submarine project will blow its budget
CROWN COPYRIGHT

Britain is in danger of another defence spending blow-up after a complex part of the new Dreadnought submarine fleet soared in price.

Engineers have told officials that a stability system for the nuclear submarines will cost more than an entire warship, stoking fears that Britain's costliest defence project is veering off budget.

UK armed forces 'face £7bn equipment funding black hole'

1 February 2019

MPs have demanded more information on the financial risks of purchasing F-35 stealth jets

The Ministry of Defence has a funding black hole of at least £7bn in its 10-year plan to equip the UK's armed forces, according to a report by the Commons spending watchdog.

- Affordability challenges
- Lead times and Programme complexity
- Ensuring availability
- Through- life cost minimisation

WORKSHOP EXERCISE

- In your tables we would like you to work together as teams
- Use your experience to generate insight into how the following areas will change in the future, what benefits they will deliver and what we need to do as a community to realise the benefits

Name badge colour	Area for discussion
Red	Atmosphere management and control
Green	Automation and the crew
Blue	Atmosphere monitoring and analysis

- 30 minutes discussion
- 10 minutes presentation