

Investigation of cylinder pre-treatments for the stability of ammonia gas reference materials

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Abstract

This report describes work to evaluate the performance of different commercial and proprietary cylinder treatments in improving the stability of ammonia reference materials in high pressure cylinders. Gas mixtures of 100 $\mu\text{mol/mol}$ and 10 $\mu\text{mol/mol}$ ammonia in nitrogen were prepared gravimetrically at both NPL and VSL. Comparative measurements at each amount-of-substance fraction were used to assess which passivation technique minimised the loss of ammonia upon preparation. The results indicate little difference between the commercial treatments, except at lower amount-of-substance fractions (10 $\mu\text{mol/mol}$). The variation observed in performance could be explained by the different abilities of the various treatments to prevent the adsorption of ammonia molecules on the internal surfaces of the cylinder. A proprietary treatment, involving initial exposure of the cylinder surface to hydrogen sulphide, seemed to provide some benefits in terms of the short-term stability of the mixtures and is thought to be most effective in stopping ammonia adsorption, although the role of residual water on the cylinder surface in reacting with ammonia is unclear.

Keywords: gas reference materials, stability, cylinder passivation, ammonia

Introduction

Accurate and stable gas reference materials of ammonia at trace amount-of-substance fractions (later referred as “amount fractions”) are crucial to underpin field measurements and to facilitate international comparability. This is especially important for ammonia currently because the gas is a key contributor to secondary atmospheric aerosol production and accurate data on its global emissions is lacking [1]. A stable reference for these measurements is required to determine trends over time and comparability between locations, and it may only be achieved with accurate, internationally comparable gas reference materials with an uncertainty as low as possible [2-5]. A recent key comparison organised by the Consultative Committee for Amount of Substance: Chemistry and Biology (CCQM-K46) was used to assess the analytical capabilities of laboratories underpinning measurements of ammonia [6]. It highlighted significant discrepancies in the measurements, as shown in Figure 1. This lack of consensus amongst National Metrology Institutes (NMIs) may result in poor instrument calibration and affect the comparability of national measurement networks. This deficiency prompted the European Metrology Research Programme MetNH₃ proposal, which aimed to develop metrological traceability for the measurement of ammonia in air using primary gas reference materials and agreed measurement protocols [3,5]. The work described in this practitioner’s report expands on the background efforts to improve the stability of primary gas reference materials of ammonia, which have prompted a new key comparison, CCQM-K117, which is currently in progress.

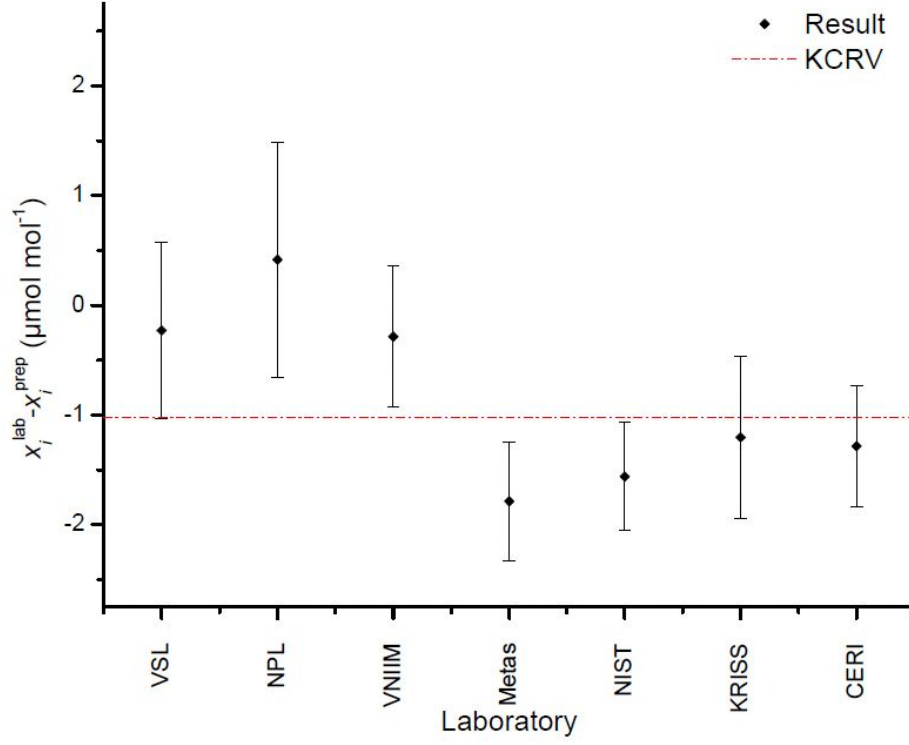


Fig. 1 Summary of the comparison results of ammonia in nitrogen (CCQM-K46); the mixtures circulated contained approximately 34 $\mu\text{mol/mol}$ ammonia in nitrogen. The y-axis displays the difference between the measured value reported by each laboratory i , x_i^{lab} , and the amount fraction from gravimetric preparation, x_i^{lab} . The dotted line shows the agreed Key Comparison Reference Value (KCRV). Taken from [6]

Gravimetric preparation of ammonia gas reference materials is often complicated by the adsorption of ammonia molecules onto the gas inner surfaces of the cylinder used for storage, during the preparation stage. To address this, a range of commercially available cylinder passivation techniques have been developed aimed at minimising the loss of ammonia. This work investigates the performance of a range of commercially available solutions.

Experimental

General

For the work described here, the National Physical Laboratory (NPL) and the Van Swinden Laboratorium (VSL), studied the suitability of different cylinder passivation techniques for the development of static gas reference materials of ammonia in nitrogen. Gas mixtures of 100 $\mu\text{mol/mol}$ and 10 $\mu\text{mol/mol}$ ammonia in nitrogen were prepared gravimetrically [7]. Both NPL and VSL prepared mixtures in Manufacturer A cylinders (A) as well as Manufacturer B cylinders (B); VSL also tested cylinders that had undergone a treatment offered by Manufacturer C (C) for reactive components such as NO_2 , SO_2 and VOCs whilst NPL also tested Manufacturer B cylinders that had undergone an additional proprietary in-house treatment (D). This treatment involved filling an evacuated cylinder with a mixture of approximately 10 $\mu\text{mol/mol}$ of hydrogen sulphide (H_2S) either in methane or nitrogen (to about 10 bar of pressure) and then incubating it inside an oven at 60°C for 72 hours. Two mixtures at each amount fraction for each passivation treatment were prepared, resulting in a total of six 100 $\mu\text{mol/mol}$ mixtures and six 10 $\mu\text{mol/mol}$ mixtures for each of NPL and VSL. The ammonia content of the mixtures was analysed by means of non-dispersive infra-red (NDIR) and photoacoustic infra-red spectroscopy. Comparative measurements at each amount fraction were used to assess which passivation technique minimised the loss of ammonia upon preparation.

Mixture preparation

At NPL, four of the six 100 $\mu\text{mol/mol}$ NH_3 in N_2 mixtures were prepared by loop injection of pure ammonia (Air Products, VLSI, 99.999 % purity) followed by addition of pure nitrogen (Air Products, BIP+, 99.99995 % purity), whilst the remaining two were prepared by dilution from high amount fraction parent mixtures (1000 $\mu\text{mol/mol}$); these parent mixtures were also prepared by loop injection of pure ammonia. The six 10 $\mu\text{mol/mol}$ mixtures were prepared by dilution of six 100 $\mu\text{mol/mol}$ parent mixtures. The hierarchy, shown in Online Resource 1, illustrates the preparation route for all 12 mixtures prepared at NPL for this study. At VSL, six mixtures of 100 $\mu\text{mol/mol}$ NH_3 in N_2 were prepared by gravimetric dilution of a 3000 $\mu\text{mol/mol}$ NH_3 in N_2 parent mixture. Six mixtures of 10 $\mu\text{mol/mol}$ NH_3 in N_2 were prepared by gravimetric dilution from a 300 $\mu\text{mol/mol}$ NH_3 in N_2 parent mixture. At both institutions, the gravimetric preparation procedure followed ISO 6142 [7]. The amount fractions of the 24 mixtures prepared by NPL and VSL are summarised in Table 1 where the horizontal lines divide gas mixtures with different nominal amount fractions.

Cylinder identifier	Amount fraction / $\mu\text{mol/mol}$	Passivation Treatment
NPL11268	100.02	A
NPL11269	100.01	A
NPL1657	100.05	B
NPL1844	100.29	B
NPL1659	99.99	D
NPL1769	101.16	D
NPL11255	9.99	A
NPL11256	10.02	A
NPL1648R	10.00	B
NPL1842	10.00	B
NPL1766	10.01	D
NPL1770	9.99	D
VSL144224	100.06	A
VSL143714	99.96	A
VSL253765	100.11	B
VSL553627	100.16	B
VSL574499	99.92	C
VSL374492	100.11	C
VSL144225	10.02	A
VSL143704	9.95	A
VSL353604	10.02	B
VSL853261	10.00	B
VSL474489	10.02	C
VSL474488	10.00	C

Table 1 Gravimetric data for the NH_3 in nitrogen mixtures prepared (A = Manufacturer A, B = Manufacturer B, C= Manufacturer C for NO_2 , SO_2 , and VOCs, D = Manufacturer B with H_2S treatment). The prefix NPL or VSL in the cylinder identifier designates where these mixtures were prepared

Measurements of gravimetric mixtures

The mixtures prepared were analysed by NPL and VSL to establish which passivation treatment, if any, exhibited the best performance. At NPL, the twelve mixtures were analysed using a non-dispersive infrared spectrometer (URAS 26, AO2000, ABB Instruments). At any given time during the measurement, two cylinders of the same nominal amount fraction were connected to a 3-way valve which led to the input of the analyser; the valve allowed rapid switching between either of the two cylinders connected to it. Cylinders were equipped with a low-volume regulator (Swagelok, HF series) to adjust the pressure of the gas to meet the requirements of the analyser. All lines consisted of Sulfinert[®]-treated Swagelok stainless steel tubing (1/16" outer diameter). Each individual cylinder line (*i.e.* upstream the 3-way valve) was equipped with a vent line: in order to minimise stabilisation times, each mixture was vented for five minutes prior to sampling. Typical measurement stabilisation times ranged from 20 to 40 minutes. Once a mixture had been sampled, the 3-way valve was switched to the other mixture connected to the sampling line; the mixture that had been sampled would then be replaced with one to sample. This routine was repeated until all the mixtures were measured. The analyser response was recorded during the measurement as the voltage output of the instrument. In addition, a zero measurement was also performed by flowing ultra-pure nitrogen into the NDIR spectrometer. The final instrument response for each mixture was calculated as the average of the last 5 minutes of sampling (200 data points) for the mixture minus the voltage recorded for the zero measurement. At VSL, the analysis of the mixtures was performed using a photoacoustic infrared analyser (Innova 1412 Photoacoustic Field Gas-Monitor). The sampling system consisted of one mass flow controller and one reducing valve connected to a twelve port multi-position valve. All tubing used was Sulfinert[®]-treated stainless steel. The six cylinders of the same nominal amount fraction were connected to the multi position valve. This set-up was chosen to ensure that the analysis results were only influenced by the different performance of the cylinder treatment and not by the sampling system. All tubing was flushed with the NH₃ in N₂ mixtures and left pressurised overnight and flushed again the following day before starting the measurement. To minimise stabilisation times, a pre-mixture with nominally the same amount fraction was used to flush the analyser for one hour. The response of each mixture was then recorded during the total sampling time to check for drift during the analysis. The sampling time for the 100 µmol/mol mixtures was thirty minutes and sixty minutes for the 10 µmol/mol mixtures. The final response of each mixture is the average of the last 10 minutes (20 individual samples) of the sampling period. The series was measured twice on different days, in the same order. This means that the mixtures were not disconnected between measurements. The analyser was not calibrated in absolute terms before use as the sole purpose of the measurements was to compare the two sets of six mixtures.

Results and discussion

For each mixture, a response factor (RF) was calculated as the ratio of the instrument response (I) and the ammonia amount fraction of the mixture (x_{NH_3}), as shown in equation (1):

$$RF = \frac{I}{x_{\text{NH}_3}} \quad (1)$$

For the response factors calculated for the mixtures, the instrument response used in equation (1) was corrected for the analyser's zero, as discussed above. The use of response factors over absolute instrument response was preferred as it highlighted the effects of adsorption onto cylinder walls independently of the amount fraction of the mixture. The response factors for all the mixtures prepared by both NPL and VSL are compared in Figures 2 and 3. The results from NPL are normalised to the highest response factor measured at NPL and likewise the result from VSL are normalised to the highest response factor measured at VSL. The error bars represent the maximum variation of the signal over the period of stable instrument response. This represents a conservative estimate of the uncertainty.

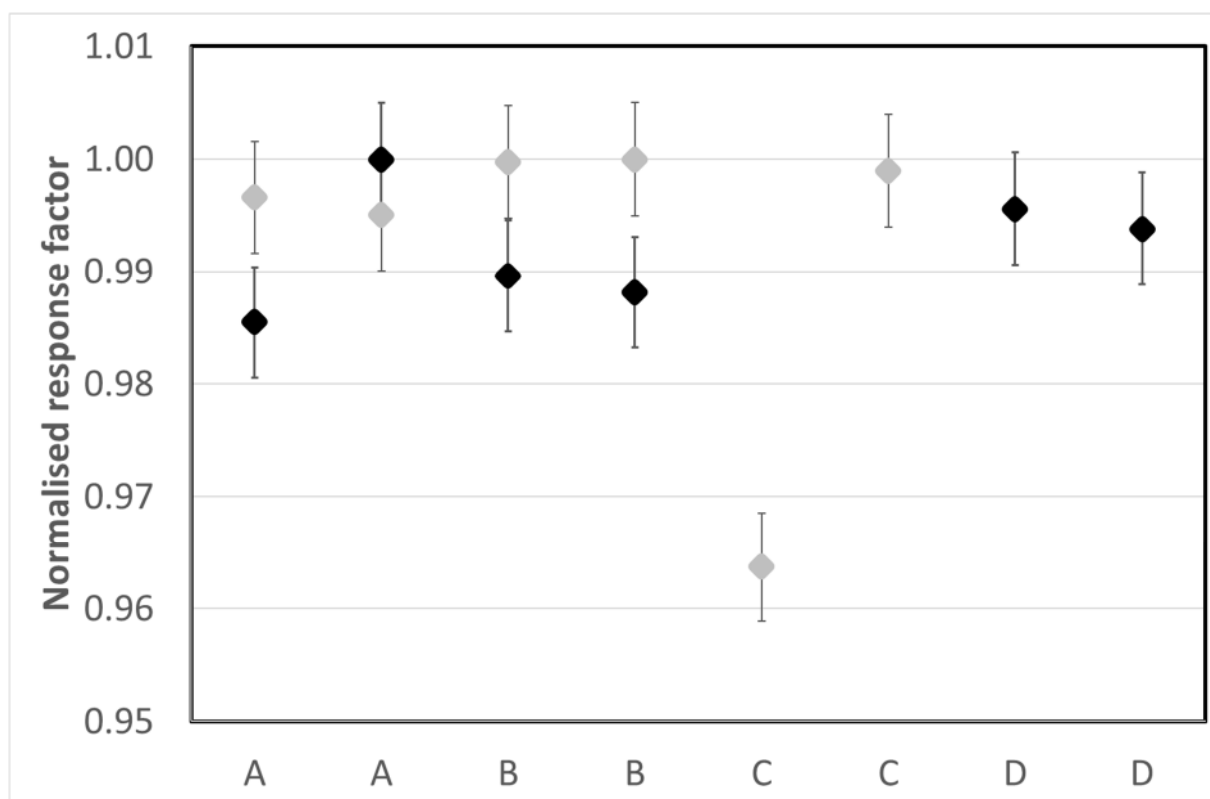


Fig. 2 Normalised response factors for the 100 µmol/mol NH₃ in N₂ mixtures from NPL (black diamonds) and VSL (grey diamonds)

At the 100 $\mu\text{mol/mol}$ level, little or no difference was seen between the different cylinder coatings at the level of uncertainty – around 1 to 2 % – with which amount fraction reference values can be confidently established. When the paired data is considered there was some evidence that the NPL H_2S treatment, Type D, was an improvement on the Type B coating alone. These replicate findings were also observed with other reactive gases [4]. Where there are significant differences seen between cylinder pairs (for instance Type A at NPL and Type C at VSL) this is most likely due to the variability in the production and treatment during cylinder production rather than a function of the property of the cylinder treatment itself.

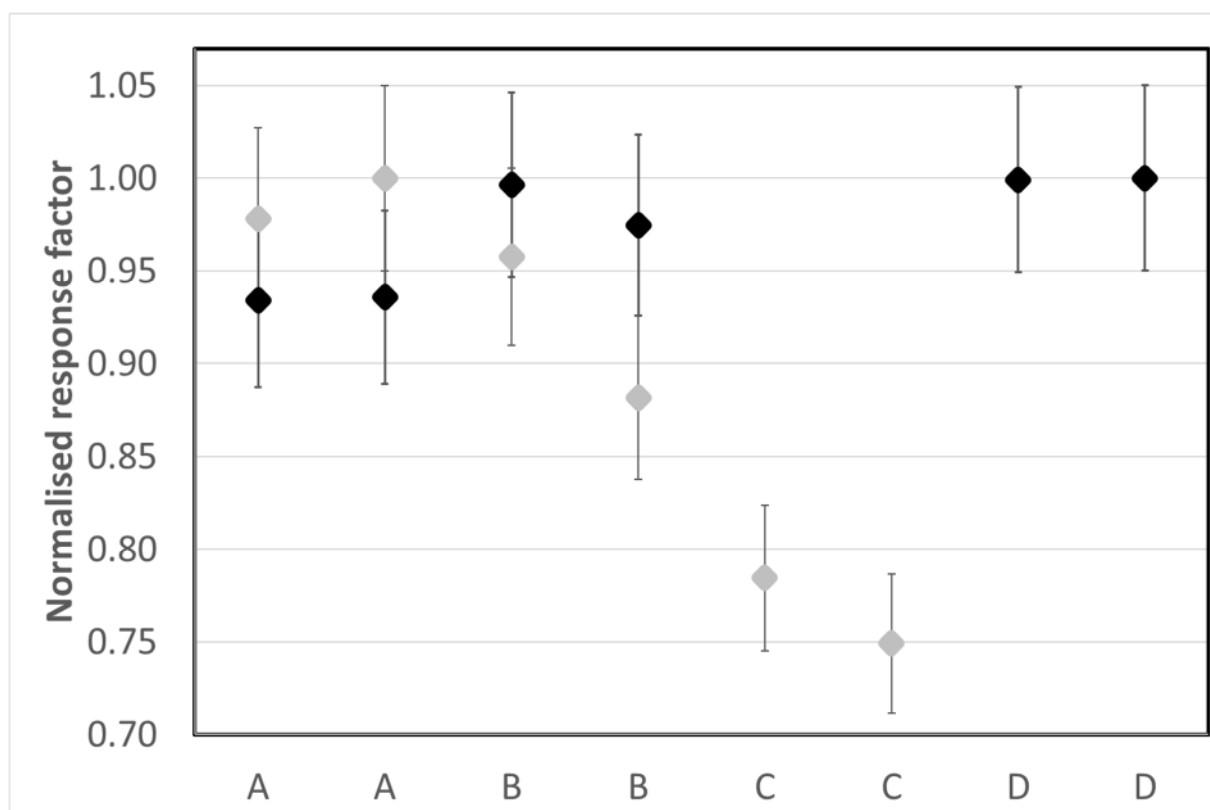


Fig. 3 Normalised response factors for the 10 µmol/mol NH₃ in N₂ mixtures from NPL (black diamonds) and VSL (grey diamonds)

At 10 $\mu\text{mol/mol}$, the differences in performance are larger. Significant relative losses are observed for the Manufacturer C cylinders – albeit this is a treatment designed to deal with other reactive species such as NO_2 , SO_2 and VOCs [8], rather than ammonia – and based on these limited results, this cylinder type did not seem suitable for ammonia gas reference materials at 10 $\mu\text{mol/mol}$. NPL found that both Manufacturer A cylinders showed significant ammonia losses, whilst VSL did not observe this. Conversely VSL observed more significant losses for Manufacturer B than NPL did. The results from NPL again show that the additional in-house treatment on Manufacturer B cylinders makes an appreciable difference from the standard treatment of such Manufacturer particularly at the 10 $\mu\text{mol/mol}$ level.

The variability in performance across all the cylinder types becomes more significant in relative terms as the amount fraction decreases and could well be the origin of the discrepancies seen in CCQM-K46 which are of the order of 1 $\mu\text{mol/mol}$. An approximate calculation suggests that a monolayer of ammonia molecules (based on a molecular diameter of 0.26 nm) adsorbed on to the cylinder surface would account for a loss of 0.3 $\mu\text{mol/mol}$ at an amount fraction of 100 $\mu\text{mol/mol}$ and 100 bar pressure. This was confirmed by decant studies aiming to determine the extent of NH_3 adsorption on cylinder walls. Briefly, mixtures at nominally 100 $\mu\text{mol/mol}$ and 10 $\mu\text{mol/mol}$ were prepared in Manufacturer A and B cylinders and then decanted into cylinders from the same manufacturer. The ammonia content of both parent and daughter mixtures was then measured to determine any changes due to the decant process. The results are presented in Table 2 and show a loss of ammonia upon decant between 0.3 and 0.9 $\mu\text{mol/mol}$ for mixtures of amount fraction 100 $\mu\text{mol/mol}$ in Manufacturer A and B cylinders. The average loss was 0.5 $\mu\text{mol/mol}$.

It is therefore conceivable that the different performance of the cylinder coatings might be a function of their varying ability to prevent one or more layers of ammonia physically adsorbing to the cylinder. Equally the role of water on the cylinder surface reacting chemically with the ammonia is unknown since, unlike for untreated cylinders, treated cylinders are not heated during evacuation in case this damages the treatment. Differing amounts of residual water in cylinders may result in differing performance.

Passivation Treatment	Amount fraction / $\mu\text{mol/mol}$	Amount fraction change upon decant/ $\mu\text{mol/mol}$
B	100.00	-0.50
B	99.97	-0.54
B	9.99	-0.70
B	9.98	-0.14
A	100.03	-0.86
A	100.04	-0.28
A	10.00	-0.49
A	10.01	-0.67

Table 2 Data on the adsorption of NH_3 on cylinder walls (A = Manufacturer A, B = Manufacturer B). The first four mixtures were prepared at NPL whilst the last four at VSL

Conclusions

The performance of three commercially available cylinder passivation techniques in the preparation of static ammonia reference materials was tested by NPL and VSL, as well as that of an H₂S cylinder treatment developed at NPL. Such proprietary treatment, applied to Manufacturer B cylinders, appeared to improve the cylinder performance, especially at the 10 µmol/mol level. However, there is no extensive data on how repeatable the performance of this treatment is when used for ammonia mixtures although at NPL a good stability is achieved using it for other gas components. It appears that a single passivation treatment that outperformed all the others could not be identified: the results of NPL and VSL on Manufacturer A and B cylinders seemed somewhat conflicting, and this is attributed to the variability in performance between cylinders that had nominally undergone the same treatment. However, our results show that Manufacturer C cylinders, specifically designed for reactive species such as NO₂, SO₂ and VOCs, are unsuitable for the preparation of ammonia standards at the 10 µmol/mol level. It is possible that the differences in performance are a result of the ability of different treatments to prevent multiple layers of ammonia adsorption to the cylinder surface – as in the case of the NPL proprietary treatment. Equally the role of residual surface water chemically reacting with ammonia is unknown, as it is its variability across cylinder types, as well as competing adsorption processes between H₂O and NH₃ [9]. It has to be highlighted that none of the coatings considered in this paper were specifically designed for use with trace ammonia, since this is an emerging requirement in gas metrology and gas cylinder technology. More work is needed on a larger set of cylinders to enhance the trustworthiness of the results. Preferably new types of passivation treatments would be tested in the same manner. Further decant studies indicate that in the best performing cylinders (Manufacturer A and B) approximately 0.5 µmol/mol are lost to the cylinder surfaces. This corresponds to the absorption of 1 or 2 monolayers of ammonia on the cylinder walls. Finally, this study has not investigated the long-term performance of these cylinder treatments, a property very relevant to reference material producers. A further study looking at this aspect should also be included in future work.

Compliance with ethical standards

Funding See below Acknowledgments

Conflicts of interest/Competing interests None. This work is original, unpublished, and is not being considered elsewhere

Availability of data and material See Supplementary 1, Supplementary 2 and Supplementary 3 Excel files

Code availability Not applicable

Acknowledgments

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Figure and table captions

Fig. 1 Summary of the comparison results of ammonia in nitrogen (CCQM-K46); the mixtures circulated contained approximately 34 $\mu\text{mol/mol}$ ammonia in nitrogen. The y-axis displays the difference between the measured value reported by each laboratory i , x_i^{lab} , and the amount fraction from gravimetric preparation, x_i^{lab} . The dotted line shows the agreed Key Comparison Reference Value (KCRV). Taken from [6]

Online Resource 1 Hierarchy of the mixtures prepared at NPL

Table 1 Gravimetric data for the NH_3 in nitrogen mixtures prepared (A = Manufacturer A, B = Manufacturer B, C = Manufacturer C for NO_2 , SO_2 , and VOCs, D = Manufacturer B with H_2S treatment). The prefix NPL or VSL in the cylinder identifier designates where these mixtures were prepared

Fig. 2 Normalised response factors for the 100 $\mu\text{mol/mol}$ NH_3 in N_2 mixtures from NPL (black diamonds) and VSL (grey diamonds)

Fig. 3 Normalised response factors for the 10 $\mu\text{mol/mol}$ NH_3 in N_2 mixtures from NPL (black diamonds) and VSL (grey diamonds)

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