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M4R PROJECT NUMBER 10532 – DEVELOPMENT OF A CYLINDER PASSIVATION TECHNOLOGY FOR ENHANCED STABILITY OF GASEOUS SAMPLES AND GASEOUS FUEL REFERENCE MATERIALS

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M4R Project number 10532 – Further development of a cylinder passivation technology for enhanced stability of gaseous samples and gaseous fuel reference materials

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Approved on behalf of NPL by
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1 INTRODUCTION

The stability of chemical compounds in gas cylinder is influenced by the cylinder surface. Several compounds are considered reactive or sticky as ammonia or water for example. The development of new surface treatment or passivation for gas cylinder is a critical aspect to expand the lifetime of gas calibrant or to reduce uncertainties.

Effetech Ltd has a long experience in gas cylinder passivation development especially with "Performax" passivation. In a previous M4R project (reference number 10211), NPL performed some stability testing on "Performax" cylinder from Effectech Ltd [1].

In the meantime, Effectech Ltd developed a novel cylinder treatment improving the Performax treatment. This new treatment called "DB Gold" is a more advanced cylinder treatment that has the potential to be more effective in stabilising reactive compounds in aluminium gas cylinder than the previous treatment "Performax". This treatment is expected to be more effective at allowing challenging components to remain stable within the aluminium cylinder. It would allow the production of new stable reference materials for the reactive compounds to support growing sector (i.e. hydrogen fuel, environmental monitoring). The treatment has the potential to be successful in multiple challenging areas, such as the atmospheric monitoring area (i.e. producing ozone precursors reference materials with stable reference materials at nmol/mol levels).

To estimate the potential of the "DB Gold" passivation, Effectech Ltd provided NPL with a small batch of this prototype treatment in order to test the stability of a set of challenging compounds: water, ammonia, formaldehyde, oxygen and 30 components ozone precursors. The objective is to evaluate the potential of the new "DB Gold" surface treatment and identify future perspective to develop further this passivation with Effectech Ltd.

2 STUDY DESIGN

Based on Effectech Ltd's interest and NPL expert knowledge, four compounds considered unstable or with insufficient stability in state-of-the-art gas cylinder in hydrogen matrix were selected: formaldehyde, ammonia, oxygen and water.

Another group of 30 compounds known as 'O3P' (ozone precursor) was selected for stability testing on the atmospheric monitoring area. The ozone precursor compounds are: ethane, ethene, propane, propene, *i*-butane, *n*-butane, ethyne, trans-2-butene, 1-butene, cis-2-butene, *i*-pentane, *n*-pentane, 1,3-butadiene, trans-2-pentene, 1-pentene, 2-methylpentane, *n*-hexane, isoprene, *n*-heptane, benzene, 2,2,4-trimethylpentane, *n*-octane, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzeneand 1,2,3-trimethylbenzene. All the compounds will be evaluated at amount fraction of 4-5 nmol/mol in nitrogen matrix.

NPL's proposed to carry out a short-term stability study on these 5 compounds or group of compounds covering the two areas identified as hydrogen fuel and atmospheric monitoring. NPL will prepare gravimetric mixture of the selected compounds in DBGold cylinder and then measured within a few days of preparation to compare the measured value with the gravimetric reference value (theoretical amount fraction). A second measurement after 1-2 weeks will then be carried out and the measured value again compared to the gravimetric value. These time periods are considered acceptable as adsorption mechanisms to internal surfaces of the cylinder are rapid and loses due to these mechanisms would be captured by these measurements. This will allow any initial losses and short-term stability to be measured to allow assessment of the suitability of the treatment for use in these areas.

2.1 PRIMARY REFERENCE MATERIAL PREPARATION

2.1.1 Hydrogen matrix

All samples were prepared gravimetrically by dilution of NPL Primary Reference Materials (PRMs) in high purity hydrogen (99.9999 %, BIP+, Air Products). This was done using a well purged gas transfer line. The gas transfer line used was a 1/16” (Thames Restek, UK) treated tubing with Swagelok® connections with a minimum-dead-volume (MDV) connection (developed by NPL) at each end to connect to the cylinder. All components used were treated with Silconert® passivation (Thames Restek, UK). Purging was done via cyclic pressure purging a minimum of six times at each end of the filling line (the line was pressurised with filling gas then depressurised to displace residual air from the line).The cylinder used to prepare each sample was weighed against a tare cylinder (of equal size and shape) on a top pan electronic balance of type XPE26003LC (Mettler Toledo, US) using an automated weighing facility (KRISS, SK). The sample cylinders were weighed once they had been evacuated (before gas addition) and again after each addition. The mass of the PRM transferred was calculated using the mass difference between the cylinder before and after gas transfer [2]. The cylinders were rolled for 2 hours to homogenise the gas mixture after the preparation.

The gas mixtures prepared in the Effectech Ltd DBGold cylinders were prepared in the following manner:

The ammonia reference gas mixture was prepared in DBGold cylinder number D991018. This mixture was prepared using an NPL PRM containing around 5 μmol/mol ammonia in hydrogen and high purity hydrogen (99.9999 %, BIP+, Air Products). The targeted value was 400 nmol/mol.

The formaldehyde reference gas mixture was prepared in DBGold cylinder number D991013. This mixture was prepared using an NPL PRM with 11 μmol/mol formaldehyde in hydrogen and high purity hydrogen (99.9999 %, BIP+, Air Products). The targeted value was 600 nmol/mol.

The oxygen reference gas mixture was prepared in DBGold cylinder number D927368. This mixture was made from an NPL PRM containing 50 μmol/mol oxygen and 2800 μmol/mol nitrogen in hydrogen and high purity hydrogen (99.9999 %, BIP+, Air Products). Nitrogen had to be present in the cylinder for safety purposes, the nitrogen was not measured as part of this study. The targeted value for the oxygen was 5 μmol/mol.

The water reference gas mixture was prepared in DBGold cylinder number D990983. The mixture was made from an NPL PRM containing 50 μmol/mol water in hydrogen and high purity hydrogen (99.9999 %, BIP+, Air Products). The targeted value was 5 μmol/mol.

Table 1: Amount fractions of binary mixtures in hydrogen prepared for the DBGold short stability study.

Component	Cylinder ID	Amount fraction (μmol/mol)	Gravimetric uncertainty (μmol/mol) (*k*=1)
Ammonia	D991018	0.381	0.0013
Formaldehyde	D991013	0.592	0.0163
Oxygen	D927368	5.07	0.027
Water	D990983	5.08	0.013

2.1.2 Nitrogen matrix

All samples were prepared gravimetrically by dilution of NPL Primary Reference Materials (PRMs) in high purity nitrogen (99.9999 %, BIP+, Air Products). This was done using a well purged gas transfer line. The gas transfer line used was a 1/16” (Thames Restek, UK) treated tubing with Swagelok®

connections with a minimum-dead-volume (MDV) connection (developed by NPL) at each end to connect to the cylinder. All components used were treated with Silconert® passivation (Thames Restek, UK). Purging was done via cyclic pressure purging a minimum of six times at each end of the filling line (the line was pressurised with filling gas then depressurised to displace residual air from the line).The cylinder used to prepare each sample was weighed against a tare cylinder (of equal size and shape) on a top pan electronic balance of type XPE26003LC (Mettler Toledo, US) using an automated weighing facility (KRISS, SK). The sample cylinders were weighed once they had been evacuated (before gas addition) and again after each addition. The mass of the PRM transferred was calculated using the mass difference between the cylinder before and after gas transfer [2]. The cylinders were rolled for 2 hours to homogenise the gas mixture after the preparation.

The ozone precursor reference gas mixture was prepared in DBGold cylinder number D990968. This mixture was prepared using an NPL PRM with 200 nmol/mol of ozone precursor compounds and high purity nitrogen (99.99998 %, BIP+, Air Products). The ozone precursor compounds are: ethane, ethene, propane, propene, *i*-butane, n-butane, ethyne, trans-2-butene, 1-butene, cis-2-butene, *i*-pentane, *n*-pentane, 1,3-butadiene, trans-2-pentene, 1-pentene, 2-methylpentane, *n*-hexane, isoprene, *n*-heptane, benzene, 2,2,4-trimethylpentane, *n*-octane, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzeneand 1,2,3-trimethylbenzene. The targeted value was 4 nmol/mol for all compounds.

Table 2: List of gravimetric amount fraction and uncertainties for 30 components in the ozone precursor mixture in cylinder D990968.

Component	Amount fraction (nmol/mol)	Gravimetric uncertainty (nmol/mol) (*k*=1)
Ethane	4.242	0.0075
Ethene	4.157	0.012
Propane	4.185	0.0050
Propene	4.160	0.0050
i-butane	4.263	0.0049
n-butane	4.225	0.0049
Ethyne	4.382	0.025
trans-2-butene	4.240	0.0053
1-butene	4.216	0.0050
cis-2-butene	4.228	0.0052
i-pentane	4.171	0.0047
n-pentane	4.189	0.0048
1,3-butadiene	4.274	0.0094
trans-2-pentene	4.210	0.0053
1-pentene	4.280	0.0049
2-methylpentane	4.395	0.0052
n-hexane	4.395	0.0051
Isoprene	4.379	0.0049
n-heptane	4.403	0.0050
Benzene	3.723	0.0049
2,2,4-trimethylpentane	4.132	0.0046
n-octane	4.145	0.0047
Toluene	3.620	0.0047
Ethylbenzene	3.915	0.0048
m-xylene	3.847	0.0047
p-xylene	3.770	0.0046
o-xylene	3.747	0.0050
1,3,5-trimethylbenzene	3.803	0.0088
1,2,4-trimethylbenzene	3.835	0.013
1,2,3-trimethylbenzene	3.807	0.019

2.2 ANALYTICAL METHODS

2.2.1 Ammonia analysis

Ammonia in cylinder D991018 was analysed on 02/07/2021, 20/07/2021 and 13/08/2021 using selected ion flow tube coupled with mass spectrometry (SIFT-MS), Voice 200 Ultra (Anatune, UK). The reagent ions used were H_3O^+ and O_2^+, the reaction products NH_4^+ and NH_3^+ respectively were measured and quantified by the SIFT-MS. Calibration was performed using dynamic standards. They were generated using a mass flow controller (MFC) system (Bronkhorst, NL) by dilution of an NPL PRM (20 µmol/mol of ammonia in hydrogen) with high purity hydrogen (99.9999 %, BIP+, Air Products). The calibration encompassed the expected ammonia amount fraction with dynamic standard at 400 nmol/mol of ammonia for the first measurement and a calibration curve covering the range 200 – 400 nmol/mol and 100 – 400 nmol/mol ammonia in hydrogen for the following measurements respectively.

2.2.2 Formaldehyde analysis

The formaldehyde in cylinder D991018 was analysed on 12/07/2021, 22/07/2021 and 18/08/2021 using SIFT-MS, Voice 200 Ultra (Anatune, UK). The reagent ion used was H_3O^+ and reaction product CH_3O^+ was measured and quantified by the SIFT-MS. Calibration was performed using dynamic standards. They were generated using a MFC system (Bronkhorst, NL) by dilution of an NPL PRM (11 µmol/mol of formaldehyde in hydrogen) with high purity hydrogen (99.9999 %, BIP+, Air Products). The calibration encompassed the expected formaldehyde amount fraction and was produced as a matching 600 nmol/mol formaldehyde in hydrogen point for the first two measurements and a calibration curve of points covering the range 50-650 nmol/mol of formaldehyde in hydrogen for the last measurement.

2.2.3 Oxygen

The oxygen in cylinder D927368 was analysed on 07/07/2021, 21/07/2021 and 01/09/2021 using a 7890A gas chromatograph (GC) (Agilent Technologies, UK) coupled with a pulsed discharge helium ionisation detector (VICI, CH). The method used two Molesieve 5A capillary columns, one 30 m x 0.53 mm x 0.50 µm and one 50m x 0.53 mm x 0.50 µm with helium carrier gas. The loop size used for sample injection was 1 ml. Calibration was performed against a NPL PRM of nominal amount fraction 5 µmol/mol oxygen in helium.

2.2.4 Ozone precursor Analysis

The ozone precursor mixture in the cylinder D990968 was analysed on 02/07/2021 and 04/08/2021 using a GC (Scion Instruments 456, UK) coupled with a Scion Instruments flame ionization detector (FID) (Scion Instruments, UK). The method uses two columns; an Rxi®-5Sil MS column (L = 60 m, D = 0.32 mm, FT = 1.0 µm) (Restek, US) and an Rt® Alumina DOND/Na2SO4 (L = 30 m, D = 0.32 mm, FT = 5 µm((Restek, US) using hydrogen carrier gas.

The GC-FID system was also fitted with a sample pre-concentrator (Scion Instrument, UK) which is cooled to a temperature of -185°C before being heated to 190°C to release the components. Calibration was done with a matching standard of nominal amount fraction 4 nmol/mol of the ozone precursor components.

2.2.5 Water Analysis

The water in cylinder D990983 was analysed on 28/07/2021 on a quartz crystal microbalance, QMA401 (Michell, US). Gases are sampled directly from the gas cylinder to the analyser, via a HF series pressure regulator (3.4 bar outlet) (Swagelok, UK) and a second high precision flow regulator (model: RP10SS-MSB-0240-SW1/4”-040, LNI Schmidlin, CH) that was used to keep the pressure at 1 bar gauge into the analyser (flow to 0.333 L/min).

The second measurement on 13/08/2021 was performed on a SPARK cavity ring down spectrometer (Tiger Optics, US). Gases were sample directly gas from the cylinder to the analyser, via a HF series

pressure regulator (3.4 bar) (Swagelok, UK) and a second high precision flow regulator (model: RP10SS-MSB-0240-SW1/4”-040, LNI Schmidlin, CH). The flow into the instrument was then controlled using a needle valve (Swagelok, UK).
Calibration was performed using NPL PRMs of nominal amount fractions of 2 and 10 µmol/mol water in hydrogen.

3 RESULTS

3.1 DBGOLD CYLINDER PERFORMANCE FOR AMMONIA IN HYDROGEN

The analysis of ammonia in hydrogen matrix for the DBGold cylinder was performed within 24 hours and 2 weeks after preparation. An additional third measurement was performed one month after preparation. The results summarised in the table below show that the measured amount fraction within 24 hours agreed with the gravimetric value within a 95% confidence level. However, the measurement after two weeks showed a 23% loss from the gravimetric amount fraction. The additional measurement after 1 month showed the amount fraction remained similar to the second measurement rather than decaying further.

Table 3: Summary of results for stability of ammonia (400 nmol/mol) in hydrogen matrix in DBGold cylinder.

Cylinder reference D991018	Gravimetric value	Measured value within 24 hours	Measured value after 2 weeks	Measured value after 1 month
Ammonia amount fraction (nmol/mol)	381	369	295	296
Uncertainty (*k*=2) (nmol/mol)	2.5	30	20	21

3.2 DBGOLD CYLINDER PERFORMANCE FOR FORMALDEHYDE IN HYDROGEN

The analysis of formaldehyde in hydrogen matrix for the DBGold cylinder was performed within 24 hours and 1 week after preparation. An additional third measurement was performed one month after preparation. The results in the table below show that the amount fraction of formaldehyde in the DBGold cylinder remained stable for the duration of the measurements (1 month) showing there was no significant loss within the uncertainty of measurement. The DBGold cylinder, therefore, seem suitable for ensuring formaldehyde stability at around 600 nmol/mol in hydrogen matrix.

Table 4: Summary of results for stability of formaldehyde (600 nmol/mol) in hydrogen matrix in DBGold cylinder.

Cylinder reference D991013	Gravimetric value	Measured value within 24 hours	Measured value after 1 week	Measured value after 1 month
Formaldehyde amount fraction (nmol/mol)	592	608	576	616
Uncertainty (*k*=2) (nmol/mol)	33	51	50	28

3.3 DBGOLD CYLINDER PERFORMANCE FOR OXYGEN IN HYDROGEN

The analysis of oxygen in hydrogen matrix for the DBGold cylinder was performed within 24 hours and 2 weeks after preparation. The results in the table show there was agreement with the gravimetric value within the uncertainty within 24 hours on the first measurement. The measurement after 2 weeks showed there was a significant decay of oxygen amount fraction. Further analysis after one month shows continued decay of oxygen amount fraction in the DBGold cylinder.

Table 5: Summary of results for stability of oxygen (5 µmol/mol) in hydrogen matrix in DBGold cylinder.

Cylinder reference D927368	Gravimetric value	Measured value within 24 hours	Measured value after 1 week	Measured value after 1 month
Oxygen amount fraction (µmol/mol)	5.07	4.99	4.79	4.64
Uncertainty (*k*=2) (µmol/mol)	0.054	0.074	0.157	0.103

3.4 DBGOLD CYLINDER PERFORMANCE FOR OZONE PRECOURSOR COMPOUNDS IN HYDROGEN

The analysis of the ozone precursor mixture of compounds (ethane, ethene, propane, propene, i-butane, n-butane, ethyne, trans-2-butene, 1-butene, cis-2-butene, i-pentane, n-pentane, 1,3-butadiene, trans-2-pentene, 1-pentene, 2-methylpentane, n-hexane, isoprene, n-heptane, benzene, 2,2,4-trimethylpentane, n-octane, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzeneand 1,2,3-trimethylbenzene) was performed after 24 hours and 1 month after preparation. The results in the table below show that the components all remained stable within uncertainty for the one-month period of the short study.

Table 6: summary of ozone precursor mixture (4 nmol/mol) measurement in cylinder D990968. The compounds m-xylene and p-xylene are validated as a sum of the two compounds as they cannot be separated.

Component	Gravimetric value and uncertainty (*k*=2) (nmol/mol)	Measurement after 24 hours and uncertainty (*k*=2) (nmol/mol)	Measurement after 1 month and uncertainty (*k*=2) (nmol/mol)
Ethane	4.242 ± 0.016	4.30 ± 0.13	4.19 ± 0.09
Ethene	4.157 ± 0.024	4.28 ± 0.13	4.23 ± 0.09
Propane	4.185 ± 0.010	4.20 ± 0.09	4.21 ± 0.09
Propene	4.160 ± 0.010	4.17 ± 0.09	4.16 ± 0.09
i-butane	4.263 ± 0.010	4.24 ± 0.11	4.26 ± 0.11
n-butane	4.225 ± 0.010	4.26 ± 0.09	4.22 ± 0.09
Ethyne	4.382 ± 0.050	4.46 ± 0.22	4.57 ± 0.22
trans-2-butene	4.240 ± 0.012	4.23 ± 0.09	4.21 ± 0.09
1-butene	4.216 ± 0.010	4.22 ± 0.09	4.17 ± 0.09
cis-2-butene	4.228 ± 0.012	4.22 ± 0.09	4.21 ± 0.09
i-pentane	4.171 ± 0.010	4.18 ± 0.09	4.15 ± 0.09
n-pentane	4.189 ± 0.010	4.20 ± 0.09	4.18 ± 0.09
1,3-butadiene	4.274 ± 0.020	4.25 ± 0.09	4.35 ± 0.09
trans-2-pentene	4.210 ± 0.012	4.20 ± 0.09	4.19 ± 0.09
1-pentene	4.280 ± 0.010	4.28 ± 0.09	4.28 ± 0.09
2-methylpentane	4.395 ± 0.012	4.39 ± 0.09	4.40 ± 0.09
n-hexane	4.395 ± 0.012	4.38 ± 0.09	4.34 ± 0.09
Isoprene	4.379 ± 0.010	4.37 ± 0.09	4.42 ± 0.09
n-heptane	4.403 ± 0.010	4.40 ± 0.09	4.39 ± 0.09
Benzene	3.723 ± 0.010	3.71 ± 0.08	3.69 ± 0.08
2,2,4-trimethylpentane	4.132 ± 0.010	4.14 ± 0.09	4.13 ± 0.09
n-octane	4.145 ± 0.010	4.15 ± 0.09	4.14 ± 0.09
Toluene	3.620 ± 0.010	3.62 ± 0.10	3.59 ± 0.10
Ethylbenzene	3.915 ± 0.010	3.93 ± 0.10	3.90 ± 0.10
m-xylene	3.847 ± 0.010	7.63 ± 0.20	7.61 ± 0.20

p-xylene	3.770 ± 0.010		
o-xylene	3.747 ± 0.010	3.76 ± 0.10	3.75 ± 0.10
1,3,5-trimethylbenzene	3.803 ± 0.018	3.82 ± 0.10	3.81 ± 0.10
1,2,4-trimethylbenzene	3.835 ± 0.026	3.85 ± 0.10	3.85 ± 0.10
1,2,3-trimethylbenzene	3.807 ± 0.038	3.83 ± 0.10	3.83 ± 0.10

3.5 DBGOLD CYLINDER PERFORMANCE FOR WATER IN HYDROGEN

The analysis of water in hydrogen matrix for the DBGold cylinder was performed 24 hours after and 2 weeks after preparation. The results in the table show that the amount fraction of water within the table agreed within a 95% confidence level (*k*=2 uncertainty) with the gravimetric value and remained stable for the two-week duration of the short stability study. These results show that DBGold cylinders seem suitable for keeping water stable at amount fractions around 5 µmol/mol in hydrogen matrix.

Table 7: Summary of results for stability of water (5 µmol/mol) in hydrogen matrix in DBGold cylinder.

Cylinder reference D990983	Gravimetric value	Measured value after 24 hours	Measured value after 2 weeks
Water amount fraction (µmol/mol)	5.08	5.28	5.14
Uncertainty (*k*=2) (µmol/mol)	0.025	0.27	0.26

4 CONCLUSION

The preliminary tests for the DBGold treatment investigated four challenging compounds in hydrogen (water, formaldehyde, oxygen and ammonia) and a selection of 30 ozone precursor compounds at challenging amount fractions in nitrogen (ethane, ethene, propane, propene, i-butane, *n*-butane, ethyne, trans-2-butene, 1-butene, cis-2-butene, *i*-pentane, *n*-pentane, 1,3-butadiene, trans-2-pentene, 1-pentene, 2-methylpentane, *n*-hexane, isoprene, *n*-heptane, benzene, 2,2,4-trimethylpentane, *n*-octane, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzeneand 1,2,3-trimethylbenzene).

The study shows that, of the components tested in the DBGold cylinder, the 30 ozone precursor compounds at 4 nmol/mol in nitrogen, water at 5 µmol/mol in hydrogen and formaldehyde at 600 nmol/mol in hydrogen were stable within uncertainty for more than 2 weeks (1 month for the formaldehyde and ozone precursor compounds and 2 weeks for the water). The analysis done for the ammonia and oxygen showed agreement with the gravimetric amount fraction on the measurements within 24 hours, however, measurements after 1-2 weeks showed that there was significant decay of these components in the cylinder from the gravimetric amount fraction. The ammonia amount fraction seemed to remain stable after the initial decay, as shown by additional measurement taken on the cylinder, however, the oxygen amount fraction seemed to continue to experience decay of amount fraction compared to the gravimetric amount fraction.

The DBGold cylinder seems to be a promising passivation treatment for low µmol/mol water and high nmol/mol formaldehyde in hydrogen and for the mix of 30 ozone precursor compounds listed above at low nmol/mol levels in nitrogen. Further analysis would be required to determine the stability of these compounds over a longer time. For ammonia and oxygen, despite the initial measurement value showing agreement, the compound began to decay after a short amount for time. Further studies would be required to investigate this instability.

5 REFERENCES

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