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


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# Introduction

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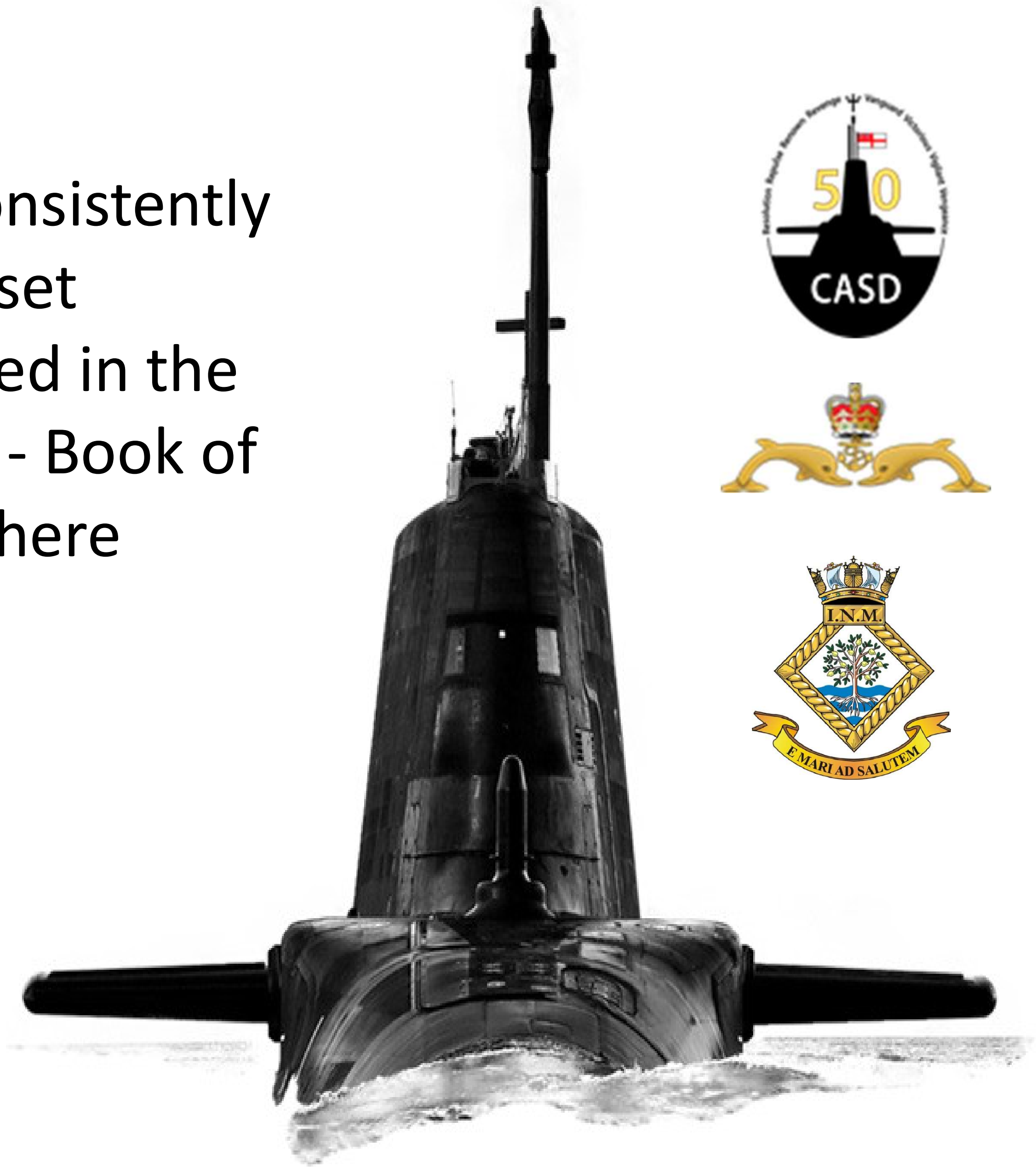
Under its duty of care, the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere.

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)



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

# VOC removal by high temperature catalysts

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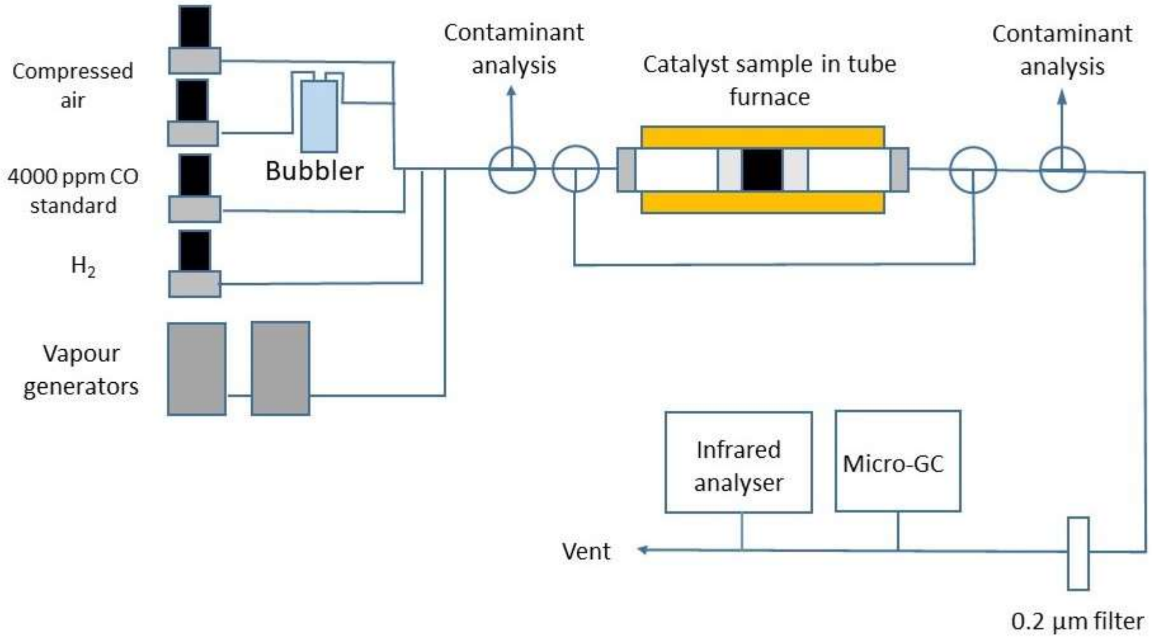
# High temperature catalyst - Experimental

- 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*



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# 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



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# VOC exposure to low temperature catalysts

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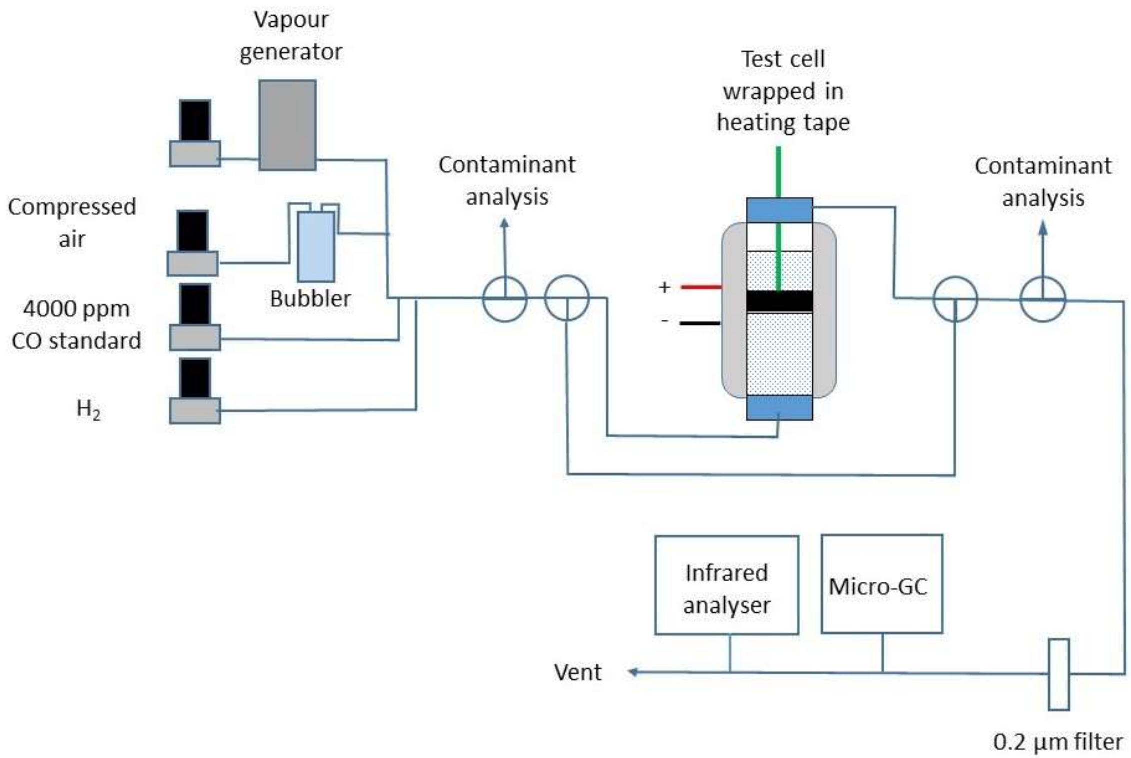
# Low temperature catalyst - Experimental

- 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*



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# 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 | |



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# 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



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# Low temperature catalyst – VOC removal

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

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

# Any questions

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