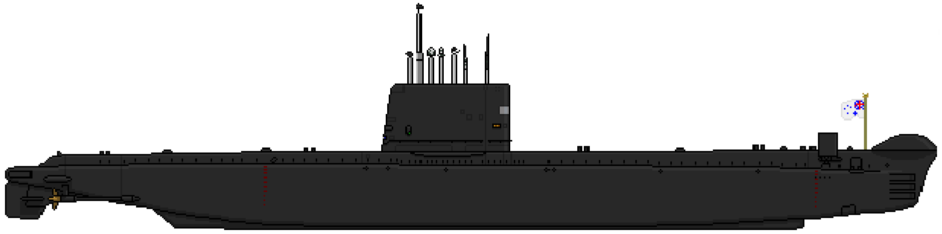
KEY DEVELOPMENTS IN SUBMARINE AIR MONITORING AND AIR PURIFICATION DURING THE PAST 20 YEARS

W. Mazurek

SAMAP Conferences

- 1994 Adelaide, Australia — 1st
- 1997 Portsmouth, UK — 2nd
- 2000 Toronto, Canada — 3rd
- 2003 Emden, Germany — 4th
- 2005 Uncasville, CT., USA — 5th
- 2007 Amsterdam, Netherlands — 6th
- 2009 San Diego, USA — 7th
- 2011 Taranto, Italy — 8th
- 2013 New Orleans, USA — 9th
- 2015 Den Helder, Netherlands — 10th

Diesel-Powered Submarines 1970s (eg. Oberon Class 1957-1978)

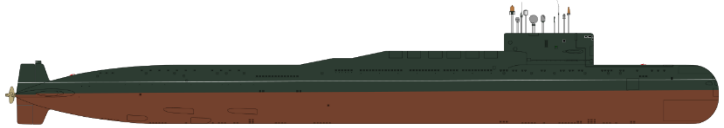


- Air Monitoring:
  - Colorimetric Tubes (eg. Drager)
- Air Purification:
  - Carbon Dioxide Absorption Unit (CDAU) Soda Lime
  - Oxygen Candles
  - CO/H_2 Burner (oxidation catalyst) Pd/Al_2O_3

CDAU

CO/H2 Burner

Nuclear-Powered Submarines 1970s



- Air Monitoring
  - Central Atmosphere Monitoring System (Mass Spectrometer)
  - IR CO monitor
- Air Purification
  - Regenerative CO_2 Removal (Amine Scrubber, Molecular Sieves)
  - Non-Regenerative (soda lime, lithium hydroxide)
  - Electrolyser (O_2)
  - High Temperature CO/H_2 Burner
  - Charcoal Filter
  - Electrostatic precipitator (aerosols)

REGENERATIVE CO_2 REMOVAL

- Much interest in regenerative CO2 removal
- Mostly for nuclear-powered submarines but also for AIP
- Move away from current MEA scrubber for CO2

CONCERNS ABOUT MEA (MonoEthanolAmine) SCRUBBER

- Initially adapted for nuclear-powered submarines from industrial applications

- What is driving research on regenerative CO2 removal
- Toxicity MEA
  - Exposure Limit: 0.5 ppm air concentration
  - Fugitive emissions from the MEA scrubber

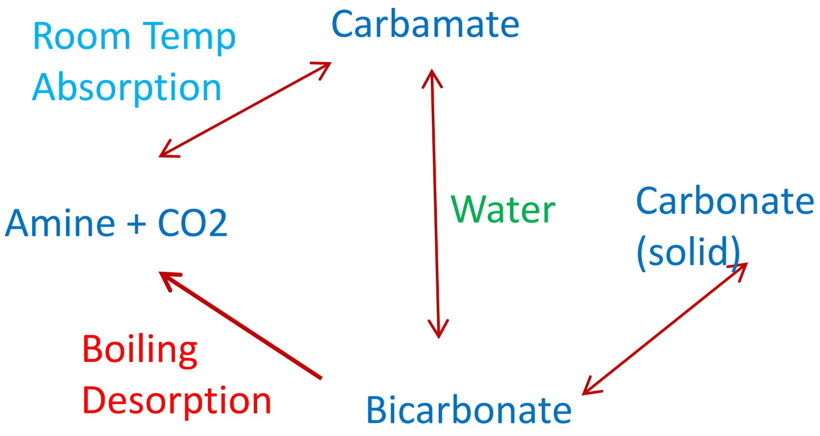
- Agricultural design
  - Operator training required
  - Monitoring solution concentrations

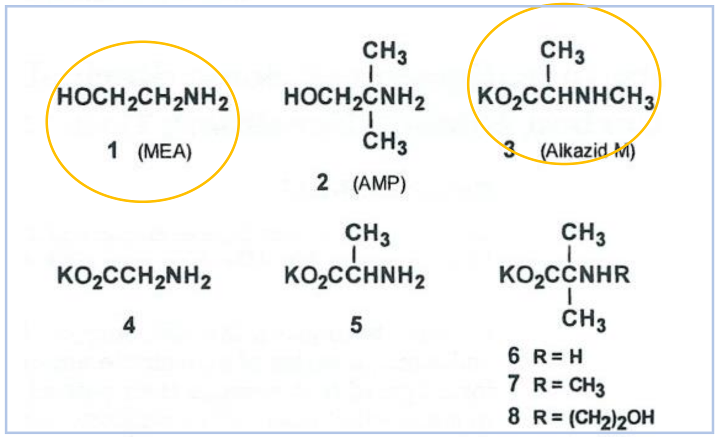
Regenerative CO_2 Scrubber (MEA)

Is MEA the best choice ?

- Installed on RAN COLLINS class submarines and Japanese Sōryū class AIP submarines
  - adapted from RN nuclear-powered submarines
  - Reaction Mechanisms – Robert Hook, DSTO

    Ind. Eng. Chem. Res. **1997**, *36*, 1779–1790

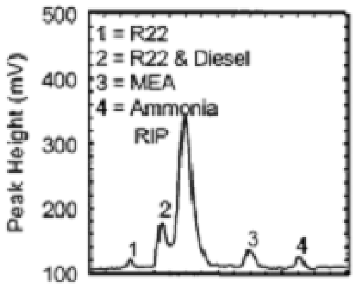




1. All 8 amines absorbed and released CO2
2. MEA and Alkazid absorbed/desorbed best
3. All formed precipitates except MEA and Alkazid
4. 7&8 are not suited to working at low CO2 levels

MEA Emissions

- **Monitoring**:
- Colorimetric tubes (real-time) – not specific to MEA
- Absorption into acid soln - retrospective anal,
- **IMS** - Gan (DSTO), Corino (CSIRO), "*Selective detection of alkanolamine vapors by ion mobility spectrometry with ketone reagent gases*". Anal Chem. 2000 Feb 15;72(4):807-15.
- Conc of interest 0.5 ppm



Sea trial for MEA monitor

H R Bollan, J L Brokenshire and M H Lunn, SAMAP 2000

"The Development and Sea Trials of Prototype Fixed-Point and Portable Ion Mobility Spectrometers for Monitoring Monoethanolamine on board Submarines"

1.Long-term stability > 8 months

2. Appropriate dynamic range

3. Good response time

Concentrations of up to 2.5 ppm found during sea trials

MOD (UK)

GRASEBY DYNAMICS

Acknowledged Leaders in Vapour Detection

Product Specification for MEA

Reduction in Amine and Ammonia Emissions from the MEA Scrubber

- **Tony Aitchison,** Submarine Atmospheres Group, Maritime Platforms and Equipment, QinetiQ – Sea, Haslar, Gosport, SAMAP 2005.
- Investigation of filter materials in the air outlet from the MEA scrubber, MEA MPC_{90} = 0.5 vppm
  - 3 impregnated activated carbons produced by different manufacturers
  - natural zeolite
  - macroporous Ion Exchange Resin
  - existing Ion Exchange filter
- Tests were performed in the laboratory by passing humidified air through MEA and through an absorption test bed containing the filters under investigation. Monitoring was by Drager ammonia tubes (no discrimination between ammonia and MEA)
- Macroporous Ion Exchange Resin (Puralite MN500)
  - Significant improvement in MEA /ammonia retention
  - Double absorption capacity
  - Higher cost

Other Sources of MEA Leaks from the MEA Scrubber

- MEA solution penetrates pump seals, this has been overcome with the use of
  - Fix:
  - Magnetically coupled pumps
  - Immersion pumps
- Carry-over of MEA into the CO_2 compressor causes fouling of the compressor lubricating oil, leading to compressor failure. This is only a hazard in the sense that it disables the scrubber.
  - Fix: Larger capacity compressor oil sump and regular oil changes .
- Transfer of MEA from container to scrubber can lead to spillage.
  - Fix: Liquid transfer system

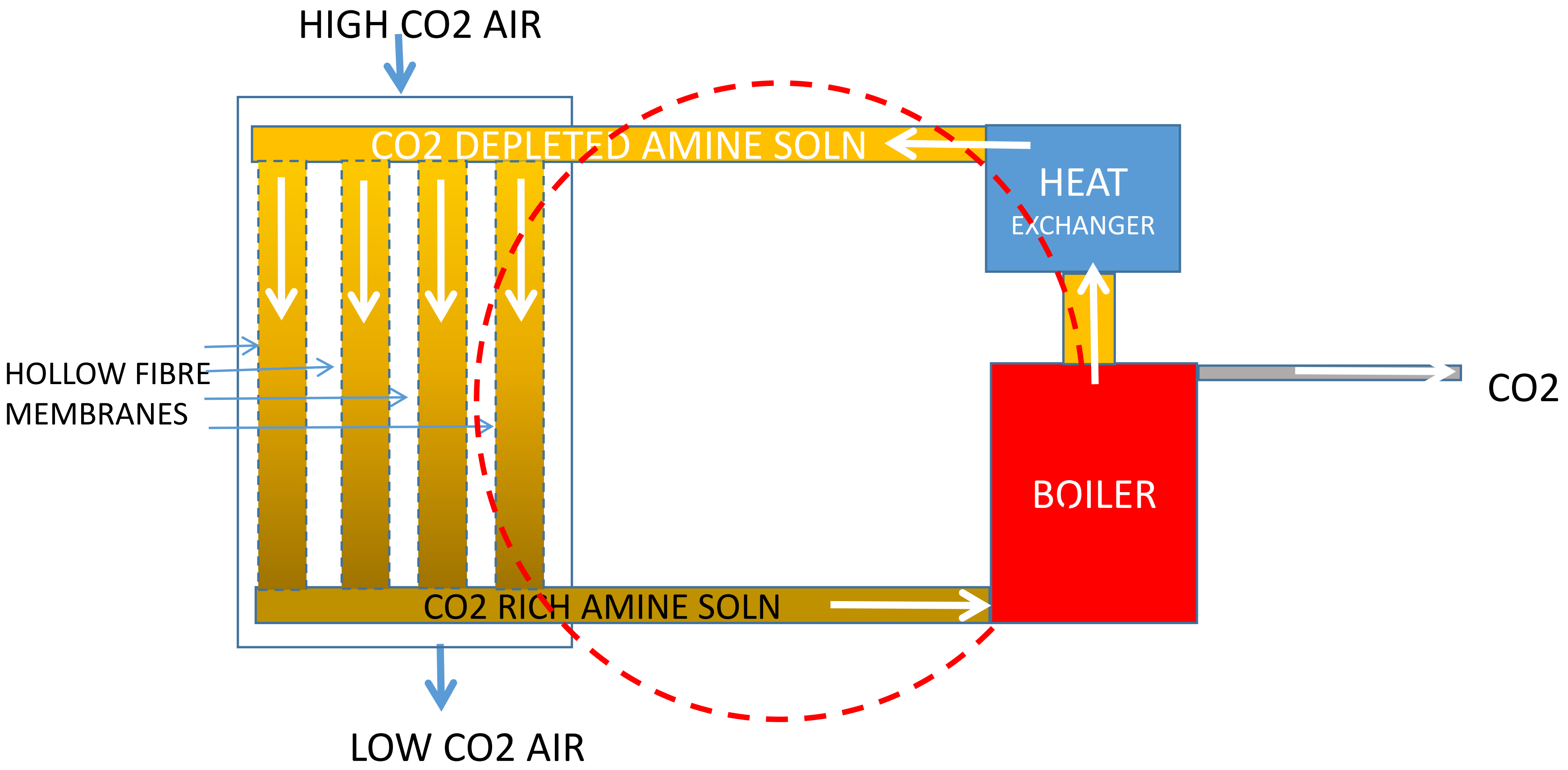
Regenerative CO2 Membrane Scrubber

Martin Jensen, et al. Netherlands, RNLN, SAMAP 2003, 2005

1. A hollow fibre membrane separates CO_2 laden air and amine solution
2. CO_2 passes through the membrane and reacts with the amine
3. The CO_2 rich amine (carbamate) passes into a boiler where the CO_2 is liberated.

ADVANTAGE: NO EXPOSURE OF AMINE TO AIR

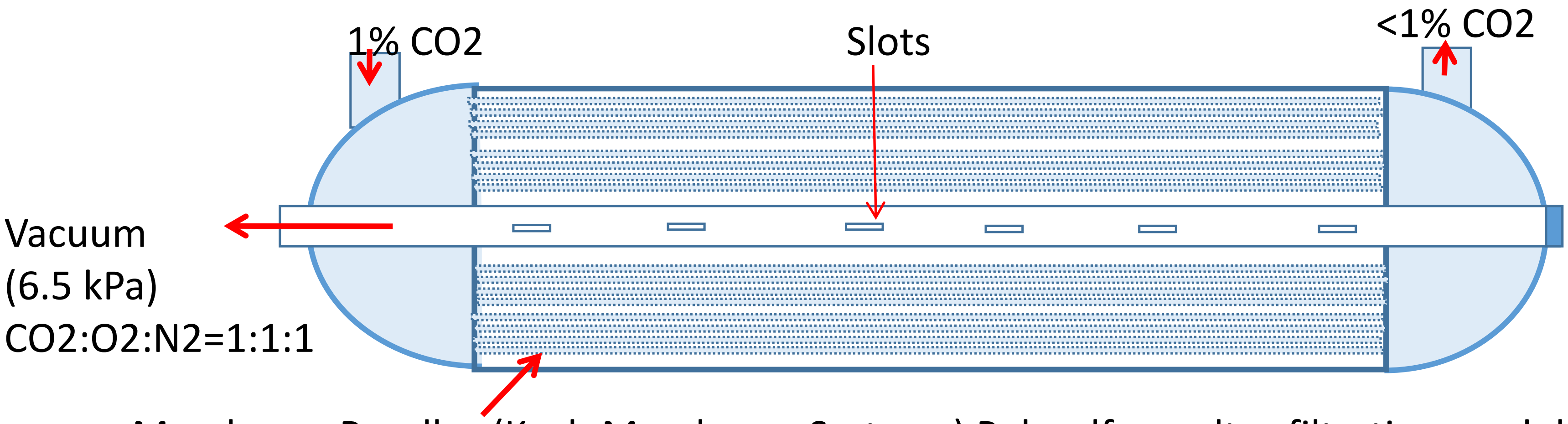
DISSADVANTAGE: REQUIRES DEMINERALISED WATER



Hollow Fibre Membrane CO_2 Removal
Amine-Facilitated Transport

- A Hedley, S Earwicker DERA, UK, 1990s in collaboration with University of Twente, The Netherlands
- Technology Demonstrator: Wellman Defence Plc, G Toft, S Cassidy and Mark Lund "Supported Liquid Membranes for Carbon Dioxide Removal from Submarine Atmospheres: Experiences with a Technology Demonstrator" *31st International Conference on Environmental Systems,* Orlando Florida, July 9-12, 2001

(1) Amine absorbed into the membrane from aqueous soln; (2) Excess removed by vacuum
(3) 1% CO2 introduced fibre bore (3) Vacuum applied to the outer side of the fibre



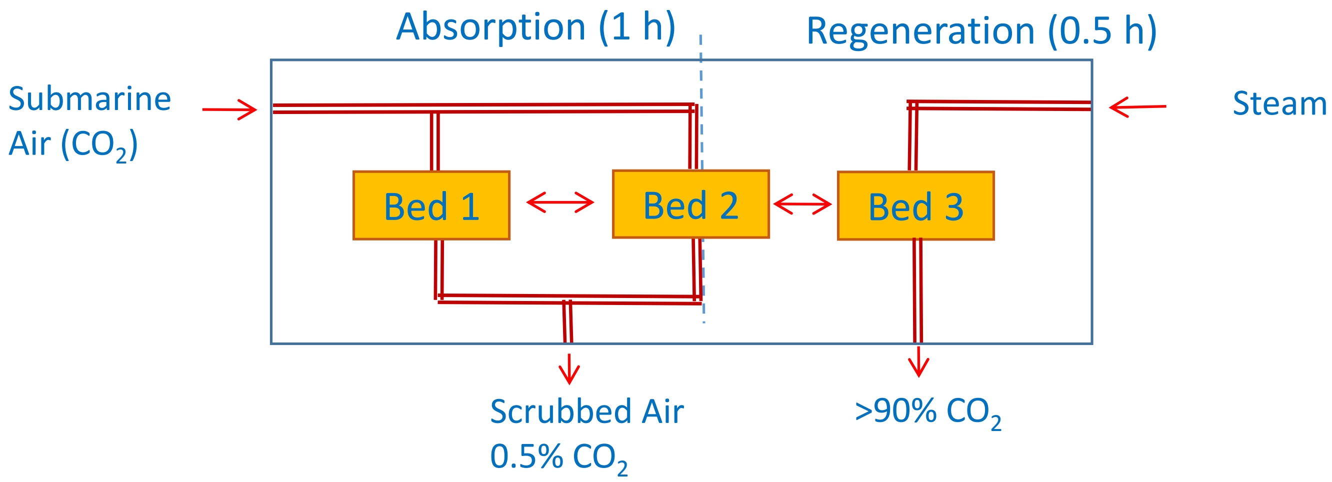
Membrane Bundles (Koch Membrane Systems) Polysulfone ultra-filtration module

Major Limitations: Low Permeation Rates, Insufficient selectivity

Regenerative Solid Amine CO2 Scrubber

Ion Exchange Resin

- Lutz Schauer and Hans-Christian Spetzler, Dornier GmbH (now EADS) SAMAP 94; W Raatschen, A Kreis, T Stuffler, H Mosebach, Contamination Control on Submarines - Technology Transfer from Space to Sub Sea, SAMAP 2003
- Solid amine CO_2 scrubber based on an primary amine exchange ion resin initially developed for spacecraft
- Trialed in Swedish submarine



United Technologies Company, USA has a similar system for spacecraft (Ben Bishop, Advanced Atmosphere Control Systems, SAMAP 2009)

Regenerative Solid Amine CO2 Scrubber

Amine-Impregnated Silica

- USN – Mesoporous silica nanoparticles, amine-impregnated (eg Polyethyleneimine, Propylamine[#]) Advanced Carbon dioxide Removal Unit – Granular Bed

([#]Z Bacsik, R Atluri, A E Garcia-Bennett and N Hedin, *Temperature-Induced Uptake of CO2 and Formation of Carbamates in Mesocaged Silica Modified with n-Propylamines*, Langmiur 26(12) 10013-10024 (2010).)

- Advantages cf Liquid Amines
  - Low heat of regeneration
  - Low cost
  - Better containment
- Disadvantages cf Liquid Amines
  - Low capacity although Ion Exchange Resin is of a similar capacity to MEA solution
  - High cost
  - Leaks

USN ACRU PROGRAM

UTC Aerospace Systems, USA.

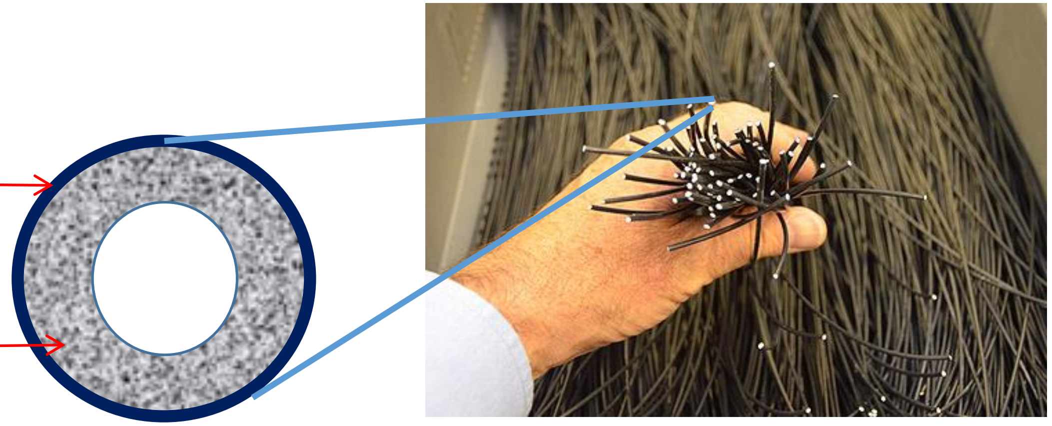
(formerly Hamilton-Sundstrand)

- Technology demonstrator - Done
- Full scale prototype - Being tested
- Qualification - 2016
- Production - 2018/19

Absorption Media Tube (AMT) Technology
Regenerative CO2 Removal

G Toft , QinetiQ, SAMAP 2013
Meso-porous Silica(MPS)/Polyethyleneimine (PEI) -
Hollow Fibre :
1. Polysulfone/Zeolite
2. Polysulfone/MPS/PEI
(Nano- Porous Solutions Ltd)
0.7% CO_2

Desorption: Thermal/Vacuum



CO_2 Removal: Cryogenics (France)

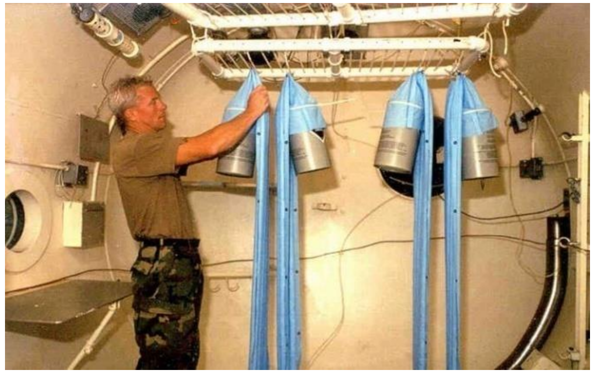
- AIP Submarine: MESMA (Module d'Energie Sous-Marine Autonome) Bry-Peel, Kerros, Rouzies, SAMAP 94
- Use of LOX heat exchanger to condense CO_2 (-170°C) to 0.7%
  - Also removes organic vapours including refrigerant gases

- Nuclear-Powered: DGA/L' Air Liquide: Pulse Tube Cryo-Cooler (-150°C) E Jouandon *et al,* SAMAP 2013
  - Can maintain CO_2 levels at <0.5%
  - Also removes organic vapours including refrigerant gases.
  - Currently
    - molecular sieve for CO_2 removal is replaced every 2 patrols and
    - charcoal filter is replaced twice during one patrol.

- These cryogenic systems reduce reliance on consumables, manpower and maintenance which is particularly important in nuclear-powered submarines where there is plentiful power and long missions..

Non-Regenerative CO2 Removal

- Soda Lime
- Granules
  - Canisters
  - Curtains (Bartelle)
  - . -



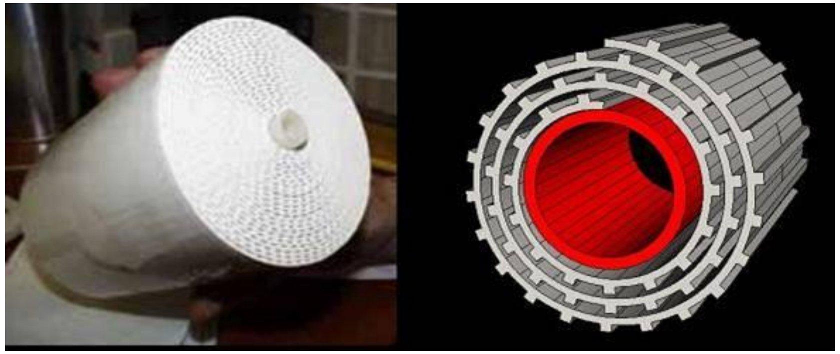
Lithium Hydroxide

Granules

Canisters

Curtains

Sheets (Micropore)



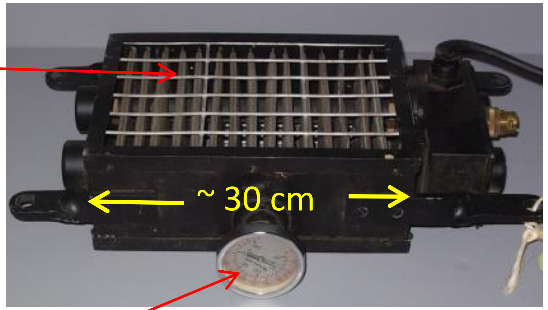
Relocateable Soda Lime Canisters

CASPA (MP Plc)
Self-Contained Batteries, Fan, Granules,
Snow-storm filled – high packing density
High Tech

DSTO Modification
MP canister fitted with electronics cooling fan –
Low Tech

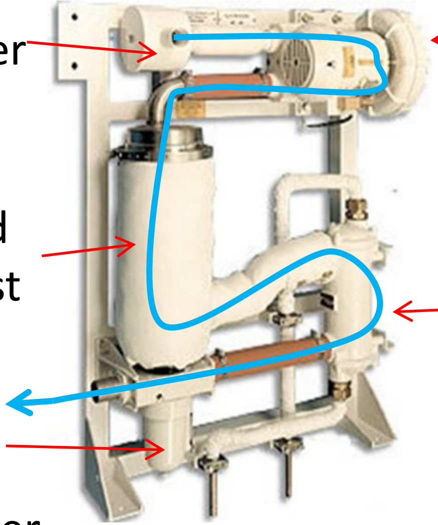
CO/H_2 "Burner"

Oberon Class Submarines 1960s



Pd/Al2O3
Diffusion
Electrically heated (60° - 120° C)

Collins Class Submarines 1990s



Low Temp Cat , Effective at Ambient Temps
Pt/Pd/SnO2
Engine Room
Fan Driven
Manufacturer: Atmosphere Control International, Corac Plc (Formerly , Wellman, CJB) www.naval-technology.com

VOC Removal
(Fuel Vapour, Material Off-Gassing)

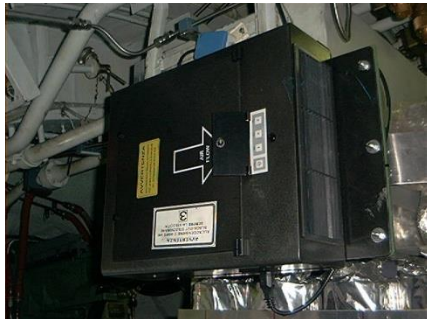
- Cryogenics – DCN (France) – Previously mentioned
  - MESMA
  - Pulse Tube cooling
- Gold Nanoclusters Marta Santiago[a], Zaira Blázquez[a], Edurne Galindo[a], Leonor Alves[b], Jordi Llorca[b,c] and Ernest Mendoza[a,b] , SAMAP 2013
  - Room Temp Removal (oxidation) : Formaldehyde, CO
- Pd/Al2O3, Pt/Pd/SnO2 (more active)
  - Designed for CO/H2 some Volatile Organic Compounds oxidized (eg. Ethanol, Toluene, Hexane, Acetone, Trichloroethane) *DeNola et al. SAMAP 2007.*

VOC Removal

D.A.TECH.
Depollution Air Technology

- Koala : Pelosi Italian Submarine, SAMAP 2003
- CO, SOx, NOx, VOCs, Particulates
- Filtration and electrostatic precipitation (?)
- 19 Units throughout the submarine
- **1. Mechanical Filter (HEPA ?),**
- **2. Special Activated Carbon Filter, (1 kg, 30 days)**
- **3. Ionic Filter (?)**
- **4. Germicide Lamp (UV lamp ?),**
- **5. Ionizer**

- **Small Units suitable for retro-fitting**



AIR QUALITY MONITORING

(Mazurek et al., SAMAP 2007)

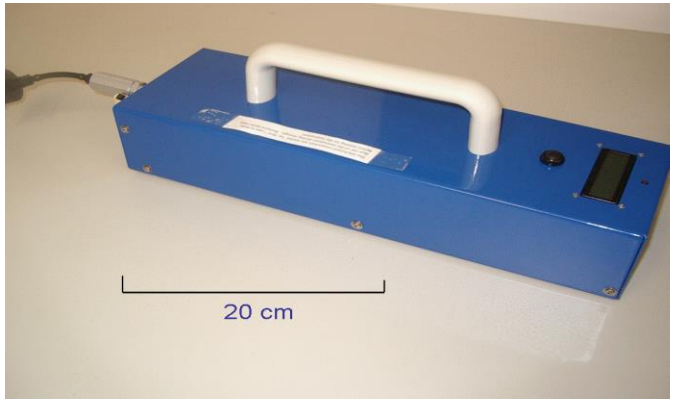
- Submarine Escape Monitor
  - DSTO/Scottish Anglo (Analox) plc, 1994
  - Hanhela and Hook, DSTO
    - Replacement for Colorimetric tubes
    - Continuous monitoring of CO_2 and O_2
    - Pressure corrected (7 bar)
    - Portable
    - Battery Life 7 days.
    - Waterproof case
    - Shock resistant.

Analox and Anagas hyperbaric O_2 and CO_2 monitors (1990s)

Analox Escape monitor for O_2, CO_2

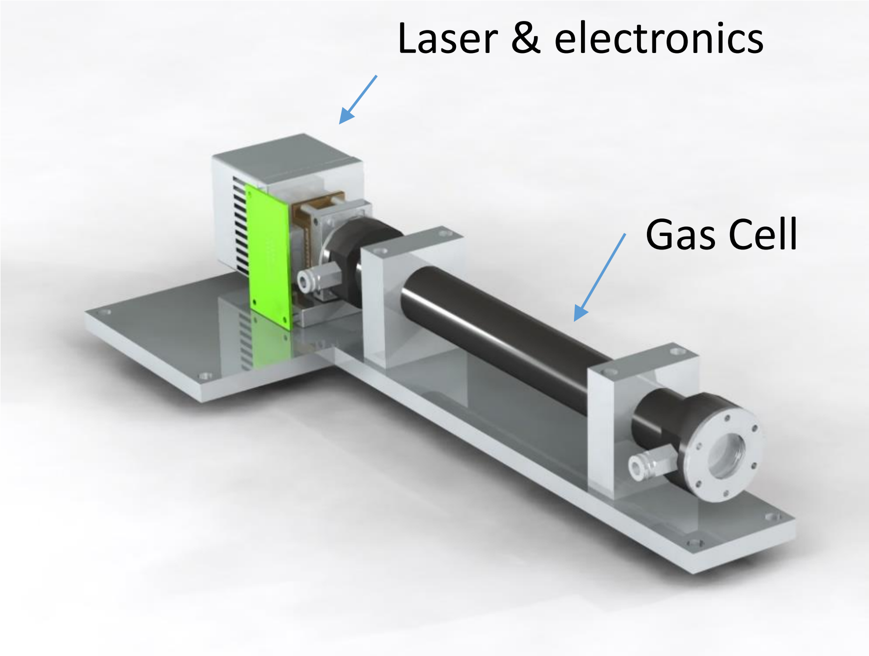
AIR QUALITY MONITORING
CO

- Electrochemical detectors unsuitable due to interference with H_2
- IR detection
  - NDIR – Bench-top only, for < 30 ppm, $\lambda = 2.3/4.7\ \mu m$
  - Tunable Diode Laser (Hanhela et al, SAMAP 2011) Southwest Sciences, Santa-Fe, NM
    - Battery powered, portable
    - Linear response 0-300 ppm CO
    - Sensitivity ±1 ppm, 0-30 ppm 15 day Submarine Trial
    - Multiple pass cell 9m
    - Inexpensive laser



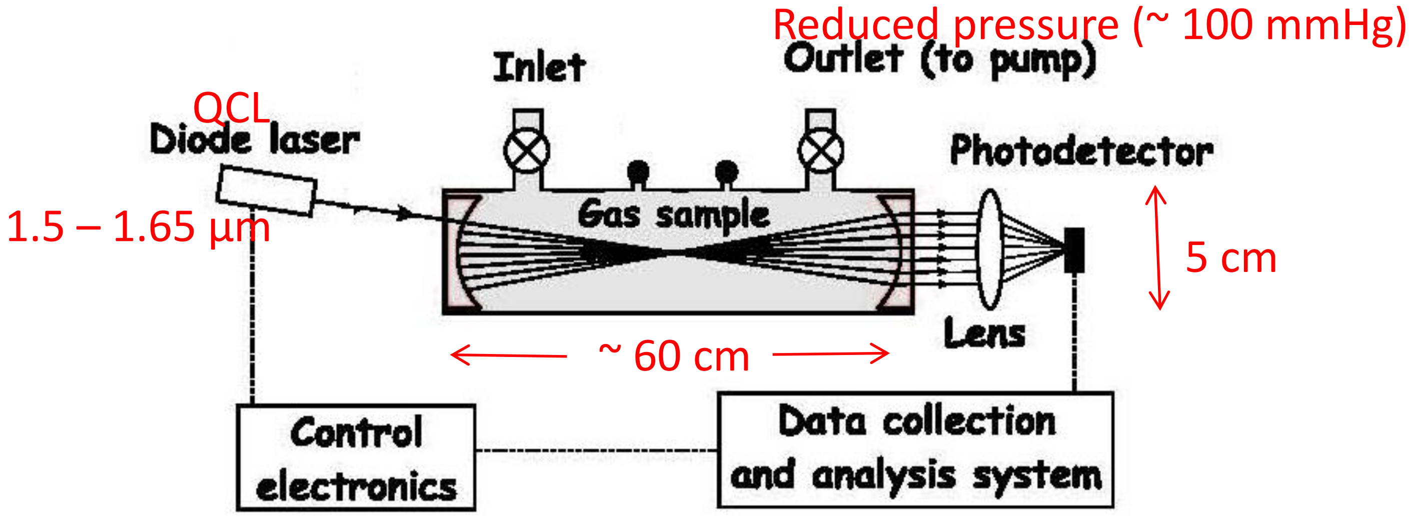
AIR QUALITY MONITORING
CO (IR, Cont.)

- Tunable Quantum Cascade Laser – Analox/TDL Sensors V. Brown and R.J. Holdsworth, SAMAP 2009; Mark Elkin∗ and Mark Lewis† SAMAP2013
- Bench - top
  - Linear 10 – 200 ppm CO
  - Noise ± 1/4 ppm
  - λ = 7.37 µm fundamental high abs
  - Expensive laser



AIR QUALITY MONITORING
CO (IR, Cont.)

- Los Gatos Research LGR's Off-Axis Integrated Cavity Output Spectroscopy (ICOS) (patented 2001): Cavity-Enhanced Absorption Technique, SAMAP 2009
- Cell: effective optical path length ~ 4 km
- Used in environmental studies high sensitivity
- CO (36 ppb), CO_2, CH_4, NH_3, HCl



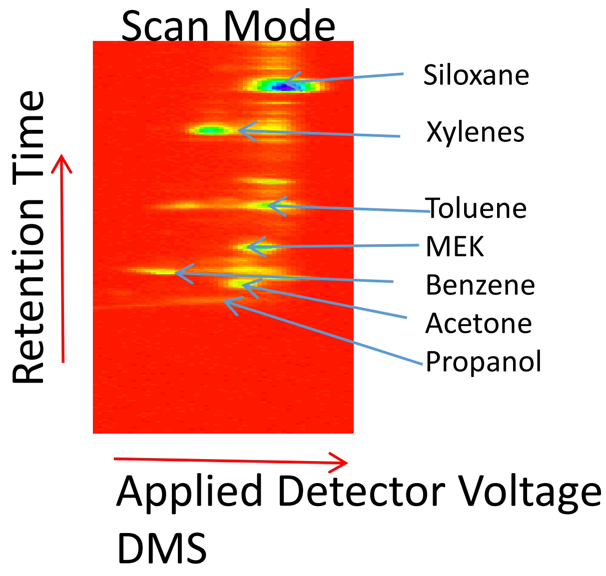
AIR QUALITY MONITORING
ANITA FTIR Analysing Interferometer for Ambient Air

- T. Stuffler, H. Mosebach, D. Kampf, A. Honne, H. Odegard, H. Schumann-Olsen, G. Tan; SAMAP 2007
- detect and quantify quasi on–line and simultaneously 32 trace gases with ppm or sub-ppm detection limits

Methanol, ethanol, 2-propanol, 1-butanol, formaldehyde , Acetaldehyde, propionaldehyde,
butyraldehyde, toluene, m-xylene, o-xylene, p-xylene, ethyl benzene, ethyl acetate
n-butyl acetate, dichloro methane, Freon 11, Freon 12, Halon 1301, Freon 113,
perfluoro propane , n-hexane, acetone, 2-butanone, hexamethyl cyclo-trisiloxane
octamethyl cyclo-tetrasiloxane, decamethyl cyclo-pentasiloxane, ammonia, carbon monoxide,
methane, carbon dioxide, water

AIR QUALITY MONITORING
SIONEX Micro GC

- Limero and Cheng “Potential for Measurement of Trace Volatile Organic Compounds in Closed Environments Using Gas Chromatograph/Differential Mobility Spectrometer”, SAMAP 2007



- Features:
  - No consumables !
  - Std GC column
  - Air as Carrier Gas
  - Detectors:
    - Differential Mobility Spectrometer ,(ions undergo an oscillating radio frequency field where the difference in mobility between the high and low fields is measured)
    - Ion Mobility Spectrometer (time of flight of ions across a drift tube, in an electric field)
  - Coupled to a Laptop

AIR QUALITY MONITORING
Femto Scan GC-IMS

- Based on the Graseby, Smiths Detection (Chemical Agent Monitor) the Femto Scan GC-IMS is similar to the Sionex

- 5m column fast GC

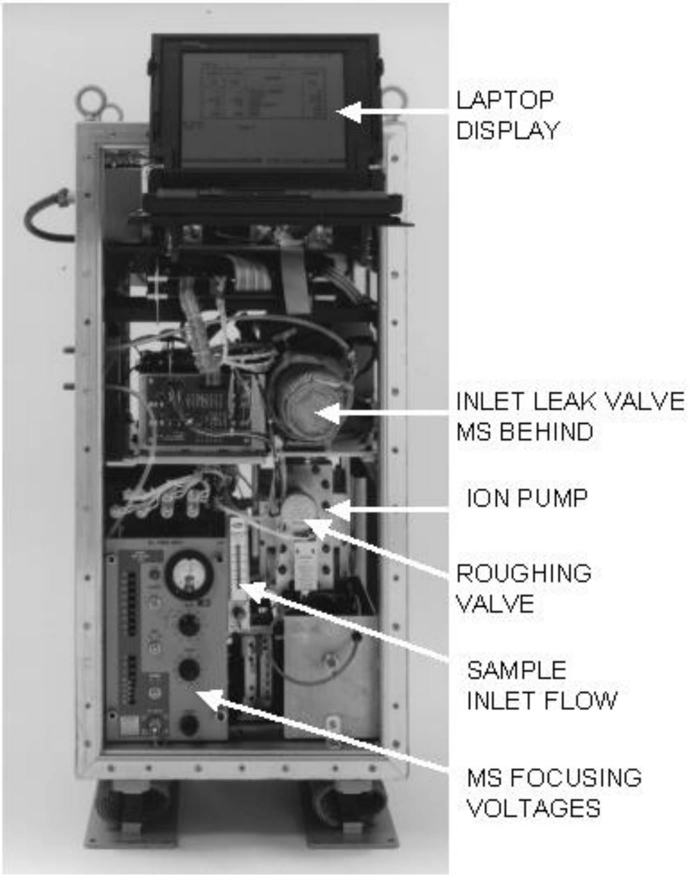
CAM

Femto Scan
GC-IMS

AIR QUALITY MONITORING
Mini-CAMS

- M Koslin and RM Carson, SAMAP94
- Cut-down version of the CAMS II, designed for conventional submarines - never sold
- Magnetically scanned singled focusing mass spectrometer.
  - ≤ 25 gases
  - Detection limit: 1ppm
  - Mass range: 1-160 amu
  - Accuracy: 5%
  - Precision: 3%
  - Time between calibrations, overhauls: >2 y

1 m



160 kg

AIR QUALITY MONITORING
CAMS

- **1970s -** CAMS Mark I: single-focusing magnetic sector mass spectrometer.
  - 8 gases including life gases and refrigerants
  - Mass range 2 -135 amu
  - Detection limit 10 ppm
- **1990s -** CAMS Mark II: double-focusing magnetic sector mass spectrometer with scanning capability..
  - ≤25 gases: life gases, refrigerants, aliphatic and aromatic hydrocarbons, and trace contaminants
  - Mass range 2-300 ppm
  - Detection Limit 1 ppm.
  - High maintenance cost
- **2012 -** CAMS IIA: single focusing magnetic sector analyzer, (Nui et al., SAMAP 2007)
  - ≤25 gases
  - Updated electronics
  - Simpler and cheaper than Mk II
  - Elimination of complex and difficult-to-manufacture components.

AIR QUALITY MONITORING
Predecessors of CAMS I
(1960s)

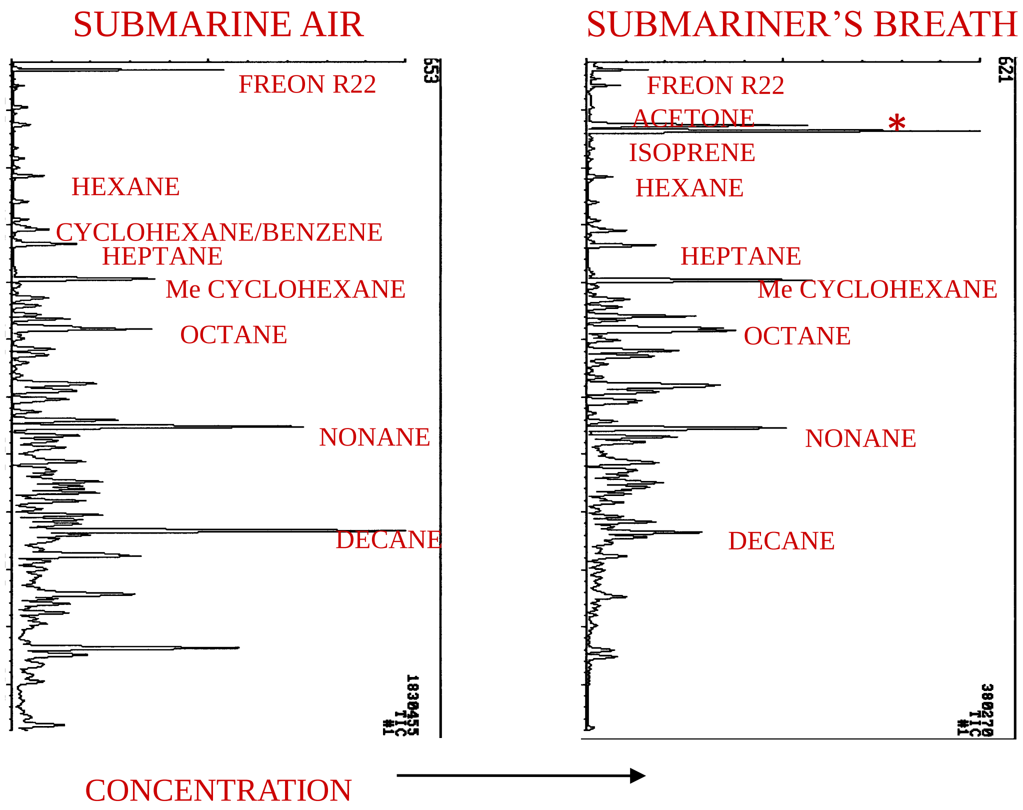
- Infrared Instruments (USN): for CO, Hydrocarbons, Refrigerants
  - Long path length cells (120 cm) to increase sensitivity
  - Pressure cells (7 atm) “ “ “
- Gas Chromatograph, automated (USN, RN): for all gases
- All were unreliable with the exception of a Perkin-Elmer IR CO monitor
- Has anything changed ?

Bio-Monitoring

- The ultimate in exposure monitoring
  - Air quality monitoring only covers inhalation-not dermal or ingestion
  - Complementary to retrospective air monitoring
  - Needs to be non-invasive
  - Needs to be related to blood

Exhaled Breath

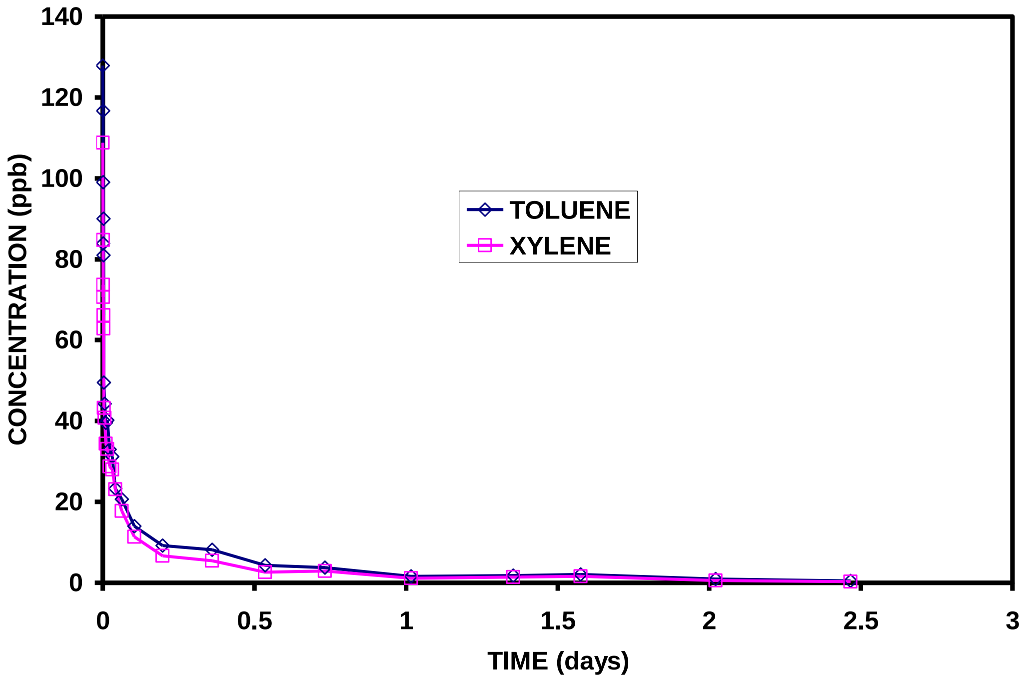
- Diesel Fuel Vapour – Major submarine air contaminant
  - Exposure through:
    - Inhalation
    - Dermal
  - Breath samples collected dock-side
  - Analysed by GC-MS in the lab.



- G. DeNola, P. J. Hanhela, T. –H. Gan and W. Mazurek , Submarine Atmosphere Program at DSTO, SAMAP 2007
- G. DeNola, P. J. Hanhela, T. –H. Gan and W. Mazurek ”Analysis of Volatile Organic Compounds in the Exhaled Breath of Submariners” Breath 2009, Dortmund, Germany.

Elimination of Hydrocarbons from Exhaled Breath

- Anecdotal evidence from submariners : diesel odour exudes from the body well after disembarkation
- Analysis of breath samples from a submariner over a period of 2.5 days showed a decay in hydrocarbon concentrations over this period.
- So what ?
- Significant improvement from Oberons to Collins submarines.
- Nitrile rubber gloves for mechanics.



SUBMARINE ODOUR

- The role of odour is undervalued in submarine air monitoring.
  - Air quality in submarines and everyday life if subjectively assessed by odour
  - You can have the best air quality but if there is a trace of odorous air contaminant no one will be convinced.
- Diesel powered submarines have a characteristic odour.
  - Diesel fuel vapor
  - Diesel fuel residue
  - > C6 aldehydes (typically C9) from cooking oil oxidation (aerosols and vapour)

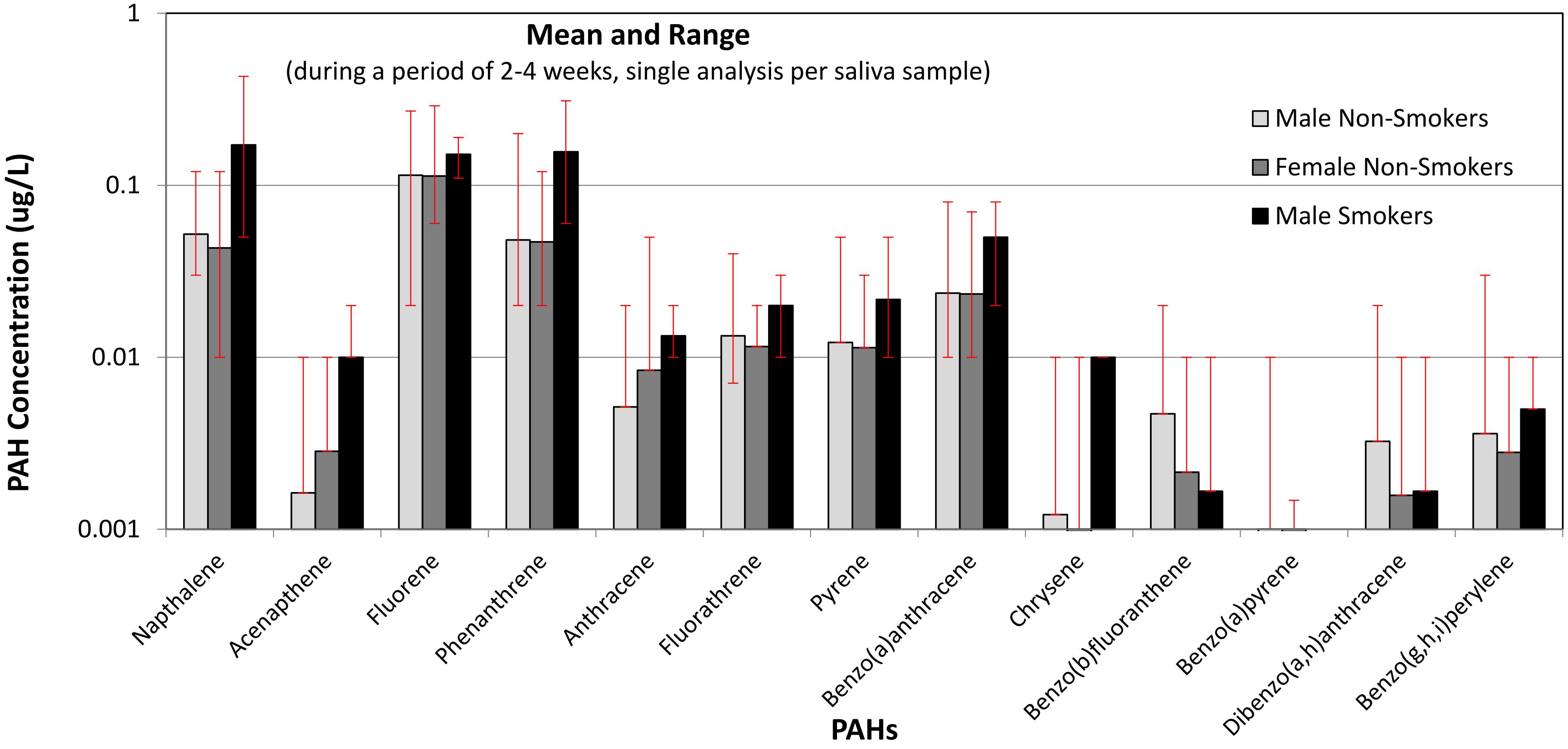
LIMITATIONS OF EXHALED BREATH ANALYSES FOR EXPOSURE MONITORING

- Largely affected by short-term exposure
- Limited to volatile compounds
  - For semi-volatile compounds
    - Blood (traditional)
    - Urine – parent compounds, metabolites (eg PAH exposure in Al smelting industry)
    - Saliva – used for drug monitoring in pharmaceutical industry

SALIVA PAHs

SMOKERS/NON-SMOKERS

(Mazurek et al SAMAP 2013)



Exposure Regulations

- Diesel Exhaust
  - 0.2 mg/m3, Diesel Particulate Matter, scheduled for 2006 (Gan and Mazurek, SAMAP 2003)
  - Implementation: MO LCDR Dr Jodie Bailey (2004)

- Fuel Vapour
  - Total Organics: 7.5 ppm (continuous exposure RN MPC90) 100 ppm reduced to 15 ppm Diesel Fuel ACIGH (2002)

- Smoking
  - Banned: Canada (Implementation MO LCDR Dr Debbie Pestell, SAMAP 2007)
  - Allowed: US, UK, France, Italy, Germany, Spain, Australia (discretion of CO)

- Carbon Dioxide
  - 0.5% - Continuous Exposure, (close to the limit of existing technology) EC Limits
  - Importance of short-term fluctuations (J James, SAMAP 2013)

Thank you !

Regenerative CO_2 Scrubber (MEA)

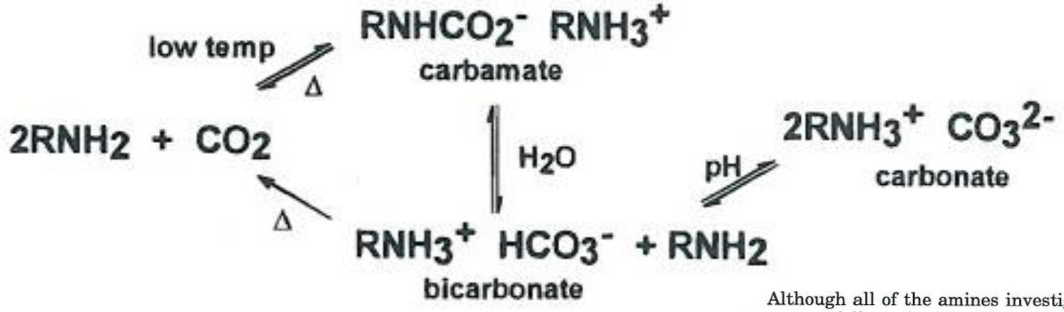
(MonoEthanolAmine)

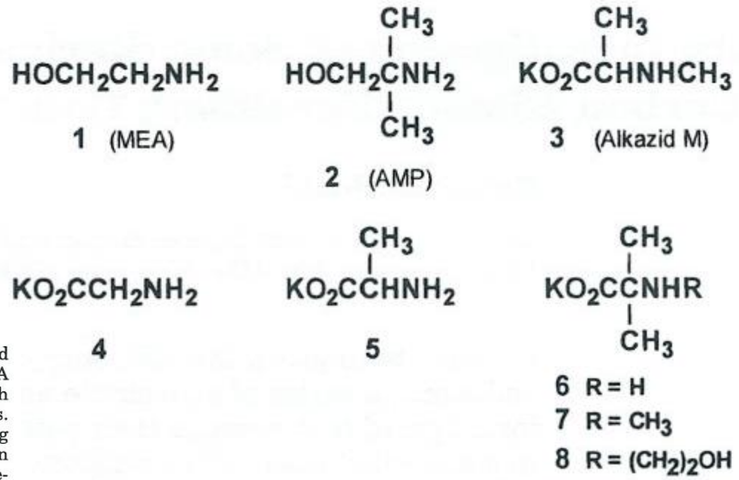
- Installed on COLLINS class submarines
  - – adapted from RN nuclear-powered submarines

- Reaction Mechanisms – Robert Hook, DSTO

Ind. Eng. Chem. Res. **1997,** *36,* 1779−1790

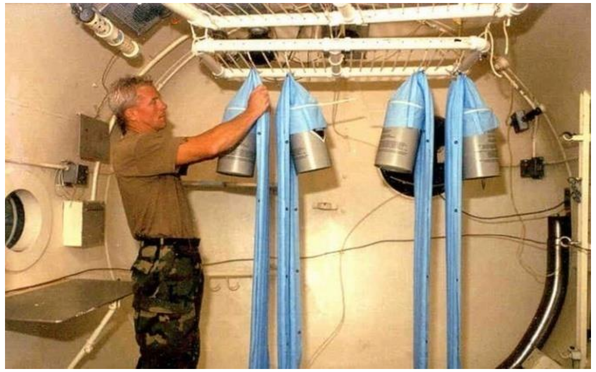
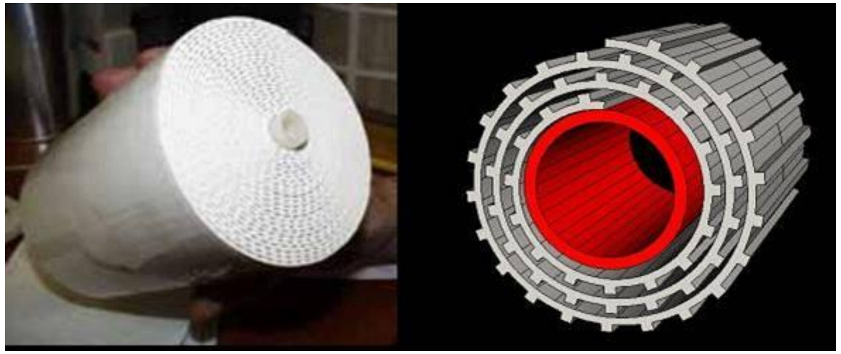
An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds

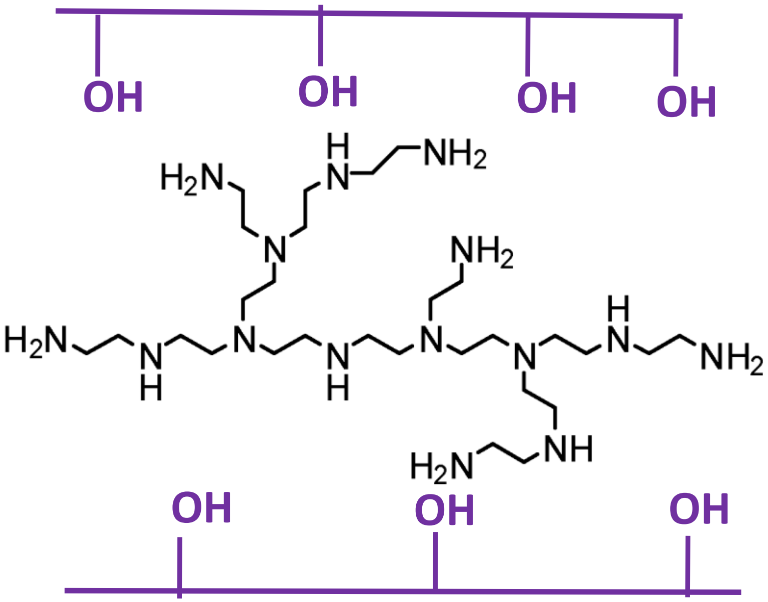


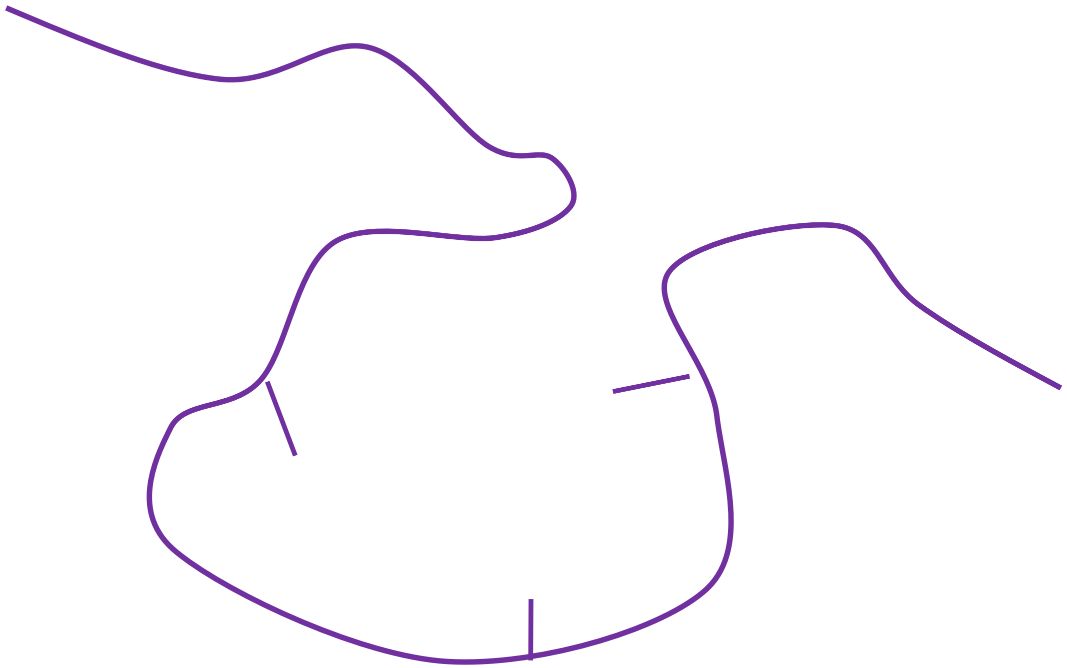


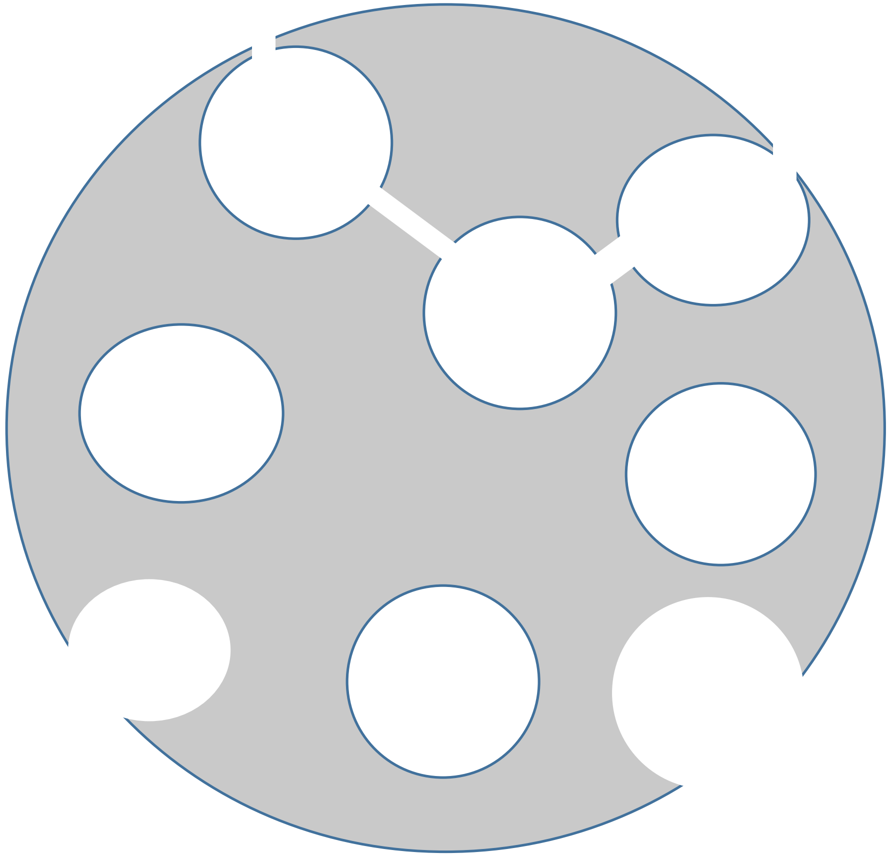
Although all of the amines investigated were found to successfully cycle CO_2, with the exception of MEA (**1**) and Alkazid M (**3**), each suffered problems with either absorption, desorption, or precipitation of salts. The α-dimethylamine function is successful in driving the absorption equilibrium to bicarbonate, but an alternative to the potassium carboxylate group is required to achieve reduced volatility and solubilization of all reaction species. Only Alkazid M (**3**) is likely to fulfill submarine-based scrubber requirements. α-Dimethylamines may be more suited to use in industrial processes where CO_2 partial pressures are higher.

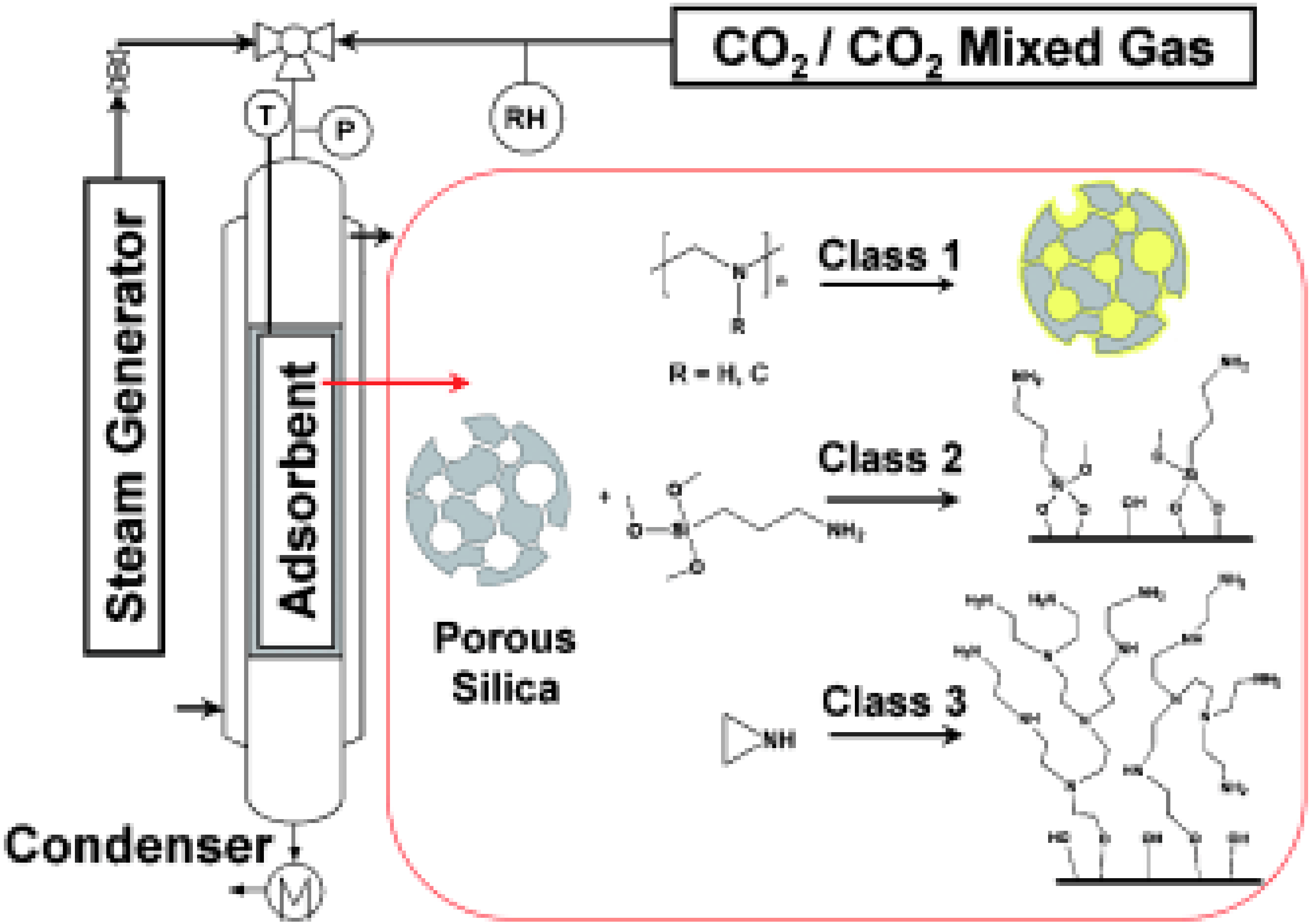

Sofnolime 1.0 - 2.5mm granules

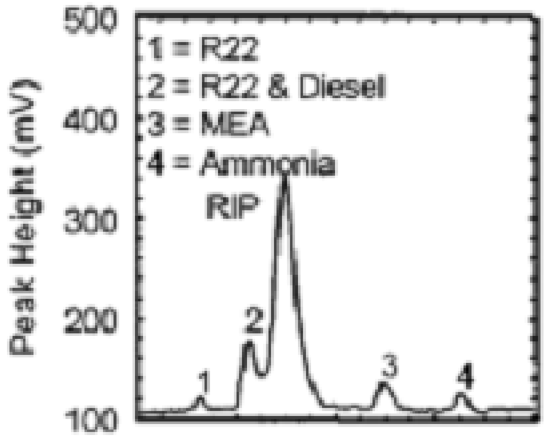





OH
OH
OH
OH
H2N
H
N
NH2
N
NH2
H2N
N
H
N
N
H
N
N
H
N
NH2
H2N
NH
OH
OH
OH






CO2 / CO2 Mixed Gas
RH
T
P
Steam Generator
Adsorbent
Condenser
M
Porous Silica
Class 1
R = H, C
Class 2
Class 3
NH


500
400
300
200
100
Peak Height (mV)
1 = R22
2 = R22 & Diesel
3 = MEA
4 = Ammonia
RIP
1
2
3
4


CAM