Bilateral comparison of primary reference materials (PRMs) containing methanol, ethanol and acetone in nitrogen

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Abstract
A range of oxygenated volatile organic compounds (OVOCs) are present in the atmosphere as a result of direct emissions and as products of atmospheric oxidation. Long-term measurements are important to understand changes to these emission sources and atmospheric oxidation processes. Accurate and stable traceable gaseous primary reference materials are needed to underpin rigorous quality assurance and quality control at monitoring stations such as those organised by the World Meteorological Organization Global Atmosphere Watch (WMO-GAW) programme. The development of a capability for providing traceable primary reference materials (PRMs) of OVOCs is of paramount importance due to the increasing prevalence of these compounds in the urban atmosphere and also because there is currently no Central Calibration Laboratory (CCL) for these components within the WMO-GAW programme. This EURAMET bilateral comparison demonstrates the measurement compatibility (≤3%) for three OVOCs (methanol, ethanol and acetone) at nominally 5 μmol mol⁻¹ between two National Metrology Institutes: the National Physical Laboratory (NPL), UK and the Van Swinden Laboratorium (VSL), the Netherlands. The comparison shows that a gravimetric method for value assignment is applicable to acetone but that a more complicated procedure must be employed to value assign methanol and ethanol due to corrections for adsorption effects, which can be as large as 10% of the nominal value. This work demonstrates the importance of making appropriate corrections to ensure the accuracy of these reference materials. NPL and VSL used different approaches to make these corrections providing confidence and independent verification. This work supports new calibration and measurement capabilities for methanol, ethanol and acetone in the range of 1 μmol mol⁻¹ –10 μmol mol⁻¹ with expanded uncertainties of 6.9% (3%), 7.3% (3%) and 1.7% (2%) for NPL (VSL), respectively, to be realized in the key comparison database and supports the development of the required traceability infrastructure to underpin long-term global measurements of these OVOCs.

Keywords Comparison · Methanol · Ethanol · Acetone · Adsorption · Primary reference materials

Introduction
Oxygenated volatile organic compounds (OVOCs) are present in the atmosphere as a result of atmospheric oxidation of hydrocarbons, direct emissions from vegetation, e.g. growing plants and/or plant debris, and other direct emission sources that include evaporation of oxygenated solvents or fuels used in industrial processes, and incomplete combustion from motor vehicles, stationary sources and biomass burning. OVOCs are generally more reactive than alkanes and play an active role in the atmospheric chemistry responsible for tropospheric ozone formation in both polluted and remote environments. Three of the most prevalent OVOCs in the atmosphere are methanol, ethanol and acetone, which have observed amount fractions in the ranges of (0.1–10) nmol mol⁻¹, (0.02–240) nmol mol⁻¹ and (0.2–2) nmol mol⁻¹, respectively [1–4]. These three OVOCs are now amongst the most abundant compounds observed in urban atmospheres [5, 6] as a result of changes in contributions from different sources to total emissions [7, 8]. Methanol, ethanol and acetone have been identified, by the World Meteorological Organisation Global Atmosphere Watch (WMO-GAW) programme, as key compounds that should be globally monitored in the long-term [9]. After methane, methanol is the next most abundant organic gas in
the global atmosphere and is a significant source of tropospheric carbon monoxide and formaldehyde. Methanol is also important as it has major sources in the biosphere and is an abundant oxidation product. Ethanol is of interest as a tracer of alternative fuel use due to its increasing use as a biofuel, that is leading to a growing atmospheric burden [10]. Acetone is an abundant oxidation product and is a source of free radicals in the upper troposphere [11].

The long-term atmospheric measurements of the amount fractions of these OVOCs are important to enable the evaluation of changes in both emissions and atmospheric oxidation processes. A prerequisite for accurately measuring these compounds at monitoring stations is having high-quality stable primary standards, which assure the quality and integrity of long-term measurements. This is critical to ensure the accuracy of the measurements and for the rigorous determination of long-term compositional trends. The published strategy of the WMO-GAW programme [12] emphasizes the importance of quality assurance and quality control at all global, regional and contributing stations within the network [13]. A principle of the WMO-GAW quality assurance system is to ensure the provision of full traceability to primary standards such as multicomponent gas mixtures maintained by National Metrology Institutes (NMIs) who disseminate this metrological traceability through primary reference materials (PRMs) providing traceability to the International System of Units (SI). The WMO-GAW programme has established data quality objectives for methanol, ethanol and acetone of < 20 % [9]. Requirements for primary standards to be used for field calibrations would be at amount fractions of ≤ 100 nmol mol\(^{-1}\) in an air matrix with stabilities of ≥ 2 years and with uncertainties of < 10 % so as to ensure that the uncertainties of the primary standards do not dominate the overall measurement uncertainty. Primary standards are often produced in a balance of nitrogen as this is simpler and provides better stability than air but once established a transition to an air matrix can be envisaged.

The development of a robust and accurate capability for providing traceable PRMs of OVOCs is of paramount importance as there is currently no Central Calibration Laboratory (CCL) for these components within the WMO-GAW programme. In contrast to simple hydrocarbons, mixtures with OVOCs are much more challenging to prepare in high pressure gas cylinders as a result of their lower vapour pressures, dipole moments and in the case of alcohols the formation of hydrogen bridges, which decreases volatility substantially compared to similar weight hydrocarbons increasing the proportion that adsorbs to the cylinder walls. Amount fractions in the PRMs are determined by purity analysis and gravimetry. However, adsorption losses to the internal surfaces within the cylinder and cylinder valve during preparation can result in amount fractions in the mixture that are lower than determined from gravimetry, often by more than the gravimetric uncertainty [14, 15]. The magnitude of the adsorption is dependent on the internal surface of the cylinder and the amount fraction of the components. A given amount adsorbed on a surface leads to a reduction of the amount fraction of that component in the gas mixture. The amount that is adsorbed to the surface is limited by the availability of active sites resulting in an absolute adsorption effect as opposed to a relative one that becomes non-negligible as amount fraction decreases [16]. Some cylinder passivation treatments perform better than others at minimizing this surface adsorption [17].

Equally important to the development of primary standards for OVOCs is the evaluation of their compatibility. Previous work in CCQM-K93 [14] has looked at international comparability for the preparation of binary mixtures of ethanol in nitrogen at amount fractions typically used to calibrate evidential breath analysers in many countries (120 µmol mol\(^{-1}\)) but to the best of our knowledge this is the first comparison to investigate the accuracy of multi-component oxygenated volatile organic compounds gas reference materials in the low µmol mol\(^{-1}\) amount fraction range, where adsorption loses become increasingly important. This comparison was undertaken between the National Physical Laboratory (NPL), UK and the Van Swinden Laboratory (VSL), the Netherlands, within the framework of the European Association of National Metrology Institutes (EURAMET) and is intended to develop the necessary infrastructure to support long-term global measurements of these OVOCs within the WMO-GAW programme and other national, regional and global monitoring networks. This paper demonstrates the comparability of PRMs containing nominally 5 µmol mol\(^{-1}\) of methanol, ethanol and acetone in a balance of nitrogen between the two aforementioned NMIs. While this amount fraction is nominally higher than that required for primary standards it is an important step towards reaching compatibility at the required lower amount fraction ranges.

**Experimental methods**

**Preparation of comparison mixture**

A batch of three NPL primary reference materials (NPL PRMs) containing methanol, ethanol, acetone, n-hexane, propane and benzene at nominal amount fractions of 5 µmol mol\(^{-1}\) were prepared in March 2015 at NPL. They were prepared gravimetrically according to ISO 6142-1 [18] in 10 L aluminium cylinders (Luxfer) with Spectraseal pretreatment (BOC). The hydrocarbon components (n-hexane, propane and benzene) were not included in the comparison but were present as internal references to be used to assess the stability, e.g. n-hexane is known to be stable in
this cylinder type for more than 5 years [17]. After preparation, all three mixtures were analysed approximately every three weeks for nine months. After nine months of stability measurements, one mixture was sent to VSL in January 2016 (NPL-A475). The remaining two mixtures (NPL-A481 and NPL-A482) were kept at NPL and were analysed periodically. After the comparison mixture was returned from VSL in October 2016, all three mixtures were re-analysed three more times over a 5-month period. At the conclusion of the comparison two years of stability data had been collected on all three mixtures.

**Stability assessment**

Stability of the comparison mixture was assessed by tracking the ratios of the GC-FID responses of methanol, ethanol and acetone relative to an internal reference (n-hexane) [19, 20]. Least squares fit straight line regressions were modelled to the temporal evolution of these three ratios to determine if there was any statistically significant change in amount fraction of any of the measurands in the comparison mixture (NPL-A475). The slopes from the straight line regression analysis were evaluated with an analysis of variance (ANOVA) test using the ‘StatsLinearRegression’ function in IGOR pro 8.04 (Wavemetrics) [21, 22] to determine whether they were significantly different to zero using an F-test, i.e. no drift in amount fraction during the timeline of the comparison.

**Preparation of in‑house reference materials at NPL and VSL**

At NPL, one PRM (NPL-A420) was used for this comparison. It was prepared gravimetrically according to ISO 6142-1 [18] in October 2013 and from different pure starting materials than the comparison mixture but in a similar 10 L aluminium cylinder (Luxfer) with Spectra Seal II passivation and 10 L aluminium cylinders with passivation from TAKACHIHO. They were prepared at 5 µmol mol⁻¹–10 µmol mol⁻¹ by combining binary mixtures that had been prepared gravimetrically at nominally (50–100) µmol mol⁻¹ in nitrogen (Air Products, BIP⁺) by liquid injection [23]. The purity of nitrogen (Air Products, BIP⁺) was checked for water, methanol, ethanol and acetone impurities. Organic impurities and the water content of the ethanol, methanol and acetone used for the preparation of the gas reference materials, were quantified. All nominally pure liquids had a stated purity better than 99 %.

**Analytical methodologies**

At NPL, a gas chromatograph equipped with a flame ionisation detector (GC-FID, Agilent Technologies 6890) equipped with 6-port gas sampling valve (Valco VICI) and a capillary GC column (Agilent J&W, DB-624, 75 m × 0.53 mm, 1.0 µm) was used for the analysis. All cylinders were connected to the GC system with a low dead-volume connector and 1/16” Sulfinert® coated sample line and an NPL custom-designed flow restrictor, which were all purged thoroughly with the OVOC gas mixtures before use. A capillary column of approximately 50 mL min⁻¹ was used to flush the sampling loop (250 µL) of the 6-port gas sampling valve. At least 10 measurements were performed in all cases and the last five runs of each were used for the calculations.

At VSL, a GC-FID (Interscience) equipped with a thermal desorption system (UNITY 2 series and Air server, Markes International) was used for the analysis. The GC was equipped with two FID detectors working with a Dean-Switch and two chromatography columns. A cold trap type ‘Air Toxics / TO-14’ and GC column (Agilent J&W, PoraBOND U, 25 m × 0.32 mm, 7 µm) were used for the analysis. All cylinders were connected to a shared reducer through a gas auto-sampler. Six cylinders were connected to the auto-sampler. The whole system was flushed thoroughly with OVOC gas mixtures before use. All lines, cylinder connectors and the reducer were Sulfinert® coated stainless steel. The last five runs of the 20 performed for each gas reference material were used for the calculations. Three series of measurements were performed.
Value assignment

NPL assigned the amount fraction of each target component (methanol, ethanol and acetone) in the comparison mixture (NPL-A475), \( x_u \), using:

\[
x_u = x_s \bar{r}
\]

where \( x_s \) is the amount fraction of the target component in the in-house NPL PRM (NPL-A420) and \( \bar{r} \) is the average ratio of the instrument response and is calculated from:

\[
\bar{r} = \frac{2 \bar{A}_u}{(\bar{A}_{s,1} + \bar{A}_{s,2})}
\]

where \( \bar{A}_u \) is the average peak area from the last five repeated measurements of the comparison mixture, \( \bar{A}_{s,1} \) is the average peak area from the last five repeated measurements of NPL-A420 before running the comparison mixture and \( \bar{A}_{s,2} \) is the average peak area from the last five repeated measurements of NPL-A420 after running the comparison mixture.

At VSL, a response factor (\( f \)) for each component in each VSL PRM (Table 1) was calculated from the average peak area of the last five repeated measurements of the VSL PRM (\( \bar{A}_s \)) and from the component amount fraction of that PRM (\( x_s \)) using:

\[
f = \frac{\bar{A}_s}{x_u}
\]

For each component the average \( f \) of the VSL PRMs and the average peak area of the last five repeated measurements of the comparison mixture (\( \bar{A}_u \)) were used to calculate the amount fraction (\( x_u \)) in the comparison mixture (NPL-A475):

\[
x_u = \frac{\bar{A}_u}{f}
\]

Uncertainty evaluation

At NPL, the standard uncertainty of the measurand, \( u(x_u) \), in the comparison mixture was calculated by:

\[
u(x_u) = \sqrt{\frac{u^2(x_s)}{x_u^2} + \frac{u^2(\bar{r})}{\bar{r}^2}}
\]

\( u(x_u) \) is the uncertainty of the amount fraction of the measurand in the NPL PRM and \( u(\bar{r}) \) is the uncertainty of the ratio, which includes, e.g. repeatability, internal blanks, peak shape (error of integration), error in the sample volume. The uncertainty in \( \bar{r} \) was calculated by:

\[
u^2(\bar{r}) = \frac{u^2(\bar{A}_u)}{\bar{A}_u^2} + \frac{u^2(\bar{A}_{s,1})}{(\bar{A}_{s,1} + \bar{A}_{s,2})^2} + \frac{u^2(\bar{A}_{s,2})}{(\bar{A}_{s,1} + \bar{A}_{s,2})^2}
\]

Expanded uncertainties were determined by multiplication of the standard uncertainties by a coverage factor of two (\( k=2 \)) corresponding to a 95 % confidence interval. The final result was determined as the average of three independent measurements and the combined uncertainty was determined by adding in quadrature the associated uncertainties for each measurement and multiplying by a coverage factor of 2 (\( k=2 \)).

At VSL, the experimental design of the measurements generated three sequences with five measured values. The standard uncertainty associated with each of the values could be readily computed from the standard deviation of the peak areas of the comparison mixture and the five VSL PRMs, and the uncertainty of the (corrected) values of the VSL PRMs, using the law of propagation of uncertainty from the GUM (Guide to the expression of uncertainty in measurement) [24]. Two contributions of additional dispersion were identified, one due to differences in the adsorption behaviour of the components of interest and another due to reproducibility effects between the three sequences. For quantifying both contributions, meta-analysis using the

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Table 1 Gravimetric and corrected amount fractions with expanded uncertainties of the in-house PRMs used by NPL and VSL to assign values to the comparison mixture

| PRM     | Component | Amount fraction (μmol mol⁻¹) | Gravimetric | Corrected |
|---------|-----------|-----------------------------|-------------|-----------|
| NPL-A420| Methanol  | 4.987 ± 0.014               | 4.549 ± 0.110 |
|         | Ethanol   | 5.076 ± 0.010               | 4.780 ± 0.113 |
|         | Acetone   | 4.991 ± 0.008               | 4.889 ± 0.117 |
| VSL37633| Methanol  | 4.932 ± 0.001               | 4.828 ± 0.042 |
|         | Ethanol   | 5.026 ± 0.003               | 4.988 ± 0.043 |
|         | Acetone   | 5.029 ± 0.002               | 5.048 ± 0.044 |
| VSL113219| Methanol | 5.077 ± 0.001               | 4.973 ± 0.043 |
|          | Ethanol   | 5.005 ± 0.002               | 4.950 ± 0.043 |
|          | Acetone   | 4.998 ± 0.001               | 4.985 ± 0.043 |
| VSL113218| Methanol | 4.998 ± 0.001               | 4.824 ± 0.042 |
|          | Ethanol   | 5.003 ± 0.002               | 4.908 ± 0.043 |
|          | Acetone   | 4.993 ± 0.001               | 4.972 ± 0.043 |
| VSL276328| Methanol | 4.513 ± 0.001               | 4.280 ± 0.037 |
|          | Ethanol   | 4.996 ± 0.002               | 4.867 ± 0.042 |
|          | Acetone   | 5.004 ± 0.001               | 4.975 ± 0.043 |
| VSL453258| Methanol | 10.090 ± 0.002              | 9.758 ± 0.085 |
|          | Ethanol   | 9.966 ± 0.002               | 9.974 ± 0.086 |
|          | Acetone   | 10.027 ± 0.002              | 10.122 ± 0.088 |
DerSimonian-Laird model [25] was used to obtain the excess variance. The median excess standard deviation due to differences in the adsorption behaviour was 0.033 µmol mol⁻¹ for methanol, 0.010 µmol mol⁻¹ for ethanol and 0.011 µmol mol⁻¹ for acetone, based on the five PRMs. The reproducibility effect was negligible.

An adsorption correction was developed for ethanol and methanol, whereas for acetone it was deemed sufficient to account for the two effects in the uncertainty budget, supplementary to the contributions from static gravimetric gas mixture preparation and the verification. The values obtained for the correction of the amount fraction acetone were very close to zero, considering the experimental uncertainty. The correction was based on the analytical results obtained with a dynamic gravimetric method for gas mixture preparation based on continuous injection (ISO 6145-4) [26] was used. The differences between the analytical and gravimmetrical values have been taken as corrections, with an uncertainty component due to between-cylinder effects. The different cylinder treatments behaved sufficiently similar. The difference between analytical and gravimmetrical values for the 10 µmol mol⁻¹ PRM was somewhat larger for methanol than for the 5 µmol mol⁻¹, but the pool of data was too small to conclude that the adsorption differs at the two amount fraction levels. For ethanol and acetone, the differences were small and did not show any dependency on the amount fraction at all.

The result of the amount fraction of the three components (methanol, ethanol and acetone) was computed as the weighted mean of the 15 measured values, taking into consideration the dependencies between these measured values. The covariance matrix associated with the vector of 15 measured values was created by propagating the standard uncertainties of the peak areas of the transfer standards, the peak areas of the gravimetric standards, and the amount fractions of the gravimetric standards. The weighted mean is obtained by solving the resulting linear set of equations and using the covariance matrix for the weighting. The expanded uncertainty is obtained by multiplying the standard uncertainty by a coverage factor of two.

### Results

#### Correction of in-house PRMs for preparative losses

The gravimetric amount fractions of methanol and ethanol in NPL PRM (NPL-A420) were corrected for adsorption of the target components to the cylinder wall and valve during preparation. Scanlon and Willis [27] used GC-FID responses and known amount fractions to determine effective carbon number (ECN) for a range of compounds. By adapting this work it is possible to relate the amount fraction of compound $i$ in mixture NPL-A420 ($x_{i,d}$) to the GC-FID response of $i$ in mixture NPL-A420 ($A_{i,d}$) relative to the amount fraction ($x_{r,p}$) and GC-FID response of n-hexane ($A_{r,p}$), an inert internal reference that does not undergo adsorption loss. This equation (Eq. 7) requires estimates of ECNs for compound $i$ ($Z_i$) and n-hexane ($Z_r$) to be used.

$$x_{i,d} = \frac{Z_i \times A_{i,d} \times x_{r,p}}{Z_r \times A_{r,p}} \quad (7)$$

Using Eq. 7, the amount fraction or ECN of compound $i$ can be calculated for any mixture relative to an inert internal reference. Rearranging Eq. 7 in terms of $Z_r$ for a higher amount fraction mixture ($p$) gives:

$$Z_r = \frac{Z_i \times x_{i,p} \times A_{r,p}}{A_{i,p} \times x_{r,p}} \quad (8)$$

In the absence of any losses the ECN of compound $i$ is independent of amount fraction. Substituting Eq. 8 into Eq. 7 produces Eq. 9. This approach provides a method, independent of ECN, to determine the amount fraction of compound $i$ in mixture NPL-A420 ($x_{i,p}$) from the gravimetric amount fractions of n-hexane in NPL-A420 ($x_{r,p}$) and in a higher amount fraction mixture $p$ ($x_{r,p}$) and the measured GC-FID response of n-hexane in NPL-A420 ($A_{r,d}$) and in a higher amount fraction mixture $p$ ($\bar{A}_{r,p}$):

$$x_{i,d} = \frac{x_{i,p} \times \bar{A}_{r,p} \times A_{i,d} \times x_{r,d}}{A_{i,p} \times x_{r,p} \times \bar{A}_{r,d}} \quad (9)$$

The $\bar{A}_{r,p}$ and $\bar{A}_{i,p}$ values were determined from three separate analyses of two different 50 µmol mol⁻¹ mixtures prepared from different pure materials. The $A_{i,d}$ and $A_{r,d}$ values were determined from the average of 42 separate analyses of NPL-A420 conducted on the same GC-FID instrument during the comparison. This approach assumes that ECN for the internal reference (n-hexane) is independent of amount fraction. Data for n-hexane, shows no significant difference in ECN between the 5 ($5.92 \pm 0.01$) µmol mol⁻¹ and 50 ($5.91 \pm 0.01$) µmol mol⁻¹ mixtures when propane, a similar aliphatic hydrocarbon, is used as the internal reference. The gravimetric and corrected data based on Eq. 9 for NPL-A420 are shown in Table 1, which shows an adsorption loss of 9 % ± 3 % and 6 % ± 2 % for methanol and ethanol, respectively. The corrected values for NPL-A420 were used to value assigned the comparison mixture (NPL-A475).

The five VSL PRMs (VSL376333, VSL113219, VSL113218, VSL276328 and VSL453258) were verified against an independent primary method based on dynamic preparation of primary gas mixtures (in the range of 2 µmol mol⁻¹ to 7 µmol mol⁻¹) using ISO 6145-4 [26]. The in-situ gas mixtures were obtained by controlled...
evaporation of a gravimetric liquid mixture, containing the OVOC pure components, and their dilution in a known flow of dry and clean air. The verification results were used to develop a correction on the gravimetric amount fractions due to cylinder wall and valve adsorption. As in the case of the comparison mixture, the calculation of the VSL PRMs analytical values was based on the response factor approach. Scrutinising the verification results of the three measurements series of each VSL PRM using meta-analysis demonstrated that there were no other uncertainties to account for than the uncertainty arising from the in-situ prepared primary gas mixtures. For methanol and ethanol, a mean correction of the gravimetric value was calculated and the uncertainty associated with the three observed differences was propagated using the law of propagation of uncertainty. For acetone, the value of the correction for the gravimetric value was set to zero, and the uncertainty of the evaluation of the adsorption effect was included in the uncertainty budget. The gravimetric data and the corrected data of the five VSL PRMs used in this comparison are shown in Table 1. The somewhat larger analytical result for the 10 µmol mol⁻¹ standard is attributed to analytical variability. This variability has been taken into account when evaluating the uncertainty of the assigned amount fractions, including that for the amount fraction of acetone.

### Measurement results and comparison mixture stability

Table 2 shows a summary of the measurement results submitted by NPL and VSL for this comparison. Both laboratories made three independent measurements of the comparison mixture under repeatability conditions on different days with reported relative standard deviations of ≤ 1 %. These independent measurements are labelled as NPL#1, NPL#2, NPL#3, VSL#1, VSL#2 and VSL#3 in Table 2. Table 2 also shows the average of these three measurements for each institute, and these are labelled as NPL results and VSL results in Table 2. The uncertainties associated with these values represented the uncertainties of each institute to provide these reference materials and will be the uncertainty levels sought as calibration and measurement capabilities (CMCs). These were 6.9 %, 7.3 % and 1.7 % (NPL) and 3 %, 3 % and 2 % (VSL) for methanol, ethanol and acetone, respectively.

| Laboratory | Component | Date       | Result (µmol mol⁻¹) | Uncertainty (µmol mol⁻¹) (%) | Repeatability (%) |
|------------|-----------|------------|---------------------|-----------------------------|-------------------|
| NPL #1     | Methanol  | 23/04/2015 | 4.62                | 1.02                        | 1.02              |
|            | Ethanol   |            | 4.61                | 0.66                        | 0.66              |
|            | Acetone   |            | 5.13                | 0.92                        | 0.92              |
| NPL #2     | Methanol  | 14/05/2015 | 4.55                | 0.46                        | 0.46              |
|            | Ethanol   |            | 4.60                | 0.35                        | 0.35              |
|            | Acetone   |            | 5.12                | 0.37                        | 0.37              |
| NPL #3     | Methanol  | 04/06/2015 | 4.63                | 0.71                        | 0.71              |
|            | Ethanol   |            | 4.63                | 0.26                        | 0.26              |
|            | Acetone   |            | 5.14                | 1.10                        | 1.10              |
| NPL result | Methanol  | 16/03/2017 | 4.60                | 0.32 (6.9)                  | 6.9               |
|            | Ethanol   |            | 4.62                | 0.33 (7.3)                  | 7.3               |
|            | Acetone   |            | 5.13                | 0.09 (1.7)                  | 1.7               |
| VSL #1     | Methanol  | 22/06/2016 | 4.70                | 0.41                        | 0.41              |
|            | Ethanol   |            | 4.70                | 0.08                        | 0.08              |
|            | Acetone   |            | 5.11                | 0.21                        | 0.21              |
| VSL #2     | Methanol  | 27/06/2016 | 4.69                | 0.33                        | 0.33              |
|            | Ethanol   |            | 4.69                | 0.11                        | 0.11              |
|            | Acetone   |            | 5.12                | 0.18                        | 0.18              |
| VSL #3     | Methanol  | 04/07/2016 | 4.74                | 0.27                        | 0.27              |
|            | Ethanol   |            | 4.71                | 0.24                        | 0.24              |
|            | Acetone   |            | 5.11                | 0.18                        | 0.18              |
| VSL result | Methanol  | 26/01/2017 | 4.71                | 0.14 (3.0)                  | 3.0               |
|            | Ethanol   |            | 4.70                | 0.14 (3.0)                  | 3.0               |
|            | Acetone   |            | 5.11                | 0.10 (2.0)                  | 2.0               |
NPL’s measurements were all made between April and June 2015 while VSL’s were made in June and July 2016. Therefore, the stability of the comparison mixture is important to verify over this timescale to ensure the robustness of the comparison. Figure 1 shows the ratio of the measurands relative to n-hexane for the comparison mixture (NPL-A475) and the other two mixtures (NPL-A481, NPL-A482) prepared in the same batch for the duration of the comparison (March 2015–March 2017). Least squares straight line regression analysis was performed to determine whether any change in the amount fraction of the three measurands in the comparison mixture was statistically significant. The results of an ANOVA test demonstrated that there was no statistically significant change for any of the three measurands (methanol, $F = 2.75 < F_{\text{crit}} = 4.67$, $p < 0.05$; ethanol, $F = 1.35 < F_{\text{crit}} = 4.67$, $p < 0.05$; acetone ($F = 0.01 < F_{\text{crit}} = 4.67$, $p < 0.05$), where $F$ denotes the observed value of the $F$ statistic, $F_{\text{crit}}$ the critical value and $p$ the probability. Using the linear regression fits, the amount fractions of methanol, ethanol and acetone for the travelling standard (NPL-A475) were determined for the time periods of the NPL and VSL measurements (shown in Fig. 1). From this analysis the amount fractions of methanol, ethanol and acetone were estimated to be 2.3 %, −0.6 % and −0.06 % different between these two periods, respectively. In the case of ethanol and acetone these differences are small in relation to the reported uncertainties of the assigned values for NPL (7.3 % and 1.7 %) and VSL (3 % and 2 %), respectively. For methanol, the difference is similar to VSL’s reported uncertainty of 3 % and about a third of NPL’s uncertainty of 6.9 %. However, the positive change in methanol would in effect bring the assigned values of NPL and VSL into even closer agreement if any changes in amount fraction had occurred. However, as the results of the ANOVA test indicated that the mixture was stable no corrections have been made to the amount fraction of the comparison mixture (NPL-A475).

**Comparison results**

Figure 2 and Table 3 show the results of the comparison between the assigned values and the gravimetric value ($x_{\text{prep}}$) of the comparison mixture (NPL-A475). Figure 2 shows that
for methanol and ethanol the assigned values from the NPL and VSL measurement results are lower than the gravimetric values ($x_{\text{prep}}$) of the comparison cylinder (NPL-A475) by approximately 9 % and 5 % for methanol and ethanol, respectively. This is the result of adsorptive losses of these compounds to the cylinder valve and walls during preparation. For acetone, the NPL and VSL results both agree (<0.6 %), within the uncertainties ($U(x_{\text{lab}})$) of the gravimetric value ($x_{\text{prep}}$), demonstrating that adsorption of acetone to the cylinder valve and walls was minimal such that no correction for adsorption loss is necessary.

Figure 3 and Table 4 show the results of the observed differences between NPLs and VSLs assigned values of methanol, ethanol and acetone in the comparison mixture (NPL-A475) in both absolute ($\mu$mol mol$^{-1}$) and relative (%) terms. These were determined by subtracting VSLs results from those of NPLs. The results show that for methanol and ethanol NPLs assigned values are lower than VSLs by 2.4 % and 1.8 %, respectively, while for acetone NPLs assigned value was higher than VSLs by 0.5 %. The expanded uncertainties shown in Fig. 3 and Table 4 are determined by combining in quadrature the uncertainties associated with NPL and VSL assigned values of the comparison mixture. The relative difference was determined by dividing the difference (NPL-VSL) by the NPL assigned value and multiplying by 100 %.

Figure 3 shows there is good agreement, within the uncertainties, between the NPL and VSL measurement results when corrections for adsorption losses for methanol and ethanol are included.

### Conclusions

The results of this bilateral comparison demonstrate agreement, within the stated expanded uncertainties, between NPL and VSL for methanol, ethanol and acetone with observed differences of $-2.37 \pm 7.57$ %, $-1.84 \pm 7.86$ % and $0.43 \pm 2.85$ %, respectively. The results of this comparison support the ability of NPL and VSL to assign accurate values to their reference materials of methanol, ethanol and acetone with uncertainties of 3 % (6.9 % for NPL) for methanol, 3 % (7.3 % for NPL) for ethanol and 2 % (1.7 % for NPL) for acetone. These results will be used to support NPL’s and VSL’s calibration and measurement verification.
capabilities (CMC) for acetone, methanol and ethanol in air and/or nitrogen at amount fractions from 1 μmol mol−1 to 10 μmol mol−1. For methanol and ethanol this is contingent on ensuring that adsorptive losses within the in-house PRMs used for value assignment have been appropriately corrected. The work presented here shows that for lower amount fraction OVOC PRMs (≤ 10 μmol mol−1) the amount fraction determined by gravimetry is not accurate if the effects of adsorption during preparation are not taken into account. The fact that NPL and VSL used different approaches to make these corrections provides both confidence and independent verification. Given that the atmospheric abundance of these compounds in the remote atmosphere at WMO-GAW global background stations is in the low nmol mol−1 range further work to develop lower amount fraction PRMs at the 100 nmol mol−1 level is important and should be the focus of future work. Adsorption losses can be expected to be even more challenging at the lower amount fractions (nmol mol−1) requirement by monitoring stations but the approaches outlined here provide the basis for ensuring the accuracy of these PRMs when they are developed. Recent advances in gravimetric preparation to minimise adsorption have been demonstrated for PRMs of water at 10 μmol mol−1 showing an improvement of about 4 % in accuracy thus providing a gravimetric preparation method to achieve lower uncertainties than reported in this work and this will be one of the focuses of future work [28].

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