CIPM MRA
Comparison reports

CCQM-K174

Methanol, ethanol and acetone in air

KEY COMPARISON

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CCQM-K174 Oxygenated volatile organic compounds in nitrogen

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Field

Amount of substance

Subject

Amount fraction of oxygenated volatile organic compounds in nitrogen (track C key comparison)

1 Introduction

A series of oxygenated volatile organic compounds (oxy-VOCs) is found in the atmosphere and they are present both from direct emissions as well as products of atmospheric chemistry. Their long-term behaviour is important to determine both emissions and oxidation processes. The development of a capability for providing traceable reference standards of oxy-VOCs is of paramount importance to underpin rigorous quality assurance and quality control for the long-term monitoring of the levels of these components in the atmosphere.

A first bilateral comparison was organised by EURAMET [1], targeting the amount fractions of methanol, ethanol and acetone at a level of 5 μmol mol^{-1}. In this first key comparison, the same measurands are targeted, but at lower amount fraction levels. Thereby, this key comparison constitutes a further step towards the development of measurement standards for the atmospheric monitoring of these compounds.

This key comparison aims to support Calibration and Measurement Capabilities (CMCs) for the amount fractions of three key oxy-VOCs (acetone, methanol and ethanol) as representatives of a larger family of environmentally-relevant oxy-VOCs. It was organised on behalf of the CCQM Gas Analysis Working Group (CCQM-GAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) in accordance with the provisions of the CIPM Mutual Recognition Arrangement (CIPM MRA) [2, 3] of the International Committee for Weights and Measures (CIPM).

2 Design of the key comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: Participating national metrology institutes (NMIs) and designated institutes (DIs) in CCQM-K174

Acronym	Country	Institute
CMI	CZ	Czech Metrology Institute, Prague, Czech Republic
LNE	FR	Laboratoire national de métrologie et d'essais, Paris, France
METAS	CH	Eidgenössisches Institut für Metrologie, Bern, Switzerland
NIM	CN	National Institute of Metrology, Beijing, China
NMISA	ZA	National Metrology Institute of South Africa, Lynnwood Ridge, South Africa
NPL	GB	National Physical Laboratory, Teddington, United Kingdom
VSL	NL	Van Swinden Laboratorium, Delft, The Netherlands

2.2 Measurement standards

The nominal ranges of amount fractions of the targeted components in the mixtures are given in table 2.

Table 2: Nominal composition of mixtures, given in amount fractions

Component	Amount fraction $x/(\mathrm{nmol\,mol^{-1}})$
methanol	100 – 1000
ethanol	100 – 1000
acetone	100 – 1000
nitrogen	Balance

Considering that the degree of adsorption decreases in the order methanol → ethanol → acetone [1], it was decided to prepare gas mixtures with amount fractions decreasing in that order. The nominal amount fractions were 900 $\mathrm{nmol\,mol^{-1}}$ for methanol, 500 $\mathrm{nmol\,mol^{-1}}$ for ethanol and 200 $\mathrm{nmol\,mol^{-1}}$ for acetone.

The travelling standards were prepared gravimetrically in accordance with the instructions in ISO 6142-1 [4, 5]. The preparation started with binary mixtures of 200 $\mu\mathrm{mol\,mol^{-1}}$ methanol, 150 $\mu\mathrm{mol\,mol^{-1}}$ ethanol, 100 $\mu\mathrm{mol\,mol^{-1}}$ acetone, and 100 $\mu\mathrm{mol\,mol^{-1}}$ *n*-hexane in nitrogen. *n*-Hexane was added as tracer component. The binary mixtures of methanol and ethanol were prepared in Luxfur UK aluminium cylinders with a water volume of 10 L. The mixtures of acetone and n-hexane were prepared in Luxfur UK aluminium cylinders with a volume of 10 L. All mixtures were prepared using the syringe method [4, 5]. The syringe was weighted using a robot [6]. All mixtures were prepared in BIP+ nitrogen from Air Products.

The purity of the materials was assessed in accordance with ISO 19229 [7]. The results are shown in tables 3-7.

Table 3: Purity assessment of acetone (Sigma Aldrich), expressed in amount fractions (μmol mol^{-1})

Component	x	$u(x)$
water	620	124
acetone	999380	124

Table 4: Purity assessment of methanol (Sigma Aldrich), expressed in amount fractions (μmol mol^{-1})

Component	x	$u(x)$
water	655	33
methanol	999345	33

Table 5: Purity assessment of ethanol (Merck), expressed in amount fractions (μmol mol^{-1})

Component	x	$u(x)$
water	344	28
ethanol	999656	28

Table 6: Purity assessment of n-hexane (Merck), expressed in amount fractions (μmol mol^{-1})

Component	x	$u(x)$
water	75	8
n-hexane	991487	650
3-methyl pentane	2940	290
methyl cyclopentane	5498	550

Table 7: Purity assessment of nitrogen (Air Products, BIP+ 6.0), expressed in amount fractions (μmol mol^{-1})

Component	x	$u(x)$
argon	5	3
methane	0.008	0.005
carbon monoxide	0.015	0.009
carbon dioxide	0.010	0.006
hydrogen	0.025	0.015
water	0.010	0.006
nitrogen	999 995	6
oxygen	0.005	0.003

Table 8: Composition of the grandparent multicomponent mixture expressed in amount fractions calculated in accordance with ISO 6142-1 (nmol mol^{-1})

Component	x	$u(x)$
methanol	35953.2	2.5
ethanol	20017.2	1.1
acetone	7990.7	0.5
n-hexane	9978.1	6.1

The binary mixtures were used to prepare a multicomponent mixture with the amount fractions in the desired ratios (table 8). From this grandparent mixture, two parent mixtures were prepared with a dilution factor of 4. These parent mixtures were used to prepare the set of travelling standards for this key comparison. The standard uncertainties in table 8 were computed in accordance with ISO 6142-1 [4, 5] and do only account for the preparation using static gravimetry, including the effects from the purity analysis of the materials used.

The amount fractions of methanol, ethanol and acetone as obtained from static gravimetry are given in table 9. The standard uncertainties in table 9 were computed in accordance with ISO 6142-1 [4,5] and do only account for the preparation using static gravimetry.

Table 9: Amount fractions of methanol, ethanol and acetone in travelling standards calculated in accordance with ISO 6142-1 (nmol mol^{-1})

		methanol		ethanol		acetone	
laboratory	Mixture	x	$u(x)$	x	$u(x)$	x	$u(x)$
CMI	VSL2A1185	900.82	0.06	501.54	0.03	200.21	0.01
LNE	VSL2A1174	900.26	0.07	501.23	0.03	200.09	0.01
METAS	VSL2A1162	901.07	0.07	501.68	0.03	200.26	0.01
NIM	VSL2A1160	900.91	0.06	501.59	0.03	200.23	0.01
NMISA	VSL2A1183	900.50	0.06	501.36	0.03	200.14	0.01
NPL	VSL2A1164	900.80	0.06	501.53	0.03	200.20	0.01
VSL	VSL2A1165	899.72	0.07	500.93	0.03	199.97	0.01

2.3 Measurement protocol

The measurement protocol requested each laboratory to perform at least 3 measurements with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants about the nominal amount fraction ranges (see table 2). The laboratories were also requested to submit a summary of their uncertainty evaluation used for calculating the uncertainty of their result.

2.4 Schedule

The schedule of this key comparison was as follows (table 10).

Table 10: Schedule of CCQM-K174

Date	Event
Dec 2020	Agreement of draft protocol
Feb 2021	Registration of participants
Jun 2021	Preparation of mixtures
Jul-Oct 2021	Characterisation of mixture compositions
Nov 2021	Dispatch of mixtures
Dec 2021 – Mar 2022	Measurements
Aug 2022	Return of cylinder
Aug 2022	Measurement report due
Sep – Dec 2022	Re-characterisation of the mixtures
Mar 2025	Draft A report available

2.5 Measurement methods used by the participants

A summary of the methods, the dates of measurement, and the way in which metrological traceability has been established is given in table 11. It is worth noting the variety of approaches used for preparing the calibration standards [4, 8–10] in this key comparison.

Table 11: Summary of the analytical techniques, calibration approaches and measurement periods

Laboratory	Date	Calibration	Standards	Matrix	Technique
CMI	Mar-Apr 2022	Bracketing	Gravimetry (ISO 6142-1)	Nitrogen	GC/FID
LNE	Feb-Mar 2022	Bracketing	Gravimetry (ISO 6142-1)	Nitrogen	GC/FID
METAS	May 2022	Multipoint	Permeation (ISO 6145-10)	Nitrogen	GC/FID
NIM	Apr 2022	Single point	Mass flow controllers (ISO 6145-7)	Nitrogen	GC/FID
NMISA	Aug 2022	Single point	Gravimetry (ISO 6142-1)	Nitrogen	GC/FID
NPL	Jun-Jul 2022	Multipoint	Gravimetry (ISO 6142-1)	Nitrogen	GC/FID
VSL	Aug 2022	Single point	Diffusion (ISO 6145-8)	Nitrogen	GC/FID

2.6 Characterisation of the travelling standards

The coordinating laboratory operates several facilities for preparing calibration gas mixtures with metrologically traceable compositions. At low amount fraction levels, generally dynamic gravimetric methods [8–10] are preferred over static gravimetry [4, 5] as these dynamic methods are generally less susceptible to interactions between the calibration gas mixture and contact surfaces. In this key comparison, diffusion in accordance ISO 6145-8 [9] was used to characterise the travelling standards.

Diffusion in accordance ISO 6145-8 [9] is, as static gravimetry, a method by which the composition of the calibration gas mixtures can be calculated from first principles, in this instance the composition of the raw materials, the molar masses of the components, and the mass flow rates. The model that was used is similar to that of ISO 6142, where the major difference is that the masses have been replaced by mass flow rates [11].

The basis of the method is that two or more flows of gas are combined together to form a calibration gas mixture. Glass diffusion cells are used to obtain a constant mass flow rate of vapour from organic

liquids, in this key comparison from methanol, ethanol and acetone. The system is kept under dry, high-purity nitrogen to prevent oxidation of the raw materials and the uptake of water. The diffusion cells are weighed at regular time intervals and their mass is recorded as a function of time. From these data, the mass flow rate is computed. For said components, data from the mass flow rate are available that spans several refills of the diffusion cells. The mass flow rate is generally very stable, with the exception just after a refill of the diffusion cell. Stabilisation time was allowed to obtain a stable mass flow rate.

The diffusion system was used to calibrate a gas chromatograph (GC) equipped with a flame ionisation detector (FID), which was used to perform the analyses used for the homogeneity and stability study. This GC is regularly used for the analysis of gas mixtures with volatile organic compounds (VOCs) or oxy-VOCs. In the case of VOCs, 20 injections are performed per gas mixture, and only the last 5 ones are used to obtain the instrument response. All cylinders are connected to a single regulator, for previous experience indicated that there can be a substantial between-regulator effect when each of the cylinders is equipped with its own regulator.

The diffusion system was assumed to be a stable reference and it was used to analyse the suite of travelling standards, together with a check and some spare mixtures. The check mixture was used to assess the stability of the dynamic system in combination with the GC/FID. Some of the mixtures that resided at VSL for the entire period were also analysed during the time that the travelling standards were at the premises of the participating laboratories.

Based on long-term performance, the relative expanded uncertainty of the diffusion system is in the order of 2 % to 3 % ($k = 2$). In this report, this relative expanded uncertainty was used to attach a scale to the measurement results obtained from the GC/FID. The analysis of mixtures containing oxy-VOCs is generally associated with a greater uncertainty than the analysis of VOCs, which only for heavier VOCs such as trimethylbenzenes has a larger uncertainty (see also VSL's participation in CCQM-K10.2018 [12]).

2.7 Evaluation of stability and batch homogeneity

The assessment of the homogeneity and stability was performed on a single set of measurement data. These data are summarised in figures 1–3. The stability assessment was performed first, for each travelling standard separately. Once the value and uncertainty were determined, the homogeneity of the batch of travelling standards was evaluated. This homogeneity assessment aimed primarily at assessing that the cylinder passivation performed similarly between the travelling standards.

For all component amount fractions in all travelling standards, stability was demonstrated. The results for the stability of the amount fraction methanol indicate a slight trend in the results. For the purpose of this key comparison, the amount fraction at the date(s) of measurement of the laboratories have been determined, thus minimising the effect of the drift in the measurement data on the key comparison reference values (KCRVs).

From the stability study data, the amount fractions at the time of measurement were obtained by interpolation. These were used to assess the differences in the amount fractions of the components of the mixtures. These differences are summarised in table 12. In these calculations, the relative expanded uncertainty of the diffusion and analytical systems was assumed to be 3 % for methanol and 2 % for ethanol and acetone. A fixed-effects model was used to perform the calculation [13,14]. The differences were calculated with respect to the weighted mean and the standard uncertainty was calculated accordingly.

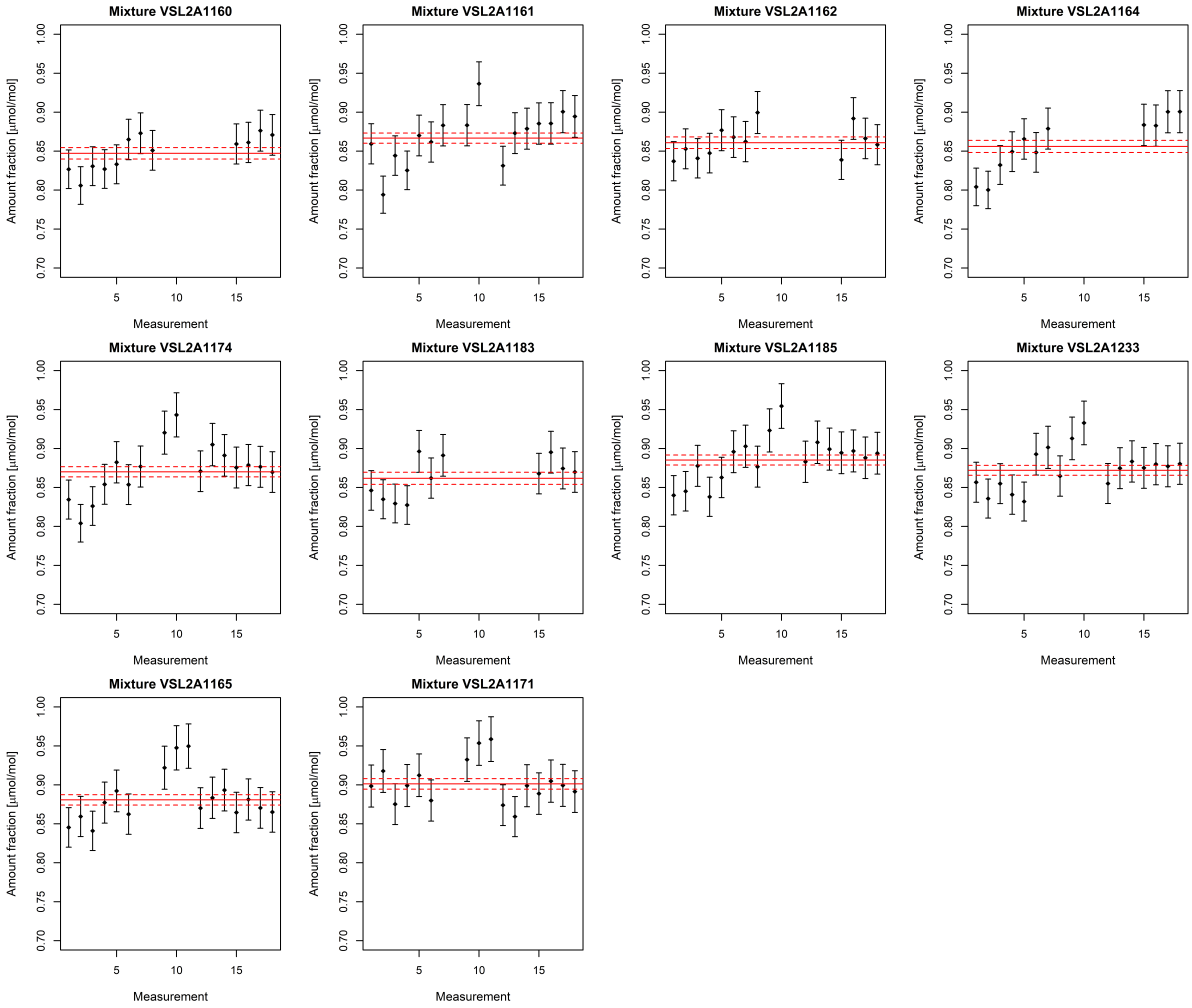


Figure 1: Results of the homogeneity study of the travelling standards of CCQM-K174 before and after analysis by the participating laboratories for methanol. The uncertainty bars indicate expanded uncertainties ($k = 2$).

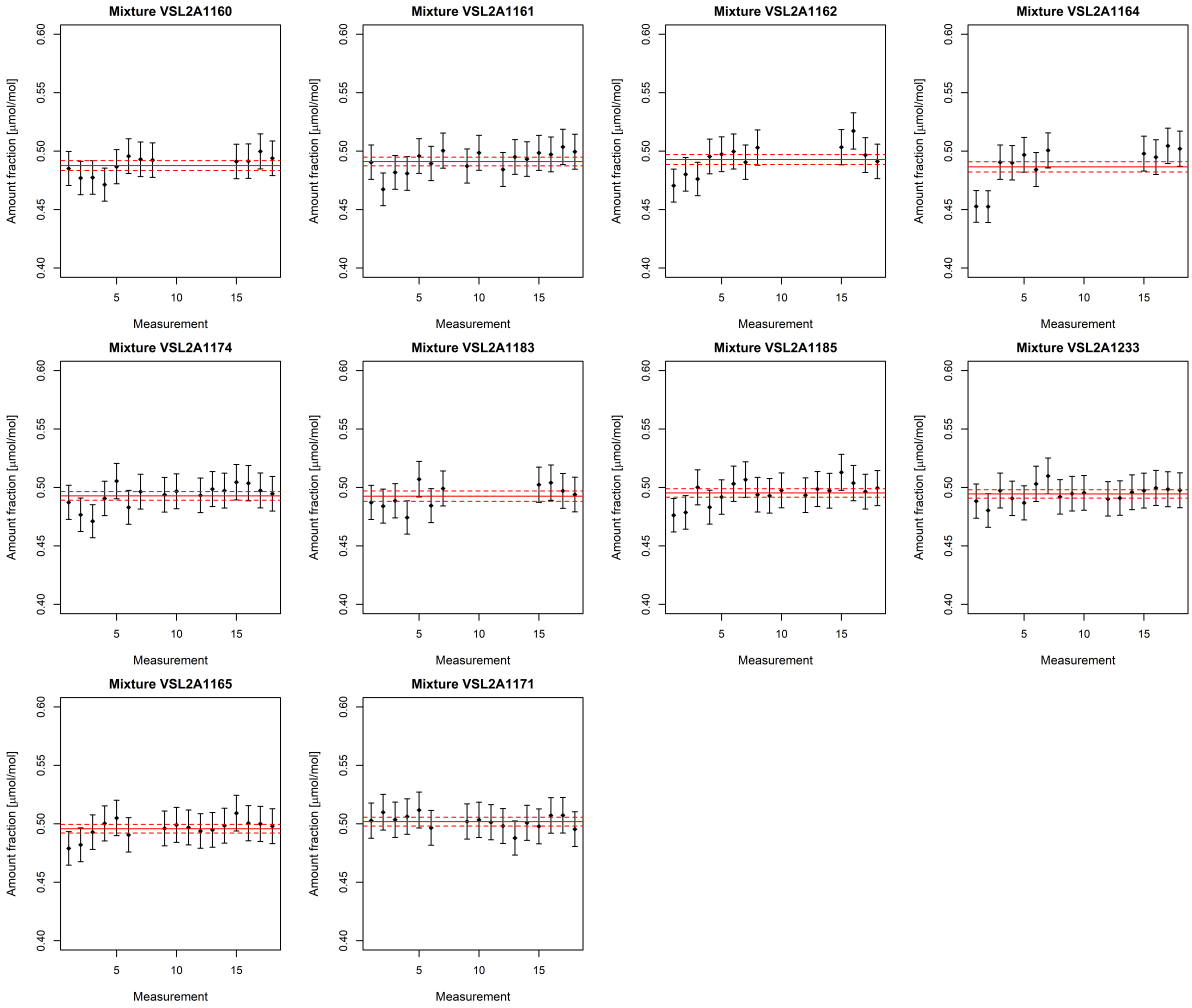


Figure 2: Results of the homogeneity study of the travelling standards of CCQM-K174 before and after analysis by the participating laboratories for ethanol. The uncertainty bars indicate expanded uncertainties ($k = 2$).

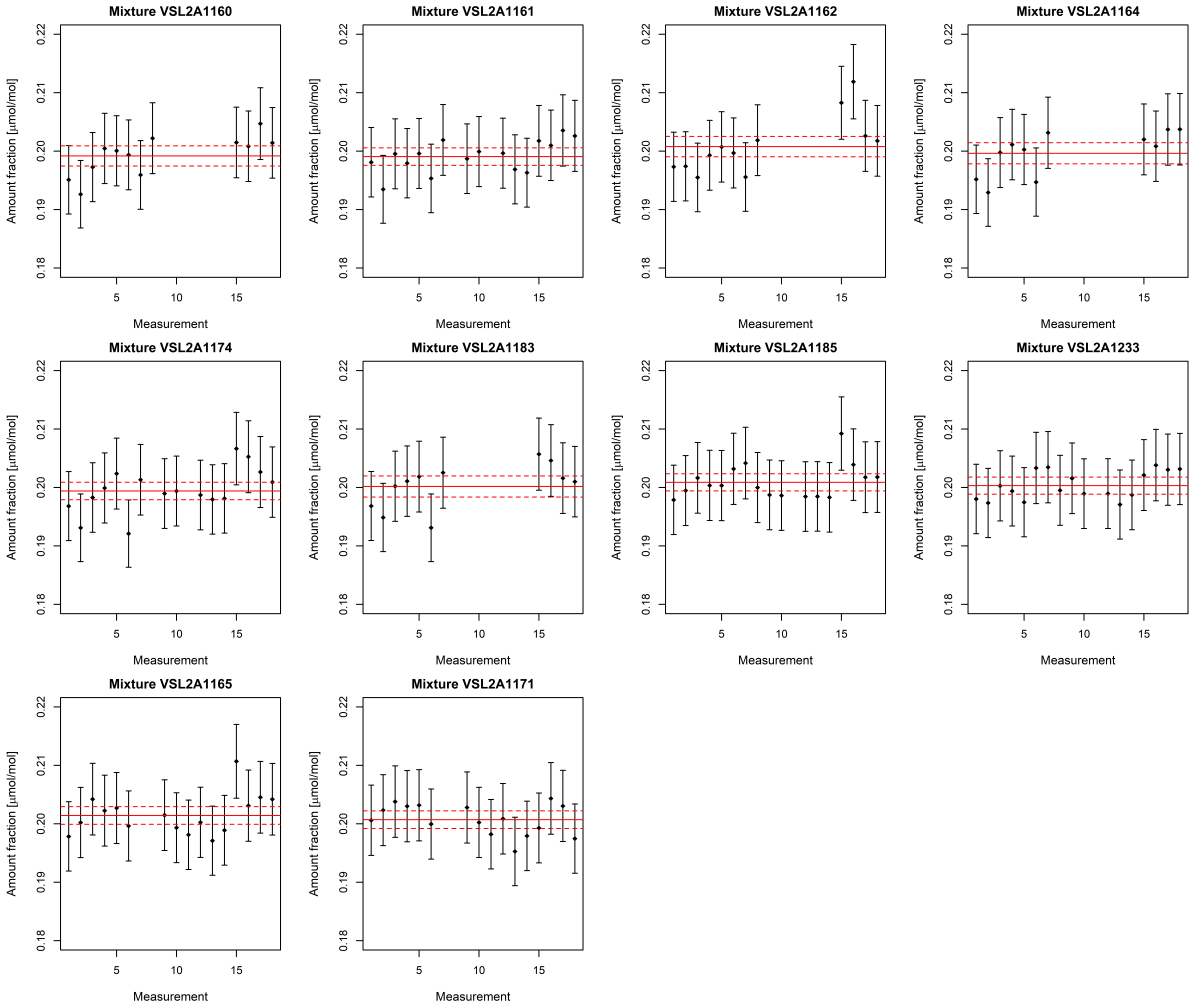


Figure 3: Results of the homogeneity study of the travelling standards of CCQM-K174 before and after analysis by the participating laboratories for acetone. The uncertainty bars indicate expanded uncertainties ($k = 2$).

The differences are generally small and below the standard uncertainty. For methanol, there are a few travelling standards where the absolute value of difference is just above the standard uncertainty.

Table 12: Differences and associated standard uncertainties in the amount fractions of methanol, ethanol and acetone between the travelling standards (nmol mol^{-1})

	Methanol		Ethanol		Acetone	
Laboratory	δ	$u(\delta)$	δ	$u(\delta)$	δ	$u(\delta)$
CMI	14.9	12.3	1.9	6.9	0.4	2.8
LNE	-3.1	12.0	-2.1	6.8	-1.6	2.8
METAS	-4.1	12.0	1.9	6.9	1.4	2.8
NIM	-17.1	11.8	-5.1	6.8	-1.6	2.8
NMISA	1.9	12.1	1.9	6.9	0.4	2.8
NPL	-0.1	12.0	-2.1	6.8	-0.6	2.8
VSL	8.9	12.2	3.9	6.9	1.4	2.8

The differences between the amount fractions from static gravimetry and dynamic gravimetry using diffusion are shown in table 13. The standard uncertainties in table 13 were propagated based on the standard uncertainties computed in accordance with ISO 6142-1 [4, 5] and ISO 6145-8 [9].

The data of the comparison of the two methods shows that the performance of the gas cylinders used for the travelling standards is fairly homogeneous. The largest differences in adsorption are for methanol, which surface both in the between cylinder-effects displayed in table 12 as well as in the differences between the amount fractions computed from static gravimetry and diffusion (table 13). The KCRVs for the amount fractions ethanol and acetone could have been established based on the static gravimetric preparation of ISO 6142-1, provided that the uncertainty associated with the determination of the losses is taken into account.

Table 13: Differences and associated standard uncertainties in the amount fractions of methanol, ethanol en acetone between static gravimetry and diffusion (nmol mol^{-1})

	methanol		ethanol		acetone	
Laboratory	Δx	$u(\Delta x)$	Δx	$u(\Delta x)$	Δx	$u(\Delta x)$
CMI	20	13	7	7	-0.8	3.0
LNE	37	13	10	7	1.1	3.0
METAS	39	13	7	7	-1.7	3.0
NIM	52	13	14	7	1.2	3.0
NMISA	32	13	6	7	-0.9	3.0
NPL	35	13	11	7	0.2	3.0
VSL	25	13	4	7	-2.0	3.0

The differences in table 13 are generally greater than two times the standard uncertainty for methanol, of the order of the standard uncertainty for ethanol and typically smaller than the standard uncertainty for acetone. For the latter component, several of the differences are negative. It is also visible that if the difference for the amount fraction methanol is large (relative to the other mixtures), then this is also true for the differences for the amount fraction ethanol and acetone. This pattern suggests

that the adsorption in the cylinders is not identical. As the value assignment using diffusion is based on GC-measurements, these effects are taken into account in the KCRVs.

2.8 Key comparison reference value

The KCRVs were established based on the data from the diffusion system used to dynamically prepare the calibration gas mixtures used to perform a multipoint calibration of the GC. The principles of the diffusion method for preparing calibration gas mixtures are described in ISO 6145-8 [9]. The performance of the diffusion system with respect to the preparation of calibration gas mixtures with various kinds of VOCs has been monitored over decades. The baseline for the uncertainty is a relative expanded uncertainty of 2.0 % ($k = 2$) for the amount fractions ethanol and acetone and 3.0 % for the amount fraction methanol, due to the fact that this component shows more adsorption. This relative expanded uncertainty has been verified in the past in comparisons of benzene, toluene, ethylbenzene, xylenes (BTEX) primary standard gas mixtures (PSMs) with the calibration gas mixtures prepared by said system. This cross-validation showed good comparability between the PSMs and the calibration gas mixtures from the diffusion system and vice versa.

The data reduction was performed using a Bayesian hierarchical model [15] with weakly informative priors for the mean, the excess standard deviation and the within-group standard deviations. The details of this model have been published elsewhere [16]. In the calculation of the KCRVs, the model was used to reduce the data from figures 1–3 to obtain the mean and standard uncertainty for the amount fractions methanol, ethanol and acetone. These means coincided with the interpolations performed as the stability assessment, but the Bayesian model offers a more comprehensive evaluation of the measurement uncertainty [17, 18].

The mass flow rate from diffusion is stable over years. Instability occurs only when refilling the diffusion cells, in which case the first mass measurements from the refilled cells indicate departures of the regular diffusion rate. During the design and implementation of this key comparison, any refilling of the cells was carefully planned an sufficient lag time between refilling and calibrating the GC was taken to ensure that the mass flow rate had stabilised again. An analysis of historical data revealed that, within the uncertainty of the mass flow rate over time, there was no meaningful impact due to the filling level of the diffusion cells.

The amount fractions of the targeted components (methanol, ethanol and acetone) were calculated in accordance with ISO 6145-8 [9] taking into consideration the adjustments arising from the purity analysis (see tables 14, 15 and 16). The GC was calibrated using a multipoint calibration and the data were processed in accordance with ISO 6143 [19, 20].

2.9 Degrees of equivalence

The unilateral degree of equivalence for laboratory j for a given component is defined as

$$d_j = y_{\text{lab},j} - y_{\text{KCRV},j} \tag{1}$$

and its associated expanded uncertainty.

The degrees of equivalence were defined as the difference between the amount fraction reported by the participant and the KCRV computed for travelling standard j. The expanded uncertainty was computed from the standard uncertainty using a coverage factor $k = 2$.

3 Results and discussion

3.1 Methanol

The reported results for the amount fraction methanol are shown in figure 5. The uncertainty bars indicate expanded uncertainties ($k = 2$). The reported results of CMI used in the body of this report are the ones submitted in the key comparison. In the measurement report, corrected results are given that are consistent with the measurement report. As these results arrived well after the agreement and disclosure of the KCRVs and degrees of equivalence, there is a discrepancy between these results. This statement applies to all three measurands in this key comparisons.

The degrees of equivalence for the amount fraction methanol are shown in figure 4. The results of NIM, NMISA and NPL are not consistent with the KCRV. For NIM and NPL, the lower bound of the coverage interval of the degree of equivalence is slightly above $d = 0$. The remaining degrees of equivalence differ minimally from zero. Small deviations in the measured amount fraction methanol or a mild underrating of the measurement uncertainty may explain the degrees of equivalence for NIM and NPL. The result of NMISA is much larger off, probably due to an unrecognised systematic effect in the measurement.

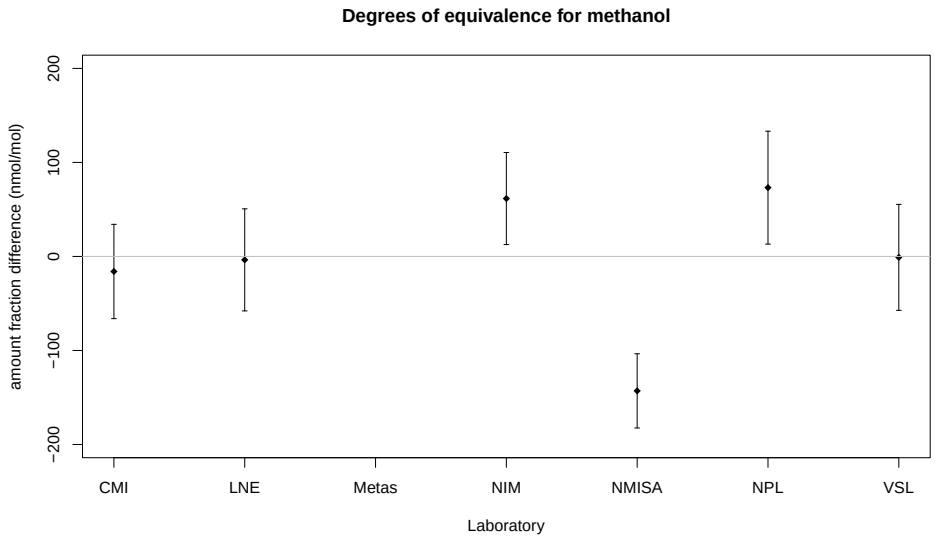


Figure 4: Degrees of equivalence for the amount fraction methanol (nmol mol^{-1}).

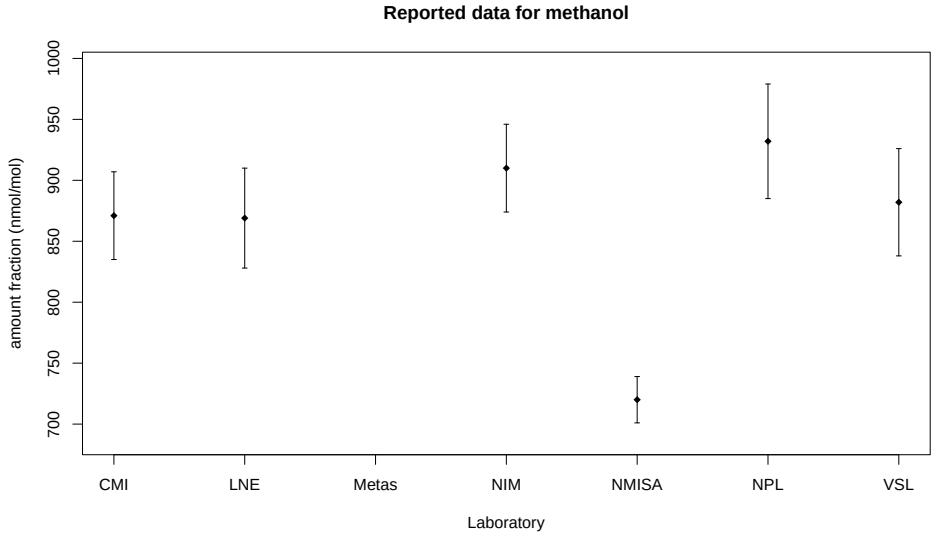


Figure 5: Reported results for the amount fraction methanol (nmol mol^{-1}).

The KCRVs, their associated standard uncertainties, the reported results and the degrees of equivalence for the amount fraction methanol are shown in table 14. The relative standard uncertainties associated with the KCRV is approximately 1.5 % and dominated by the diffusion system. For the amount fraction methanol, the relative expanded uncertainties reported by the participants range from 2.6 % to 5.0 %.

Table 14: Results, key comparison reference values and degrees of equivalence for the amount fraction methanol (nmol mol^{-1})

Lab	Mixture	x_{lab}	$U(x_{\text{lab}})$	k_{lab}	x_{KCRV}	$U(x_{\text{KCRV}})$	$u(x_{\text{KCRV}})$	k_{KCRV}	d	$U(d)$	k
CMI	VSL2A1185	871	36	2.0	887	35	17	2.0	-16	50	2.0
LNE	VSL2A1174	869	41	2.0	873	36	18	2.0	-4	54	2.0
Metas	VSL2A1162				862	33	16	2.0			2.0
NIM	VSL2A1160	910	36	2.0	848	33	17	2.0	62	49	2.0
NMISA	VSL2A1183	720	19	2.0	863	35	17	2.0	-143	39	2.0
NPL	VSL2A1164	932	47	2.0	859	37	19	2.0	73	60	2.0
VSL	VSL2A1165	882	44	2.0	883	35	18	2.0	-1	56	2.0

The weighted mean of the laboratory results, not adjusted for the differences between the travelling standards is for the amount fraction methanol 810 nmol mol^{-1} with a standard uncertainty of 7 nmol mol^{-1}. The results of five of the participants (see figure 5) are mutually consistent with each other.

3.2 Ethanol

The results for the amount fraction ethanol are shown in figure 6. The uncertainty bars indicate expanded uncertainties ($k = 2$). Four results are mutually consistent with each other.

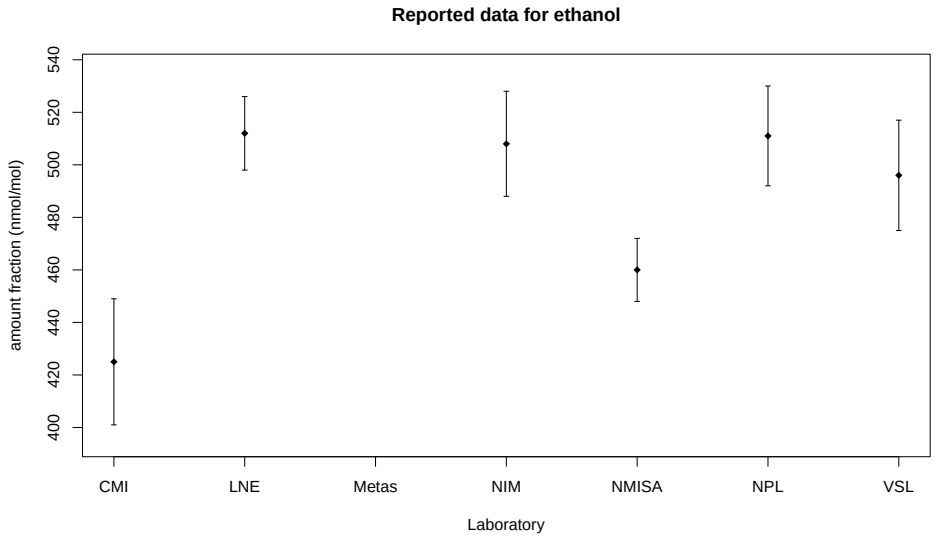


Figure 6: Reported for the amount fraction ethanol (nmol mol^{-1}).

The degrees of equivalence for the amount fraction ethanol are shown in figure 7. The results of CMI, LNE and NMISA are not consistent with the KCRV.

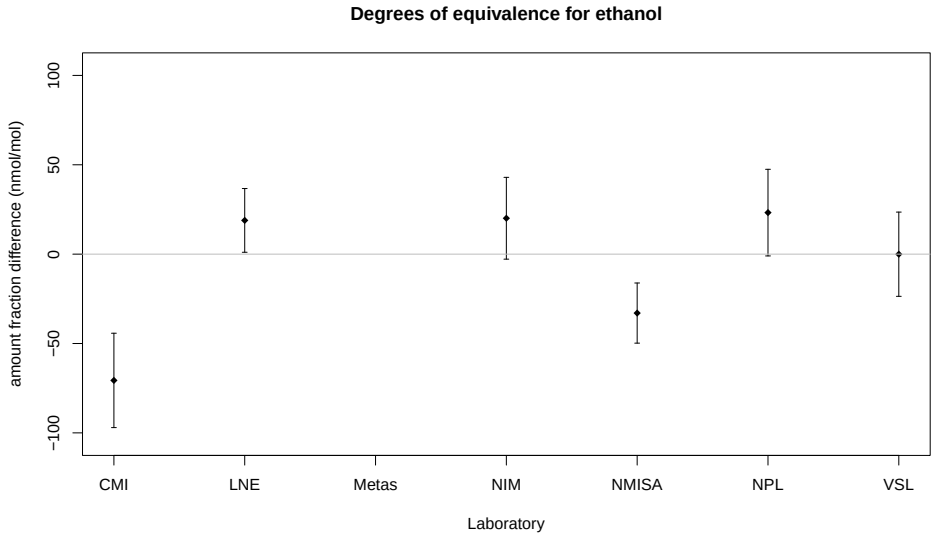


Figure 7: Degrees of equivalence for the amount fraction ethanol (nmol mol^{-1}).

The KCRVs, their associated standard uncertainties, the reported results and the degrees of equivalence for the amount fraction ethanol are shown in table 15. The relative standard uncertainties associated with the KCRV is approximately 1.3 % and dominated by the diffusion system. For the amount fraction ethanol, the relative expanded uncertainties reported by the participants range from 2.6 % to 5.6 %.

Table 15: Results, key comparison reference values and degrees of equivalence for the amount fraction ethanol (nmol mol^{-1})

Lab	Mixture	x_{lab}	$U(x_{lab})$	k_{lab}	x_{KCRV}	$U(x_{KCRV})$	$u(x_{KCRV})$	k_{KCRV}	d	$U(d)$	k
CMI	VSL2A1185	425.0	24.0	2.0	495.6	11.0	5.5	2.0	-70.6	26.4	2.0
LNE	VSL2A1174	512.0	14.0	2.0	493.1	11.0	5.5	2.0	18.9	17.8	2.0
Metas	VSL2A1162				493.4	12.5	6.3	2.0			2.0
NIM	VSL2A1160	508.0	20.0	2.0	487.9	11.1	5.6	2.0	20.1	22.9	2.0
NMISA	VSL2A1183	460.0	12.0	2.0	493.0	11.8	5.9	2.0	-33.0	16.8	2.0
NPL	VSL2A1164	511.0	19.0	2.0	487.8	15.0	7.5	2.0	23.2	24.2	2.0
VSL	VSL2A1165	496.0	21.0	2.0	496.0	10.7	5.4	2.0	-0.0	23.6	2.0

3.3 Acetone

The reported results for the amount fraction acetone are shown in figure 8. The uncertainty bars indicate expanded uncertainties ($k = 2$). Six results are mutually consistent.

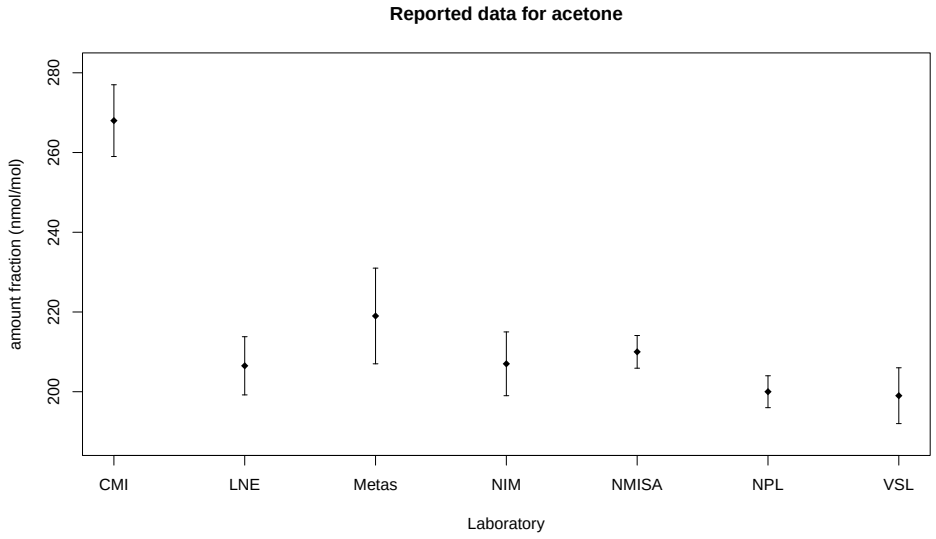


Figure 8: Reported results for the amount fraction acetone (nmol mol^{-1}).

The degrees of equivalence for the amount fraction acetone are shown in figure 9. The results of CMI, METAS and NMISA are not consistent with the KCRV. In all three cases, the coverage interval of the degree of equivalence does just not include zero, which is necessary for consistent results.

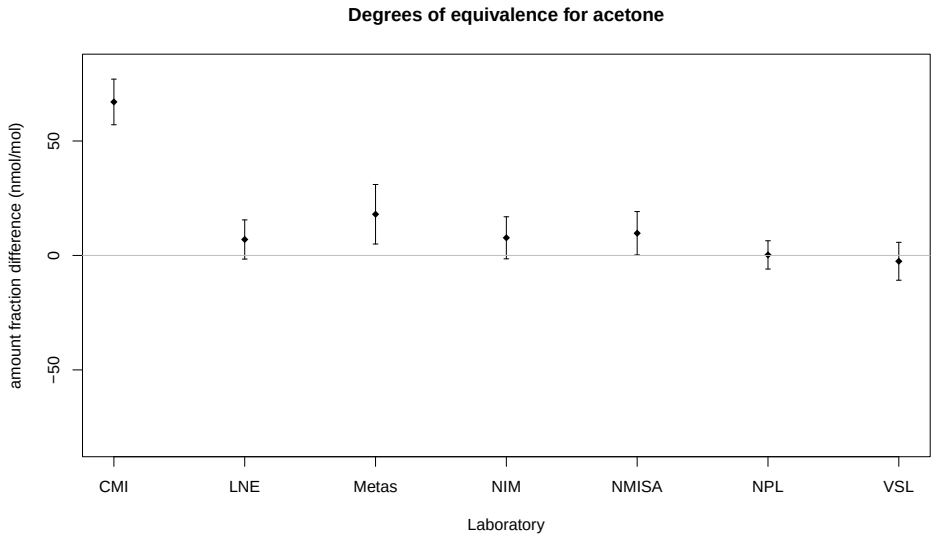


Figure 9: Degrees of equivalence for the amount fraction acetone (nmol mol^{-1}).

The KCRVs, their associated standard uncertainties, the reported results and the degrees of equivalence for the amount fraction acetone are shown in table 16. The relative standard uncertainties associated with the KCRV is approximately 1.1 % and dominated by the diffusion system. For acetone, the relative expanded uncertainties reported by the participants range from 2.0 % to 5.4 %.

The experience with the performance of analytical systems is that the stickier the component is, the poorer the performance. Typically, the relative expanded uncertainty decreases from methanol → ethanol → acetone. The stated relative expanded uncertainties of NIM, NPL and VSL show such trend. It should be considered that the effect is possibly less pronounced because of the decreasing amount fraction from methanol to acetone.

Table 16: Results, key comparison reference values and degrees of equivalence for the amount fraction acetone (nmol mol^{-1})

Lab	Mixture	x_{lab}	$U(x_{\text{lab}})$	k_{lab}	x_{KCRV}	$U(x_{\text{KCRV}})$	$u(x_{\text{KCRV}})$	k_{KCRV}	d	$U(d)$	k
CMI	VSL2A1185	268.0	9.0	2.0	200.9	4.3	2.1	2.0	67.1	10.0	2.0
LNE	VSL2A1174	206.5	7.3	2.0	199.5	4.5	2.2	2.0	7.0	8.6	2.0
Metas	VSL2A1162	219.0	12.0	2.0	201.0	5.0	2.5	2.0	18.0	13.0	2.0
NIM	VSL2A1160	207.0	8.0	2.0	199.3	4.5	2.3	2.0	7.7	9.2	2.0
NMISA	VSL2A1183	210.0	4.1	2.0	200.3	4.7	2.4	2.0	9.7	9.5	2.0
NPL	VSL2A1164	200.0	4.0	2.0	199.8	4.7	2.3	2.0	0.2	6.2	2.0
VSL	VSL2A1165	199.0	7.0	2.0	201.5	4.4	2.2	2.0	-2.5	8.3	2.0

4 Support to CMCs

The support of CMC claims is described in more detail in the ”GAWG strategy for comparisons and CMC claims” [21]. The results of this key comparison can be used to support CMC claims for analysis of methanol, ethanol and acetone in nitrogen or air from 100 nmol mol^{-1} up to 10 µmol mol^{-1}. The

relative expanded uncertainty is presumed to be constant over said amount fraction intervals. CMCs for reference materials are supported as far as the characterisation goes. This key comparison does not provide evidence for other parts of the uncertainty budget, such as stability and between-cylinder effects.

With the performance shown for the amount fraction acetone, CMCs can be supported for the amount fractions acetonitrile, methyl ethyl ketone and methacrolein over the same amount fraction interval. CMCs for the amount fraction methyl vinyl ketone can be supported based on the performance shown for the amount fraction ethanol over the same amount fraction interval.

5 Conclusions

There is good agreement between the results. METAS could only analyse acetone in the provided travelling standards. The stated relative expanded uncertainties generally decrease from methanol to acetone. Some degrees of equivalence that have a coverage interval that does just not include the KCRV suggest that the measurement uncertainty may be underrated slightly.

The key comparison shows that for ethanol and acetone, static gravimetry could have been used to establish the KCRV, provided that the uncertainty associated with the difference between dynamic and static gravimetry is taken into account. For methanol, the adsorption effect is larger, so here clearly the diffusion method is to be preferred as source for an independent KCRV.

The great diversity of methods used for preparing calibration gas mixtures and analysis used by the participants underlines that there are many pathways to provide calibration services for gas mixtures and instruments for these challenging components in nitrogen, which all have the potential of providing consistent results.

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CCQM-K174

Completion date

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A List of symbols

- d difference with respect to the key comparison reference value
- δ difference between static gravimetry and dynamic gravimetry using diffusion.
- k coverage factor
- U expanded uncertainty
- u standard uncertainty
- x amount fraction

B Measurement reports of the participating institutes

Report Form CCQM-K174 oxygenated VOCs

Laboratory name: Czech metrology institute

Cylinder number: 961185

Authors: Miroslav Bárta, Luděk Král

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	11.3.2022	0.883	2.0	10
Ethanol	11.3.2022	0.344	3.5	10
Acetone	11.3.2022	0.266	2.2	10

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	26.3.2022	0.903	3.9	10
Ethanol	25.3.2022	0.480	4.0	10
Acetone	25.3.2022	0.259	4.1	10

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	2.4.2022	0.789	3.2	10
Ethanol	2.4.2022	0.310	3.7	10
Acetone	2.4.2022	0.256	3.4	10

Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Methanol	3.1.2023	0.858	0.036	2
Ethanol	3.1.2023	0.378	0.024	2
Acetone	3.1.2023	0.260	0.009	2

[1] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

Calibration standards

The preparation was done by two steps procedure. In first step we made a pre-mixture for each component to 40 l cylinders. Each compound was injected by glass syringe to the 40 l evacuated cylinder. This caused that all compounds were transfer to gases phases immediately. Then followed dilution by nitrogen to 50 µmol/mol. In second step these pre-mixtures were used for further dilution. The final amount fraction was 1 µmol/mol and 0,5 µmol/mol for each compound of interest and these mixtures was used as calibration standards. The gravimetric preparation follows the EN ISO 6142-1.

	Cylinder no.	Mass of acetone (g)	Mass of nitrogen (g)	Amount fraction (µmol/mol)	Uabs (µmol/mol)
Pre-mixture	517201	0.21100	5070.53	24.6	0.1
PRM	002453	0.00088	799.50	0.634	0.003
PRM	466388	0.00126	579.62	1.540	0.008

	Cylinder no.	Mass of EtOH (g)	Mass of nitrogen (g)	Amount fraction (µmol/mol)	Uabs (µmol/mol)
Pre-mixture	517196	0.12520	6482.522	11.75	0.02
Pre-mixture	259011	0.79550	6365.087	75.97	0.20
PRM	925241	0.00069	786.816	0.514	0.001
PRM	685285	0.00251	1491.076	1.009	0.009

	Cylinder no.	Mass of methanol (g)	Mass of nitrogen (g)	Amount fraction (µmol/mol)	Uabs (µmol/mol)
Pre-mixture	258994	0.14880	6505.893	20.00	0.02
PRM	002452	0.00051	888.084	0.342	0.001
PRM	685284	0.00139	1136.336	0.705	0.002

The purity of the parent gases and liquids is based on the manufacturers' specifications.

Nitrogen 6.0

H2O	≤	0.5 ml. m^{-3}
O_2	≤	0.5 ml. m^{-3}
CO_2	≤	0.1 ml. m^{-3}
CO	≤	0.1 ml. m^{-3}
CnHn	≤	0.1 ml. m^{-3}

Acetone

Content	min.	99.50 %
Non-volatile compounds	max.	0.001 %
Acids (as CH_3C00H)	max.	0.003 %
Water	max.	0.30 %

Methanol

Content	min.	99.80 %
Non-volatile compounds	max.	0.001 %
Acids (as HCOOH)	max.	0.002 %
Water	max.	0.1 %

Ethanol

Content	min.	99.80 %
Acids (as CH_3C00H)	max.	0.004 %
Non-volatile compounds	max.	0.002 %
Water	max.	0.20 %

Instrumentation

The analysis of gas mixture was carried out by GC-FID. The column was Rt-U-BOND (Restek) 30 m, 0.53 mm ID, 20 µm df (polar column incorporating DVB ethylene glycol-dimethylacrylate polymer). Injection to column was done by 1 ml loop through gas liner (1 mm inner diameter). All sampling lines in GC were heated at 100 °C. Owen temperature program was isotherm at 150 °C. Whole temperature program took 4 min.

Calibration method and value assignment

Two points calibration curves were prepared for each compound. Used formulae for calculation of compositions of PRM.

$$y_k = \frac{\sum_{j=1}^{r}\left(\frac{x_{k,j}\cdot m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}$$

Where:

- y_k is amount of substance fraction of component *k* in the prepared mixture
- $x_{k,j}$ is amount of substance fraction of component *k* in parent gas or liquid *j*
- m_j is mass added of parent gas or liquid *j*
- $x_{i,j}$ is amount of substance fraction of component *i* in parent gas or liquid *j*
- M_i is the molar mass of the component *i*

The final composition of PRM.

	Cylinder number	Amount fraction (µmol/mol)
Methanol	002452	0.342
Methanol	685284	0.705
Ethanol	925241	0.514
Ethanol	685285	1.009
Aceton	002453	0.634
Aceton	466388	1.540

Every PRM was measured several hours to make sure that whole system is properly flush out. Last ten values was taking account.

Uncertainty evaluation

Standard uncertainty $u^2(y_{k,grav})$

$$u^2\left(y_{k,grav}\right) = \sum_{i=1}^{q}\left(\frac{\partial_{y_k}}{\partial M_i}\right)^2 \cdot u^2\left(M_i\right) + \sum_{j=1}^{r}\left(\frac{\partial y_k}{\partial m_j}\right)^2 \cdot u^2(m_j) + \sum_{j=1}^{r}\sum_{i=1}^{q}\left(\frac{\partial y_k}{\partial x_{i,j}}\right)^2 \cdot u^2\left(x_{i,j}\right)$$

Where:

- y_k amount of substance fraction of component *k* in the prepared mixture
- m_j weight of compound j
- M_i molar mass of compound i
- $x_{j,j}$ amount of substance fraction of component i in the parent gas or liquid j
- m_j weight of compound j

Expressions for sensitivity coefficients appearing in previous formula follows:

$$\frac{\partial y_k}{\partial m_j} = \frac{1}{n_\Omega}\frac{x_{kj}}{\overline{M_j}} - \frac{n_k}{n_\Omega^2}\frac{1}{\overline{M_j}}$$

$$\frac{\partial y_k}{\partial M_i} = -\frac{1}{n_\Omega}\sum_{j=1}^{p}\frac{x_{kj}m_j}{\overline{M_j^2}}x_{ij} + \frac{n_k}{n_\Omega{}^2}\sum_{j=1}^{p}\frac{m_j}{\overline{M_j^2}}x_{ij}$$

$$\frac{\partial y_k}{\partial x_{ij}} = -\frac{1}{n_\Omega}\frac{x_{kj}m_j}{\overline{M_j^2}}M_i + \frac{n_k}{n_\Omega^2}\frac{m_j}{\overline{M_j^2}}M_i \ (for\ i \neq k)$$

$$\frac{\partial y_k}{\partial x_{kj}} = \frac{1}{n_\Omega}\left(-\frac{x_{kj}m_j}{\overline{M_j^2}}M_k + \frac{m_j}{\overline{M_j}}\right) + \frac{n_k}{n_\Omega^2}\frac{m_j}{\overline{M_j^2}}M_i$$

Where:

$$n_k = \sum_{j=1}^{p}\frac{x_{kj}m_j}{\overline{M}_j}$$

$$n_\Omega = \sum_{j=1}^{p}\frac{m_j}{\overline{M}_j}$$

$$\overline{M}_j = \sum_{i=1}^{q}x_{ij}M_i$$

Where:

- y_k amount of substance fraction of component *k* in the prepared mixture
- $x_{k,j}$ amount of substance fraction of component k in the parent gas or liquid j
- n_k molar amount of component k
- m_j mass added of parent gas or liquid j
- n_Ω molar amount of final mixture
- M_i molar mass of compound i
- $x_{j,j}$ amount of substance fraction of component i in the parent gas or liquid j

- M_i molar mass of compound i

Uncertainty of weighing u_{mi}

$$u_{m_i} = \sqrt{u_{m_{iA}}^2 + u_{m_{iB}}^2}$$

Where:

- u_{miA} uncertainty type A
- u_{miB} uncertainty type B

$$u_{m_{iA}} = \sqrt{\frac{1}{n(n-1)} \cdot \sum_{j=1}^{n} (q_j - \overline{q})^2}$$

Where:

- n number of measurement
- q_j random value
- $\overline{q}$ arithmetic mean

$$u_{miB} = \sqrt{u_{cal}^2 + \left(\frac{digit}{2\sqrt{3}}\right)^2}$$

Where:

- u_{cal} uncertainty of calibration of scales

Uncertainty of molecular mass u_{Mi}

For a compound of general formula A_xB_y is valid equation

$$u_{Mi} = \sqrt{x^2 \cdot u_a^2 + y^2 \cdot u_b^2}$$

Where:

- x coefficient of element A
- u_a uncertainty of molecular mass of element A
- y coefficient of element B
- u_b uncertainty of molecular mass of element B

Uncertainty of purity of default material $u_{xi,j}$

$$u_{x_{i,j}} = 1 - KC$$

Where:

- KC coefficient of purity

$$KC = 0.5 \cdot (1 + 0.01 \cdot P)$$

Where:

- P percent expression of purity (%)

Expanded uncertainty

$$U_{(y_k;grav)} = 2 \cdot u_{(y_k;grav)}$$

Where:

- $U_{(yk;grav)}$ standard uncertainty

The example of uncertainty budget of reference material is given in following table.

Uncertainty component	Uncertainty source	Standard uncertainty	Sensitivity coefficient	Contribution to final uncertainty
$u(m_a)$	Weighting of the component A	1.07E-03 g	9.58E-05 $mol \cdot mol^{-1} \cdot g^{-1}$	1.03E-07 $mol \cdot mol^{-1}$
$u(m_{matrix})$	Weighting of the matrix	2.25E-03 g	1.90E-09 $mol \cdot mol^{-1} \cdot g^{-1}$	4.27E-12 $mol \cdot mol^{-1}$
$u(M_a)$	Molar mass of component A	9.71E-04 $g \cdot mol^{-1}$	-2.60E-07 $mol^2 \cdot mol^{-1} \cdot g^{-1}$	-2.52E-10 $mol \cdot mol^{-1}$
$u(M_{matrix})$	Molar mass of matrix	8.08E-05 $g \cdot mol^{-1}$	-4.29E-07 $mol^2 \cdot mol^{-1} \cdot g^{-1}$	-3.47E-11 $mol \cdot mol^{-1}$
$u(x_a)$	Mole fraction of component A in parental gas	9.98E-01 $mol \cdot mol^{-1}$	2.40E-08	2.40E-08 $mol \cdot mol^{-1}$
$u(x_{matrix})$	Mole fraction of matrix in parental gas	8.08E-05 $mol \cdot mol^{-1}$	-1.20E-05	-9.71E-10 $mol \cdot mol^{-1}$
$u_{(stability)}$	Stability of mixture	1.71E-02 $mol \cdot mol^{-1}$	2.40E-08	4.10E-10 $mol \cdot mol^{-1}$

Report Form CCQM-K174 oxygenated VOCs

Laboratory name: LNE

Cylinder number: D961174

Authors: Christophe Sutour

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	21/02/22	868.0	0.31	5
Ethanol	21/02/22	513.2	0.37	5
Acetone	21/02/22	207.1	0.14	5

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	25/02/22	868.0	0.14	5
Ethanol	25/02/22	511.7	0.13	5
Acetone	25/02/22	206.1	0.13	5

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	08/03/22	872.1	0.28	5
Ethanol	08/03/22	511.5	0.15	5
Acetone	08/03/22	206.2	0.07	5

Results

Component	Date (dd/mm/yy)	Result (nmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Methanol	21/02-08/03/22	869	41	2
Ethanol	21/02-08/03/22	512	14	2
Acetone	21/02-08/03/22	206.5	7.3	2

Calibration standards

1. Method of preparation

   The oxy-VOC binary reference gas mixtures were produced by gravimetric method according to the standard ISO 6142-1. The pure compounds were introduced in a vaccum cylinder (Experis for VOC Airproducts cylinders). The cylinder was successively weighed on a Mettler mass comparator to calculate the mass of the compounds introduced in the cylinder. The amount fraction of the gas mixture is calculated from the purity, the molar mass and the mass of each compound.

– Weighing data for ethanol

GravCalc Version 2.3.1

Gravimetric composition of cylinder Etha_N2_0038

OUTPUTS

=======

Component	Value µmol/mol	Standard uncertainty µmol/mol	% u/c
N2	999900.2586	0.04872292	0.000
Ethanol	99.63081172	0.03920075	0.039
H2O	0.06036313	0.00152537	2.527
CnHm	0.04999502	0.02886464	57.735
CO2	0.00005000	0.00002887	57.736
H2	0.00005000	0.00002887	57.736
O2	0.00005000	0.00002887	57.736
CO	0.00005000	0.00002887	57.736

INPUTS

======

File	Mass (g)	u/c (g)
Pur\N2_Alpha2_F9	1602.554	0.03800
Pur\ETHA_pur_006	0.26266	0.00010

Purity composition of parent gas for ethanol

INPUT DATA FILES
==========

°°°°°°°°°°°° Pur\N2_Alpha2_F902.txt °°°°°°°°°°°°

Component	Value mol/mol	Standard uncertainty (mol/mol)
N2	0.9999999498	0.0000000289
H2O	0.0000000001	0.0000000000
O2	0.0000000001	0.0000000000
CO	0.0000000001	0.0000000000
CO2	0.0000000001	0.0000000000
H2	0.0000000001	0.0000000000
CnHm	0.0000000500	0.0000000289

°°°°°°°°°°°° Pur\ETHA_pur_0062.txt °°°°°°°°°°°°

Component	Value mol/mol	Standard uncertainty (mol/mol)
ethanol	0.9993950000	0.0000154000
H2O	0.0006050000	0.0000153000

– Weighing data for methanol

GravCalc Version 2.3.1

Gravimetric composition of cylinder MetOH_N2_0001

OUTPUTS

=======

Component	Value µmol/mol	Standard uncertainty µmol/mol	% u/c
N2	999900.3017	0.05718482	0.000
methanol	99.58615417	0.04924936	0.049
CnHm	0.04999502	0.02886464	57.735
H2O	0.03682012	0.00150476	4.087
imp_methanol	0.02511130	0.00251053	9.998
H2	0.00005000	0.00002887	57.736
O2	0.00005000	0.00002887	57.736
CO	0.00005000	0.00002887	57.736
CO2	0.00005000	0.00002887	57.736

Purity composition of parent gas for methanol

INPUTS

=======

File	Mass (g)	u/c (g)
Pur\N2_Alpha2_F9	1464.841	0.04000
Pur\METOH_pur_00	0.16695	0.00008

INPUT DATA FILES

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°°°°°°°°°°°° Pur\N2_Alpha2_F902.txt °°°°°°°°°°°°

Component	Value mol/mol	Standard uncertainty (mol/mol)
N2	0.9999999498	0.0000000289
H2O	0.0000000001	0.0000000000
O2	0.0000000001	0.0000000000
CO	0.0000000001	0.0000000000
CO2	0.0000000001	0.0000000000
H2	0.0000000001	0.0000000000
CnHm	0.0000000500	0.0000000289

°°°°°°°°°°°° Pur\METOH_pur_0001.txt °°°°°°°°°°°°

Component	Value mol/mol	Standard uncertainty (mol/mol)
methanol	0.9993790000	0.0000294000
H2O	0.0003690000	0.0000151000
imp_methanol	0.0002520000	0.0000252000

– Weighing data for acetone

GravCalc Version 2.3.1

OUTPUTS

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Component	Value µmol/mol	Standard uncertainty µmol/mol	% u/c
N2	999899.1732	0.05149131	0.000
acetone	100.156219	0.03730351	0.037
H2O	0.59967076	0.01941549	3.238
CnHm	0.04999496	0.02886460	57.735
imp_acetone	0.02055843	0.00205544	9.998
H2	0.00004999	0.00002887	57.736
O2	0.00004999	0.00002887	57.736
CO	0.00004999	0.00002887	57.736
CO2	0.00004999	0.00002887	57.736

INPUTS

======

File	Mass (g)	u/c (g)
Pur\N2_Alpha2_F9	1551.629	0.03700
Pur\ACE_pur_0001	0.32289	0.00012

Purity composition of parent gas for acetone

INPUT DATA FILES

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°°°°°°°°°°°° Pur\N2_Alpha2_F902.txt °°°°°°°°°°°°

Component	Value mol/mol	Standard uncertainty (mol/mol)
N2	0.9999999498	0.0000000289
H2O	0.0000000001	0.0000000000
O2	0.0000000001	0.0000000000
CO	0.0000000001	0.0000000000
CO2	0.0000000001	0.0000000000
H2	0.0000000001	0.0000000000
CnHm	0.0000000500	0.0000000289

°°°°°°°°°°°°° Pur\ACE_pur_0001.txt °°°°°°°°°°°°°

Component	Value mol/mol	Standard uncertainty (mol/mol)
Acetone	0.9938440000	0.0002000000
H2O	0.0059500000	0.0001930000
imp_acetone	0.0002040000	0.0000204000

2. Verification procedure

   The three binary RGM of oxy-VOCs in nitrogen at 100 µmol/mol were verified with permeation reference method for methanol and acetone and with another gravimetric gas mixture for ethanol. The results of this analysis were taken into account in the uncertainty budget of the RGM according to the ISO 6142-1.

Instrumentation

The method used for the analysis of oxy-VOCs was based on a GC-FID (Agilent 7890) equipped with an on-column pre-concentration system. A Silconert 2000 sample loop was used to inject 60 ml of the sample at the top of capillary column (HP-Plot U 30m-0.53mm-20µm) that was cooled down to -60°C by a liquid nitrogen cryo trap system (JAS) to refocus the sample. The system was heated to 150°C to perform the final injection.

All the parts of the analytical system were coated with Silconert 2000 and a LNE's restrictor was used with the cylinders instead of pressure reducer to avoid adsorption of the oxy-VOCs on the different parts of the system.

Calibration method and value assignment

The GC-FID was calibrated (bracketing method) with gas mixtures obtained by a two stages dynamic dilution (SONIMIX 7100 and external mass flow controllers) of the oxy-VOCs binary gas mixtures at 100 µmol/mol. Twenty GC runs were performed to obtain the stability of the measurements and the last 5 runs were used to calculate the averaged area and the standard deviations.

The values assigned for oxy-VOCs was calculated using the equation below:

$$C_i = 0.5 \times A_i \times C_e \times \left(\frac{F_{1b} \times F_2}{A_1} + \frac{F_{1a} \times F_2}{A_2}\right) \quad \textbf{Equation 1}$$

Where:

C_i: Amount fraction result of the compounds i

A_i: Average of the area of component i (last 5 runs)

C_e: Amount fraction of the gravimetric standard at 100 µmol/mol

F_{1b}: Dilution factor of the first stage dilution for the reference gas mixture produced before the analysis of the comparison gas mixture

F_2: Dilution factor of the second stage dilution

A_1: Average of the area of the first standard of the component (last 5 runs)

F_{1a}: Dilution factor of the first stage dilution for the reference gas mixture produced after the analysis of the comparison gas mixture

A_2: Average of the area of the second standard of the component (last 5 runs)

Uncertainty evaluation

The uncertainty evaluation is established by combining the uncertainty on the amount fractions of the standard gas mixture and the repeatability and reproducibility standard deviations of the measurements; they are calculated according to the law of propagation of uncertainty (Equation 2).

$$u_c^2(y) = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 \times u^2(x_i) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left(\frac{\partial f}{\partial x_i}\right)\left(\frac{\partial f}{\partial x_j}\right)u(x_i, x_j) \qquad \textbf{Equation 2}$$

The table 1 shows an example for the determination of the methanol amount fraction and the associated expanded uncertainty on the first day of the measurements.

Table 1: Uncertainty budget on the methanol amount fraction analysis for VSL cylinder N° D961174 (21/02/2022)

Variable	Unit	Value	u(Xi)	Sensib. C(Xi)	C(Xi).u(Xi)	Contributions
Amount fraction of gravimetric standard	nmol/mol	9.959×10^{4}	1.882×10^{3}	8.715×10^{-3}	1.640×10^{1}	68.88%
Dilution factor F_{1b}		9.073×10^{-2}	9.073×10^{-4}	4.774×10^{3}	4.331	4.80%
Dilution factor F_2		9.931×10^{-2}	9.931×10^{-4}	8.740×10^{3}	8.680	19.29%
Dilution factor F_{1a}		9.065×10^{-2}	9.065×10^{-4}	4.797×10^{3}	4.348	4.84%
Area of the first standard		1.909×10^{2}	4.300×10^{-1}	-2.269	-9.757×10^{-1}	0.24%
Area of the unknown gas mixture		1.843×10^{2}	5.700×10^{-1}	4.710	2.684	1.84%
Area of the second standard		1.90×10^{2}	2.70×10^{-1}	-2.29	-6.18×10^{-1}	0.10%
Result for methanol	**nmol/mol**	**868**	**40**	**k=2**		

Table 2: Uncertainty budget on the ethanol amount fraction analysis for VSL cylinder N° D961174 (21/02/2022)

Variable	Unit	Value	u(Xi)	Sensib. C(Xi)	C(Xi).u(Xi)	Contributions
Amount fraction of gravimetric standard	nmol/mol	9.96×10^{4}	2.69×10^{2}	5.15×10^{-3}	1.39	4.16%
Dilution factor F_{1b}		5.40×10^{-2}	5.40×10^{-4}	4.75×10^{3}	2.56	14.22%
Dilution factor F_2		9.93×10^{-2}	9.93×10^{-4}	5.17×10^{3}	5.13	57.06%
Dilution factor F_{1a}		2.16×10^{2}	8.00×10^{-1}	2.37	1.90	7.82%
Area of the first standard		2.25×10^{2}	5.70×10^{-1}	-1.14	-6.49×10^{-1}	0.91%
Area of the unknown gas mixture		5.39×10^{-2}	5.39×10^{-4}	4.77×10^{3}	2.57	14.31%
Area of the second standard		2.24×10^{2}	7.30×10^{-1}	-1.15	-8.37×10^{-1}	1.52%
Result for ethanol	**nmol/mol**	**513.2**	**13.6**	**k=2**		

Table 3: Uncertainty budget on the acetone amount fraction analysis for VSL cylinder N° D961174 (21/02/2022)

Variable	Unit	Value	u(Xi)	Sensib. C(Xi)	C(Xi).u(Xi)	Contributions
Amount fraction of gravimetric standard	nmol/mol	1.00×10^{5}	1.24×10^{3}	2.07×10^{-3}	2.56	49.93%
Dilution factor F_{1b}		2.24×10^{-2}	2.24×10^{-4}	4.61×10^{3}	1.03	8.13%
Dilution factor F_2		9.93×10^{-2}	9.93×10^{-4}	2.09×10^{3}	2.07	32.74%
Dilution factor F_{1a}		1.22×10^{2}	1.70×10^{-1}	1.70	2.90×10^{-1}	0.64%
Area of the first standard		1.31×10^{2}	8.00×10^{-2}	-7.89×10^{-1}	-6.31×10^{-2}	0.03%
Area of the unknown gas mixture		2.24×10^{-2}	2.24×10^{-4}	4.62×10^{3}	1.04	8.20%
Area of the second standard		1.31×10^{2}	2.60×10^{-1}	-7.93×10^{-1}	-2.06×10^{-1}	0.32%
Result for acetone	**nmol/mol**	**207.1**	**7.3**	**k=2**		

The final uncertainty is the quadratic sum of the maximal uncertainty calculated for the three determinations and the standard deviation of the three determinations.

$$u = \sqrt{u_c^2 + std_{repro}^2}$$

With:

u_c : Maximal uncertainty calculated for the three measurements
Std_{repro} : Standard deviation of the three determinations of the amount fractions under reproducibility conditions

References

ISO 6142-1

Report Form CCQM-K174 oxygenated VOCs

Laboratory name: METAS

Cylinder number: D961162

Authors: Maitane Iturrate-Garcia, Tobias Bühlmann, Céline Pascale

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol*	-	-	-	-
Ethanol*	-	-	-	-
Acetone	30/05/2022	0.218	1.6	6

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol*	-	-	-	-
Ethanol*	-	-	-	-
Acetone	31/05/2022	0.221	1.6	9

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol*	-	-	-	-
Ethanol*	-	-	-	-
Acetone	01/06/2022	0.218	2.0	8

Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Methanol*	-	-	-	-
Ethanol*	-	-	-	-
Acetone	01/06/2022	0.219	0.012	2

* Due to issues with the analytical system, METAS cannot provide data for methanol and ethanol.

[1] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

Calibration standards

Because of issues with the analytical system, METAS could not measure methanol and ethanol. The generation of the calibration standards would have followed the same procedure that for the acetone calibration standards described below.

The acetone calibration standards were generated dynamically using a portable generator (ReGaS1, METAS) based on the permeation and dilution methods [1, 2]. ReGaS1 has a Dynacalibrator® Model 150 oven (VICI Metronics, WA, USA), whose temperature is controlled by comparison between the set temperature and the value measured by a calibrated Tweener-Thermistor-Thermometer 1504 (5 kΩ; Fluke, WA, USA). To minimise surface effects, the oven surface, as well as tubing and MFCs in contact with RGMs, are coated with SilcoNert®2000. ReGaS1 two-stage dilution system comprises one thermal mass flow meter (MFM; Red-y GSM, Vögtlin Instruments GmbH, Switzerland) and four thermal mass flow controllers (MFCs; Red-y GSC, Vögtlin Instruments GmbH, Switzerland). All parameters (time, flows, temperatures, pressure, calculated permeation rates and calculated amount fractions) are monitored in real time and recorded into *.csv* files by a software, which was developed by METAS written in LabView (NI, TX, USA). Flow and temperature elements were calibrated against METAS primaries.

A calibrated acetone permeation unit (Fine Metrology, Italy; assessed purity = 99. 4 %) was placed in ReGaS1 oven two weeks before starting the measurements to guarantee the stability of the membrane. The calibration consisted of measuring the mass loss of the permeation unit with time under controlled temperature and pressure conditions. This calibration was performed using one of METAS coated (SilcoNert®2000) stainless steel primary magnetic suspension balances (MSBs; TA instruments, Germany; former Rubotherm GmbH) at set values (calibration temperatures were set at 38 °C, 40 °C and 44 °C and absolute pressure at 1080 mbar). A continuous carrier gas flow – nitrogen from distillation of liquid nitrogen with quality > 5.0 – was passed through the permeation chamber at a set value of 170 mL/min. The MFM measuring the total flow and the temperature probe measuring the chamber temperature were calibrated against METAS primaries. For each calibration point, the permeation unit was kept at constant conditions (i.e. pressure, temperature and flows) for seven days, until the mass loss became linear over time, to ensure membrane stability. Measurements were automatically corrected for MSB drift and buoyancy effects by means of two reference weights.

Three calibration standards were generated for each measurement at different amount fraction levels using ReGaS1. For that purpose, the oven temperature was set at 44 °C, absolute pressure at 1080 mbar, carrier gas flow at 0.170 L/min and the dilution gas flow at 1.8 L/min, 0.9 L/min and 0.45 L/min. Each calibration standard was generated for at least 2 hours before considering it stable and, therefore, using them for the instrument calibration.

Instrumentation

The instrument used in this key comparison was an automatic thermal desorber (ATD) TurboMatrix 350 coupled to a Clarus 500 GC-FID (Perkin Elmer Inc., MA, USA). The capillary column selected for these measurements was a DuraBond DB-624 (Agilent, CA, USA; length = 30 m, ID = 0.32 mm and film thickness = 1.8 µm). Tenax TA was the sorbent material of the cold trap.

The GC method was set as initial GC oven temperature: 40 °C (held for 2 minutes), followed by a ramp to 200 °C at 5 °C/min (held for 2 minutes).

The ATD method used was:

- valve transfer heated to 230 °C and the tubes to 220 °C
- cold trap heated from -30 °C to 280 °C at a temperature rate of 40 °C/s
- set times: 1 min for purging, 10 min for desorption
- set flows: 5 mL/min (outlet split flow), 50 mL/min (desorption flow) and 2 mL/min (flow through the column)

The GC-FID was used as off-line method. Therefore, calibration standards and samples were loaded into sorbent tubes as explained below.

Calibration method and value assignment

Calibration standards were loaded into sorbent tubes prior analysis. Commercial stainless steel tubes (1/4" x 3.5 ") packed with multibed sorbent material: Carbograph 2 (mesh 60/80) – Carbograph 1 (40/60) – Carbosieve^{TM} SIII (60/80) (Camsco, TX, USA) were used. The sorbent tubes, before being loaded, were conditioned for 2.5 hours at a temperature of 325 °C using a TC-20 tube conditioner (Markes International Ltd., UK) connected to a nitrogen supply (same nitrogen as describe above).

The tube loading was performed using a loading system developed by METAS. The main elements of this system are four MFCs (Red-y GSC, Vögtlin Instruments, Switzerland), an upstream pressure controller (DELTA Smart II Pressure, Brooks Instrument GmbH, Germany), an external pump and eight pneumatic valves (Swagelok, OH, USA). System purging was done overnight passing nitrogen at ca. 100 mL/min before each new measurement to ensure residual compounds from previous measurements were eliminated.

The system was flushed with the calibration standards for at least 2 hours at around 330 mL/min before sampling. For blanks, N_2 was also passed through the system for 2 hours at ca. 350 mL/min. After that time, the sorbent tubes (three each run without caps) were connected to the glass tube openings of the loading system by the groove-side and to the MFC by the other side through PFA tubing. During the loading, some overflow (ca. 55 mL/min) was let to ensure there is enough flow to load the three tubes. Once the loading time was over, sorbent tubes were closed with their brass caps. The loading time for the calibration standards was 10 minutes, setting the MFCs of the loading system at 30 mL/min (loading volume = 300 mL). A similar procedure was used for the transfer standard samples. In this case, the loading time was 5 minutes (loading volume = 150 mL). Instead of flushing the loading system with the transfer standard for several hours, the system was flushed nine times by opening and closing the cylinder valve. This was followed by 2 minutes of flushing at a flow around 100 mL/min. Estimation of internal blanks was done by loading sorbent tubes with N_2 at different volumes (N_2-1x (150 mL), N_2-2x (300 mL) and N_2-4x (600 mL), respectively).

The same analysis sequence was used for all the measurements. The three first GC-FID runs were discarded (conditioned empty tubes). After that, the sequence was as follows:

- 3 replicates of the calibration standard at low amount fraction level
- 3 replicates of the transfer standard
- 3 replicates of the calibration standard at medium amount fraction level
- 6 replicates of the transfer standard
- 3 replicates of the calibration standard at high amount fraction level

- 3 replicates of blanks (only nitrogen)
- 3 replicates of "empty" tubes (i.e. conditioned tubes without loading)

The following equations were used for the value assignment. The first step was to estimate the permeation rate of the acetone permeation unit placed in ReGaS1 using the exponential curve obtained during its calibration at three temperatures in MSB (Equation 1).

$$q_{m_ReGaS1} = a \cdot e^{b \cdot T} \quad \text{[Eq. 1]}$$

where,

q_m: permeation rate (in ng/min)
a: intercept of the calibration curve
b: slope of the calibration curve
T: temperature of the permeation chamber or oven (in °C)

After that, the amount fraction of the calibration standards was estimated using Equation 2.

$$X_{acetone} = q_m \cdot purity \cdot \left(\frac{V_{m_gas}}{M_{m_comp}}\right) \cdot f_{dil1} + X_{res} \quad \text{[Eq. 2]}$$

where,

$X_{acetone}$: amount fraction of acetone in the calibration standards (in nmol/mol)

q_m: permeation rate of the acetone permeation unit (in ng/min)

purity: purity of the permeation unit (no units)

V_{m_gas}: molar volume of the carrier/dilution gas (in L/mol)

M_{m_comp}: molar mass of acetone (in g/mol)

f_{dil1}: first step dilution fraction (no units)

X_{res}: residual amount fraction of acetone in the dilution gas (in nmol/mol)

Because the gas flows during the loading of the sorbent tubes ware the same, instead of estimating the loaded mass of calibration standard in the sorbent tubes (Equation 3), the loaded amount was calculated by multiplying the amount fraction of the calibration standard by the loading time. This results in a loaded amount with the unit nmol/mol·min. Both methods resulted in the same results.

$$m_{compound} = \frac{q_m \cdot q_{v_loading} \cdot t_{loading}}{q_{v_total}} \quad \text{[Eq. 3]}$$

where,

$m_{compound}$: loaded mass of acetone (in ng)

q_m: permeation rate of the calibrated permeation units (in ng/min)

$q_{v_loading}$: loading MFC flows of the loading system (in mL/min)

$t_{loading}$: loading time (in minutes)

q_{v_total}: total dilution flow measured by ReGaS1 MFM during the generation (in mL/min)

Two calibration parameters (slope and intercept) per measurement were obtained by linear regression using the least square method (Equations 4.a-c) [3]. All the peak areas were previously corrected by the blank peak areas for acetone.

$$n_{loaded} = a + b \cdot A_{peak} \quad \text{[Eq. 4.a]}$$

$$b_j = \frac{\sum_1^3 \left(n_{loaded_{RGMi}} - \bar{n}\right) \cdot \left(A_{peak_{RGMi}} - \overline{A_{peak}}\right)}{\sum_1^3 (n_{RGMi} - \bar{n})^2} \quad \text{[Eq. 4.b]}$$

$$a_j = \overline{A_{peak}} - b_j \cdot \bar{n} \quad \text{[Eq. 4c]}$$

where,

n_{loaded}: loaded amount of each calibration standard in the sorbent tubes (in nmol/mol·s)

a_j: intercept of the calibration curve obtained for measurement j (in nmol/mol·s)

A_{peak}: peak area of the loaded amount of each calibration standard measured with the GC-FID system (in units of area (u.a.))

b_j: slope of the calibration curve obtained for measurement j (in (nmol/mol·s)/u.a.)

$\bar{n}$: mean loaded amount of the three calibration standards in the sorbent tubes (in nmol/mol·s)

$\overline{A_{peak}}$: mean peak area of the three calibration standards measured with the GC-FID system (in u.a.)

Finally, the acetone amount fraction in the transfer standard was estimated as the average of the amount fractions calculated for each of the three measurements according Equation 5.

$$X_{acetone_j} = \frac{\overline{A_{peak_cyl}} - a}{b \cdot t_{load}} \quad \text{[Eq. 5]}$$

where,

$X_{acetone_j}$: estimated amount fraction for measurement j (in nmol/mol)

A_{peak_cyl}: average peak area of the replicates of transfer standard measured for each measurement (in u.a.)

a: intercept of the calibration curve (in nmol/mol·s)

b: slope of the calibration curve (in (nmol/mol·s)/u.a.)

t_{load}: loading time set for the value assignment (in s)

Uncertainty evaluation

To obtain the final result for acetone, a weighted average of the tree measurements was determined, taking into account the associated uncertainties (Equation 6). The combined uncertainty of the acetone amount fraction considered the combined uncertainty of each measurement and the standard uncertainty associated to the repeatability of the analytical method (i.e. pooled standard deviation of the measurement results).

$$X_{acetone_D961162} = \frac{\sum_{j=1}^{3} X_{acetone_j}}{3} \quad \text{[Eq. 6]}$$

where,

$X_{acetone_D961162}$: acetone amount fraction estimated for transfer standard D961162 (in µmol/mol)

$X_{acetone_j}$: acetone amount fraction estimated during measurement j, with j = 1,..,3 (in µmol/mol)

The contributions to the relative combined standard uncertainty of each measurement came mainly from the calibration standards and loading system (Equation 7.a). In turn, the contributions to the uncertainty of the calibration standards were the estimation of the permeation rate, the long-term stability of the permeation rate, the dilution flows and the purity of the permeation unit (Eq. 7.b). The uncertainty coming from the loading system was mainly due to the uncertainty of the loading time.

$$\frac{u(X_{acetone_j})}{X_{acetone_j}} = \sqrt{\frac{u(X_{cal_ij})^2}{X_{cal,ij}^2} + \frac{u(t_{load})^2}{t_{load}^2}} \quad \text{[Eq. 7.a]}$$

where,

$u(X_{acetone_j})$: uncertainty of the acetone amount fraction estimated in measurement j (in nmol/mol)

$X_{acetone_j}$: acetone amount fraction estimated in measurement j (in nmol/mol)

$u(X_{cal_ij})$: uncertainty of the acetone amount fraction in the calibration standard i (i = 1, …,3) (in nmol/mol)

X_{cal_ij}: acetone amount fraction in the calibration standard i (i = 1, …,3) for measurement j (j = 1, …, 3) (in nmol/mol)

$u(t_{load})$: uncertainty of the loading time (in s)

t_{load}: loading time (in s)

$$\frac{u(X_{cal_ij})}{X_{cal_ij}} = \sqrt{\frac{u(q_{m_ReGaS1})^2}{q_{m_ReGaS1}^2} + \frac{u(q_{v_i})^2}{q_{v_i}^2} + \frac{u(F_{stab})^2}{F_{stab}} + \frac{u(purity)^2}{purity}} \quad \text{[Eq. 7.b]}$$

where,

$u(q_{m_ReGaS1})$: uncertainty of the estimated permeation rate for ReGaS1 conditions

q_{m_ReGaS1}: estimated permeation rate under ReGaS1 conditions

$u(q_{v_i})$: uncertainty of the total gas flow used to generate each calibration standard

q_{v_i}: total gas flow used to generate each calibration standard

$u(F_{stab})$: uncertainty due to the long term stability of the permeation rate

F_{stab}: factor that considers the long term stability of the permeation rate

u(purity): uncertainty due to the purity level of the permeation unit

purity: purity of the permeation unit; values ranging between 0 and 1

An example of combined uncertainty of one of the calibration standards for one of the measurements can be found in the following table. The main sources of uncertainty are indicated.

	Units	Value	Standard uncertainty	Uncertainty type	Distribution	Uncertainty contribution		Index
						nmol/mol	%	%
q_{m_ReGaS1}	ng/min	194.9	0.7			0.043	0.2	22.7
q_v	mL/min	1975.6	3.0	B	normal	-0.057	0.2	30.2
PU	no units	0.9940	0.0025	B	triangular	0.093	0.3	49.2
F_{stab}	mL/min	1.000	0.001	B	normal	0.11	0.3	58.2
$u(X_{cal1_1M01})$	nmol/mol	37.85	0.21					

The estimated amount fraction of acetone for the transfer standard D961162 and its combined and expanded uncertainty (coverage factor k = 2) are shown in the table below.

	Units	Value	Standard Uncertainty	Uncertainty type	Distribution	Uncertainty contribution (%)	Index (%)
$X_{acetone_M01}$	µmol/mol	0.218	0.004	A	normal	1.6	27.1
$X_{acetone_M02}$	µmol/mol	0.221	0.004	A	normal	1.6	27.1
$X_{acetone_M03}$	µmol/mol	0.218	0.005	A	normal	2.0	33.9
repeatability	no units			A		0.7	11.9
$X_{acetone_D961162}$	µmol/mol	**0.219**					
$u(X_{acetone_D961162})$	µmol/mol	0.006					
$U(X_{acetone_D961162})$	µmol/mol	**0.012**					

References

[1] ISO 6145-10:2002 Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Part 10: Permeation method.

[2] ISO 6145-7:2018 Gas analysis – Preparation of calibration gas mixtures using dynamic methods – Part 7: Thermal mass-flow controllers.

[3] Cantrell, C.A. (2008). Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmospheric Chemistry and Physics, 8, 5477 – 5487.

Authorship

Maitane Iturrate-Garcia, Tobias Bühlmann, Céline Pascale

CCQM-K174 oxygenated VOCs

Laboratory name: National Institute of Metrology (NIM), China

Cylinder number: D961160

Authors: Haomiao Ma, Defa Wang, Zhe Bi

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	2/4/2022	0.912	0.6%	3
Ethanol	2/4/2022	0.498	0.6%	3
Acetone	2/4/2022	0.205	0.3%	3

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	6/4/2022	0.906	0.9%	3
Ethanol	6/4/2022	0.514	1.2%	3
Acetone	6/4/2022	0.208	0.7%	3

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	7/4/2022	0.905	0.2%	3
Ethanol	7/4/2022	0.498	0.4%	3
Acetone	7/4/2022	0.205	0.3%	3

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	12/4/2022	0.920	0.6%	3
Ethanol	12/4/2022	0.516	0.2%	3
Acetone	12/4/2022	0.210	0.3%	3

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates

Methanol	13/4/2022	0.911	0.8%	3
Ethanol	13/4/2022	0.505	1.1%	3
Acetone	13/4/2022	0.208	0.2%	3

Measurement #6

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	15/4/2022	0.908	1.0%	3
Ethanol	15/4/2022	0.515	0.2%	3
Acetone	15/4/2022	0.207	0.5%	3

Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Methanol	20/10/2022	0.910	0.036	2
Ethanol	20/10/2022	0.508	0.020	2
Acetone	20/10/2022	0.207	0.008	2

Calibration standards

In order to obtain the calibration standard of OVOCs in N_2 of 0.5 µmol/mol，PRMs of 250 µmol/mol OVOCs in cylinder prepared according to ISO6142-1:2015 was then diluted by using BIP nitrogen. RPMs of 250 µmol/mol OVOCs was gravimetrically prepared. In preparation step, the OVOCs were injected into a vacuum 4 L cylinder by 3 syringes. The purity data was showed in Table 1, 2 and 3. The mass of injected ethanol was around 0.19 g, methanol was 0.13 g, acetone was 0.24 g (Sartorius, capacity 230 g, resolution 10 µg), and the mass of N_2 was around 460 g by using comparator (Mettler Toledo, capacity 26 kg, resolution 1 mg). The relative uncertainty of 250 µmol/mol OVOCs was 0.3%(k=1), which was estimated based on only gravimetric data and purity data. Internal consistency of 5 PRMs in 250 µmol/mol were checked by using GC-FID (Agilent 7890A, VB-WAX 30 m×0.25 mm×0.25 µm). Results showed that all PRMs agreed with each other within 0.5%, and it was taken as the uncertainty contribution from verification. Equal-decanting method was used to evaluate the absorption effect of cylinder internal wall. Results indicated loss of OVOCs due to absorption effect was less than 0.3%, and thereby it was taken as additional uncertainty contribution of absorption effect. Finally, the combined uncertainty of PRMs of 250 µmol/mol OVOCs was estimated as 0.7% (k=1). The two PRMs used were listed in Table 4.

Table 1. The purity data of Methanol

Component	Amount fraction (%)	Standard Uncertainty (%)	Method
H_2O	0.261	0.026	Karl Fischer
Methanol	99.739	0.026	

Table 2. The purity data of Ethanol

Component	Amount fraction (%)	Standard Uncertainty (%)	Method
H_2O	0.226	0.023	Karl Fischer
Ethanol	99.774	0.023	

Table 3. The purity data of Acetone

Component	Amount fraction (%)	Standard Uncertainty (%)	Method
H_2O	0.175	0.018	Karl Fischer
Acetone	99.825	0.018	

Table 4. PRMs of 250 μmol/mol

Cyl. No.	Component	Amount fraction (μmol/mol)	Exp.Uncertainty (μmol/mol)	Exp.Relative Uncertainty	Balance
212903102#	Methanol	251.8	3.5	1.4%	N_2
	Ethanol	248.1	3.5	1.4%	
	Acetone	250.5	3.5	1.4%	
212903106#	Methanol	247.6	3.5	1.4%	N_2
	Ethanol	245.9	3.4	1.4%	
	Acetone	244.0	3.4	1.4%	

A dilution device consisting of two mass flow controllers calibrated was used to dilute the PRM of 250 μmol/mol OVOCs to standard gas of 0.5 μmol/mol. Considering the bias as well as the stability of the dilution device, the uncertainty due to dilution process was conservatively estimated as 0.8%. The uncertainty of 0.5 μmol/mol OVOCs was estimated as 1.1%(k=1).

Instrumentation

The GC-FID (Agilent 7890A) , equipped with a capillary column of Stabilwax (60 m×0.32 mm×1 μm), was adopted to measure OVOCs content. The parameters of GC used were set as: Oven=40 ℃, Carrier gas (He) flow rate=10 mL/min, Split ratio=5:1. The data was collected by using the Agilent workstation.

Calibration method and value assignment

In order to cancel the drift effect of GC on the measurement result, A-B-A mode was used. The standard and sample were injected alternatively. The OVOCs concentrations in the sample were assigned according to single-point calibration, the equation as follow.

$$C_{\mathrm{spl}} = C_{\mathrm{std}} \times f = (C_{\mathrm{PRM}} \times DR) \times f \quad (1)$$

C_{spl}: Concentration of OVOCs in comparison sample, μmol/mol;

C_{std}: Concentration of OVOCs in calibration standard, μmol/mol;

C_{PRM}: Concentration of OVOCs in PRM, μmol/mol;

DR: Dilution rate;

f: Area ratio of sample to standard.

Uncertainty evaluation

According to equation (1), combined uncertainty of measurement result was estimated as equation (2).

$$u_{\mathrm{rel}}(C_{\mathrm{spl}}) = \sqrt{{u_{\mathrm{rel}}}^2(C_{\mathrm{std}}) + {u_{\mathrm{rel}}}^2(f)} = \sqrt{{u_{\mathrm{rel}}}^2(C_{\mathrm{PRM}}) + {u_{\mathrm{rel}}}^2(DR) + {u_{\mathrm{rel}}}^2(f)} \quad (2)$$

The relative uncertainty in measurement result conservatively is 2.0%(k=1), and the expanded uncertainty is 4.0%(k=2).

Table 5. Uncertainty budgets

Component	u_{rel} (derived from PRMs)	u_{rel} (derived from dilution)	$u_{\mathrm{rel}}(C_{\mathrm{std}})$	$u_{\mathrm{rel}}(f)$	$u_{\mathrm{rel}}(C_{\mathrm{spl}})$	$U_{\mathrm{rel}}(C_{\mathrm{spl}})$ k=2
Methanol	0.7%	0.8%	1.1%	0.6%	1.2%	2.4%
Ethanol	0.7%	0.8%	1.1%	1.7%	2.0%	3.9%
Acetone	0.7%	0.8%	1.1%	1.0%	1.5%	3.0%

Report Form CCQM-K174 oxygenated VOCs

Laboratory name: National Metrology Institute of South Africa (NMISA)

Cylinder number: D96 1183

Authors: Nompumelelo Leshabane, Gumani Ethel Mphaphuli, Wilson Matlhatse Magobo, Mudalo Isabel Jozela

Table 1. Nominal amount fraction ranges for the comparison sample

Component	Amount fraction ranges
Acetone (C_3H_6O)	0.1 – 1.0 x 10^{-6} mol.mol^{-1}
Methanol (CH_3OH)	0.1 – 1.0 x 10^{-6} mol.mol^{-1}
Ethanol (C_2H_5OH)	0.1 – 1.0 x 10^{-6} mol.mol^{-1}

1. Measurement results

Measurement #1

Component	Date (dd/mm/my)	Result (µmol.mol^{-1})	Standard deviation (% relative)	Number of replicates
Methanol	03/08/2022	0.7248	0.0002	2
Ethanol	02/08/2022	0.4560	0.0015	4
Acetone	02/08/2022	0.2134	0.0033	4

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol.mol^{-1})	Standard deviation (% relative)	Number of replicates
Methanol	03-04/08/2022	0.7299	0.0096	2
Ethanol	03/08/2022	0.4581	0.0013	2
Acetone	03/08/2022	0.2134	0.0062	3

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol.mol^{-1})	Standard deviation (% relative)	Number of replicates
Methanol	04/08/2022	0.7296	0.0113	2
Ethanol	04/08/2022	0.4585	0.0029	4
Acetone	04/08/2022	0.2134	0.0052	3

Comparison sample results

Component	Date (dd/mm/yy)	Result (µmol.mol^{-1})	Expanded uncertainty (µmol.mol^{-1})	Coverage factor
Methanol	03-04/08/2022	0.728	0.019	2
Ethanol	02-04/08/2022	0.458	0.012	2
Acetone	02-04/08/2022	0.213	0.0041	2

2. Calibration standards

Purity analysis of the starting materials

Purity assessment of the high purity methanol, ethanol and acetone used the Karl Fischer titration method for the quantification of moisture content. The organic impurities on the high purity chemicals were quantified using the manufacturer's specifications. The purity assessment of BIP^{TM} nitrogen was done on the Agilent GC using traceable primary standard gas mixtures containing components with amount fractions similar to the impurities found in the high purity BIP^{TM} nitrogen. **Table 2 to 6** show purity tables for the high purity starting materials used to prepare calibration standards that value-assigned the comparison sample.

Table 2. Purity table for high purity methanol

Component	Amount fraction (µmol.mol^{-1})	Expanded uncertainty (µmol.mol^{-1}) *k=2*
CH_3OH	994709.00	91.65
H_2O (moisture)	5291.00	91.65

Table 3. Purity table for high purity ethanol

Component	Amount fraction (µmol.mol^{-1})	Expanded uncertainty (µmol.mol^{-1}) *k=2*
Acetone	5.00	5.77
Isopropanol	50.00	57.73
1-propanol	50.00	57.73
Methanol	50.00	57.73
3-methyl-1-butanol	250.00	288.68
H_2O (moisture)	1169.17	24.16
C_2H_5OH	998425.83	4.70

Table 4. Purity table for high purity acetone

Component	Amount fraction (µmol.mol^{-1})	Expanded uncertainty (µmol.mol^{-1}) *k=2*
C_3H_6O	991498.58	81.17
H_2O (moisture)	8501.42	81.17

Table 5. Purity table for high purity hexane

Component	Amount fraction (µmol.mol^{-1})	Expanded uncertainty (µmol.mol^{-1}) *k=2*
C_6H_{14}	990000.00	1154.70
H_2O (moisture)	2000.00	1150.00

Table 6. Purity table for Built-in purifier nitrogen

Component	Amount fraction (µmol.mol^{-1})	Expanded uncertainty (µmol.mol^{-1}) *k=2*
CO	0.076	0.088
CO_2	0.063	0.073
CH_4	0.021	0.024
C_2H_6	0.020	0.023
Ar	20.562	1.902
O_2	0.005	0.006
H_2O	0.010	0.012
H_2	1.643	0.351
N_2	999977.599	1.938

Method of preparation

Multi-component primary standard gas mixtures (PSGMs) containing acetone, ethanol, and methanol with hexane as an internal standard in nitrogen used for analysis and value assignment for the comparison gas mixture were prepared in accordance with ISO 6142-1:2015 (Gas analysis – Preparation of calibration gas mixtures – Gravimetric method). The standards used were prepared using a three-step dilution method from high purity acetone, hexane, ethanol, and methanol sourced from Sigma Aldrich and the diluent gas of BIP^{TM} nitrogen was sourced from Air Products. **Figure** 1 shows the production diagram of the multi-component PSGMs. The gravimetric amount fractions of the prepared PSGMs are detailed in **Table 7**. The gravimetric amount fractions of the PSGMs were verified using ISO 6143:2001 (Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures).

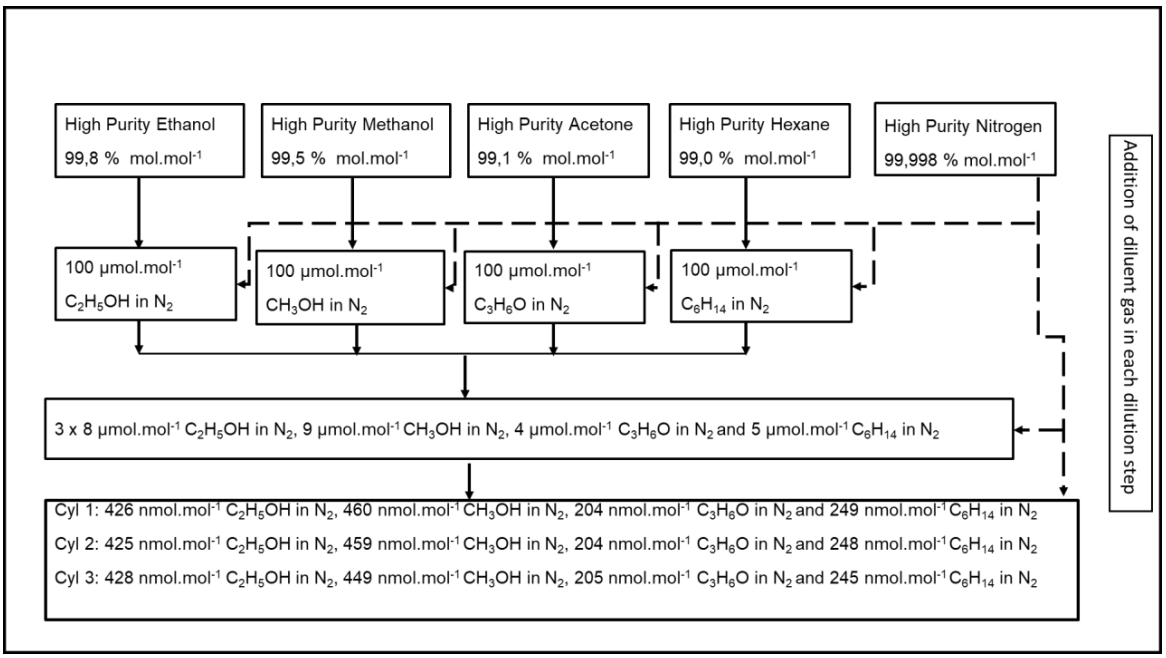


Figure 1. Schematic diagram for the production of multi-component primary standard gas mixtures of acetone, ethanol, methanol, and hexane in nitrogen.

Table 7. Gravimetric and corrected amount fractions with expanded uncertainties of the primary standard gas mixtures used for value assignment of the comparison sample

Cylinder number	Component	Gravimetric amount fraction and expanded uncertainty (µmol.mol^{-1}) U (*k*=2)	Corrected amount fraction and expanded uncertainty (µmol.mol^{-1}) U (*k*=2)
M39 5435	Acetone	0.2043 ± 0.0001	0.2104 ± 0.0005
	Methanol	0.4598 ± 0.0005	0.4672 ± 0.0029
	Ethanol	0.4263 ± 0.0012	0.3773 ± 0.0009
D62 6413	Acetone	0.2038 ± 0.0001	0.2063 ± 0.0009
	Methanol	0.4587 ± 0.0005	0.4775 ± 0.0058
	Ethanol	0.4252 ± 0.0012	0.3721 ± 0.0019
D67 9629	Acetone	0.2051 ± 0.0001	0.2076 ± 0.0006
	Methanol	0.4490 ± 0.0006	0.2937 ± 0.0027
	Ethanol	0.4284 ± 0.0005	0.3721 ± 0.0011

3. Instrumentation

The calibration standard(s) and comparison sample were analysed using gas chromatography coupled with dual flame ionisation detectors (GC-FID). Hydrogen served as a carrier gas while the components of interest in the multi-component gas mixtures were separated using a capillary HP-INNOWAX column. The instrument conditions are shown in **Table 8**.

Table 8. GC-FID analytical conditions for the analysis of Oxy-VOC's

Instrument ID	**Agilent Technologies (7890B)**
Column	60 m x 320 µm x 0.5 µm capillary HP-INNOWAX
Oven Temperature	60 °C and held for 0.8 minutes and ramped at a rate of 40 °C /min to 100 °C for 0.5 minutes
Detector	FID
Detector Temperature	270 °C
Carrier Gas	Hydrogen
Sample Flow	35 mℓ.min^{-1}

Single-point calibration method was used to analyse the comparison sample. A calibration standard which contained nominal values of 204 nmol.mol^{-1}, 460 nmol.mol^{-1} and 426 nmol.mol^{-1} for acetone, methanol and ethanol respectively was used to determine the amount fractions of the mentioned components in the comparison sample.

Adsorption study

Studies have shown that components are more likely to adsorb or desorb on the inner surfaces of gas cylinders and transfer lines based on their chemical bonding and molecular structures (Leuenberger et.al., 2015). Therefore, adsorption losses to the cylinder surfaces and transfer lines should be considered in order to produce accurate and reliable reference gas mixtures as this may cause variations in the gravimetric amount fraction. To consider the adsorption of components of interest in the prepared reference gas mixtures, an adsorption study was performed using the GC responses and gravimetric amount fractions to correct the gravimetric amount fraction due to adsorption losses. Hexane was added to the reference gas mixtures as an internal standard that is known to have negligible adsorption losses to the cylinder surfaces. Following the adsorption study, the corrected gravimetric amount fractions, and associated uncertainties for NMISA standards were used to value assign the comparison sample. **Equation 1** was used to calculate the corrected gravimetric value and **Equation 2** and **3** were used to calculate the standard and expanded uncertainty associated with the corrected gravimetric value.

$$x_{i,d} = \frac{x_{i,p} \times \bar{A}_{r,p} \times \bar{A}_{i,d} \times x_{r,d}}{\bar{A}_{i,p} \times x_{r,p} \times \bar{A}_{r,d}} \quad (1)$$

$$u(x_{i,d}) = x_{i,d} \sqrt{\left(\frac{u(x_{i,p})^2}{x_{i,p}{}^2}\right) + \left(\frac{u(\bar{A}_{r,p})^2}{\bar{A}_{r,p}{}^2}\right) + \left(\frac{u(\bar{A}_{i,d})^2}{\bar{A}_{i,d}{}^2}\right) + \left(\frac{u(x_{r,d})^2}{x_{\mathrm{r,d}}{}^2}\right) + \left(\frac{u(\bar{A}_{i,p})^2}{\bar{A}_{i,p}{}^2}\right) + \left(\frac{u(x_{r,p})^2}{x_{\mathrm{r,p}}{}^2}\right) + \left(\frac{u(\bar{A}_{r,d})^2}{\bar{A}_{r,d}{}^2}\right)} \quad (2)$$

$$U_{i,d} = u(x_{i,d}) \times 2 \quad (3)$$

Where,

$x_{i,p}$ is the amount fraction of the component of interest in the pre-mixture

$u_{x(i,p)}$ is the gravimetric uncertainty of the component of interest in the pre-mixture

$x_{r,p}$ is the amount fraction of n-hexane (internal standard) in the pre-mixture

$u_{x(r,p)}$ is the gravimetric uncertainty of the n-hexane in the pre-mixture

$x_{r,d}$ is the amount fraction of n-hexane in ppb level mixture

$u_{x(r,d)}$ is the gravimetric uncertainty of the n-hexane in the ppb level mixture

$\bar{A}_{r,p}$ is the GC-FID response of n-hexane in the pre-mixture

$u_{\bar{A}_{r,p}}$ is the estimated standard deviation of the mean (ESDM) of n-hexane in the pre-mixture

$\bar{A}_{r,d}$ is the GC-FID response of n-hexane in the ppb level mixture

$u_{\bar{A}_{r,d}}$ is the ESDM of n-hexane in the ppb level mixture

$\bar{A}_{i,d}$ is the GC-FID response of component of interest in the ppb level mixture

$u_{\bar{A}_{i,d}}$ is the ESDM of the component of interest at ppb level mixture

$\bar{A}_{i,p}$ is the GC-FID response of the component of interest in the pre-mixture

$u_{\bar{A}_{i,p}}$ is the ESDM of the component of interest in the pre-mixture

$x_{i,d}$ is the corrected amount fraction of component of interest in the ppb level mixture

$u_{i,d}$ is the corrected standard uncertainty of component of interest in the ppb level mixture

$U_{i,d}$ is the corrected expanded uncertainty of component of interest in the ppb level mixture

4. Calibration method and value assignment

The GC-FID was calibrated utilising NMISA developed primary standards gas mixtures for the single-point calibration method. The single-point calibration formulae were adopted as shown in **Equation 4** in order to assign the comparison sample value.

$$x_{Sample} = \frac{y_{Sample}}{y_{Reference}} \times x_{Reference} \quad (4)$$

Where x_{Sample} is the amount fraction of the comparison sample, $x_{Reference}$ is the amount fraction of the NMISA calibration standard, y_{Sample} is the analytical response of the comparison sample and $y_{Reference}$ is the analytical response of the NMISA calibration standard.

5. Uncertainty evaluation

Evaluation of uncertainty depends mostly on a known measurement model. The different parameters from the measurement model contribute to the uncertainty of the measurement result. Therefore, uncertainty is evaluated based on measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the result, the uncertainties are either considered or neglected.

A list of potential uncertainty sources considered is given and compiled from ISO-Standards, ISO-6142-1:2015 and ISO-6143:2001. The uncertainty contributors associated with the value assignment of Oxy-VOCs (acetone, methanol, and ethanol) amount fraction were as follows:

a. Short-term stability of the Oxy-VOCs gas mixtures (Estimated standard deviation of the mean)
b. Adsorption of the component-of-interest on the inner surface of the cylinder
c. Verification uncertainty (Repeatability)

All the uncertainty contributors are calculated as combined standard uncertainties which contribute to the value assignment of comparison sample. The predicted amount fraction for each component in the comparison sample was averaged, and standard deviation was calculated using **Equation 5**. The combined standard uncertainty is calculated as a combination of all the uncertainty contributors as the sum of square of all the uncertainty contributors as shown in **Equation 6**. The uncertainties of each measurement result were combined as shown in **Equation 7**.

$$S = \sqrt{\frac{\sum(x_i - \bar{x})^2}{(n-1)}} \quad (5)$$

Where S is the standard deviation, x_i is the predicted amount fraction, $\bar{x}$ is the average of the predicted amount fraction and n is the total number of replicates.

$$u_c\,(\mathrm{y}) = \sqrt{\sum_{i=1}^{N}[c_i u(x_i)]^2} \quad (6)$$

Where $u_c\,(y)$ represents the combined standard uncertainty, c_i is the sensitivity coefficient for input *i,* $u(x_i)$ represents the uncertainty estimates for input x_i

$$u_c = \sqrt{\Sigma(u_{Meas(i)}{}^2)/n} \quad (7)$$

Where u_c is the combined uncertainty, $u_{Meas(i)}$ is the standard uncertainty of measurement i and n, the total number of measurements. The combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor *k = 2*, at a confidence level of 95,45%.

5.1 Detailed uncertainty budget:

The uncertainty contributors and corresponding relative expanded uncertainties are detailed in **Table 9** for each component.

Table 9. Uncertainty evaluation for Oxy-VOCs in nitrogen

Component	Uncertainty source x_i	Evaluation Type (A or B)	Assumed distribution	Standard uncertainty $u(x_i)$,(µmol.mol^{-1})	Expanded Uncertainty, U (k=2) (µmol.mol^{-1})	% REU
Acetone	Verification	Type A	Normal	0.0021	0.0041	1.9
	Stability	Type A	Normal	0.0001		
	Adsorption	Type A	Normal	0.0005		
Methanol	Verification	Type A	Normal	0.0095	0.019	2.6
	Stability	Type A	Normal	0.0017		
	Adsorption	Type A	Normal	0.0030		
Ethanol	Verification	Type A	Normal	0.0059	0.012	2.6
	Stability	Type A	Normal	0.0008		

Adsorption	Type A	Normal	0.0010

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Report Form CCQM-K174 oxygenated VOCs

Laboratory name: National Physical Laboratory

Cylinder number: D961164

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	29/06/2022	0.936	1.78	5
Ethanol	29/06/2022	0.511	1.20	5
Acetone	29/06/2022	0.199	0.82	5

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	12/07/2022	0.929	1.42	5
Ethanol	12/07/2022	0.510	1.05	5
Acetone	12/07/2022	0.200	0.49	5

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Methanol	25/07/2022	0.930	1.11	4
Ethanol	25/07/2022	0.514	1.01	4
Acetone	25/07/2022	0.201	0.53	4

Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Methanol	25/07/2022	0.932	0.047	2
Ethanol	25/07/2022	0.511	0.019	2
Acetone	25/07/2022	0.200	0.004	2

Calibration standards

One NPL primary reference material (NPL PRM; NG1040) of nominally 50 µmol mol^{-1} methanol, ethanol, acetone (Table 1) and n-hexane in nitrogen (BIP$^+$, Air Products) was gravimetrically prepared in accordance with ISO 6142-1 in 10 litre aluminium cylinders, (Luxfer) with a proprietary passivation treatment of the internal surfaces (BOC Spectraseal), from pure sources (Sigma Aldrich). *n*-hexane was included in the mixture as an internal reference and is not part of the comparison. The purity of all sources is given in Tables 2 – 5. This NPL PRM mixture was prepared in one stage by dilution of the four pure sources by indirect filling using a transfer vessel, followed by the addition of high purity nitrogen (BIP$^+$, Air Products) via direct filling. Following preparation this NPL PRM (NG1040) was validated against existing in house NPL PRMs to verify the integrity of the preparation. This NPL PRM was dynamically diluted with high purity nitrogen (BIP+, Air Products) using a dilution system based on sonic nozzles (Sonimix, LNI Swissgas). This dynamically generated reference standard was used to value assign amount fractions to the comparison mixture (travelling standard).

Table 1. Amount fractions of methanol, ethanol and acetone in NPL PRM NG1040 and associated gravimetric uncertainties.

Component	**Amount fraction (µmol mol^{-1})**	**Standard uncertainty (µmol mol^{-1})**
methanol	49.17	0.03
ethanol	50.98	0.02
acetone	49.71	0.02

The purity of the methanol (Sigma-Aldrich), ethanol (Thermo Fisher Scientific), acetone (Acros Organics) and nitrogen (BIP+, Air Products) were determined according to ISO 19229:2015 and all were > 99.7 % (see Tables 3, 4 and 5). For methanol, ethanol and acetone all components with the exception of water were analysed by GC-FID/MS. The amount fraction of water was taken from the certificate of analysis. For ethanol, no peaks were observed in the GC-FID/MS analysis so the amount fraction of impurities was taken from the certificate of analysis. The nitrogen purity was determined from the certificate of analysis.

The uncertainty of an amount fraction was estimated based upon a rectangular distribution between zero and the value of the detection limit of the analytical method, thus assuming that there is an equal likelihood that the impurity may be present in the material at a level up to the value of the detection limit. An unexpected impurity therefore forms a rectangular probability distribution from which its standard uncertainty is given by equation (1):

$$u(x_{ij}) = \frac{L_{ij}}{2\times\sqrt{3}} \quad (1)$$

Where L_{ij} is the limit of detection of component i in parent gas j
u is the standard uncertainty
x_{ij} is the amount-of-substance fraction of component i in parent j.

The standard uncertainty in the amount fraction of the ‘pure’ component was determined using the law for the propagation of uncertainty shown in equation (2):

$$u^2(x_{kj}) = \sum_{i=1;i\neq k}^{n} u^2(x_{ij}) \quad (2)$$

Table 2. Methanol purity table

Component	Amount fraction (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
methanol	999990.00	19.03
H_2O	10.00	1.00

Table 3. Ethanol purity table

Component	Amount fraction (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
ethanol	999793.24	57.73
acetic acid	1.80	0.52
methanol	2.00	0.58
isopropanol	3.00	0.87
H_2O	199.96	57.72

Table 4. Acetone purity table

Component	Amount fraction (µmol mol-1)	Standard uncertainty (µmol mol-1)
acetone	997070.41	806.34
methanol	51.12	20.73
acetaldehyde	86.32	8.63
H_2O	2792.15	806.34

Table 5. Nitrogen purity table

Component	Amount fraction (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
N_2	999999.4817	0.8735
Ar	0.5000	0.0500
O_2	0.0050	0.0025
C_xH_y	0.0050	0.0050
H_2O	0.0050	0.0020
CH_4	0.0010	0.0010
H_2	0.0010	0.0010
NO	0.0005	0.0003

SO_2	0.0005	0.0003
CO	0.0003	0.0002

Instrumentation and measurement procedure

The amount fraction of methanol, ethanol and acetone were measured using a gas chromatograph fitted with a flame ionisation detector (GC-FID; Scion 456). The capillary column used was 105 m x 0.32 um, df = 1.8 um DB-624 (Restek Corporation). The oven had an initial temperature of 30°C and was held at this temperature for 15 minutes. It was then heated at a rate of 25°C per minute to 200°C giving a total run time of 23 minutes. Hydrogen was used as the carrier gas with a head pressure of 138 kPa. Sample pre-concentration was conducted by flowing the sample through a cryogenic pre-concentration trap consisting of glass beads cooled to -180 °C with liquid nitrogen for a period of nominally five minutes at a flow rate of nominally 50 ml/min. The sample volume was recorded using a mass flow meter (Vögtlin, Red-y), which was used to correct any differences between sample volumes. During injection of the sample into the GC the preconcentration trap was heated to 200°C and held for 15 minutes to ensure complete transfer. Sample pre-concentration was necessary to ensure adequate peak areas were observed in the GC-FID to enable robust and repeatable data to be produced.

Before measuring any gas mixtures, the analyser response to the balance gas (nitrogen) was recorded. As only a baseline was recorded, no balance gas correction was applied. The instrument response was monitored until stable and once stable the last five injections for each amount fraction were recorded. The points in the calibration curve were generated in a randomised order to minimise the effects of analyser drift and were run in blocks to ensure stable readings. The response from the comparison mixture was also recorded for five injections and the normalised response was averaged. All sample line tubing, connectors, flow controllers and unions were SilcoNert 2000 treated to minimise adsorption affects.

Calibration method and value assignment

Amount fraction values for all three components were assigned to the comparison mixture based on an inverse evaluation using XLGENLINE (in the GDR mode) (Cox et al., 2003, ISO/TS 28037:2010(E)) from a calibration curve generated from the dynamic dilution of the NPL PRM (NG1040) in accordance with ISO 6143:2006. The calibration curve contained between 5 to 7 points across the range of 0.1 – 2 µmol mol^{-1}.

Uncertainty evaluation

The estimated uncertainty for the measurement includes the following components:

- Purity analysis
- Gravimetric preparation and verification
- Analytical validation (system repeatability of the GC response).
- Curve fitting routine

The analyte content (x) of the comparison mixture was calculated from an inverse evaluation using the XLGENLINE software. Standard uncertainties included in the XLGENLINE software for x (amount

fraction) were contributions from purity, gravimetric preparation and verification and for y (instrument response) were the repeatability of the GC response.

The inverse evaluation used the analysis function x = G(y), which was determined to be linear for all components:

$$x = b_0 + b_1 y$$

The uncertainty was determined within the XLGENLINE software using:

$$u^2(x) = \left(\frac{\partial G}{\partial y}\right)^2 u^2(y) + \sum_{j=0}^{N} \left(\frac{\partial G}{\partial b_j}\right)^2 u^2(b_j)$$

The final result was determined as the average of the three measurement results and the total uncertainty was determined as the sum of squares of the three standard uncertainties added in quadrature. The reported expanded uncertainty is based on the total standard uncertainty multiplied by a coverage factor of 2 (k=2), providing a level of confidence of approximately 95%.

References

ISO 6143:2006. Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures.

ISO 19229:2019. Gas analysis - Purity analysis and the treatment of purity data.

Cox, M. G., Forbes A B, Harris P. M. and Smith I. M. (2003). The classification and solution of regression problems for metrology. Technical Report CMSC 24/03 (Teddington, UK: National Physical Laboratory).

Authorship

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Report Form CCQM-K174 oxygenated VOCs

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Table 1. Nominal amount fraction ranges for the comparison sample

Component	Amount fraction ranges
Acetone (C_3H_6O)	0.1 – 1.0 x 10^{-6} mol.mol^{-1}
Methanol (CH_3OH)	0.1 – 1.0 x 10^{-6} mol.mol^{-1}
Ethanol (C_2H_5OH)	0.1 – 1.0 x 10^{-6} mol.mol^{-1}

1. Measurement results

Measurement #1

Component	Date (dd/mm/yy)	Result (mol.mol^{-1})	Standard deviation (% relative)	Number of replicates
Methanol	04/08/22	8.70 x 10^{-7}	0.37	5
Ethanol	04/08/22	4.94 x 10^{-7}	0.35	5
Acetone	04/08/22	2.00 x 10^{-7}	0.44	5

Measurement #2

Component	Date (dd/mm/yy)	Result (mol.mol^{-1})	Standard deviation (% relative)	Number of replicates
Methanol	07/08/22	8.83 x 10^{-7}	0.51	5
Ethanol	07/08/22	4.95 x 10^{-7}	0.64	5
Acetone	07/08/22	1.97 x 10^{-7}	0.50	5

Measurement #3

Component	Date (dd/mm/yy)	Result (mol.mol^{-1})	Standard deviation (% relative)	Number of replicates
Methanol	10/08/22	8.93 x 10^{-7}	0.16	5
Ethanol	10/08/22	4.98 x 10^{-7}	0.36	5
Acetone	10/08/22	1.99 x 10^{-7}	0.47	5

Comparison sample results

Component	Date (dd/mm/yy)	Result (µmol.mol^{-1})	Expanded uncertainty (µmol.mol^{-1})	Coverage factor
Methanol		0.882	0.044	2
Ethanol	---	0.496	0.021	2
Acetone		0.199	0.007	2

2. Calibration standards

Purity information

In general, the purity analysis was performed in accordance with ISO 19229:2019 [1]. Water contents in the liquid chemicals (methanol, ethanol and acetone) were measured using Karl Fischer titration method. The organic impurities in these chemicals were analysed using GC-MSD/FID. The results (see below table) showed the purities of these pure liquids are better than 99 %. The nitrogen used as balance gas is the Built-in-Purifier type from Air Products, BIP+ quality. The purity of nitrogen was checked for water and methanol, ethanol and acetone content.

Liquid chemical	Component	Fraction (mol/mol)	Uncertainty (mol/mol)
Methanol	methanol	0.999723850	0.000055230
	water	0.000276150	0.000055230
Ethanol	ethanol	0.999732650	0.000053470
	water	0.000267350	0.000053470
Acetone	acetone	0.999380400	0.000123920
	water	0.000619600	0.000123920

Method of preparation

Static gas mixture (as control mixture) with the same nominal amount fractions was prepared gravimetrically in accordance with ISO 6142-1:2015 [2].

Dynamically prepared gas mixtures (using diffusion method in accordance with ISO6145-8:2005 [3]) in the range covering the nominal level of the comparison were used as calibration standards. One point calibration method (in accordance with ISO 12963: 2017 [4]) was used. Prior to the measurement of the comparison, multi-point calibration of the instrument and the dynamic method was performed.

3. Instrumentation

Instrument:

The instrument is a thermal desorption gas chromatography (TD-GC, Interscience, Trace GC, Thermo) equipped with two Flame Ionization Detectors (FID), UNITY 2 Air Server autosampler (Markes). A Dean's switch sends the gas sample to two columns and two FID detectors.

Capillary column 1: Stabilwax (Restek, 30m x 0.32 mm x 1.0µm) which was not used for the components concerned.

Capillary column 2: PoraBOND U (Agilent, 25m x 0.32 mm x 7µm)

Cold trap: multi-bed sorbent trap for air toxics cooled at - 20 °C and heated at 300 °C. Sampling flow 20 mL/min, Sampling time 8 min, Sampled volume 160 mL.

Sampling is ensured by a pump and MFC.

Sample handling:

The mixture together with other identical oxy-VOCs mixtures (control mixtures) were connected to an autosampler (VSL Spin) which was equipped with a multi-positions valve (VICI), Stainless Steel (SS) silconert 2000 coated lines of 1/16"diameter and with a shared pressure reducer (SS silconert 2000 coated). The autosampler was connected with a SS silconert 2000 coated,1/16"diameter line to one channel of the GC autosampler (UNITY 2 from Markes). The pressure reducer was flushed 8 consecutive times before connection and then set to 1 bar (a).

For each measurement, the mixture(s) were analyzed 20 times and the last 5 runs (run 16-20) were used for the calculation.

4. Calibration method and value assignment

Calibration method:
Dynamic prepared gas mixtures (in accordance with ISO 6145-8:2005 Diffusion method [3]) were used for the calibration. One-point calibration method (in accordance with ISO 12963: 2017 [4]) was applied. The comparison mixture and the dynamic gas standards were analysed in the same period (within 1 week) and mostly within the same sequence. At least one dynamic gas mixture containing comparable amount fractions as the nominal fractions of the comparison mixture was generated.

Value assignment:

For the value assignment, calculated values against dynamic method were used.

A Response Factor (*f*) for each component was calculated from the average peak area of the last five repeated measurements of the dynamically generated gas mixture ($\overline{A}_d$) and from the component amount fraction of that dynamic mixture (x_d) using:

$$f = \frac{\bar{A}_d}{x_d} \qquad \text{Equation 1}$$

For each component the average $f(\overline{f}_d)$ of the dynamically generated gas mixtures and the average peak area of the last five repeated measurements of the comparison mixture ($\overline{A}_s$) were used to calculate the amount fraction (x_s) in the comparison gas mixture:

$$x_s = \frac{\bar{A}_s}{\overline{f}_d} \qquad \text{Equation 2}$$

Where x_s is the calculated value.

In total, there were 3 measurements performed on the comparison gas mixture, the average calculated amount fraction ($\overline{x}_s$) for each component is taken as the assigned value.

5. Uncertainty evaluation

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they either have to be taken into account or they can be neglected.

Generally speaking, the measurement model of ISO 6142-1 is used at VSL for the gravimetrically prepared gas mixtures (such as for the control mixture) and the ISO 6143:2001 [5] is used for determination of composition of gas mixtures.. Uncertainties from weighing, molar masses and the purity of the materials used is propagated using the law of propagation of uncertainty of the Guide to the expression of Uncertainty in Measurement (GUM) [6]. VSL uses an in-house made software to

calculate the uncertainty of preparation based on the work of Alink and van der Veen [7]. Knowledge gained during the bilateral comparison with NPL [8] are also very useful for this work.

For the evaluation of the uncertainty of the comparison mixture, the expanded uncertainties of the assigned values were calculated using the following Equations.

$$u_i^2 = \left(\frac{x_{std}}{n}\right)^2 + u(R)^2 + u(prep)^2$$ Equation 3

Where,

u_i	is the uncertainty of each measurement
x_{std}	is the standard deviation of the GC responses (those taken into account for calculation)
n	is the number of sample injections (those taken into account during calculation)
$u(R)$	is the reproducibility of the dynamic method
$u(prep)$	is the uncertainty of the preparation of dynamic mixtures

$$u_{combined}^2 = \frac{u_1^2+u_2^2+\cdots+u_m^2}{m} + x_{MAD}^2$$ Equation 4

Where,

$u_{combined}$	is the combined uncertainty of the assigned value
$u_{1\ldots m}$	is the standard uncertainty of each measurement (u_i) calculated using Equation 3
m	is the number of measurements
MAD	is the median of absolute differences (see Equation 5-6)

The absolute differences (d_i) are calculated according to Equation 5:

$$d_i = |x_i - x_{med}|$$ Equation 5

Where,

x_i	is the calculated amount fraction value of each measurement
x_{med}	is the median of the calculated amount fraction values from all measurements

And x_{MAD}, the uncertainty contribution due to the spread of measurement results is calculated according to Equation 6, where the number 1.4826 is the scale factor for normally distributed data:

$$x_{MAD} = 1.4826 \times median\ (d_i)$$ Equation 6

Eventually, the expanded uncertainty (U) is calculated as:

$$U = k \times u_{combined}$$ Equation 7

Where,

k	is the coverage factor

The main uncertainty sources of these assigned values of the comparison mixture are uncertainties from the measurements of the mixture (analytical variance) and uncertainties from the calibration (dynamic method).

6. References

[1] ISO 19229:2019 Gas analysis — Purity analysis and the treatment of purity data.

[2] ISO 6142-1:2015 Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures.

[3] ISO 6145-8:2005 Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 8: Diffusion method.

[4] ISO 12963:2017 Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration.

[5] ISO 6143:2001 Gas Analysis – Comparison Methods for Determining and Checking the Composition of Calibration Gas Mixtures.

[6] JCGM 100:2008 GUM 1995 with minor corrections – Evaluation of measurement data - Guide to the Expression of Uncertainty in Measurement (GUM).

[7] Alink A. and Van der Veen A.M.H., "Uncertainty calculations for the preparation of primary gas mixtures. Part 1: Gravimetry", Metrologia **37**, 641-650 (2000).

[8] Worton, D. R., Moreno, S., Brewer, P.J., Li, J., Baldan, A. and Van Der Veen, A. M. H. 'Bilateral comparison of primary reference materials (PRMs) containing methanol, ethanol, and acetone in nitrogen', Accreditation and Quality Assurance **27**, 265-274 (2022).

7. Authorship

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Acronyms

BTEX benzene, toluene, ethylbenzene, xylenes. 11

CCQM Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology. 1

CCQM-GAWG CCQM Gas Analysis Working Group. 1

CIPM International Committee for Weights and Measures. 1

CIPM MRA CIPM Mutual Recognition Arrangement. 1

CMC Calibration and Measurement Capability. 1, 16, 17

FID flame ionisation detector. 6

GC gas chromatograph. 6, 11

KCRV key comparison reference value. 6, 10–17

oxy-VOC oxygenated volatile organic compound. 1, 6

PSM primary standard gas mixture. 11

VOC volatile organic compound. 6, 11