

International Comparison CCQM-K10.2018: BTEX in Nitrogen at 5 nmol mol⁻¹

Final Report

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Coordinating laboratory

National Institute of Standards and Technology (NIST)

Subject

Comparison of BTEX in nitrogen (Track C)

Organizing body

CCQM-GAWG

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1 Overview

The key comparison CCQM-K10.2018 was designed to assess laboratory capabilities for the preparation and value assignment of primary reference mixtures (PRMs) containing BTEX (benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene and *o*-xylene) in nitrogen at a nominal amount fraction of 5 nmol mol⁻¹. It was a follow-up to the previous key comparisons CCQM-K7 [1] and CCQM-K10 [2].

Two parallel studies comprised this key comparison. The first study, deemed henceforth as the “gravimetric study”, was a Model 2 comparison [3] aimed at comparing gravimetric capabilities for the preparation of BTEX PRMs. Seven participating laboratories submitted gravimetrically prepared BTEX mixtures, which were analyzed by NIST referencing a control standard. The gravimetric values of the control standard, as determined by NIST, were used as the key comparison reference values (KCRVs) for the gravimetric study.

The second study, deemed the “comparative study”, was a Model 1 comparison [3] designed to evaluate analytical capabilities for the value assignment of a BTEX PRM. For this study, NIST prepared one BTEX mixture, which was measured consecutively by three participating laboratories. The KCRVs for the comparative

study were determined as a consensus value based on the participants' measurement results including any excess variance.

To provide a link to the gravimetric study, the comparative mixture was also analyzed by NIST using the control standard from the gravimetric study, and these values were incorporated into the KCRV consensus values.

This key comparison was considered to present an analytical challenge, and was therefore designated as a Specialized Comparison (Track C).

2 Design and organization of the key comparison

2.1 Quantities and units

The measurands for CCQM-K10.2018 were the amount-of-substance fractions (hereafter abbreviated as “amount fractions”) of benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene and *o*-xylene (BTEX) in nitrogen, at a nominal quantity value of 5 nmol mol⁻¹.

2.2 Participants

This key comparison included a total of 10 participants, 7 in the gravimetric study and 3 in the comparative study, which are listed in Table 1.

2.3 Schedule

The schedule for the key comparison is shown in Table 2.

3 Gravimetric study

3.1 Participant samples

For the gravimetric study, each participant was required to provide one cylinder containing a gaseous mixture of BTEX in nitrogen at a nominal amount fraction of 5 nmol mol⁻¹. The mixtures were to be prepared and verified by the participants using their usual procedures. The key comparison protocol required the final amount fractions of BTEX to be within ± 0.2 nmol mol⁻¹ of the nominal value, and the cylinder pressure to be at minimum 10 MPa.

Table 1. CCQM-K10.2018 participants.

| Study | Acronym | Country | Institute |
|-------------|---------|---------|--|
| Gravimetric | KRISS | KR | Korea Research Institute of Standards and Science |
| | LNE | FR | Laboratoire National de Métrologie et d'Essais |
| | NIST | US | National Institute of Standards and Technology |
| | NMISA | ZA | National Metrology Institute South Africa |
| | NPL | GB | National Physical Laboratory |
| | VNIIM | RU | D.I. Mendeleyev Institute for Metrology |
| | VSL | NL | Van Swinden Laboratorium |
| Comparative | METAS | CH | Federal Institute of Metrology |
| | UBA | DE | Federal Environment Agency Germany Umweltbundesamt |
| | CHMI | CZ | Czech Hydrometeorological Institute |

Figure 1 shows the reported amount fractions of BTEX in the mixtures prepared by the participants. All participants submitted mixtures within the required interval (as indicated by the dashed lines), with the exception of NIST's reported values for benzene, toluene and *p*-xylene. An overview of the different cylinders used by the participants to prepare their mixtures is included in Table 3.

The methods by which the participants prepared their samples, including preparation procedures, purity analyses, and uncertainty budgets, are detailed in the participant reports (see Appendix B), and summarized in Table 4.

The participants were asked to verify the stability of their mixtures before shipping the cylinders to NIST, and to perform follow-up stability testing after their return. There were no reported issues regarding mixture instability, i.e., none of the participants reported any changes in the compositions of their mixtures, outside of what was already accounted for in their uncertainty budgets. Therefore, no corrections or adjustments were made to the participants' reported gravimetric values for this comparison.

Table 2. CCQM-K10.2018 schedule.

| Date | Gravimetric study | Comparative study |
|--------------|--|--|
| Nov–Jun 2018 | NMI preparation of gravimetric standards | NIST preparation of measurement sample |
| Apr–Sep 2018 | NMI shipment of standards to NIST | NIST shipment of sample to METAS |
| Jul–Oct 2018 | NIST measurement of NMI standards | METAS analysis; shipment to UBA |
| Nov–Feb 2019 | NIST analysis of key comparison data | UBA analysis; shipment to CHMI |
| Dec–Apr 2019 | NIST return of samples to NMIs | CHMI analysis; shipment to NIST |
| Apr 2019 | NMI reanalysis for stability | NIST reanalysis for stability |
| Oct 2019 | Distribution of Draft A Report to participants | |
| May 2021 | Distribution of Draft B Report | |
| Jan 2022 | Final approval by GAWG | |

3.2 Control mixture

All participant samples were analyzed against a single analytical control, APE1228481. The control was used to monitor and correct for instrument drift, ensuring consistent sample measurements throughout the study.

The control mixture was prepared gravimetrically by NIST in a 20 L aluminum gas cylinder treated with Experis¹ by Air Products, Belgium. The amount fractions and their associated expanded uncertainties are listed in Table 5.

The control mixture was prepared by gravimetric dilution of a parent mixture, CC460929, containing nominal 250 nmol mol^{−1} BTEX in nitrogen (Table 6). The parent mixture was prepared in a 30 L aluminum gas cylinder treated with Megalife¹ by Airgas, LLC, USA. The pure BTEX components were transferred into the cylinder by means of individual, pre-weighed glass capillary tubes. The prepared parent mixture was analyzed against previously prepared NIST standards to verify its gravimetric values (not shown).

¹Certain commercial equipment, instruments, or materials are identified in this report in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

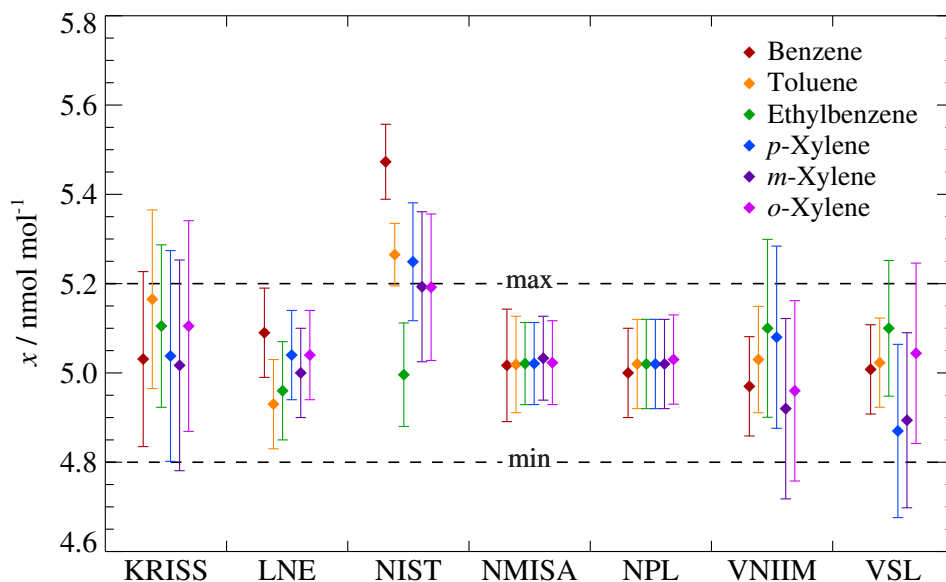


Figure 1. Gravimetrically determined amount fractions (x) of the BTEX components in the participants' samples. Error bars represent the associated expanded ($k = 2$) uncertainties.

Table 3. Cylinders used to prepare participant samples.

| Participant | Sample number | Volume / L | Pressure / MPa ^a | Treatment type | Preparation date |
|-------------|---------------|------------|-----------------------------|----------------|------------------|
| KRISS | D517490 | 10 | 7.6 | Experis | Nov 20 2017 |
| LNE | 1029123 | 10 | 12.0 | Experis | Jan 26 2018 |
| NIST | CC412027 | 30 | 10.5 | Megalife | May 30 2018 |
| NMISA | D626613 | 10 | 11.7 | Fluorination | Apr 18 2018 |
| NPL | D618315 | 10 | 11.4 | Experis | Apr 09 2018 |
| VNIIM | 5603810 | 5 | 11.0 | Aculife III+IV | Jun 28 2018 |
| VSL | VSL136606 | 5 | 12.4 | Experis | Apr 04 2018 |

^a Measured upon arrival to NIST.

Table 4. Sample preparation and measurement procedures reported by participants.

| Participant | Transfer method | Dilution steps / nmol mol ⁻¹ | Analytical technique | Verification method |
|-------------|-----------------------------------|---|---|-------------------------------|
| KRISS | Binary micro-syringes | 10000 → 100 → 5 | GC-FID ^a with preconcentration | Gravimetric standards |
| LNE | Binary syringes | 44000 → 2000 → 100 → 5 | GC-FID with preconcentration | Dynamic dilution ^b |
| NIST | Binary capillary tubes | 250 → 5 | GC-FID with preconcentration | Gravimetric standards |
| NMISA | Liquid mixture; syringe injection | 10000 → 2000 → 100 → 5 | GC-FID with preconcentration | Gravimetric standards |
| NPL | Binary 3-way transfer vessels | 100000 ^c → 10000 → 200 → 5 | GC-FID with preconcentration | Gravimetric standards |
| VNIIM | Not reported | 20000 → 300 → 5 | GC-MS ^d | Gravimetric standards |
| VSL | Liquid mixture; transfer line | 25000 → 2500 → 500 → 50 → 5 | GC-FID with preconcentration | Gravimetric standards |

^a Gas chromatography–flame ionization detection.

^b Dilution of a gravimetric standard at 2 μmol mol⁻¹.

^c Individual binary mixtures prepared at this level.

^d Gas chromatography–mass spectrometry.

Table 5. Amount fractions, y , of BTEX in the control mixture (APE1228481), and associated uncertainties for 95 % coverage, $U_{95\%}(y)$, which represent a blanket relative uncertainty of 4 %.

| | / nmol mol ⁻¹ | |
|------------------|--------------------------|---------------|
| | y | $U_{95\%}(y)$ |
| Benzene | 5.101 | 0.204 |
| Toluene | 4.907 | 0.196 |
| Ethylbenzene | 4.656 | 0.186 |
| <i>p</i> -Xylene | 4.892 | 0.196 |
| <i>m</i> -Xylene | 4.840 | 0.194 |
| <i>o</i> -Xylene | 4.840 | 0.194 |

NIST monitored the stability of the control mixture throughout the duration of the study in two ways: (i) by tracking the raw instrument response (i.e., GC peak areas) for each component, and (ii) by treating benzene as an internal standard, and tracking the ratio of the response of each other component to the response of benzene. The first method allows for all components in the mixture to be measured, but the data can be subject to drift or variations in the instrumentation. With the second method, relative changes in the mixture can be monitored independent of instrument drift, but the accuracy of the data is contingent upon the long-term stability of benzene.

The stability data for the control mixture, as shown in Figures 2 and 3, indicate that some degradation of toluene, ethylbenzene, and *p*-/*m*-/*o*-xylene may have occurred, while the last curve in Figure 3 indicates that the measurement system and benzene remained stable. The reason for the instability is not fully understood, and the relative change is slightly greater than what has been observed in previous stability studies [4]. Therefore, in order to mitigate any potential impact of instability on the results of this key comparison, the relative expanded uncertainties of the gravimetric amount fractions (including benzene) were increased, to a conservative estimate of 4 %, to account for any changes in the cylinder mixture over time.

3.3 Stability of participant samples

Over the course of the study, NIST monitored the stability of the mixtures prepared by the participants in the same manner as described in §3.2. The stability data

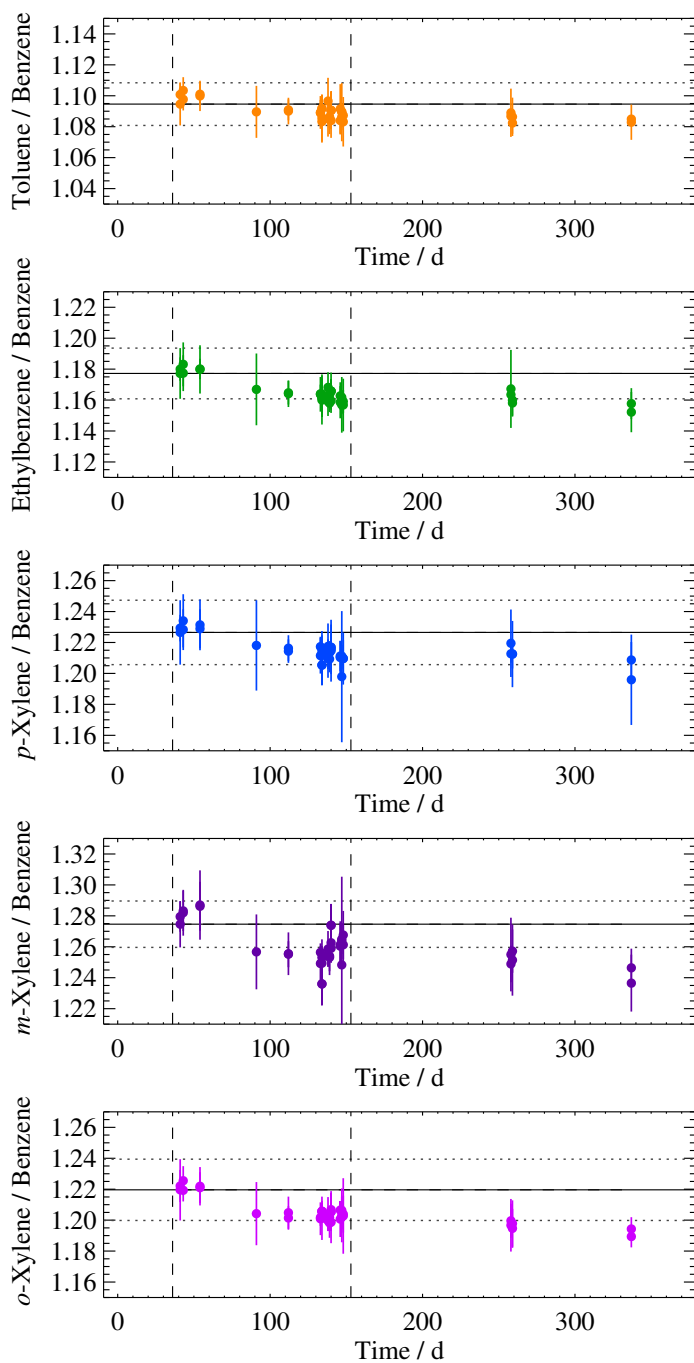


Figure 2. Stability of toluene, ethylbenzene, *p*-xylene, *m*-xylene and *o*-xylene in the control mixture, as measured by the ratio of their peak areas to the peak area of benzene over time. Error bars represent expanded ($k = 2$) uncertainties. The solid and dotted horizontal lines represent the initial response ratios and associated expanded uncertainties, respectively. The dashed vertical lines bracket the time during which the measurements for the gravimetric study took place.

Table 6. Gravimetric amount fractions, y , of BTEX in the parent mixture used to prepare the control (CC460929), and associated expanded uncertainties for 95 % confidence.

| | / nmol mol ⁻¹ | |
|------------------|--------------------------|---------------|
| | y | $U_{95\%}(y)$ |
| Benzene | 282.99 | 0.39 |
| Toluene | 272.27 | 0.37 |
| Ethylbenzene | 258.31 | 0.32 |
| <i>p</i> -Xylene | 271.41 | 0.34 |
| <i>m</i> -Xylene | 268.52 | 0.35 |
| <i>o</i> -Xylene | 268.51 | 0.34 |

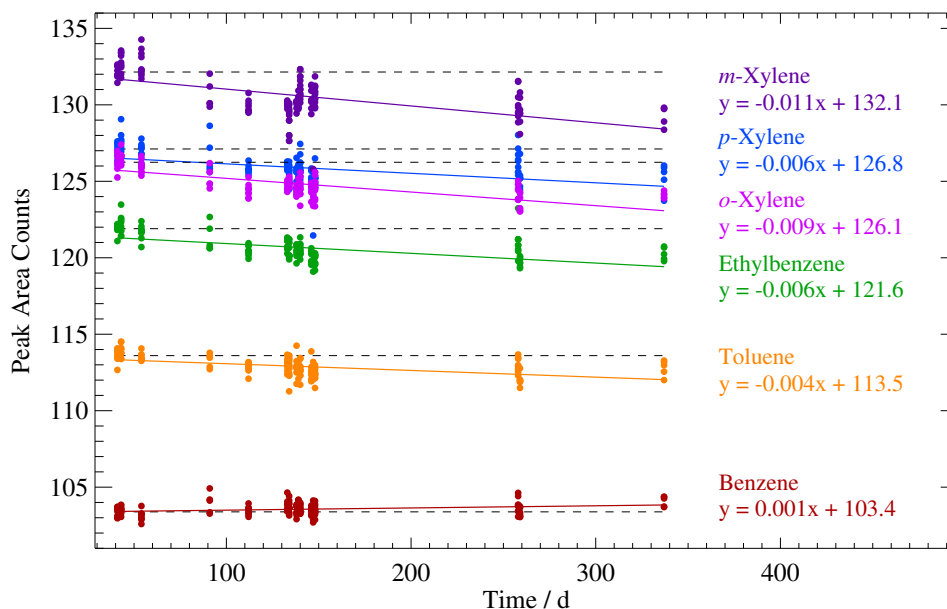


Figure 3. Stability of the BTEX components in the control mixture, as indicated by their measured GC response over time. Each data point represents one peak area measurement taken from a single replicate chromatogram.

were derived from the four measurements that were taken for the gravimetric comparison, between July and October 2018, and are plotted in Figures 4 and 5. Due to a delay in returning the cylinders to VNIIM and NMISA, NIST reanalyzed their samples one more time before shipment, in February 2019. These measurements were taken to ascertain stability of the mixtures, and were not used to determine any results for the comparison. The data for these analyses are included in Figures 4 and 5 for informational purposes only. Also included are any additional measurements of NIST's sample, which were taken as part of the long-term stability check requested from each participant.

The stability data show that most of the participants' mixtures remained stable during the comparison measurements. The exception to this were the mixtures prepared by LNE and VNIIM, which showed significant drift in instrument response over the same period. The measurement sequences were designed such that the participants' samples were measured in pairs, as described in §3.4.2. Therefore, if the observed drift were related to any instability of the measurement system, it would have also been apparent in the concurrent measurements of the other participant samples. However, no such correlations were observed. Throughout the comparison measurements, LNE was paired in the same sequence(s) with NIST, VSL and NMISA; VNIIM was paired with KRISS and NMISA.

Interestingly, after sitting idle at NIST for several months, the last measured peak areas of VNIIM's mixture returned to what they were when the sample was first analyzed. One speculation is that this behavior may have been caused by a gradual accumulation of BTEX in the cylinder valve, resulting in a highly concentrated initial sample that decreased over time with repeated use. But because VNIIM's cylinder was returned shortly after the final stability measurements were taken, no further testing was performed.

As mentioned in §3.1, the participants also performed their own stability testing on their mixtures. Since none of the participants reported any observed instability, no corrections to their gravimetric values were made.

3.4 Comparison measurements

3.4.1 Instrumentation

All measurements were performed using a gas chromatograph with flame ionization detection (GC-FID) coupled to a cryogenic preconcentrator. The BTEX components were separated using a 60 m × 0.32 mm capillary column with 0.25 μm of AT-WAX with the following temperature program: 35 °C (hold 5 min); increase

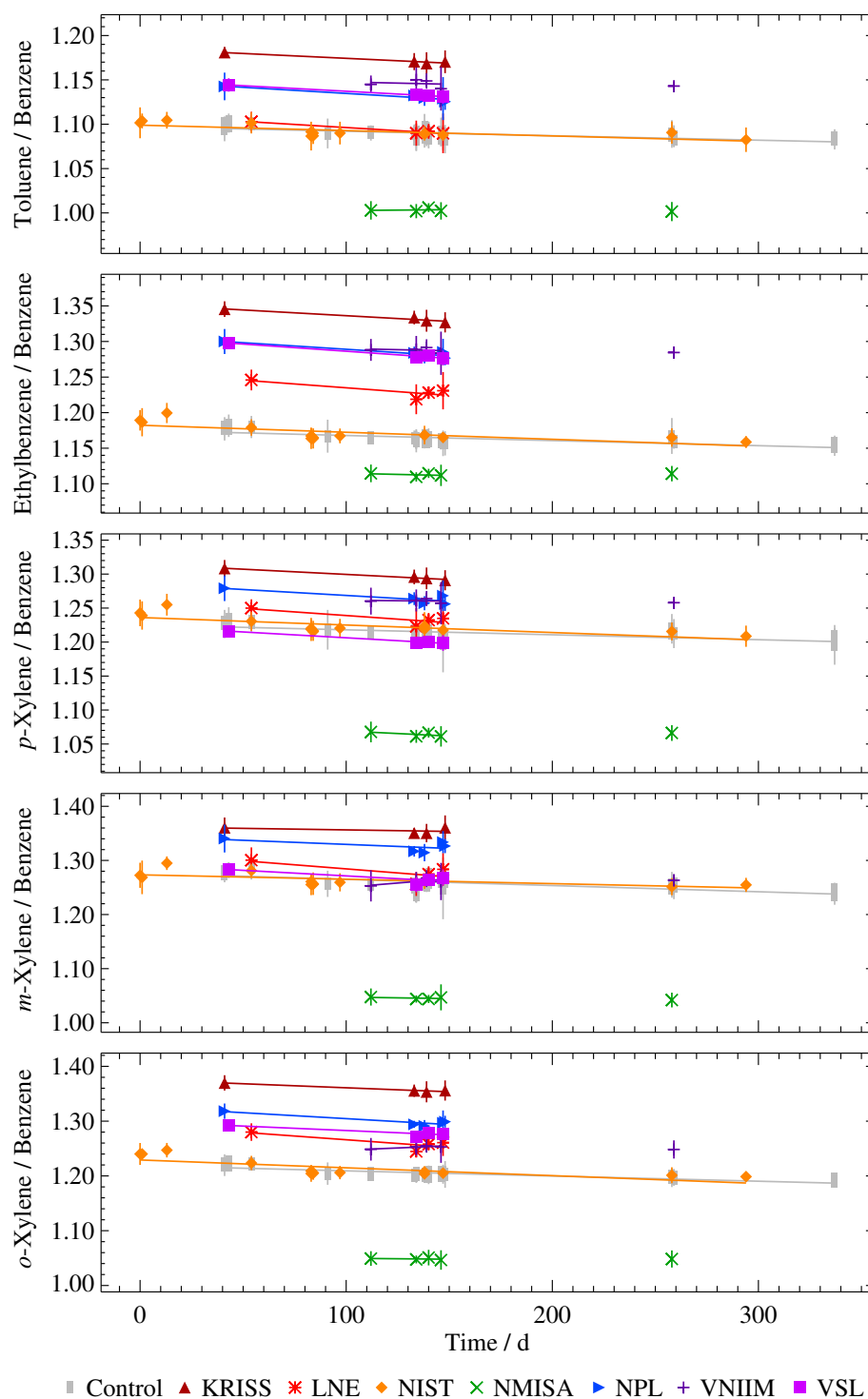


Figure 4. Stability of the participant samples and control mixture, as measured by the peak area ratios of toluene, ethylbenzene, *p*-xylene, *m*-xylene, and *o*-xylene to benzene. Error bars represent expanded ($k = 2$) uncertainties.

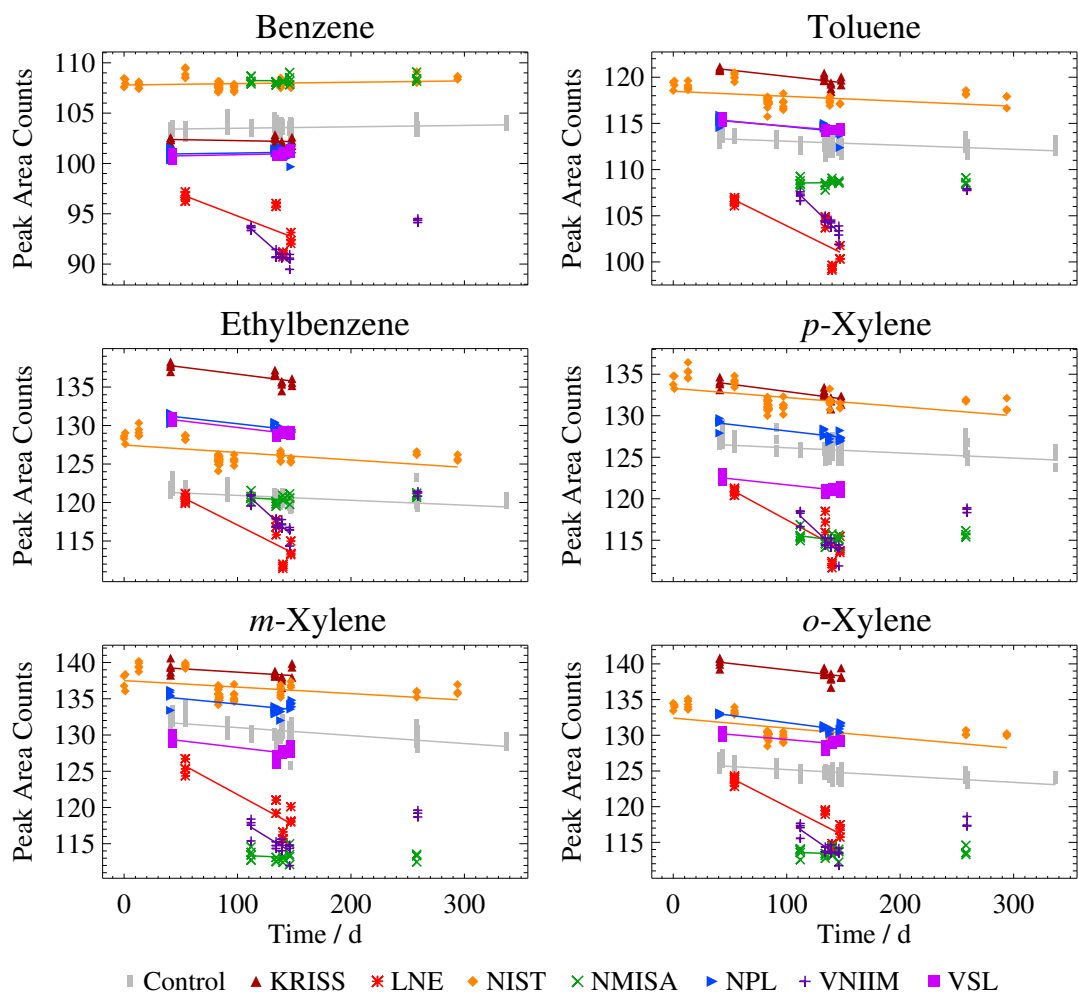


Figure 5. Stability of BTEX in each participant sample and the control mixture, as indicated by their measured GC response over time. Each point represents one peak area measurement taken from a single replicate chromatogram.

2 °C min⁻¹ to 60 °C (hold 3 min); increase 10 °C min⁻¹ to 115 °C. The FID was set to 250 °C, with a fuel flow rate of 30 mL min⁻¹ hydrogen and 400 mL min⁻¹ air. The preconcentrator was used to cryogenically trap 200 mL of sample at -100 °C, and then release the sample at 150 °C. A representative chromatogram using this method is shown for the control mixture in Figure 6.

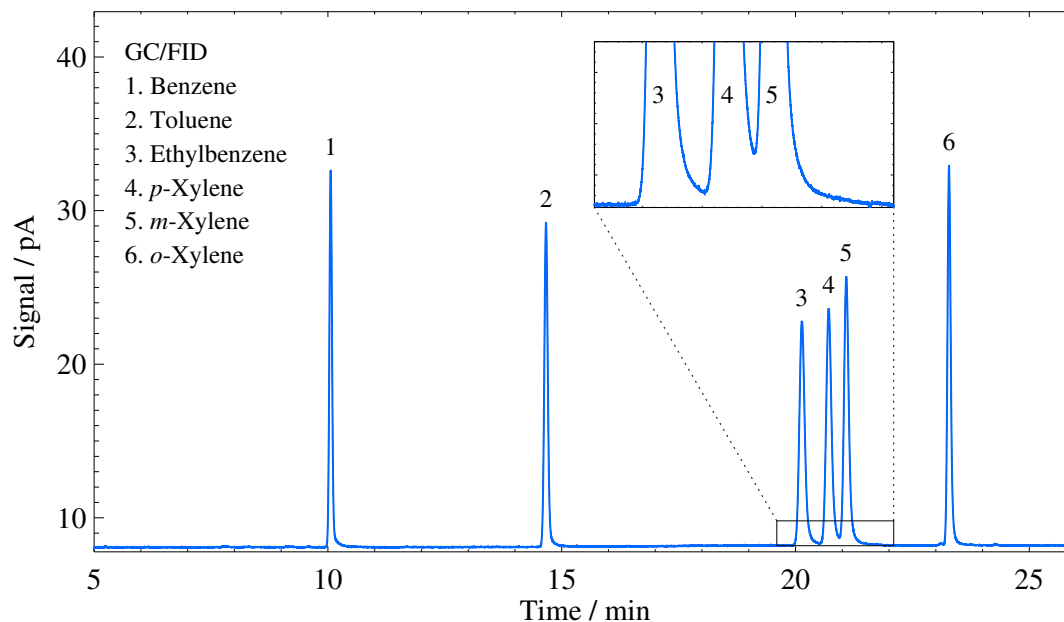


Figure 6. Sample chromatogram of the control mixture, APE1228481, nominal 5 nmol mol⁻¹ BTEX in nitrogen.

Linearity of the measurement system was verified by cryogenically trapping one NIST standard (CC412027) at incremented sample volumes from 170 mL to 220 mL, simulating a nominal amount fraction range of 4.5 nmol mol⁻¹ to 5.5 nmol mol⁻¹. The 200 mL trapping volume served as the analytical control, and response ratios of each sample volume to the control were plotted along with their calculated amount fractions (Figure 7). The resulting regression equations were determined using a generalized least-squares regression compliant with ISO 6143 [5, 6]. The results of the linearity tests demonstrated that the instrumentation was linear for all BTEX components, over the entire range of measurements comprising this key comparison.

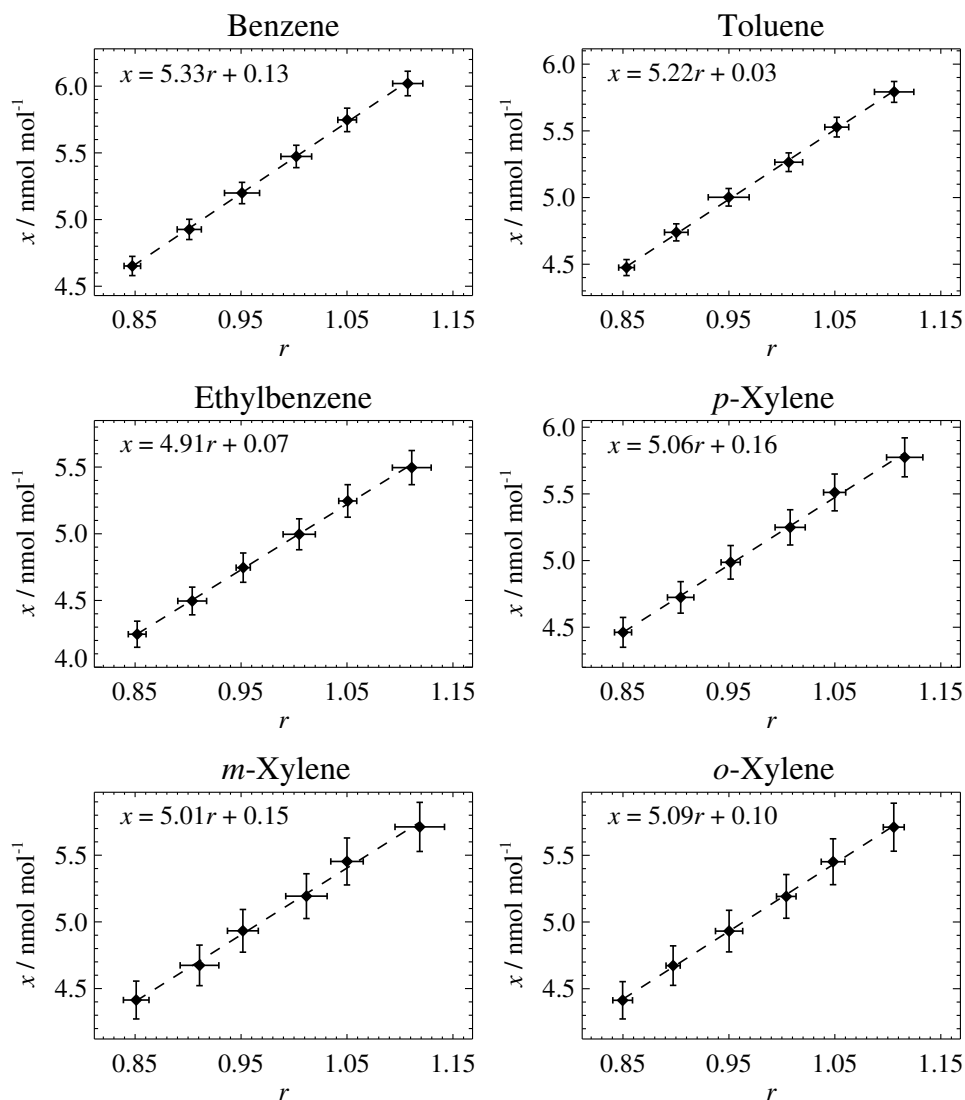


Figure 7. Linearity testing of the NIST measurement system, using one NIST standard, CC412027. The y-axis represents the simulated amount fractions, x , calculated using the gravimetric value of the standard adjusted for the trapping volume of the sample (relative to 200 mL). The x-axis represents the corresponding instrument response ratio to the control, r . Error bars represent expanded ($k = 2$) uncertainties.

3.4.2 *Measurement procedure*

The measurements for this study were taken in July through October 2018, according to the following procedure:

- (a) All participant measurements were ratios of instrumental indications to the analytical control, corrected for instrument drift over time.
- (b) The participant samples were measured four separate times, producing a total of four independent ratio measurements per sample.
- (c) Each ratio itself consisted of no less than three replicate GC injections of the participant sample and the control (measured both before and after the sample measurements).
- (d) Nearly all measurements of the participant samples were taken in pairs, bracketed by the same control measurements (e.g., Control, Participant 1, Participant 2, Control), to help identify or rule out measurement error as a cause for outlying observations.
- (e) The majority of the measurements were taken within the short time span of a few days to satisfy repeatability conditions. The sole exception to this was the first analysis, which spanned several months owing to the delayed arrival of two participant cylinders. However, the ratios for those participants whose cylinders were analyzed early showed no significant deviation from their ratios measured months later, indicating minimal impact on the conditions of repeatability.

3.5 **Results**

3.5.1 *Rationale*

The approach originally conceived for this comparison was to build a set of analysis functions using the participants' mixtures as calibrants. The analysis functions were based on the measured ratios (as described above) and reported amount fractions of the participants' mixtures. The performance criteria was the set of differences between the participants' reported amount fractions, and the corresponding amount fractions predicted from the analysis function.

This approach was hampered principally by two facts: (i) the compositions of the mixtures prepared by the participants were much closer to one another than they should have been to support reliable analysis functions; and (ii) for each of all six

measurands, there were groups of observations that deviated markedly from the trend defined by the other observations.

Therefore, due to the limitations of the original approach, the GAWG agreed to adopt an alternative approach for evaluating participant performance. This approach, which is described below, utilizes the ratios and reported values of each of the participants' mixtures to directly predict the amount fractions of BTEX in the control mixture. The corresponding KCRVs are the "true" amount fractions of BTEX in the control mixture, as determined gravimetrically by NIST (see Table 5).

3.5.2 *Ratio-based predictions for control mixture*

As explained above in §3.4.2, the results of the participant measurements comprise four ratios of instrumental indications: the numerator of each ratio is the instrumental indication observed for a participant's mixture, and the denominator is the instrumental indication for the control mixture, observed approximately contemporaneously with the indication in the numerator.

The average ratio for each component, and for each participant, summarizes the four replicated ratios, each with its own associated standard uncertainty. The DerSimonian-Laird procedure [7] was used to combine these four results, as implemented in R function `rma` of package `metafor` [8], and produce the average ratio and its associated uncertainty.

Consider the average ratio $r_p(C)$, pertaining to component C in the mixture prepared by participant P , and let $x_p(C)$ denote the corresponding amount fraction measured gravimetrically by this participant. In these circumstances,

$$\hat{y}_p(C) = \frac{x_p(C)}{r_p(C)} \quad (1)$$

is an estimate of the amount fraction of component C in the control mixture, derived from the average ratio obtained for the participant's mixture and from the participant's reported composition of this mixture.

Each of these derived estimates can then be compared to the true amount fraction of component C in the control mixture $y(C)$, as determined gravimetrically by NIST, to measure participant performance (see Table 7).

For example, one of the ratios for benzene, for the mixture prepared by KRISS, was 0.9854, and the amount fraction of benzene in that mixture, as reported by KRISS, was $5.031 \text{ nmol mol}^{-1}$. Therefore, the corresponding estimate of the amount fraction of benzene in the control mixture is

$$\hat{y}_{\text{KRISS}}(\text{benzene}) = \frac{5.031 \text{ nmol mol}^{-1}}{0.9854} = 5.106 \text{ nmol mol}^{-1}. \quad (2)$$

Table 7. Amount fractions (y) and associated standard uncertainties ($u(y)$) in the control mixture, and corresponding predictions (\hat{y}) and associated standard uncertainties ($u(\hat{y})$), based on the ratios and reported compositions of the participants' mixtures. The $u(\hat{y})$ are often smaller than the corresponding $u(y)$, in part because $u(y)$ contains a large contribution to account for mixture stability.

| / nmol mol ⁻¹ | | | | | / nmol mol ⁻¹ | | | | |
|--------------------------|------|--------|-----------|--------------|--------------------------|------|--------|-----------|--------------|
| | y | $u(y)$ | \hat{y} | $u(\hat{y})$ | | y | $u(y)$ | \hat{y} | $u(\hat{y})$ |
| Benzene | | | | | Toluene | | | | |
| KRISS | 5.10 | 0.10 | 5.11 | 0.10 | KRISS | 4.91 | 0.10 | 4.86 | 0.10 |
| LNE | 5.10 | 0.10 | 5.60 | 0.11 | LNE | 4.91 | 0.10 | 5.41 | 0.10 |
| NIST | 5.10 | 0.10 | 5.24 | 0.04 | NIST | 4.91 | 0.10 | 5.03 | 0.04 |
| NMISA | 5.10 | 0.10 | 4.80 | 0.06 | NMISA | 4.91 | 0.10 | 5.21 | 0.06 |
| NPL | 5.10 | 0.10 | 5.12 | 0.05 | NPL | 4.91 | 0.10 | 4.95 | 0.05 |
| VNIIM | 5.10 | 0.10 | 5.63 | 0.08 | VNIIM | 4.91 | 0.10 | 5.41 | 0.08 |
| VSL | 5.10 | 0.10 | 5.14 | 0.05 | VSL | 4.91 | 0.10 | 4.96 | 0.05 |
| Ethylbenzene | | | | | <i>p</i> -Xylene | | | | |
| KRISS | 4.66 | 0.09 | 4.52 | 0.08 | KRISS | 4.89 | 0.10 | 4.79 | 0.11 |
| LNE | 4.66 | 0.09 | 5.17 | 0.11 | LNE | 4.89 | 0.10 | 5.45 | 0.11 |
| NIST | 4.66 | 0.09 | 4.76 | 0.06 | NIST | 4.89 | 0.10 | 5.00 | 0.06 |
| NMISA | 4.66 | 0.09 | 5.02 | 0.05 | NMISA | 4.89 | 0.10 | 5.48 | 0.05 |
| NPL | 4.66 | 0.09 | 4.66 | 0.05 | NPL | 4.89 | 0.10 | 4.94 | 0.05 |
| VNIIM | 4.66 | 0.09 | 5.21 | 0.11 | VNIIM | 4.89 | 0.10 | 5.53 | 0.12 |
| VSL | 4.66 | 0.09 | 4.75 | 0.07 | VSL | 4.89 | 0.10 | 5.06 | 0.10 |
| <i>m</i> -Xylene | | | | | <i>o</i> -Xylene | | | | |
| KRISS | 4.84 | 0.10 | 4.72 | 0.11 | KRISS | 4.84 | 0.10 | 4.59 | 0.11 |
| LNE | 4.84 | 0.10 | 5.43 | 0.12 | LNE | 4.84 | 0.10 | 5.31 | 0.08 |
| NIST | 4.84 | 0.10 | 4.95 | 0.08 | NIST | 4.84 | 0.10 | 4.95 | 0.08 |
| NMISA | 4.84 | 0.10 | 5.79 | 0.06 | NMISA | 4.84 | 0.10 | 5.53 | 0.05 |
| NPL | 4.84 | 0.10 | 4.90 | 0.05 | NPL | 4.84 | 0.10 | 4.78 | 0.05 |
| VNIIM | 4.84 | 0.10 | 5.54 | 0.12 | VNIIM | 4.84 | 0.10 | 5.40 | 0.11 |
| VSL | 4.84 | 0.10 | 5.02 | 0.10 | VSL | 4.84 | 0.10 | 4.88 | 0.10 |

KRISS's performance for benzene will be gauged based on the difference $(5.106 \text{ nmol mol}^{-1}) - (5.101 \text{ nmol mol}^{-1})$, where $5.101 \text{ nmol mol}^{-1}$ is the gravimetric amount fraction of benzene in the control mixture.

3.5.3 KCRVs and degrees of equivalence

The unilateral degree of equivalence for each participant P is determined as

$$D_p(C) = \hat{y}_p(C) - y(C) \quad (3)$$

where $\hat{y}_p(C)$ is the participants' predicted amount fraction of component C in the control mixture, and $y(C)$ is the KCRV, represented by the true, gravimetric amount fraction of component C in the control mixture.

Considering that the uncertainty associated with each ratio $r_p(C)$ is based on a small number of degrees of freedom (the median number of degrees of freedom for the average ratios is around 6), the expanded uncertainty for 95 % coverage associated with each difference $D_p(C)$ was computed by application of the Monte Carlo method of the GUM Supplement 1 [9], based on a sample of size 10^6 .

Figure 8 depicts the unilateral degrees of equivalence, $D_p(C) \pm U_{95\%}(D_p(C))$, and Table 8 lists their values. The final calculated uncertainties are largely dominated by $u(y(C))$, which is due in part to the observed instability of the control mixture.

As shown in Figure 8, the results for KRISS, NIST, NPL, and VSL are consistently in agreement with the KCRV, while the results for LNE, NMISA, and VNIIM are biased high, with the exception of NMISA's result for benzene. The observed pattern between the results for KRISS, LNE, NIST, NPL, VNIIM and VSL is the same for all components, indicating that these participants produced mixtures which were self-consistent.

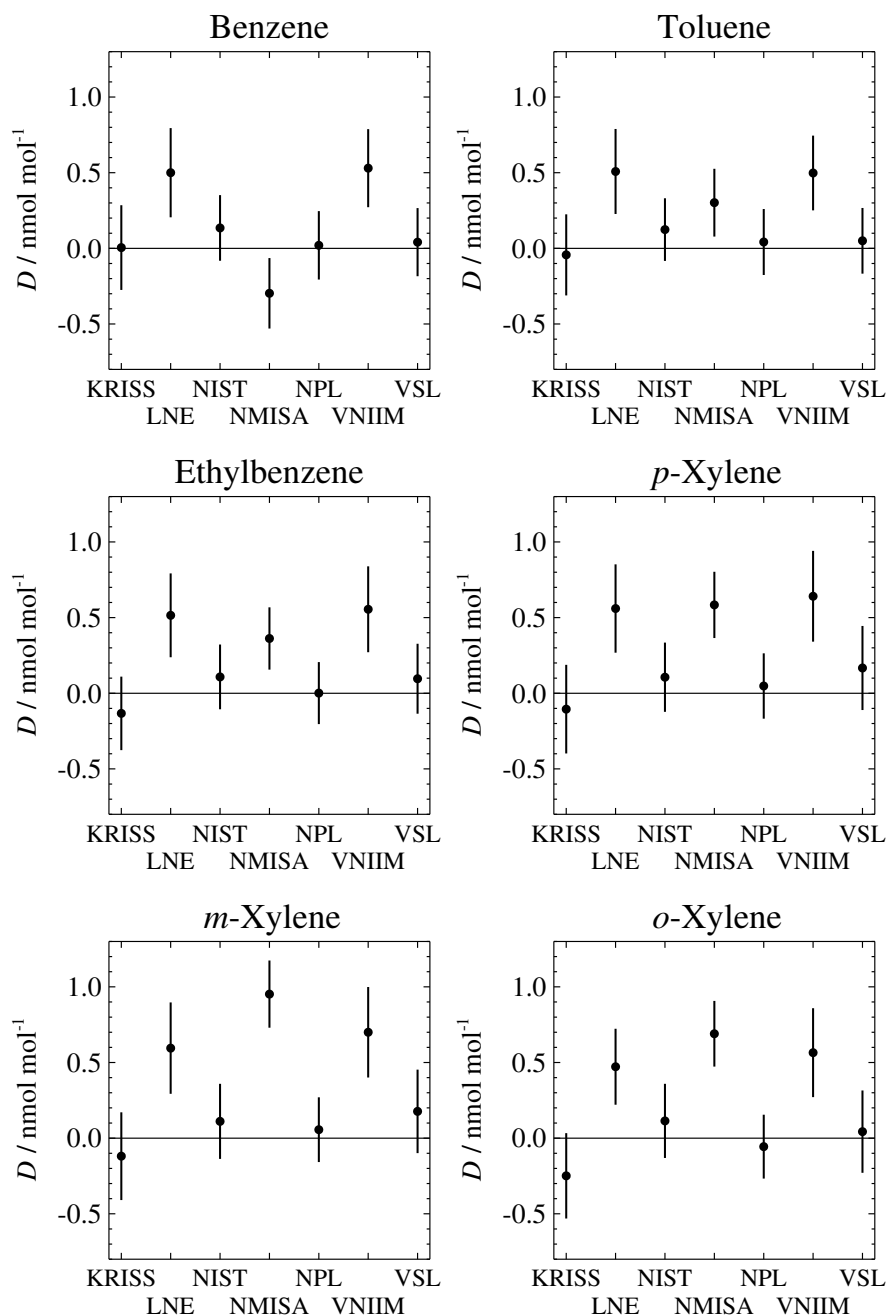


Figure 8. Degrees of equivalence between the participants' predicted amount fractions in the control mixture, based on the ratios and reported compositions of their mixtures, and the corresponding KCRVs, based on the gravimetric amount fractions determined by NIST.

Table 8. Degrees of equivalence between predicted amount fractions in the control mixture, based on ratios and reported compositions of participants' mixtures, and amount fractions in the control mixture as determined gravimetrically by NIST.

| / nmol mol ⁻¹ | | | / nmol mol ⁻¹ | | |
|--------------------------|----------|--------------------------------------|--------------------------|----------|--------------------------------------|
| | <i>D</i> | <i>U</i> _{95%} (<i>D</i>) | | <i>D</i> | <i>U</i> _{95%} (<i>D</i>) |
| Benzene | | | Toluene | | |
| KRISS | 0.005 | 0.280 | KRISS | −0.043 | 0.268 |
| LNE | 0.500 | 0.295 | LNE | 0.508 | 0.281 |
| NIST | 0.135 | 0.217 | NIST | 0.124 | 0.207 |
| NMISA | −0.297 | 0.233 | NMISA | 0.302 | 0.224 |
| NPL | 0.020 | 0.226 | NPL | 0.042 | 0.218 |
| VNIIM | 0.530 | 0.258 | VNIIM | 0.498 | 0.247 |
| VSL | 0.041 | 0.225 | VSL | 0.050 | 0.217 |
| Ethylbenzene | | | <i>p</i> -Xylene | | |
| KRISS | −0.133 | 0.243 | KRISS | −0.105 | 0.293 |
| LNE | 0.515 | 0.277 | LNE | 0.560 | 0.292 |
| NIST | 0.108 | 0.214 | NIST | 0.106 | 0.229 |
| NMISA | 0.362 | 0.206 | NMISA | 0.584 | 0.219 |
| NPL | 0.001 | 0.205 | NPL | 0.048 | 0.216 |
| VNIIM | 0.555 | 0.284 | VNIIM | 0.641 | 0.300 |
| VSL | 0.096 | 0.231 | VSL | 0.167 | 0.278 |
| <i>m</i> -Xylene | | | <i>o</i> -Xylene | | |
| KRISS | −0.119 | 0.290 | KRISS | −0.249 | 0.282 |
| LNE | 0.595 | 0.302 | LNE | 0.472 | 0.251 |
| NIST | 0.111 | 0.248 | NIST | 0.114 | 0.245 |
| NMISA | 0.952 | 0.222 | NMISA | 0.690 | 0.217 |
| NPL | 0.056 | 0.214 | NPL | −0.056 | 0.211 |
| VNIIM | 0.700 | 0.299 | VNIIM | 0.565 | 0.294 |
| VSL | 0.177 | 0.276 | VSL | 0.043 | 0.272 |

4 Comparative study

4.1 Comparative mixture

For the comparative study, NIST prepared one mixture of BTEX in nitrogen at a nominal amount fraction of 5 nmol mol⁻¹. The mixture was prepared in a 20 L aluminum Experis cylinder by gravimetric dilution of a parent mixture, CC460929 (Table 6), following the same procedure described in §3.2. Table 9 lists the amount fractions and associated uncertainties of the BTEX components in the comparative mixture.

Table 9. Amount fractions, y , of BTEX in the comparative mixture (APE1228493), and associated expanded uncertainties for 95 % coverage, $U_{95\%}(y)$.

| | / nmol mol ⁻¹ | |
|------------------|--------------------------|---------------|
| | y | $U_{95\%}(y)$ |
| Benzene | 5.275 | 0.160 |
| Toluene | 5.101 | 0.110 |
| Ethylbenzene | 4.833 | 0.140 |
| <i>p</i> -Xylene | 5.076 | 0.148 |
| <i>m</i> -Xylene | 5.029 | 0.150 |
| <i>o</i> -Xylene | 5.020 | 0.176 |

Since the comparative mixture was prepared by dilution of an aliquot of the parent mixture, a “mother-daughter” test was performed to determine whether any loss of BTEX occurred during transfer of the cylinder mixture. Approximately 0.9 MPa of parent mixture CC460929 (“mother”) was transferred into an evacuated Experis cylinder (“daughter”), and instrument response ratios of the daughter to the mother were determined. The daughter cylinder was then re-evacuated, and the experiment was repeated a second time.

Figure 9 shows the results of the mother-daughter tests, with the first and second sets of ratios indicated by the red diamonds and blue squares, respectively. On average, the response of the daughter mixture was ~1 % higher than the response of the mother, as indicated by the dashed lines.

These results, although highly unexpected, were reproduced in a separate mother-daughter test using the same parent mixture and a different Experis cylinder. That test, which was conducted twice by two different analysts, showed an increase during mixture transfer of up to 3 % (not shown).

The cause of this apparent increase is not yet understood, nor is it known whether its effects will persist or diminish over time; nonetheless, the gravimetric values of the comparative mixture were adjusted to account for the observed bias, and the corresponding uncertainties were increased accordingly.

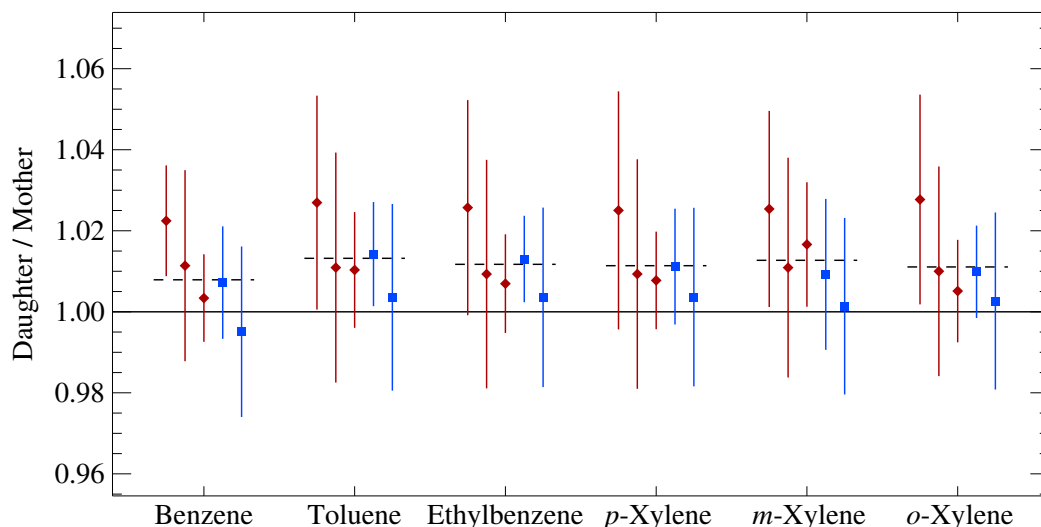


Figure 9. Mother-daughter testing of cylinder APE1228493. Each data point represents a ratio of instrumental indications, of the daughter cylinder to the mother cylinder, with the error bars representing the associated expanded ($k = 2$) uncertainty. The experiment was repeated two separate times, as indicated by the red diamonds and blue squares. The horizontal dashed lines represent the mean response ratio for each component.

NIST monitored the stability of the comparative mixture before and after shipping the cylinder to the participants, in the same manner as described in §3.2. The stability data, as shown in Figures 10 and 11, were incorporated into the overall uncertainty of the NIST determined amount fractions.

4.2 Measurement protocol

The comparative cylinder was circulated to the participants along with a stainless steel, two-stage pressure regulator equipped with a DIN 477 No. 1 fitting. The participants were asked to provide their analyzed amount fractions and associated uncertainties for the BTEX components in the mixture. Each participant was responsible for calibrating their own instrumentation or equipment used for the analysis. A description of the analytical procedure, uncertainty budget and calibration method was also requested.

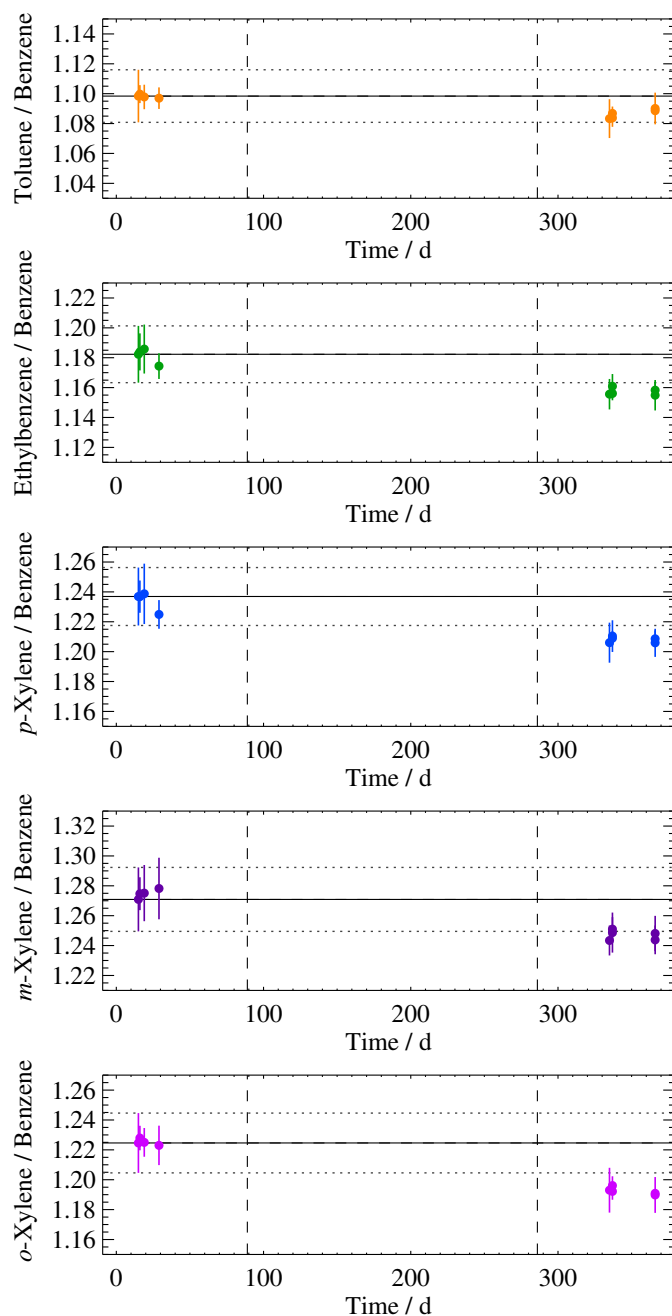


Figure 10. Stability of toluene, ethylbenzene, *p*-xylene, *m*-xylene and *o*-xylene in the comparative mixture, as measured by the ratio of their peak areas to the peak area of benzene over time. Error bars represent expanded ($k = 2$) uncertainties. The solid and dotted horizontal lines represent the initial response ratios and their associated expanded uncertainties, respectively. The dashed vertical lines bracket the time during which the comparative measurements took place.

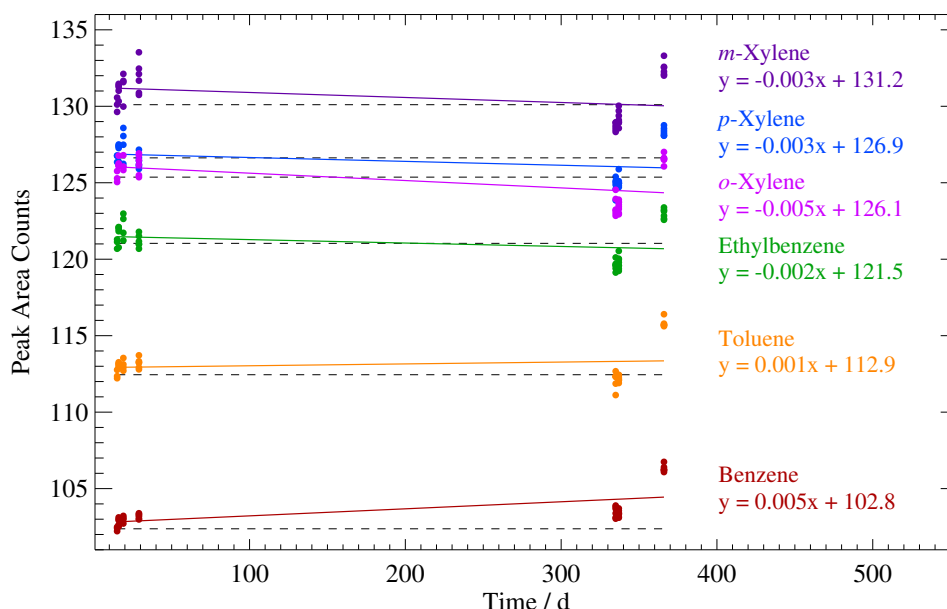


Figure 11. Stability of BTEX in the comparative mixture, APE1228493, as indicated by the measured GC response over time. Each data point represents one peak area measurement taken from a single replicate chromatogram.

4.3 Participant measurements

The methods and procedures employed by the participants to analyze the comparative mixture are described in their respective reports (see Appendix C), and summarized in Table 10.

The participants' reported amount fractions for the comparative mixture are listed in Table 11. UBA and CHMI were unable to separate *p*-xylene and *m*-xylene, and therefore reported a combined value for both components, designated hereafter as (*p+m*)-xylene. METAS separated *p*-xylene and *m*-xylene, and reported individual values for each; however, these two values were subsequently combined into one result for (*p+m*)-xylene, to be commensurate with the results of the other participants.

Also included in Table 11 are the results of measurements performed by NIST using the control mixture from the gravimetric study, APE1228481. These measurements were taken to verify the amount fractions of the comparative mixture (Table 9), and to provide a link between the gravimetric and comparative studies.

There were no significant trends in the participants' measurements to indicate any consequential impact from instability of the comparative mixture over time. As a result, no corrections to the participants' reported amount fractions were applied.

Table 10. Methods used by the participants to analyze the comparative mixture.

| Participant | Analytical method | Dates of analysis / (dd/mm/yy) | Pressure / MPa ^a |
|-------------|---|-----------------------------------|--------------------------------|
| METAS | Dynamic dilution using a home-built permeation system. All components analyzed simultaneously. GC-FID with preconcentration. | 27/08/18–04/09/18 | 12.7 |
| UBA | Static dilution of pure materials in a mixing chamber (ISO 6144). Each component measured individually. GC-FID with preconcentration. | 18/10/18–08/11/18 | 12.5 |
| CHMI | Direct comparison against an NPL PRM at nominal 10 nmol mol ^{−1} . GC-FID with preconcentration. | 14/12/18–12/03/19 | 11.2 |

^a Cylinder pressure, measured upon arrival to participating laboratory.

4.4 Results

4.4.1 KCRVs

For each component in the comparative mixture, the KCRV was determined as a consensus value on the basis of the measurements provided by UBA, CHMI and NIST. NIST’s measurements were included to provide a more reliable estimation of the KCRV, and to provide a link between the results of both the comparative and gravimetric studies. The measurements provided by METAS were excluded from the determination of the KCRV, after METAS discovered a possible error in the flow calibration of their reference gas mixture, which may have inadvertently led to a bias in their measurement results.

The consensus value was computed using the DerSimonian-Laird consensus building procedure as described by Koepke et al. [7], including the uncertainty evaluation both for the consensus value and for the degrees of equivalence. The resulting KCRVs for the comparative mixture are listed in Table 12, and plotted in Figure 12 along with the participants’ measurement results.

NIST did not formally participate in the comparative study (as shown in Table 1); therefore, only the results for METAS, UBA and CHMI are presented. Even though NIST’s measurements were included in the calculations of the KCRVs for the comparative study, NIST’s performance in this key comparison is based solely upon the results of the gravimetric study, as described in §3.

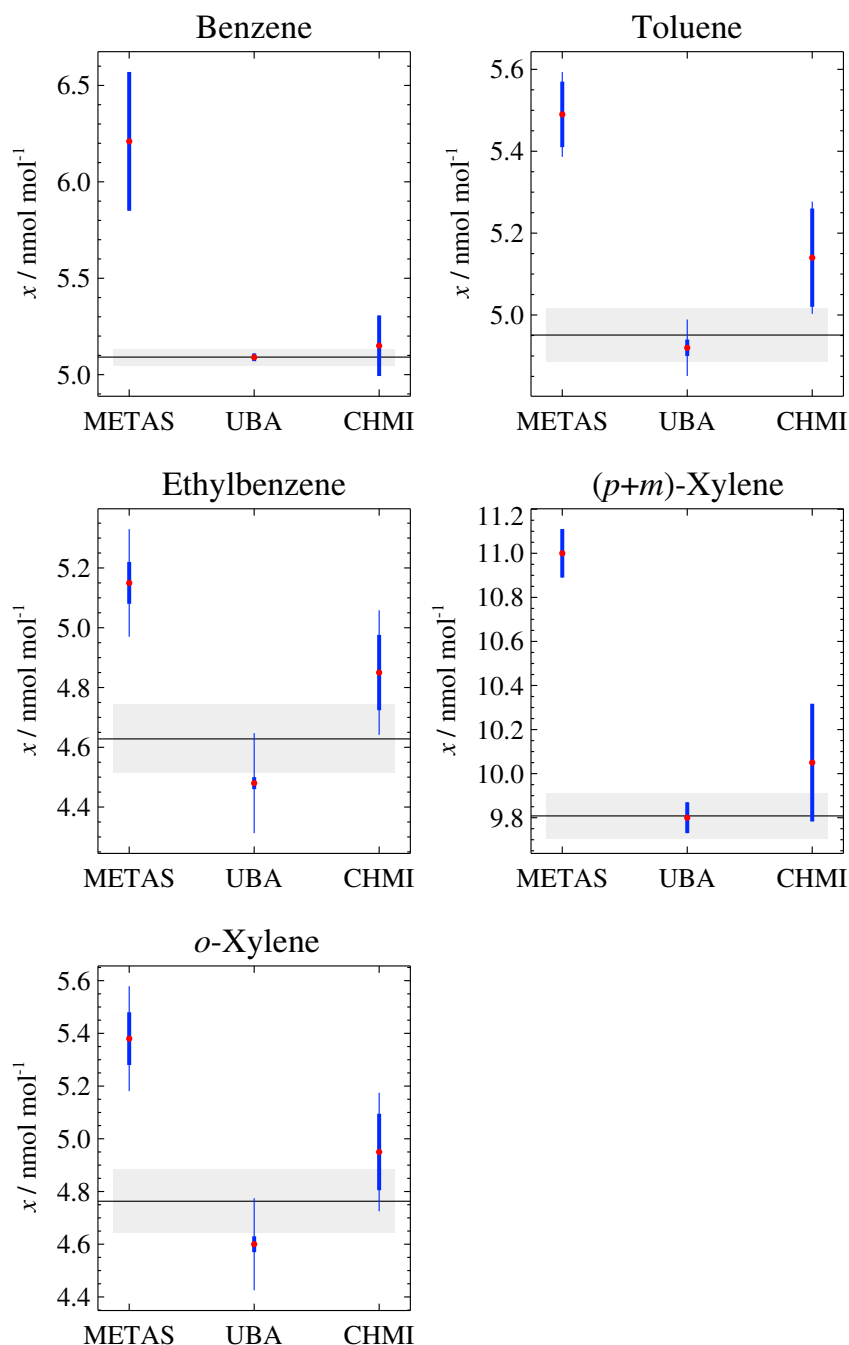


Figure 12. Participants' reported amount fractions (red dots) and associated standard uncertainties (thick blue error bars) for each component in the comparative mixture. The thin blue error bars incorporate dark uncertainty, τ , relating to excess variance between the measurements from UBA, CHMI and NIST. The horizontal black lines with grey shading depict the corresponding KCRVs and associated standard uncertainties, which include the contribution from τ .

Table 11. Amount fractions, x , of BTEX in the comparative mixture (APE1228481), and associated uncertainties for 95 % confidence, $U(x)$, as reported by the participants and measured by NIST.

| / nmol mol ⁻¹ | METAS | | UBA | | CHMI | | NIST | |
|--------------------------|-------|--------|------|--------|-------|--------|------|--------|
| | x | $U(x)$ | x | $U(x)$ | x | $U(x)$ | x | $U(x)$ |
| Benzene | 6.21 | 0.72 | 5.09 | 0.04 | 5.15 | 0.31 | 5.09 | 0.22 |
| Toluene | 5.49 | 0.15 | 4.92 | 0.05 | 5.14 | 0.24 | 4.90 | 0.21 |
| Ethylbenzene | 5.15 | 0.14 | 4.48 | 0.04 | 4.85 | 0.25 | 4.64 | 0.20 |
| (<i>p+m</i>)-Xylene | 11.00 | 0.22 | 9.80 | 0.14 | 10.05 | 0.53 | 9.72 | 0.46 |
| <i>o</i> -Xylene | 5.38 | 0.19 | 4.60 | 0.06 | 4.95 | 0.29 | 4.83 | 0.21 |

Table 12. KCRVs, μ , with expanded uncertainties for 95 % confidence, $U(\mu)$, and associated estimates of excess variance, expressed as dark uncertainty, τ .

| / nmol mol ⁻¹ | | | |
|--------------------------|-------|----------|--------|
| | μ | $U(\mu)$ | τ |
| Benzene | 5.091 | 0.084 | 0.000 |
| Toluene | 4.951 | 0.131 | 0.066 |
| Ethylbenzene | 4.628 | 0.230 | 0.166 |
| (<i>p+m</i>)-Xylene | 9.808 | 0.207 | 0.000 |
| <i>o</i> -Xylene | 4.763 | 0.242 | 0.172 |

The KCRVs were validated by comparison to the gravimetric amount fractions determined by NIST, as described in §4.1. (These gravimetric values differ from the NIST measured values described in §4.3.) As shown in Figure 13, the gravimetric values assigned to the comparative mixture agree with the KCRV determinations within the expanded uncertainties.

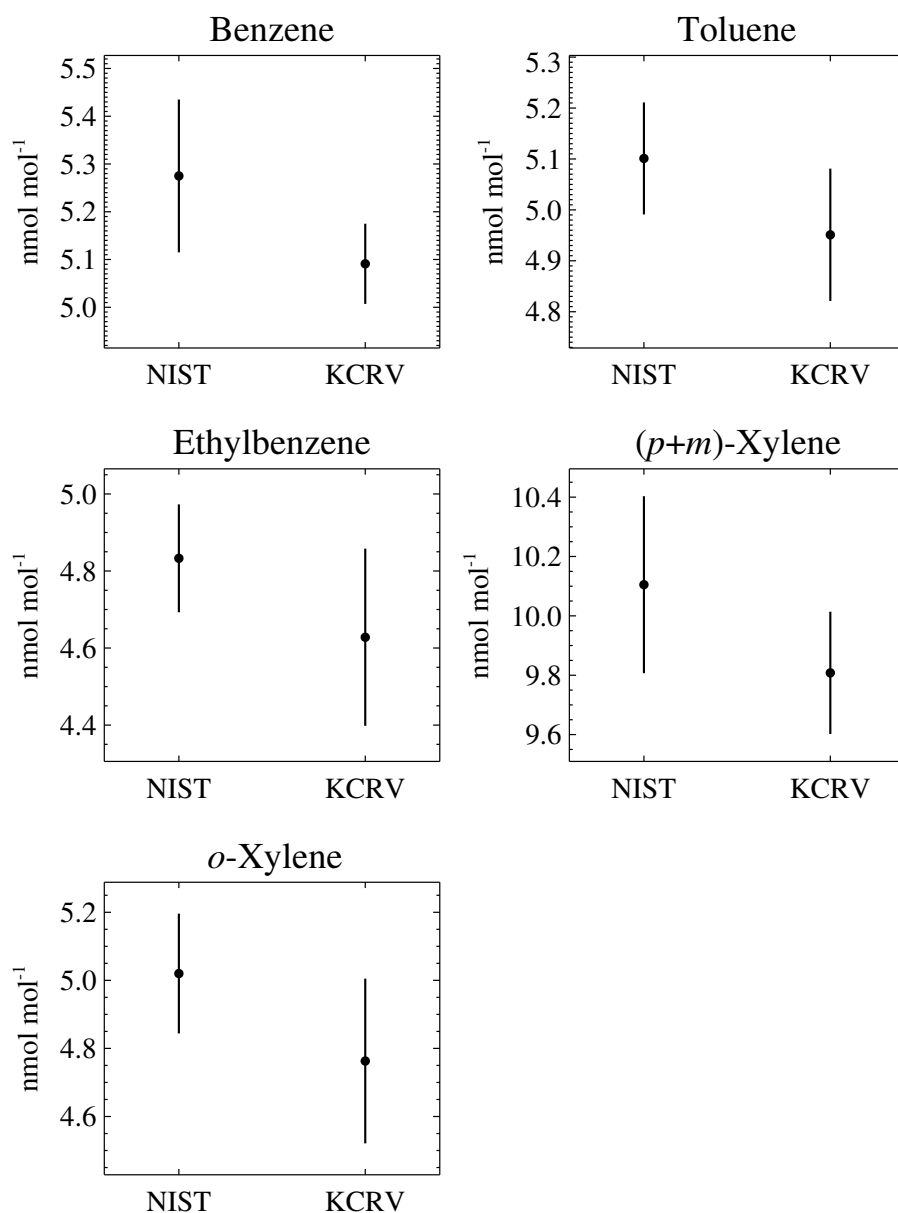


Figure 13. Gravimetric amount fractions of BTEX in the comparative mixture as determined by NIST, and corresponding consensus value estimates for the KCRV, with expanded uncertainties for 95 % confidence.

4.4.2 Degrees of equivalence

For each component in the comparative mixture, the unilateral degree of equivalence for each participant is expressed quantitatively by two terms: (i) the deviation of the participants' result from the KCRV, and (ii) the uncertainty of this deviation at 95 % confidence.

The degree of equivalence is defined as

$$D_p = x_p - \mu \quad (4)$$

where x_p is the amount fraction of the component as determined by each participant P , and μ is the KCRV. The associated expanded uncertainty, $U(D_p)$, was evaluated using a parametric statistical bootstrap estimation consistent with the GUM Supplement 1 [9], and as described by Koepke et al. [7] for the DerSimonian-Laird procedure.

The degrees of equivalence and expanded uncertainties associated with the results of this study are shown Table 13 and Figure 14. For all measurands in the comparison, UBA and CHMI agree with the KCRV within the expanded uncertainties. METAS, on the other hand, exhibits a large bias in their results. METAS speculates that this bias may be related to an error in the flow calibration during the generation of their reference gas mixture. Although the calibration was performed, the correction was apparently not taken into account and/or not saved by the software used in the generation system. This could also explain the difference of about 7 % for toluene, ethylbenzene, *p*-xylene, *m*-xylene and *o*-xylene, which is a known difference when the flow calibration is reported to 20 °C instead of 0 °C.

Table 13. Values and expanded uncertainties for the degrees of equivalence, D , between the participants' measured amount fractions of BTEX in the comparative mixture and the corresponding KCRV.

| / nmol mol ⁻¹ | | | / nmol mol ⁻¹ | | |
|--------------------------|--------|---------------|--------------------------|--------|---------------|
| | D | $U_{95\%}(D)$ | | D | $U_{95\%}(D)$ |
| Benzene | | | Toluene | | |
| METAS | 1.119 | 0.710 | METAS | 0.539 | 0.240 |
| UBA | -0.001 | 0.095 | UBA | -0.031 | 0.141 |
| CHMI | 0.059 | 0.276 | CHMI | 0.189 | 0.254 |
| Ethylbenzene | | | <i>(p+m)</i> -Xylene | | |
| METAS | 0.522 | 0.418 | METAS | 1.192 | 0.296 |
| UBA | -0.148 | 0.288 | UBA | -0.008 | 0.218 |
| CHMI | 0.222 | 0.380 | CHMI | 0.242 | 0.474 |
| <i>o</i> -Xylene | | | | | |
| METAS | 0.617 | 0.457 | | | |
| UBA | -0.163 | 0.306 | | | |
| CHMI | 0.187 | 0.411 | | | |

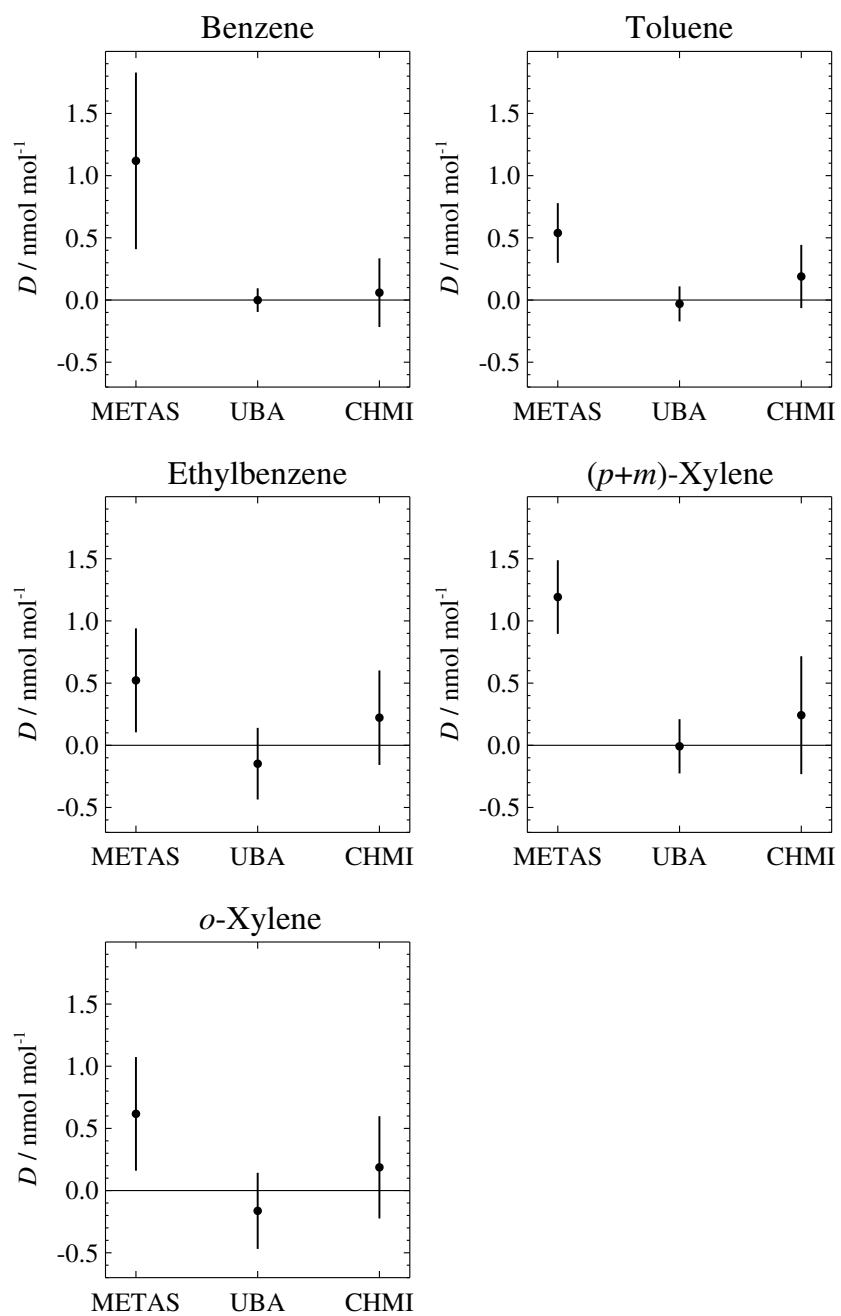


Figure 14. Degrees of equivalence and corresponding 95 % uncertainties for each component in the comparative mixture.

5 Conclusions

The results for the gravimetric study, based on the response ratios and reported compositions of the participants' mixtures, identify four participants (KRISS, NIST, NPL, and VSL) that consistently agree with the KCRV, and three participants (LNE, NMISA, and VNIIM) that are consistently biased high, with the exception of NMISA's result for benzene.

For the comparative study, the results for UBA and CHMI agree with the KCRV for all components measured. The results for METAS are biased high, which they attribute to a possible calibration error in their measurement system.

6 Supported claims

This key comparison can be used to support CMC claims for mixtures of BTEX in nitrogen from 1 nmol mol⁻¹ to 10 µmol mol⁻¹.

Over the stated range of amount fractions, the relative expanded uncertainty as calculated in accordance with the GAWG strategy [10] can be applied. Beyond this range, NMIs should justify their CMCs.

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A Gravimetric study calculations

The results for the gravimetric study, as described in §3.5, were based upon the set of differences between the participants’ predicted amount fractions of the control mixture, $\hat{y}_p(C)$, and the “true” amount fractions of the control mixture, $y(C)$, as determined gravimetrically by NIST.

The $\hat{y}_p(C)$ were calculated based on the participants’ reported amount fractions of their prepared mixtures, $x_p(C)$, and the ratios of instrumental indications to the control mixture, $r_p(C)$, using Equation 1.

The following tables list, for each BTEX component C , the reported amount fractions of the participants’ mixtures (x_p), their corresponding ratios of instrumental indications to the control mixture (r_p), and the resulting calculations for \hat{y}_p , along with their associated standard uncertainties.

A direct comparison of the values for $\hat{y}_p(C)$ and $y(C)$ are included in Table 7, and the corresponding degrees of equivalence are listed in Table 8.

Table A1. Benzene

| | x / nmol mol ⁻¹ | $u(x)$ | r | $u(r)$ | \hat{y} / nmol mol ⁻¹ | $u(\hat{y})$ |
|-------|---------------------------------|--------|--------|--------|---------------------------------------|--------------|
| KRISS | 5.031 | 0.098 | 0.9854 | 0.0029 | 5.106 | 0.101 |
| LNE | 5.09 | 0.050 | 0.9088 | 0.0154 | 5.601 | 0.110 |
| NIST | 5.473 | 0.042 | 1.0454 | 0.0031 | 5.236 | 0.043 |
| NMISA | 5.017 | 0.063 | 1.0443 | 0.0020 | 4.804 | 0.061 |
| NPL | 5.00 | 0.05 | 0.9764 | 0.0030 | 5.121 | 0.054 |
| VNIIM | 4.97 | 0.056 | 0.8827 | 0.0084 | 5.631 | 0.083 |
| VSL | 5.008 | 0.050 | 0.9741 | 0.0025 | 5.141 | 0.053 |

Table A2. Toluene

| | x / nmol mol ⁻¹ | $u(x)$ | r | $u(r)$ | \hat{y} / nmol mol ⁻¹ | $u(\hat{y})$ |
|-------|---------------------------------|--------|--------|--------|---------------------------------------|--------------|
| KRISS | 5.165 | 0.100 | 1.0619 | 0.0028 | 4.864 | 0.095 |
| LNE | 4.93 | 0.050 | 0.9105 | 0.0149 | 5.415 | 0.104 |
| NIST | 5.265 | 0.035 | 1.0464 | 0.0043 | 5.031 | 0.039 |
| NMISA | 5.019 | 0.054 | 0.9634 | 0.0033 | 5.210 | 0.059 |
| NPL | 5.02 | 0.05 | 1.0143 | 0.0031 | 4.949 | 0.052 |
| VNIIM | 5.03 | 0.060 | 0.9305 | 0.0079 | 5.406 | 0.079 |
| VSL | 5.023 | 0.050 | 1.0132 | 0.0027 | 4.958 | 0.051 |

Table A3. Ethylbenzene

| | x / nmol mol ⁻¹ | $u(x)$ | r | $u(r)$ | \hat{y} / nmol mol ⁻¹ | $u(\hat{y})$ |
|-------|---------------------------------|--------|--------|--------|---------------------------------------|--------------|
| KRISS | 5.105 | 0.091 | 1.1288 | 0.0026 | 4.522 | 0.081 |
| LNE | 4.96 | 0.055 | 0.9592 | 0.0164 | 5.171 | 0.106 |
| NIST | 4.996 | 0.058 | 1.0487 | 0.0022 | 4.764 | 0.056 |
| NMISA | 5.021 | 0.046 | 1.0006 | 0.0029 | 5.018 | 0.048 |
| NPL | 5.02 | 0.05 | 1.0780 | 0.0017 | 4.657 | 0.047 |
| VNIIM | 5.10 | 0.010 | 0.9787 | 0.0082 | 5.211 | 0.111 |
| VSL | 5.100 | 0.076 | 1.0733 | 0.0031 | 4.752 | 0.072 |

Table A4. *p*-Xylene

| | x / nmol mol ⁻¹ | $u(x)$ | r | $u(r)$ | \hat{y} / nmol mol ⁻¹ | $u(\hat{y})$ |
|-------|---------------------------------|--------|--------|--------|---------------------------------------|--------------|
| KRISS | 5.038 | 0.118 | 1.0525 | 0.0028 | 4.787 | 0.113 |
| LNE | 5.04 | 0.050 | 0.9245 | 0.0167 | 5.451 | 0.112 |
| NIST | 5.249 | 0.066 | 1.0504 | 0.0026 | 4.997 | 0.064 |
| NMISA | 5.021 | 0.046 | 0.9170 | 0.0035 | 5.476 | 0.054 |
| NPL | 5.02 | 0.05 | 1.0163 | 0.0029 | 4.940 | 0.051 |
| VNIIM | 5.08 | 0.102 | 0.9182 | 0.0064 | 5.532 | 0.118 |
| VSL | 4.870 | 0.097 | 0.9626 | 0.0039 | 5.059 | 0.103 |

Table A5. *m*-Xylene

| | x / nmol mol ⁻¹ | $u(x)$ | r | $u(r)$ | \hat{y} / nmol mol ⁻¹ | $u(\hat{y})$ |
|-------|---------------------------------|--------|--------|--------|---------------------------------------|--------------|
| KRISS | 5.017 | 0.118 | 1.0627 | 0.0024 | 4.721 | 0.112 |
| LNE | 5.00 | 0.050 | 0.9200 | 0.0181 | 5.435 | 0.120 |
| NIST | 5.193 | 0.084 | 1.0490 | 0.0028 | 4.950 | 0.081 |
| NMISA | 5.033 | 0.047 | 0.8690 | 0.0035 | 5.792 | 0.059 |
| NPL | 5.02 | 0.05 | 1.0254 | 0.0024 | 4.895 | 0.050 |
| VNIIM | 4.92 | 0.101 | 0.8882 | 0.0050 | 5.540 | 0.118 |
| VSL | 4.894 | 0.098 | 0.9755 | 0.0040 | 5.017 | 0.103 |

Table A6. *o*-Xylene

| | x / nmol mol ⁻¹ | $u(x)$ | r | $u(r)$ | \hat{y} / nmol mol ⁻¹ | $u(\hat{y})$ |
|-------|---------------------------------|--------|--------|--------|---------------------------------------|--------------|
| KRISS | 5.105 | 0.118 | 1.1120 | 0.0030 | 4.591 | 0.107 |
| LNE | 5.04 | 0.050 | 0.9489 | 0.0115 | 5.312 | 0.083 |
| NIST | 5.192 | 0.082 | 1.0482 | 0.0030 | 4.953 | 0.080 |
| NMISA | 5.023 | 0.047 | 0.9084 | 0.0026 | 5.530 | 0.054 |
| NPL | 5.03 | 0.05 | 1.0516 | 0.0018 | 4.783 | 0.048 |
| VNIIM | 4.96 | 0.101 | 0.9177 | 0.0056 | 5.405 | 0.115 |
| VSL | 5.044 | 0.101 | 1.0330 | 0.0039 | 4.883 | 0.099 |

B Gravimetric participant reports

B.1 KRISS

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : Korea Research Institute of Standards and Science

Laboratory code : KRISS

Cylinder number : D517490

NOMINAL COMPOSITION: 5×10^{-9} (nmol/mol; ppb)

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty ($k=2$) (nmol/mol) |
|----------------|-----------|---|---|---|
| Benzene | 2018-5-24 | 5.031 | 0.098 | 0.195 |
| Toluene | | 5.165 | 0.100 | 0.201 |
| Ethylbenzene | | 5.105 | 0.091 | 0.182 |
| meta-Xylene | | 5.017 | 0.118 | 0.235 |
| para-Xylene | | 5.038 | 0.118 | 0.237 |
| ortho-Xylene | | 5.105 | 0.118 | 0.235 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES.

A set of primary standard gas mixtures (PSMs) was gravimetrically prepared for the comparison. All source reagents were analyzed using GC-FID to determine their purities (based on peak areas). Micro-syringes were used to transfer the source reagents into cylinders for gravimetrically prepared PSMs at 10 $\mu\text{mol/mol}$. The PSMs were further diluted with nitrogen to 100 nmol/mol and then 5 nmol/mol (Figure 1). The PSMs at each step were analyzed against each other for verification.

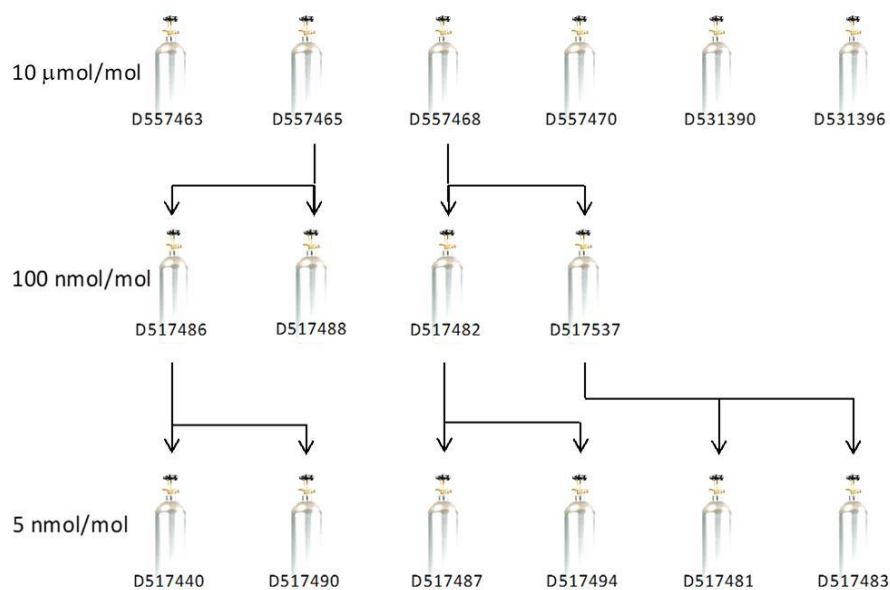


Figure 1. Hierarchy of KRISS PSMs

3. UNCERTAINTY BUDGET.

Please provide a complete uncertainty budget.

| | Benzene | Toluene | Ethyl benzene | <i>m</i> -Xylene | <i>p</i> -Xylene | <i>o</i> -Xylene |
|-------------------------|--|---------|---------------|------------------|------------------|------------------|
| Uncertainty component | Relative standard uncertainty ($k = 1$), % | | | | | |
| Gravimetric preparation | 1.14 | 1.22 | 1.12 | 1.47 | 1.48 | 1.42 |
| Verification | 1.57 | 1.51 | 1.37 | 1.82 | 1.81 | 1.80 |
| Stability | 0.14 | 0.12 | 0.16 | 0.16 | 0.17 | 0.22 |
| Combined uncertainty | 1.94 | 1.94 | 1.78 | 2.34 | 2.35 | 2.30 |

4. COMPLEMENTARY INFORMATION.

Please include information on:

- 1) a purity table with uncertainties for the benzene, toluene, ethylbenzene, meta-para-ortho-xylenes, and balance nitrogen used to prepare your standard mixture

| % | Benzene | Toluene | Ethyl benzene | <i>m</i> -Xylene | <i>p</i> -Xylene | <i>o</i> -Xylene |
|------------------|---------|---------|---------------|------------------|------------------|------------------|
| Benzene | 99.967 | 0.002 | 0.108 | - | - | 0.004 |
| Toluene | 0.002 | 99.955 | 0.026 | 0.003 | 0.010 | - |
| Ethyl benzene | - | 0.007 | 99.815 | 0.028 | 0.040 | 0.002 |
| <i>m</i> -Xylene | - | 0.002 | - | 99.703 | - | 0.017 |
| <i>p</i> -Xylene | - | 0.004 | - | - | 99.813 | 0.247 |
| <i>o</i> -Xylene | - | 0.001 | - | 0.177 | 0.010 | 99.458 |
| unknowns | 0.014 | 0.020 | 0.047 | 0.083 | 0.122 | 0.253 |
| H ₂ O | 0.017 | 0.009 | 0.005 | 0.005 | 0.006 | 0.017 |

- 2) outline of dilution series to produce final standard mixture

Please refer to Figure 1.

- 3) outline/discussion of the verification procedure applied to final mixture

A set of PSMs were prepared at each step and then one of those was chosen as a working reference. The prepared PSMs at each step were analyzed against each other for verification.

- 4) outline of any stability testing of mixture

Physical adsorption loss on internal cylinder surface at 5 nmol/mol were tested using cylinder-to-cylinder division. Results from the cylinder-to-cylinder division showed that both responses agreed with their analytical uncertainty. Two new PSMs at 5 nmol/mol were prepared again about 6 months after the preparation of the first set of PSMs and then compared. Results from the stability test showed that both old and new PSMs agreed within their analytical uncertainty. Although the results from the stability showed a good agreement, any difference was combined as additional uncertainties for estimating the final uncertainties.

- 5) cylinder pressure

about 9.3 Mpa

5. STABILITY

Results from the stability evaluation of the KRISS sample gas mixture are shown in Figure 2. All sensitivities (i.e., peak area/amount-of-substance fraction) of the KRISS sample gas mixture, which are normalized to the sensitivity of the sample reference gas mixtures, agree with each other within their associated uncertainty before its ship-out and ship-back.

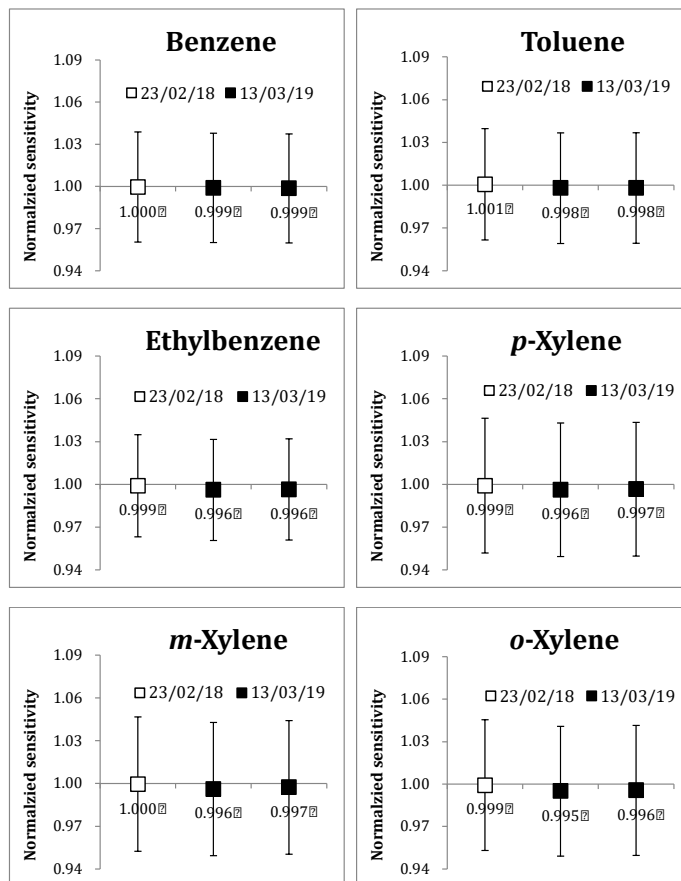


Figure 2. Results from stability evaluation

B.2 LNE

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : LNE

Laboratory code :

Cylinder number : 1029123

NOMINAL COMPOSITION: 5×10^{-9} (nmol/mol; ppb)

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|----------------|------------|---|---|--|
| Benzene | 29/01/2018 | 5.09 | 0.050 | 0.10 |
| Toluene | | 4.93 | 0.050 | 0.10 |
| Ethylbenzene | | 4.96 | 0.055 | 0.11 |
| meta-Xylene | | 5.00 | 0.050 | 0.10 |
| para-Xylene | | 5.04 | 0.050 | 0.10 |
| ortho-Xylene | | 5.04 | 0.050 | 0.10 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES.

The gas mixture is prepared according to the ISO 6142 standard.

The cylinder is evacuated with a turbo vacuum pump and weighed using a Mettler AX32004 mass comparator with a 0.1 mg resolution.

Each pure compound is injected individually in the empty cylinder with a syringe containing each pure compound. The mass of the injected pure compound is determined by weighing the syringe before and after injection on a Mettler XP505 balance with a 0.00001 g resolution.

After the injection of the 6 pure hydrocarbon compounds, the injection system is flushed with pure nitrogen (N2 BIP).

The cylinder is filled with pure nitrogen to obtain the first premix gas mixture. After stabilization in temperature the cylinder is weighed on the mass comparator to calculate the amount fraction of the compounds in the cylinder.

Three successive gravimetric dilutions are performed to obtain the final gas mixture at 5 nmol/mol.

3. UNCERTAINTY BUDGET.

Please provide a complete uncertainty budget.

UNCERTAINTY BUDGET FOR BENZENE

| Uncertainty source | Unit | Value Xi | u(Xi) | Contribution to the uncertainty % |
|---|---------|---------------------------|----------------------|-----------------------------------|
| Mass of BTEX/N ₂ premix | g | 70.4812 | $1.4 \cdot 10^{-2}$ | 0.04 |
| Mass of N ₂ | g | 1461.854 | $1.7 \cdot 10^{-2}$ | 0.00 |
| Purity of N ₂ | mol/mol | 0.99999991 | $5.2 \cdot 10^{-8}$ | 0.00 |
| Molar mass of benzene | g/mol | 78.11184 | $2.0 \cdot 10^{-3}$ | 0.00 |
| Molar mass of Toluene | g/mol | 92.13842 | $2.2 \cdot 10^{-3}$ | 0.00 |
| Molar mass of Ethylbenzene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of O-xylene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of M-xylene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of P-xylene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of Nitrogen | g/mol | 28.01348 | $9.9 \cdot 10^{-5}$ | 0.00 |
| Amount fraction of benzene in premix mixture | mol/mol | $1.1071610 \cdot 10^{-7}$ | $4.2 \cdot 10^{-11}$ | 0.15 |
| Amount fraction of toluene in premix mixture | mol/mol | $1.0713283 \cdot 10^{-7}$ | $3.9 \cdot 10^{-11}$ | 0.00 |
| Amount fraction of ethylbenzene in premix mixture | mol/mol | $1.0792587 \cdot 10^{-7}$ | $1.1 \cdot 10^{-10}$ | 0.00 |
| Amount fraction of o-xylene in premix mixture | mol/mol | $1.0949965 \cdot 10^{-7}$ | $3.8 \cdot 10^{-11}$ | 0.00 |
| Amount fraction of m-xylene in premix mixture | mol/mol | $1.087438 \cdot 10^{-7}$ | $3.8 \cdot 10^{-11}$ | 0.00 |
| Amount fraction of p-xylene in premix mixture | mol/mol | $1.0960214 \cdot 10^{-7}$ | $4.3 \cdot 10^{-11}$ | 0.00 |
| Stability | mol/mol | 0 | $0.05 \cdot 10^{-9}$ | 99.81 |

Amount fraction of benzene : $5.09 \text{ nmol/mol} \pm 0.10 \text{ nmol/mol}$

UNCERTAINTY BUDGET FOR TOLUENE

| Uncertainty source | Unit | Value Xi | u(Xi) | Contribution to the uncertainty % |
|---|---------|----------------------------|-----------------------|-----------------------------------|
| Mass of BTEX/N ₂ premix | g | 70.4812 | 1.4 10 ⁻² | 0.03 |
| Mass of N ₂ | g | 1461.854 | 1.7 10 ⁻² | 0.00 |
| Purity of N ₂ | mol/mol | 0.99999991 | 5.2 10 ⁻⁸ | 0.00 |
| Molar mass of benzene | g/mol | 78.11184 | 2.0 10 ⁻³ | 0.00 |
| Molar mass of Toluene | g/mol | 92.13842 | 2.2 10 ⁻³ | 0.00 |
| Molar mass of Ethylbenzene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of O-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of M-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of P-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of Nitrogen | g/mol | 28.01348 | 9.9.10 ⁻⁵ | 0.00 |
| Amount fraction of benzene in premix mixture | mol/mol | 1.1071610 10 ⁻⁷ | 4.2 10 ⁻¹¹ | 0.00 |
| Amount fraction of toluene in premix mixture | mol/mol | 1.0713283.10 ⁻⁷ | 3.9 10 ⁻¹¹ | 0.12 |
| Amount fraction of ethylbenzene in premix mixture | mol/mol | 1.0792587.10 ⁻⁷ | 1.1 10 ⁻¹⁰ | 0.00 |
| Amount fraction of o-xylene in premix mixture | mol/mol | 1.0949965.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.00 |
| Amount fraction of m-xylene in premix mixture | mol/mol | 1.087438.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.00 |
| Amount fraction of p-xylene in premix mixture | mol/mol | 1.0960214.10 ⁻⁷ | 4.3 10 ⁻¹¹ | 0.00 |
| Stability | mol/mol | 0 | 0.05.10 ⁻⁹ | 99.84 |

Amount fraction of toluene : 4.93 nmol/mol ± 0.10 nmol/mol

UNCERTAINTY BUDGET FOR ETHYLBENZENE

| Uncertainty source | Unit | Value Xi | u(Xi) | Contribution to the uncertainty % |
|---|---------|----------------------------|-----------------------|-----------------------------------|
| Mass of BTEX/N ₂ premix | g | 70.4812 | 1.4 10 ⁻² | 0.04 |
| Mass of N ₂ | g | 1461.854 | 1.7 10 ⁻² | 0.00 |
| Purity of N ₂ | mol/mol | 0.99999991 | 5.2 10 ⁻⁸ | 0.00 |
| Molar mass of benzene | g/mol | 78.11184 | 2.0 10 ⁻³ | 0.00 |
| Molar mass of Toluene | g/mol | 92.13842 | 2.2 10 ⁻³ | 0.00 |
| Molar mass of Ethylbenzene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of O-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of M-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of P-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of Nitrogen | g/mol | 28.01348 | 9.9.10 ⁻⁵ | 0.00 |
| Amount fraction of benzene in premix mixture | mol/mol | 1.1071610 10 ⁻⁷ | 4.2 10 ⁻¹¹ | 0.00 |
| Amount fraction of toluene in premix mixture | mol/mol | 1.0713283.10 ⁻⁷ | 3.9 10 ⁻¹¹ | 0.00 |
| Amount fraction of ethylbenzene in premix mixture | mol/mol | 1.0792587.10 ⁻⁷ | 1.1 10 ⁻¹⁰ | 1.01 |
| Amount fraction of o-xylene in premix mixture | mol/mol | 1.0949965.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.00 |
| Amount fraction of m-xylene in premix mixture | mol/mol | 1.087438.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.00 |
| Amount fraction of p-xylene in premix mixture | mol/mol | 1.0960214.10 ⁻⁷ | 4.3 10 ⁻¹¹ | 0.00 |
| Stability | mol/mol | 0 | 0.05.10 ⁻⁹ | 98.95 |

Amount fraction of ethylbenzene : 4.96 nmol/mol ± 0.11 nmol/mol

UNCERTAINTY BUDGET FOR O-XYLENE

| Uncertainty source | Unit | Value Xi | u(Xi) | Contribution to the uncertainty % |
|---|---------|----------------------------|-----------------------|-----------------------------------|
| Mass of BTEX/N ₂ premix | g | 70.4812 | 1.4 10 ⁻² | 0.04 |
| Mass of N ₂ | g | 1461.854 | 1.7 10 ⁻² | 0.00 |
| Purity of N ₂ | mol/mol | 0.99999991 | 5.2 10 ⁻⁸ | 0.00 |
| Molar mass of benzene | g/mol | 78.11184 | 2.0 10 ⁻³ | 0.00 |
| Molar mass of Toluene | g/mol | 92.13842 | 2.2 10 ⁻³ | 0.00 |
| Molar mass of Ethylbenzene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of O-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of M-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of P-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of Nitrogen | g/mol | 28.01348 | 9.9.10 ⁻⁵ | 0.00 |
| Amount fraction of benzene in premix mixture | mol/mol | 1.1071610 10 ⁻⁷ | 4.2 10 ⁻¹¹ | 0.00 |
| Amount fraction of toluene in premix mixture | mol/mol | 1.0713283.10 ⁻⁷ | 3.9 10 ⁻¹¹ | 0.00 |
| Amount fraction of ethylbenzene in premix mixture | mol/mol | 1.0792587.10 ⁻⁷ | 1.1 10 ⁻¹⁰ | 0.00 |
| Amount fraction of o-xylene in premix mixture | mol/mol | 1.0949965.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.12 |
| Amount fraction of m-xylene in premix mixture | mol/mol | 1.087438.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.00 |
| Amount fraction of p-xylene in premix mixture | mol/mol | 1.0960214.10 ⁻⁷ | 4.3 10 ⁻¹¹ | 0.00 |
| Stability | mol/mol | 0 | 0.05.10 ⁻⁹ | 99.84 |

Amount fraction of o-xylene : 5.04 nmol/mol ± 0.10 nmol/mol

UNCERTAINTY BUDGET FOR M-XYLENE

| Uncertainty source | Unit | Value Xi | u(Xi) | Contribution to the uncertainty % |
|---|---------|----------------------------|-----------------------|-----------------------------------|
| Mass of BTEX/N ₂ premix | g | 70.4812 | 1.4 10 ⁻² | 0.04 |
| Mass of N ₂ | g | 1461.854 | 1.7 10 ⁻² | 0.00 |
| Purity of N ₂ | mol/mol | 0.99999991 | 5.2 10 ⁻⁸ | 0.00 |
| Molar mass of benzene | g/mol | 78.11184 | 2.0 10 ⁻³ | 0.00 |
| Molar mass of Toluene | g/mol | 92.13842 | 2.2 10 ⁻³ | 0.00 |
| Molar mass of Ethylbenzene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of O-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of M-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of P-xylene | g/mol | 106.165 | 2.3 10 ⁻³ | 0.00 |
| Molar mass of Nitrogen | g/mol | 28.01348 | 9.9.10 ⁻⁵ | 0.00 |
| Amount fraction of benzene in premix mixture | mol/mol | 1.1071610 10 ⁻⁷ | 4.2 10 ⁻¹¹ | 0.00 |
| Amount fraction of toluene in premix mixture | mol/mol | 1.0713283.10 ⁻⁷ | 3.9 10 ⁻¹¹ | 0.00 |
| Amount fraction of ethylbenzene in premix mixture | mol/mol | 1.0792587.10 ⁻⁷ | 1.1 10 ⁻¹⁰ | 0.00 |
| Amount fraction of o-xylene in premix mixture | mol/mol | 1.0949965.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.00 |
| Amount fraction of m-xylene in premix mixture | mol/mol | 1.087438.10 ⁻⁷ | 3.8 10 ⁻¹¹ | 0.18 |
| Amount fraction of p-xylene in premix mixture | mol/mol | 1.0960214.10 ⁻⁷ | 4.3 10 ⁻¹¹ | 0.00 |
| Stability | mol/mol | 0 | 0.05.10 ⁻⁹ | 99.69 |

Amount fraction of m-xylene : 5.00 nmol/mol ± 0.10 nmol/mol

UNCERTAINTY BUDGET FOR P-XYLENE

| Uncertainty source | Unit | Value Xi | u(Xi) | Contribution to the uncertainty % |
|---|---------|---------------------------|----------------------|-----------------------------------|
| Mass of BTEX/N ₂ premix | g | 70.4812 | $1.4 \cdot 10^{-2}$ | 0.04 |
| Mass of N ₂ | g | 1461.854 | $1.7 \cdot 10^{-2}$ | 0.00 |
| Purity of N ₂ | mol/mol | 0.99999991 | $5.2 \cdot 10^{-8}$ | 0.00 |
| Molar mass of benzene | g/mol | 78.11184 | $2.0 \cdot 10^{-3}$ | 0.00 |
| Molar mass of Toluene | g/mol | 92.13842 | $2.2 \cdot 10^{-3}$ | 0.00 |
| Molar mass of Ethylbenzene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of O-xylene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of M-xylene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of P-xylene | g/mol | 106.165 | $2.3 \cdot 10^{-3}$ | 0.00 |
| Molar mass of Nitrogen | g/mol | 28.01348 | $9.9 \cdot 10^{-5}$ | 0.00 |
| Amount fraction of benzene in premix mixture | mol/mol | $1.1071610 \cdot 10^{-7}$ | $4.2 \cdot 10^{-11}$ | 0.00 |
| Amount fraction of toluene in premix mixture | mol/mol | $1.0713283 \cdot 10^{-7}$ | $3.9 \cdot 10^{-11}$ | 0.00 |
| Amount fraction of ethylbenzene in premix mixture | mol/mol | $1.0792587 \cdot 10^{-7}$ | $1.1 \cdot 10^{-10}$ | 0.00 |
| Amount fraction of o-xylene in premix mixture | mol/mol | $1.0949965 \cdot 10^{-7}$ | $3.8 \cdot 10^{-11}$ | 0.00 |
| Amount fraction of m-xylene in premix mixture | mol/mol | $1.087438 \cdot 10^{-7}$ | $3.8 \cdot 10^{-11}$ | 0.00 |
| Amount fraction of p-xylene in premix mixture | mol/mol | $1.0960214 \cdot 10^{-7}$ | $4.3 \cdot 10^{-11}$ | 0.15 |
| Stability | mol/mol | 0 | $0.05 \cdot 10^{-9}$ | 99.81 |

Amount fraction of p-xylene : $5.04 \text{ nmol/mol} \pm 0.10 \text{ nmol/mol}$

4. COMPLEMENTARY INFORMATION.

Please include information on:

- 1) a purity table with uncertainties for the benzene, toluene, ethylbenzene, meta-para-ortho-xylenes, and balance nitrogen used to prepare your standard mixture

oooooooooooo Purity table for benzene (C6H6pur_0015) ooooooooooooo

| Component | mol/mol | uncertainty |
|------------------|--------------|--------------|
| ----- | | |
| H ₂ O | 0.0002000000 | 0.0002000000 |
| benzene | 0.9996300000 | 0.0002000000 |

oooooooooooo Purity table for toluene (tolpur_0002) ooooooooooooo

| Component | mol/mol | uncertainty |
|------------------|--------------|--------------|
| ----- | | |
| toluene | 0.9986900000 | 0.0001100000 |
| H ₂ O | 0.0003000000 | 0.0001000000 |

oooooooooooo Purity table for ethylbenzene (Ebenpur_0006) ooooooooooooo

| Component | mol/mol | uncertainty |
|------------------|--------------|--------------|
| ----- | | |
| ethylbenzene | 0.9839400000 | 0.0011000000 |
| H ₂ O | 0.0006000000 | 0.0001000000 |
| benzene | 0.0000087200 | 0.0000009300 |
| toluene | 0.0003282400 | 0.0000055800 |
| p-xylene | 0.0007630100 | 0.0000148600 |
| m-xylene | 0.0000622400 | 0.0000069400 |
| o-xylene | 0.0000343800 | 0.0000009000 |
| acetophenone | 0.0067383100 | 0.0008446400 |

oooooooooooo Purity table for o-xylene (Oxylpur_0002) ooooooooooooo

| Component | mol/mol | uncertainty |
|------------------|--------------|--------------|
| ----- | | |
| H ₂ O | 0.0002000000 | 0.0001000000 |
| benzene | 0.0000250000 | 0.0000079000 |
| toluene | 0.0000070100 | 0.0000004500 |
| ethylbenzene | 0.0000024200 | 0.0000002300 |
| p-xylene | 0.0000047300 | 0.0000003900 |
| m-xylene | 0.0000041200 | 0.0000004800 |
| o-xylene | 0.9986800000 | 0.0001000000 |

oooooooooooo Purity table for m-xylene (Mxylpur_0002) oooooooooooooo

| Component | mol/mol | uncertainty |
|------------------|--------------|--------------|
| ----- | | |
| H ₂ O | 0.0004000000 | 0.0002000000 |
| benzene | 0.0000135600 | 0.0000004700 |
| toluene | 0.0000291200 | 0.0000013000 |
| p-xylene | 0.0013596400 | 0.0000472400 |
| m-xylene | 0.9955400000 | 0.0002200000 |
| o-xylene | 0.0023804800 | 0.0000776700 |
| ethylbenzene | 0.0000152800 | 0.0000010200 |
| m-tolualdehyde | 0.0000149600 | 0.0000010200 |

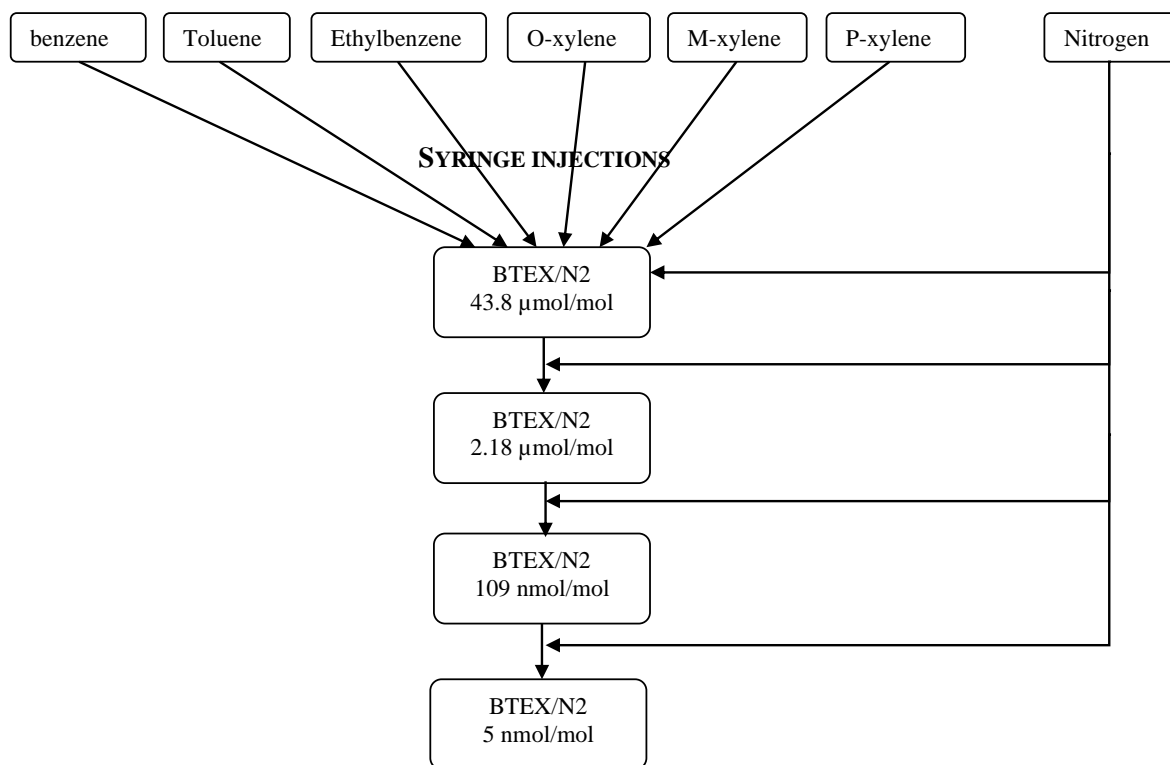
oooooooooooo Purity table for p-xylene (Pxylpur_0002) oooooooooooooo

| Component | mol/mol | uncertainty |
|------------------|--------------|--------------|
| ----- | | |
| H ₂ O | 0.0004000000 | 0.0002000000 |
| toluene | 0.0000294400 | 0.0000012500 |
| p-xylene | 0.9950100000 | 0.0002400000 |
| m-xylene | 0.0029806000 | 0.0001160000 |
| o-xylene | 0.0000032900 | 0.0000008500 |
| ethylbenzene | 0.0004357600 | 0.0000165500 |
| m-tolualdehyde | 0.0010933700 | 0.0000527200 |

oooooooooooooooooooo Purity table for nitrogen (N2_bip) oooooooooooooooooo

| Component | mol/mol | uncertainty |
|------------------|--------------|--------------|
| ----- | | |
| N ₂ | 0.9999999100 | 0.0000000520 |
| O ₂ | 0.0000000050 | 0.0000000029 |
| H ₂ O | 0.0000000100 | 0.0000000578 |
| methane | 0.0000000250 | 0.0000000144 |
| CO ₂ | 0.0000000125 | 0.0000000072 |
| CO | 0.0000000125 | 0.0000000072 |
| H ₂ | 0.0000000250 | 0.0000000144 |
| N ₂ O | 0.0000000000 | 0.0000000000 |

2) outline of dilution series to produce final standard mixture



3) outline/discussion of the verification procedure applied to final mixture

The gas mixture of 5 nmol/mol of BTEX was analyzed by GC-FID with a pre-concentration module (-20°C). The GC is a Compact GC from Interscience equipped with a CP-xylene capillary column for the separation of the compounds.

The GC is calibrated at 5 nmol/mol with a reference gas mixture obtained by diluting dynamically a gravimetric gas standard at 2 μmol/mol. The flowrates are measured with two accurate flowmeters (Molbloc). Five determinations of the chromatographic areas of BTEX peaks are performed for the two gas mixtures to determine the amount fraction of the gas mixture at 5 nmol/mol.

4) outline of any stability testing of mixture

The stability test was performed during a period of three months. The analytical results are sum up in the table below:

| | 15/02/2018 | | 08/03/2018 | | 24/04/2018 | |
|--------------|-----------------|----------|-----------------|----------|-----------------|----------|
| | Amount fraction | U(k=2) | Amount fraction | U(k=2) | Amount fraction | U(k=2) |
| | nmol/mol | nmol/mol | nmol/mol | nmol/mol | nmol/mol | nmol/mol |
| Benzene | 5.150 | 0.064 | 5.157 | 0.064 | 5.181 | 0.064 |
| Toluene | 4.962 | 0.060 | 4.978 | 0.059 | 4.915 | 0.056 |
| Ethylbenzene | 5.038 | 0.064 | 5.106 | 0.061 | 5.036 | 0.059 |
| P-Xylene | 5.096 | 0.090 | 5.097 | 0.075 | 5.036 | 0.077 |
| M-Xylene | 5.054 | 0.080 | 5.049 | 0.072 | 5.002 | 0.074 |
| O-Xylene | 5.073 | 0.091 | 5.078 | 0.008 | 5.015 | 0.079 |

5) cylinder pressure

The pressure of the final gas mixture is equal to 125 bars.

B.3 NIST

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : National Institute of Standards and Technology, USA
Laboratory code : NIST

Cylinder number : CC412027

NOMINAL COMPOSITION: 5×10^{-9} (nmol/mol; ppb)

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|----------------------|-----------|---|---|--|
| Benzene | 5/20/2018 | 5.473 | 0.042 | 0.084 |
| Toluene | 5/20/2018 | 5.265 | 0.035 | 0.070 |
| Ethylbenzene | 5/20/2018 | 4.996 | 0.058 | 0.115 |
| <i>meta</i> -Xylene | 5/20/2018 | 5.193 | 0.084 | 0.167 |
| <i>para</i> -Xylene | 5/20/2018 | 5.249 | 0.066 | 0.133 |
| <i>ortho</i> -Xylene | 5/20/2018 | 5.192 | 0.082 | 0.165 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES.

A 6-component BTEX-in-nitrogen primary standard mixture (PSM) was prepared in a 30-L aluminum gas cylinder (CC460929) equipped with CGA-590 stainless steel valve and pretreated with the proprietary process Megalife by Airgas, Pennsylvania. Pure benzene, toluene, ethylbenzene, para-xylene, meta-xylene and ortho-xylene were weighed into pre-weighed glass capillary tubes which were then weighed three times. The BTEX components were then transferred into cylinder CC460929. Airgas built in purifier (BIP) N₂ was then added to the cylinder to approximately 1850 psi to achieve an amount-of-substance fraction of approximately 250 nmol/mol. The completed cylinder was weighed three times and then rolled for two hours. BTEX mixture CC460929 was then verified against previous PSMs.

The 6-component BTEX-in-nitrogen primary standard mixture (PSM) at 5 nmol/mol for this comparison was prepared in a 30-L aluminum gas cylinder (CC412027) equipped with a CGA-590 stainless steel valve and pretreated with Megalife. The cylinder was connected to a fill manifold (Manifold # 2), along with Airgas BIP N₂. The cylinder was vented and evacuated to a pressure of approximately 3 μ mHg. The evacuated cylinder was weighed three times. It was then filled with 73.9 g of the parent BTEX mix at nominal 250 nmol/mol and weighed three times. Airgas BIP N₂ was then added to approximately 1840 psi. The cylinder was then weighed three times completed. The cylinder was then rolled for 2 hours. Mass measurements were determined using a Mettler SR64001 single-pan balance (NIST # 619572), with a capacity of 64 kg and a sensitivity of 0.1 g.

Please provide a complete uncertainty budget.

| | | | | | | | | | | | | | | | | |
|---|---------------|----------------|--------------|----------------------------|-----------------------------|---|---------------------|---|----------------------------|---|---------------------|--------------------------|--------------|---------------|----------------------|-------------------------|
| Equation: $M_{org} = M_{diff} + S + D_{org} + V_{dapor}$ | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| <div>Gas Constant0.08205 (l-atm)/(g-K) Temperature294.8600 K Air Density1.2006 g/l MW of Air28.9631 Transfer Efficiency1.00</div> | | | | | | <div>Uncert1.1547 21.7000 C 0.0024 0.0014 0.0000</div> | | <div>% EquilibriumK Factor Tube Weight Loss</div> | | <div>50% 2 0.0008</div> | | <div>0.0005</div> | | | | |
| | | | | | | | | | | | | | | | | |
| <div>VOC PurityBenzene99.997% Toluene100.000% o-Xylene99.940%</div> | | | | | | <div>ethylbenzene0.003% para-xylene0.003% meta-xyfene0.030%</div> | | <div>99.997% 100.000% 99.940%</div> | | <div>0.003% 0.003% 0.030%</div> | | | | | | |
| | | | | | | | | | | | | | | | | |
| Mass Calculations | | | | | | Mass Organic | | mg air displaced | | mg air displaced | | | | | | |
| Compound | Tube Full, mg | Tube Empty, mg | Rough wt. mg | Tube Mass Loss Sealing, mg | Uncorrected for Bouancy, mg | Vol of tube ul | Organic Density | Vol of liq ul | by org liquid 1.2 x mg liq | Vapor Press mmHg | by org vapor PV=nrt | Total mg air displaced | Mass Organic | Purity | Transfer Efficiency | Final Mass Organic, mg |
| Benzene | 37.6695 | 34.0562 | 3.6113 | 0.0008 | 3.6121 | 19.45 | 0.8788 | 4.107 | 0.004930 | 40.7 | 0.00098 | 0.00591 | 3.61798 | 99.997% | 1.00 | 3.6179 |
| Toluene | 38.0469 | 33.9499 | 4.0990 | 0.0008 | 4.0998 | 19.38 | 0.8668 | 4.729 | 0.005677 | 12.0 | 0.00028 | 0.00595 | 4.10578 | 100.000% | 1.00 | 4.1058 |
| Ethylbenzene | 33.3128 | 28.8316 | 4.4813 | 0.0008 | 4.4821 | 19.02 | 0.8668 | 5.171 | 0.006208 | 3.9 | 0.00009 | 0.00629 | 4.48834 | 99.997% | 1.00 | 4.4882 |
| para-Xylene | 42.3086 | 37.6002 | 4.7084 | 0.0008 | 4.7092 | 24.01 | 0.8610 | 5.469 | 0.006567 | 3.6 | 0.00011 | 0.00667 | 4.71588 | 100.000% | 1.00 | 4.7159 |
| meta-Xylene | 41.9260 | 37.2648 | 4.6612 | 0.0008 | 4.6620 | 23.99 | 0.8641 | 5.395 | 0.006477 | 3.4 | 0.00010 | 0.00658 | 4.66858 | 99.940% | 1.00 | 4.6658 |
| ortho-Xylene | 31.4845 | 26.8234 | 4.6611 | 0.0008 | 4.6619 | 15.27 | 0.8802 | 5.296 | 0.006359 | 2.7 | 0.00004 | 0.00640 | 4.66832 | 99.940% | 1.00 | 4.6655 |
| | | | | | | | | | | | | | | | | |
| Uncertainty Calculations | | | | | | Mass Organic | | mg air displaced | | mg air displaced | | | | | | |
| Compound | Tube Full, mg | Tube Empty, mg | Rough wt. mg | Tube Mass Loss Sealing, mg | Uncorrected for Bouancy, mg | Vol of tube ul | Organic Density | Vol of liq ul | by org liquid 1.2 x mg liq | Vapor Press mmHg | by org vapor PV=nrt | Total mg air displaced | Mass Organic | Purity Uncert | Transfer Uncertainty | Uncert Mass Organic, mg |
| Benzene | 0.0017 | 0.0013 | 0.0022 | 0.0005 | 0.0022 | 0.12 | 0.0051 | 0.024 | 0.000030 | 23.5 | 0.00057 | 0.00057 | 0.0023 | 0.003% | 0.00% | 0.0023 |
| Toluene | 0.0008 | 0.0023 | 0.0024 | 0.0005 | 0.0025 | 0.12 | 0.0050 | 0.027 | 0.000035 | 6.9 | 0.00016 | 0.00016 | 0.0025 | 0.003% | 0.00% | 0.0025 |
| Ethylbenzene | 0.0020 | 0.0013 | 0.0024 | 0.0005 | 0.0025 | 0.12 | 0.0050 | 0.030 | 0.000038 | 2.3 | 0.00005 | 0.00006 | 0.0025 | 0.003% | 0.00% | 0.0025 |
| para-Xylene | 0.0017 | 0.0019 | 0.0026 | 0.0005 | 0.0027 | 0.26 | 0.0050 | 0.032 | 0.000040 | 2.1 | 0.00006 | 0.00007 | 0.0027 | 0.003% | 0.00% | 0.0027 |
| meta-Xylene | 0.0008 | 0.0022 | 0.0023 | 0.0005 | 0.0024 | 0.25 | 0.0050 | 0.031 | 0.000040 | 2.0 | 0.00006 | 0.00007 | 0.0024 | 0.030% | 0.00% | 0.0028 |
| ortho-Xylene | 0.0007 | 0.0021 | 0.0022 | 0.0005 | 0.0022 | 0.21 | 0.0051 | 0.031 | 0.000038 | 1.6 | 0.00002 | 0.00005 | 0.0022 | 0.030% | 0.00% | 0.0026 |
| | | | | | | | | | | | | | | | | |
| Compound | mgrams | | | MW | moles | Concentration | Intermediate Uncert | N2 Purity Uncert | Conc, ppb | 95% CI | | Summary of Uncertainties | | | | Mass Factor |
| | | | | | | | | | | | | Mass Diff | S | Dorg | Dvapor | |
| Benzene | 3.6179 | 0.0023 | | 78.1118 | 4.63E-05 | 0.000000283 | 0.19 | 0.05 | 282.99 | 0.39 | Benzene | 0.0022 | 0.0005 | 0.0000 | 0.0006 | 7.8909E-07 |
| Toluene | 4.1058 | 0.0025 | | 92.1384 | 4.46E-05 | 0.000000272 | 0.18 | 0.05 | 272.27 | 0.37 | Toluene | 0.0024 | 0.0005 | 0.0000 | 0.0002 | 8.951E-07 |
| Ethylbenzene | 4.4882 | 0.0025 | | 106.1650 | 4.23E-05 | 0.000000258 | 0.15 | 0.05 | 258.31 | 0.32 | Ethylbenzene | 0.0024 | 0.0005 | 0.0000 | 0.0000 | 9.7892E-07 |
| para-Xylene | 4.7159 | 0.0027 | | 106.1650 | 4.44E-05 | 0.000000271 | 0.16 | 0.05 | 271.41 | 0.34 | para-Xylene | 0.0026 | 0.0005 | 0.0000 | 0.0001 | 1.0286E-06 |
| meta-Xylene | 4.6658</ | | | | | | | | | | | | | | | |

| CC412027 | gms from | parent | | | | | Intermediate | Nitrogen | | | |
|---------------|-----------------|-----------|------------|-------------|-------------|----------------|--------------|----------|-----------|--------|--------------|
| Compound | parent CC460929 | wt factor | grams | MW | moles | Concentration | Uncert | Purity | | | |
| | | | | | | | | Uncert | Conc, ppb | 95% CI | |
| Benzene | 73.9000 | 7.892E-07 | 5.8322E-05 | 78.12 | 7.46569E-07 | 0.000000005473 | 0.015 | 0.01 | 5.473 | 0.037 | Benzene |
| Toluene | 73.9000 | 8.956E-07 | 6.6184E-05 | 92.15 | 7.18215E-07 | 0.000000005265 | 0.014 | 0.01 | 5.265 | 0.035 | Toluene |
| Ethylbenzene | 73.9000 | 9.789E-07 | 7.2343E-05 | 106.16 | 6.81451E-07 | 0.000000004996 | 0.014 | 0.01 | 4.996 | 0.034 | Ethylbenzene |
| para-Xylene | 73.9000 | 1.029E-06 | 7.6012E-05 | 106.17 | 7.15947E-07 | 0.000000005249 | 0.014 | 0.01 | 5.249 | 0.034 | para-Xylene |
| meta-Xylene | 73.9000 | 1.018E-06 | 7.5205E-05 | 106.17 | 7.08346E-07 | 0.000000005193 | 0.013 | 0.01 | 5.193 | 0.033 | meta-Xylene |
| o-Xylene | 73.9000 | 1.018E-06 | 7.5196E-05 | 106.17 | 7.08257E-07 | 0.000000005192 | 0.014 | 0.01 | 5.192 | 0.034 | ortho-Xylene |
| | 73.90 | 0.10 | | | | | | | | | |
| | grams | | MW | moles | uncertainty | | | | | | |
| Nitrogen | 3821.25 | 1 | 28.0134 | 136.4079333 | 0.0357 | | | | | | |
| Total moles = | 136.4079376 | | | 136.4079376 | 0.0357 | | | | | | |

The following table shows the uncertainties considered in the calculations for the total standard uncertainty ($k = 1$) and the expanded uncertainty at the approximate 95 % confidence interval. They include the uncertainties in the gravimetric preparation of the mixture, the stability and the verification. The total standard uncertainty (u) is calculated by taking the square root of the sum of the squares for those three uncertainty components.

| | -----k = 1----- | | | | | | |
|----------------------|-----------------|--------------------------|--------------|-----------------------|--------------------|--------------------|-----------------|
| BTEX | Gravimetric | Stability | Verification | Total Standard | Total Std uncert | Expanded | U (95 %) CI |
| Component | Uncertainty | Uncertainty ^a | Uncertainty | Uncertainty ($k=1$) | nmol/mol ($k=1$) | Uncertainty (95 %) | nmol/mol |
| Benzene | 0.34% | 0.55% | 0.42% | 0.77% | 0.042 | 1.54% | 0.084 |
| Toluene | 0.33% | 0.54% | 0.21% | 0.67% | 0.035 | 1.34% | 0.070 |
| Ethylbenzene | 0.34% | 0.58% | 0.94% | 1.16% | 0.058 | 2.31% | 0.115 |
| <i>para</i> -Xylene | 0.33% | 0.59% | 1.07% | 1.26% | 0.066 | 2.53% | 0.133 |
| <i>meta</i> -Xylene | 0.32% | 0.52% | 1.49% | 1.61% | 0.084 | 3.22% | 0.167 |
| <i>ortho</i> -Xylene | 0.33% | 0.56% | 1.45% | 1.59% | 0.082 | 3.18% | 0.165 |

4. COMPLEMENTARY INFORMATION.

Please include information on:

- 1) a purity table with uncertainties for the benzene, toluene, ethylbenzene, meta-*para*-*ortho*-xylenes, and balance nitrogen used to prepare your standard mixture

| VOC Purity | Benzene | 99.997% | 0.003% | ethylbenzene | 99.997% | 0.003% |
|------------|------------------|----------|--------|---------------------|----------|--------|
| | Toluene | 100.000% | 0.003% | <i>para</i> -xylene | 100.000% | 0.003% |
| | <i>O</i> -Xylene | 99.940% | 0.030% | <i>meta</i> -xylene | 99.940% | 0.030% |

Balance nitrogen had less than (0.001 ± 0.001) nmol/mol present for each of the BTEX compounds.

- 2) outline of dilution series to produce final standard mixture

A parent mixture, CC460929, was prepared at nominal 250 nmol/mol in nitrogen and verified. An aliquot of this mixture was then transferred to a new cylinder, CC412027, and diluted with nitrogen to reach nominal 5 nmol/mol.

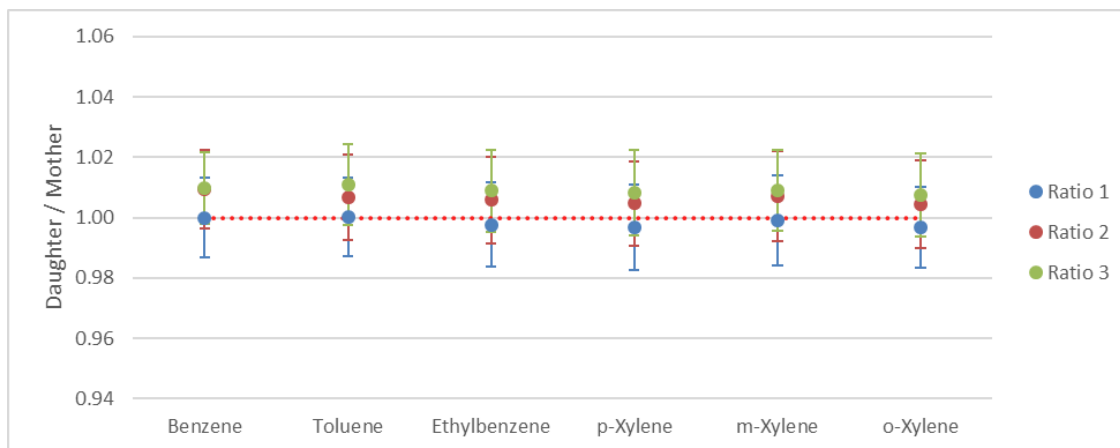
- 3) outline/discussion of the verification procedure applied to final mixture

Verification was performed by comparing the NIST BTEX sample CC412027 to three existing primary standards (PSMs). The concentration of each compound was determined by direct calculation to each PSM using the peak area responses. The average concentration was calculated, the difference between the gravimetric value of the BTEX sample and the analytical average value was determined. The difference was used as the verification uncertainty.

- 4) outline of any stability testing of mixture

Daughter/Mother testing was done on the cylinder used to prepare the NIST sample, cylinder # CC412027, for this comparison. Two hundred psi from BTEX PSM, cylinder # CC460929 (mother), at nominal 250 nmol/mol was transferred to the evacuated cylinder CC412027 (daughter). The daughter was compared to the mother by GC/FID/preconcentration. The peak area response for the daughter was divided by

that of the mother to determine a ratio. Three ratios were collected for each BTEX component in CC412027 with each ratio being an average of three replicate injects. The figure below shows those ratios plotted.



The following table gives the three ratios, the average ratio, standard deviation, and the uncertainty in %, which is the standard deviation/average ratio, for each BTEX component.

| | Benzene | Toluene | hylbenzer | <i>p</i> -Xylene | <i>m</i> -Xylene | <i>o</i> -Xylene |
|------------|---------|---------|-----------|------------------|------------------|------------------|
| | ratio | ratio | ratio | ratio | ratio | ratio |
| Ratio 1 | 1.0000 | 1.0002 | 0.9976 | 0.9967 | 0.9991 | 0.9968 |
| Ratio 2 | 1.0094 | 1.0068 | 1.0058 | 1.0047 | 1.0072 | 1.0045 |
| Ratio 3 | 1.0098 | 1.0110 | 1.0089 | 1.0084 | 1.0090 | 1.0076 |
| Average | 1.0064 | 1.0060 | 1.0041 | 1.0033 | 1.0051 | 1.0030 |
| Stdev | 0.0055 | 0.0055 | 0.0058 | 0.0059 | 0.0053 | 0.0056 |
| <i>u</i> % | 0.55% | 0.54% | 0.58% | 0.59% | 0.52% | 0.56% |

The *u* % of the ratio was added to the gravimetric uncertainty as described in section 3 on uncertainty budget.

5) cylinder pressure

The pressure in the cylinder 1500 psi at submission for the comparison.

Optional

You may provide additional data, such as raw measurement data, information on your measurement procedure, etc.

Authors: George C. Rhoderick, Cassie A. Goodman, Christina E. Cecelski, Joseph T. Hodges

B.4 NMISA

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : NMISA

Laboratory code :

Cylinder number : D62 6613

NOMINAL COMPOSITION: 5 nmol/mol

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty gravimetric ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|----------------|---------------|---|---|--|
| Benzene | 15 April 2018 | 5,017 | 0,063 | 0,23 |
| Toluene | | 5,019 | 0,054 | 0,22 |
| Ethylbenzene | | 5,021 | 0,046 | 0,21 |
| meta-Xylene | | 5,033 | 0,047 | 0,25 |
| para-Xylene | | 5,021 | 0,046 | 0,31 |
| ortho-Xylene | | 5,023 | 0,047 | 0,23 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES.

High pure liquids of at least 99.95% of benzene, ethylbenzene, p, o, m-xylene and toluene were added sequentially in one vial. The mass of each component was weighed in a syringe before addition to the vial. The total mass of all the components was calculated. The required mass of a solution containing all the components was then transferred into a pre-evacuated cylinder using the syringe. High pure nitrogen of 99.99% was used as a diluent gas. The gas mixtures of 10 $\mu\text{mol/mol}$ mole fractions were prepared. This was followed by a four-step dilution to prepare a mixture of 5 nmol/mol mole fraction.

3. UNCERTAINTY BUDGET.

Please provide a complete uncertainty budget.

Considered uncertainty budget for the comparison sample is as follows;

$$u(\text{combined}) = \sqrt{u_{(\text{gravimetric})}^2 + u_{(\text{verification})}^2 + u_{(\text{stability})}^2}$$

Table 1: Uncertainty budget associated with BTEX mole fraction

| Uncertainty Budget | | | | | | |
|-------------------------------|----------------------------|---------|--------------|----------|----------|----------|
| Uncertainty contribution | Benzene | Toluene | Ethylbenzene | m-xylene | p-xylene | o-xylene |
| | All values in relative (%) | | | | | |
| Gravimetric (u) | 1.3 | 1.1 | 0.93 | 0.93 | 0.94 | 0.94 |
| Verification (u) | 1.6 | 1.5 | 1.5 | 2.8 | 2.0 | 1.7 |
| Stability (u) | 1.2 | 1.1 | 1.1 | 0.94 | 1.1 | 1.1 |
| Combined Standard Uncertainty | 2.4 | 2.2 | 2.1 | 3.1 | 2.5 | 2.3 |
| Expanded Uncertainty | 4.8 | 4.4 | 4.2 | 6.2 | 5.0 | 4.6 |

4. COMPLEMENTARY INFORMATION.

Please include information on:

- 1) a purity table with uncertainties for the benzene, toluene, ethylbenzene, meta-para-ortho-xylenes, and balance nitrogen used to prepare your standard mixture

The final 5 nmol/mol comparison cylinder was prepared from 100 nmol/mol gas mixture (cylinder (D62 6623)). The purity table for the pre-mixture and the balance nitrogen will be shown below

Table 2: Purity table for D62 6623 (Pre-mixture for final comparison cylinder)

| D62 6623 | | |
|-------------------------------|----------------|----------|
| Component | mol/mol | |
| N ₂ | 9.99E-01 | 2.57E-06 |
| Ar | 5.39E-05 | 2.57E-06 |
| m-xylene | 1.00E-07 | 9.44E-10 |
| o-xylene | 1.00E-07 | 9.42E-10 |
| p-xylene | 1.00E-07 | 9.28E-10 |
| Ethylbenzene | 1.00E-07 | 9.28E-10 |
| Toluene | 1.00E-07 | 1.07E-09 |
| Benzene | 9.99E-08 | 1.26E-09 |
| H ₂ O | 1.00E-08 | 5.46E-09 |
| CO ₂ | 9.75E-09 | 1.07E-09 |
| H ₂ | 9.00E-09 | 4.94E-09 |
| CO | 6.85E-09 | 3.76E-09 |
| C ₂ H ₆ | 6.30E-09 | 3.46E-09 |
| O ₂ | 5.00E-09 | 2.75E-09 |
| CH ₄ | 4.29E-09 | 2.36E-09 |

Table 3: Purity table for balance nitrogen

| Balance nitrogen | | |
|-------------------------------|----------------|---------|
| Component | mol/mol | |
| Ar | 5.39E-05 | 2.7E-06 |
| C ₂ H ₆ | 6.3E-09 | 3.6E-09 |
| CH ₄ | 4.3E-09 | 2.5E-09 |
| CO | 6.9E-09 | 4E-09 |
| CO ₂ | 9.8E-09 | 1.1E-09 |
| H ₂ | 9.00E-09 | 5.2E-09 |
| H ₂ O | 1.00E-08 | 5.8E-09 |
| O ₂ | 5.00E-09 | 2.9E-09 |
| N ₂ | 9.999E-01 | 2.7E-06 |

2) outline of dilution series to produce final standard mixture

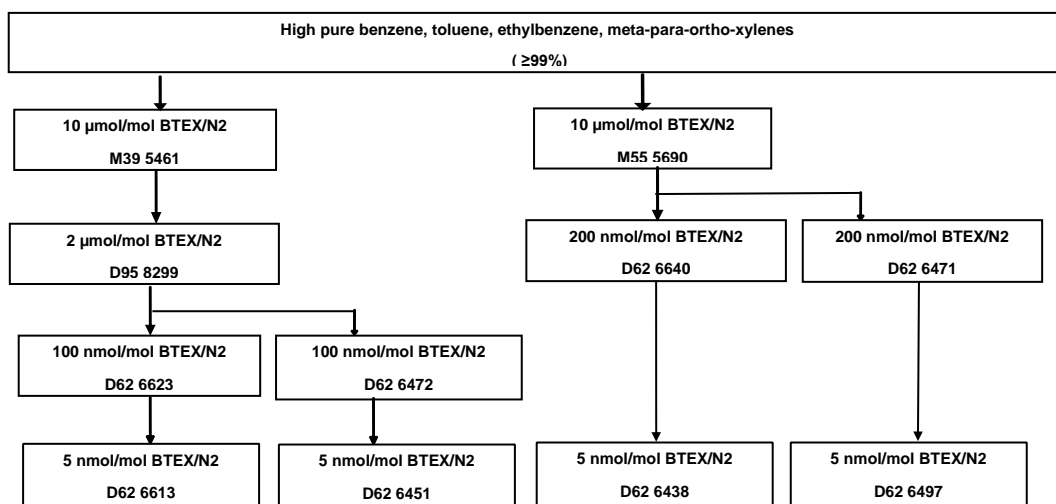


Figure 1: Production diagram of 5 nmol/mol of BTEX

3) outline/discussion of the verification procedure applied to final mixture

The analysis of the mixture was performed using the Entech 7200 cryogenic pre-concentrator coupled on the Agilent 7890B gas chromatograph. The Entech cryogenic pre-concentrator is configured with three modules, module one is for the removal of water and carbon dioxide, module two is the trapping of the btex and module three is the cryo-focuser prior to injection into the gas chromatography.

The Entech pre-concentrator conditions were as follows;

Table 4: Cryogenic pre-concentration steps

| | |
|-------------------------|---------------------------------|
| Module 1 | Empty trap operated at -40°C |
| Module 2 | Tenax trap operated at -40°C |
| Module 3 | Cryo focuser operated at -150°C |
| Volume pre-concentrated | 200ml |

The gas chromatograph conditions were as follows;

Table 5: GC conditions

| | |
|------------------|--|
| Carrier gas | Nitrogen |
| Column type | 60 m x 0.32 mm x 0.5 mm AT_WAX (heliflex) |
| Column flow | 1,2 ml/min |
| Oven programming | Initial at 40 °C hold for 3min, ramp to 60 °C at 4 °C/min, hold for 5 min and 120 °C at 10 °C/min, hold for 3min |
| FID conditions | 275°C |
| Total run time | 21,5 min |

4) outline of any stability testing of mixture

The mixture was prepared and verified after preparation, short-term stability of the comparison mixture was done. No long -term stability was performed for the comparison mixture prior to shipping

5) cylinder pressure

The cylinder left the laboratory at 132 bar.

Optional

You may provide additional data, such as raw measurement data, information on your measurement procedure, etc.

B.5 NPL

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : National Physical Laboratory
Laboratory code :

Cylinder number : D618315

NOMINAL COMPOSITION: 5×10^{-9} nmol/mol

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty ($k=2$) (nmol/mol) |
|----------------------|------------|---|---|---|
| Benzene | 09/04/2018 | 5.00 | 0.05 | 0.10 |
| Toluene | | 5.02 | 0.05 | 0.10 |
| Ethylbenzene | | 5.02 | 0.05 | 0.10 |
| <i>meta</i> -Xylene | | 5.02 | 0.05 | 0.10 |
| <i>para</i> -Xylene | | 5.02 | 0.05 | 0.10 |
| <i>ortho</i> -Xylene | | 5.03 | 0.05 | 0.10 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES

Six binary mixtures were gravimetrically prepared for each component from pure liquids (Sigma Aldrich and Acros Organics, see table below for suppliers and purity information obtained from the Certificate of Analysis) following ISO 6142. Each binary mixture was prepared at a nominal amount fraction of 100 $\mu\text{mol/mol}$ in a balance of nitrogen (BIP+, Air Products). An aliquot from each of the six mixtures was added into a single cylinder to make a multicomponent BTEX mixture in a balance of nitrogen (BIP+, Air Products). This multicomponent mixture was diluted further using nitrogen (BIP+, Air Products) to achieve the nominal composition of 5 nmol/mol. For the comparison mixture the nitrogen was flowed through an additional BIP purifier in order to remove hydrocarbons and other impurities. All mixtures were prepared in Quantum/Experis treated 10 L aluminium cylinder (Air Products). The transfer method for the binary mixtures used a vessel fitted with a three way tap to transfer the liquid into the cylinder. The vessel is evacuated and filled with the target mass of liquid. The vessel is weighed before and after the addition to the cylinder against an empty tare vessel of similar dimensions. All subsequent dilutions were performed using a short transfer line made from Sulfinert treated 1/16" tubing fitted with NPL designed minimum dead volume connections. These connections fit directly into a specially machined cylinder valve eliminating the need for regulators or cylinder stems thereby minimizing adsorption effects.

| Component | Supplier | Product Code | Lot Number | Purity of Component (%) |
|--------------|---------------|--------------|------------|-------------------------|
| Benzene | Sigma Aldrich | 401765 | SHBH7208 | 99.99 |
| Toluene | Sigma Aldrich | 244511 | STBG7960 | 99.96 |
| Ethylbenzene | Sigma Aldrich | 296848 | SHBH3700V | 99.82 |

| | | | | |
|----------------------|----------------|-----------|----------|-------|
| <i>meta</i> -Xylene | Sigma Aldrich | 296325 | STBG9458 | 99.80 |
| <i>para</i> -Xylene | Sigma Aldrich | 296333 | SHBH7708 | 99.60 |
| <i>ortho</i> -Xylene | Acros Organics | 443021000 | 1707384 | 99.25 |

Supplier and purity information

3. UNCERTAINTY BUDGET

The estimated uncertainty for the measurement contains the following components:

- Purity analysis of the BTEX components
- Gravimetric preparation (weighing and automatic weight uncertainties)
- Analytical validation

| Component | Relative Uncertainty (%) | | |
|----------------------|--------------------------|----------------------|-----------------|
| | Preparation ($k=1$) | Validation ($k=1$) | Total ($k=2$) |
| Benzene | 0.07 | 0.99 | 1.98 |
| Toluene | 0.06 | 0.99 | 1.98 |
| Ethylbenzene | 0.06 | 0.99 | 1.98 |
| <i>meta</i> -Xylene | 0.07 | 0.98 | 1.96 |
| <i>para</i> -Xylene | 0.06 | 0.99 | 1.98 |
| <i>ortho</i> -Xylene | 0.07 | 0.98 | 1.96 |

Uncertainty contributors. To calculate the combined uncertainty, the uncertainties were combined as the square root of the sum of squares. The reported uncertainty of the result is based on standard uncertainties multiplied by a coverage factor of $k=2$, providing a level of confidence of approximately 95%.

4. COMPLEMENTARY INFORMATION

Please include information on:

1) A purity table with uncertainties for the benzene, toluene, ethylbenzene, meta-para-ortho-xylenes, and balance nitrogen used to prepare your standard mixture

Purity analysis was conducted on the binary mixtures using a Varian CP-3800 Gas Chromatograph fitted with a 250 μ L injection loop. Column: 60 m x 0.32 μ m, $df = 1$ μ m RTX-Wax (Restek Corporation). No contamination peaks were observed for benzene so the purity from the Certificate of Analysis (Sigma-Aldrich, product code 401765, lot number SHBH7208) was used, see supplier and purity information table in section 2. Purity analysis of the nitrogen was conducted via a gas chromatograph fitted with a pulsed discharge helium ionisation detector (PDHID) and a cavity ring down spectrometer.

| Component | Purity of Component (μ mol/mol) | Standard uncertainty ($k=1$) (μ mol/mol) |
|-------------------------------|--------------------------------------|---|
| Toluene | 999425.78 | 78.20 |
| C _x H _y | 502.39 | 76.08 |
| Ethylbenzene | 71.83 | 18.10 |

Toluene purity table

| Component | Purity of Component (μ mol/mol) | Standard uncertainty ($k=1$) (μ mol/mol) |
|-----------|--------------------------------------|---|
|-----------|--------------------------------------|---|

| | | |
|-------------------------------|-----------|--------|
| Ethylbenzene | 998583.25 | 137.44 |
| Benzene | 1219.81 | 126.86 |
| Toluene | 116.61 | 40.17 |
| C _x H _y | 80.32 | 34.37 |

Ethylbenzene purity table

| Component | Purity of Component (μmol/mol) | Standard uncertainty (<i>k</i> =1) (μmol/mol) |
|-------------------------------|--------------------------------|--|
| <i>meta</i> -Xylene | 997007.93 | 204.50 |
| <i>ortho</i> -Xylene | 1563.55 | 156.35 |
| <i>para</i> -Xylene | 1234.90 | 123.49 |
| C _x H _y | 132.56 | 42.56 |
| Toluene | 61.06 | 17.67 |

meta-Xylene purity table

| Component | Purity of Component (μmol/mol) | Standard uncertainty (<i>k</i> =1) (μmol/mol) |
|-------------------------------|--------------------------------|--|
| <i>para</i> -Xylene | 996313.53 | 268.05 |
| Ethylbenzene | 1166.28 | 116.63 |
| <i>meta</i> -Xylene | 1122.24 | 179.88 |
| C _x H _y | 703.66 | 168.67 |
| Toluene | 435.87 | 123.33 |
| <i>ortho</i> -Xylene | 258.42 | 25.84 |

para-Xylene purity table

| Component | Purity of Component (μmol/mol) | Standard uncertainty (<i>k</i> =1) (μmol/mol) |
|-------------------------------|--------------------------------|--|
| <i>ortho</i> -Xylene | 989208.07 | 573.56 |
| <i>para</i> -Xylene | 4462.48 | 446.25 |
| C _x H _y | 3607.49 | 640.43 |
| <i>meta</i> -Xylene | 2721.96 | 272.20 |

ortho-Xylene purity table

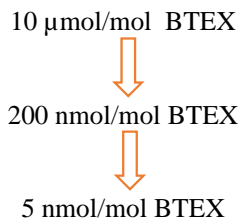
| Component | Purity of Component (μmol/mol) | Standard uncertainty (<i>k</i> =1) (μmol/mol) |
|-----------------|--------------------------------|--|
| Nitrogen | 999996.55 | 0.66 |
| Argon | 3.31 | 0.66 |
| Carbon Dioxide | 0.06 | 0.02 |
| Oxygen | 0.05 | 0.01 |
| Water | 0.01 | 0.01 |
| Carbon Monoxide | < 0.01 | 0.01 |
| Methane | < 0.01 | 0.01 |

Nitrogen purity table

2) Dilution Series

100 μmol/mol binaries of each component





3) Discussion of the verification procedure applied to final mixture

Analysed using gas chromatography against a newly prepared 5 nmol/mol BTEX reference standard (cylinder D618321). Four individual measurements were taken under repeatable conditions. An average of the calculated amount fraction has been reported and the calculated uncertainties from the four measurements were combined to give the final result. The reference standard was validated through comparison against 5 additional 'in-house' BTEX mixtures with similar amount fractions (4 – 10 nmol/mol) and two 30 component ozone precursor mixtures at nominally 4 nmol/mol from the Euramet 886 comparison.

4) Outline of any stability testing of mixture

No stability testing was carried out on this mixture

5) Cylinder pressure

100 bar (10 MPa)

Optional

You may provide additional data, such as raw measurement data and/or information on your measurement procedure.

Measurement Procedure

Analysis was conducted using a Varian CP-3800 gas chromatograph with a flame ionisation detector. Sample pre concentration of the 5 nmol/mol mixtures was conducted by flowing the sample through a pre concentration trap for a period of two minutes at a flow rate of 35 ml/min. The trap contains glass beads which are cooled to -100°C during sampling then heated in two steps, initially to 150°C and held for 35 seconds then to 190°C and held for 5 mins. The column used was a 60 m x 0.32 um, df = 1 um RTX-Wax (Restek corporation). The oven had an initial temperature of 30°C and was held at this temperature for six minutes. It was then heated at a rate of 5°C per minute to 130°C giving a total run time of 26 minutes. Helium was used as the carrier gas with a pressure of 17.8 psi and a flow of 2 ml/min. The FID was kept at a constant temperature of 280°C throughout using nitrogen as the makeup gas at a flow of 30 ml/min.

Sample Handling

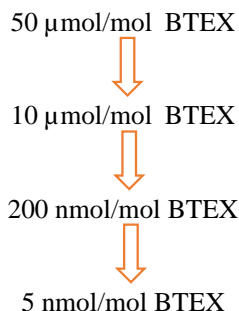
The sample line from cylinder to GC was set up using connectors and flow controllers designed at NPL to minimise dead volume. The tubing used was 1/16" and all tubing, connectors, flow controllers and unions were SilcoNert treated to minimise adsorption affects.

Elution order

Elution orders were established by measuring each of the six 100 µmol/mol binaries using the same oven and carrier gas flow conditions as above but injecting via a 250 µL sample loop rather than a sample pre concentration trap.

Reference Standard

The reference standard (cylinder D618321) used for analysing the comparison mixture was prepared using the same pure chemicals and nitrogen as the comparison mixture. The mixture was prepared by a different operator on a different day to the comparison mixture. The dilution series was as follows;



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B.6 VNIIM

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : D.I. Mendeleyev Institute for Metrology
Laboratory code : VNIIM

Cylinder number : № 5603810

NOMINAL COMPOSITION: 5×10^{-9} (nmol/mol)

Authors: L.A. Konopelko, Y.A. Kustikov, A.V. Kolobova, A.Y. Klimov, O.V. Efremova

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|----------------|------|---|---|--|
| Benzene | | 4.97 | 0.0556 | 0.11 |
| Toluene | | 5.03 | 0.0595 | 0.12 |
| Ethylbenzene | | 5.10 | 0.0996 | 0.20 |
| meta-Xylene | | 4.92 | 0.101 | 0.20 |
| para-Xylene | | 5.08 | 0.102 | 0.20 |
| ortho-Xylene | | 4.96 | 0.101 | 0.20 |

2. BRIEF DESCRIPTION YOUR PREPARATION PROCEDURES

Preparation of final mixtures was carried out from pure substances by gravimetric method in accordance with ISO 6142 from pure substances in 3 stages.

3. UNCERTAINTY BUDGET.

3.1 Benzene

| Uncertainty source X_i | | Estimate x_i | Evaluation type (A or B) | Distribution | Contribution $u_i(y)$ nmol/mol |
|--|----------------------------------|-------------------------------|--------------------------|--------------|--------------------------------|
| Purity of Nitrogen | | 999998.67 $\mu\text{mol/mol}$ | B | Normal | $3.6 \cdot 10^{-7}$ |
| Purity of Benzene | | 99.99 % | B | Normal | $6.1 \cdot 10^{-6}$ |
| Impurity of benzene in the other BTEX components | | - | B | Normal | $1.3 \cdot 10^{-4}$ |
| *Weighing 1 stage premixture (≈ 20 ppm) | benzene | 0.03199700 g | A,B | Normal | $4.6 \cdot 10^{-3}$ |
| | Other BTEX components summary | - | A,B | Normal | |
| | N ₂ | 573.34546102 g | A,B | Normal | |

| | | | | | |
|--|----------------|----------------|-----|--------|-----------------------|
| *Weighing 2 stage premixture (300 nmol/mol ⁻¹) | 1 pre-mixture | 8.65898284 g | A,B | Normal | 1.4 *10 ⁻³ |
| | N ₂ | 565.28819039 g | A,B | Normal | |
| *Weighing final mixture | 2 pre-mixture | 11.12334016 g | A,B | Normal | 9.5 *10 ⁻⁴ |
| | N ₂ | 666.09328308 g | A,B | Normal | |
| Verification | | 4.965 nmol/mol | A | Normal | 0.0554 |
| Combined standard uncertainty | | | | | 0.556 |
| Expanded uncertainty k=2 | | | | | 0.11 |

3.2 Toluene

| Uncertainty source X _i | | Estimate x _i | Evaluation type (A or B) | Distribution | Contribution u _i (y) nmol/mol |
|--|----------------------------------|----------------------------|--------------------------------|--------------|--|
| Purity of Nitrogen | | 999998.67 µmol/mol | B | Normal | 3.6*10 ⁻⁷ |
| Purity of Toluene | | 99.79 % | B | Normal | 1.3*10 ⁻⁴ |
| Impurity of toluene in the other BTEX components | | - | B | Normal | 2.5*10 ⁻⁵ |
| *Weighing 1 stage premixture (≈20 ppm) | Toluene | 0.03837400 g | A,B | Normal | 3.9 *10 ⁻³ |
| | Other BTEX components summary | - | A,B | Normal | |
| | N ₂ | 573.34546102 g | A,B | Normal | |
| *Weighing 2 stage premixture (300 nmol/mol ⁻¹) | 1 pre-mixture | 8.65898284 g | A,B | Normal | 1.4 *10 ⁻³ |
| | N ₂ | 565.28819039 g | A,B | Normal | |
| *Weighing final mixture | 2 pre-mixture | 11.12334016 g | A,B | Normal | 9.7 *10 ⁻⁴ |
| | N ₂ | 666.09328308 g | A,B | Normal | |
| Verification | | 5.034 nmol/mol | A | Normal | 0.0593 |
| Combined standard uncertainty | | | | | 0.0595 |
| Expanded uncertainty k=2 | | | | | 0.12 |

3.3 Ethylbenzene

| Uncertainty source X _i | | Estimate x _i | Evaluation type (A or B) | Distribution | Contribution u _i (y) nmol/mol |
|--|----------------------------------|----------------------------|--------------------------------|--------------|--|
| Purity of Nitrogen | | 999998.67 µmol/mol | B | Normal | 3.6*10 ⁻⁷ |
| Purity of Ethylbenzene | | 99.73 % | B | Normal | 1.1*10 ⁻⁴ |
| Impurity of Ethylbenzene in the other BTEX components | | - | B | Normal | 1.5*10 ⁻³ |
| *Weighing 1 stage premixture (≈20 ppm) | Ethylbenzene | 0.04469000 g | A,B | Normal | 3.4*10 ⁻³ |
| | Other BTEX components summary | - | A,B | Normal | |
| | N ₂ | 573.34546102 g | A,B | Normal | |
| *Weighing 2 stage premixture (300 nmol/mol ⁻¹) | 1 pre-mixture | 8.65898284 g | A,B | Normal | 1.4 *10 ⁻³ |
| | N ₂ | 565.28819039 g | A,B | Normal | |
| *Weighing final mixture | 2 pre-mixture | 11.12334016 g | A,B | Normal | 9.8 *10 ⁻⁴ |
| | N ₂ | 666.09328308 g | A,B | Normal | |

| | | | | |
|-------------------------------|----------------|---|--------|--------|
| Verification | 5.095 nmol/mol | A | Normal | 0.0995 |
| Combined standard uncertainty | | | | 0.0996 |
| Expanded uncertainty k=2 | | | | 0.20 |

3.4 meta-Xylene

| Uncertainty source X_i | | Estimate x_i | Evaluation type (A or B) | Distribution | Contribution $u_i(y)$ nmol/mol |
|--|----------------------------------|-------------------------------|--------------------------------|--------------|--------------------------------------|
| Purity of Nitrogen | | 999998.67 $\mu\text{mol/mol}$ | B | Normal | $3.5 \cdot 10^{-7}$ |
| Purity of meta-Xylene | | 99.66 % | B | Normal | $1.7 \cdot 10^{-4}$ |
| Impurity of meta-Xylene in the other BTEX components | | - | B | Normal | $5.3 \cdot 10^{-5}$ |
| *Weighing 1 stage premixture (≈ 20 ppm) | meta-Xylene | 0.04322000 g | A,B | Normal | $3.4 \cdot 10^{-3}$ |
| | Other BTEX components summary | - | A,B | Normal | |
| | N ₂ | 573.34546102 g | A,B | Normal | |
| *Weighing 2 stage premixture (300 nmol/mol ⁻¹) | 1 pre-mixture | 8.65898284 g | A,B | Normal | $1.4 \cdot 10^{-3}$ |
| | N ₂ | 565.28819039 g | A,B | Normal | |
| *Weighing final mixture | 2 pre-mixture | 11.12334016 g | A,B | Normal | $9.4 \cdot 10^{-4}$ |
| | N ₂ | 666.09328308 g | A,B | Normal | |
| Verification | | 4.915 nmol/mol | A | Normal | 0.101 |
| Combined standard uncertainty | | | | | 0.101 |
| Expanded uncertainty k=2 | | | | | 0.20 |

3.5 para-Xylene

| Uncertainty source X_i | | Estimate x_i | Evaluation type (A or B) | Distribution | Contribution $u_i(y)$ nmol/mol |
|--|----------------------------------|-------------------------------|--------------------------------|--------------|--------------------------------------|
| Purity of Nitrogen | | 999998.67 $\mu\text{mol/mol}$ | B | Normal | $3.6 \cdot 10^{-7}$ |
| Purity of para-Xylene | | 99.73 % | B | Normal | $1.5 \cdot 10^{-3}$ |
| Impurity of para-Xylene in the other BTEX components | | - | B | Normal | $9.9 \cdot 10^{-5}$ |
| *Weighing 1 stage premixture (≈ 20 ppm) | para-Xylene | 0.04443000 g | A,B | Normal | $3.4 \cdot 10^{-3}$ |
| | Other BTEX components summary | - | A,B | Normal | |
| | N ₂ | 573.34546102 g | A,B | Normal | |
| *Weighing 2 stage premixture (300 nmol/mol ⁻¹) | 1 pre-mixture | 8.65898284 g | A,B | Normal | $1.4 \cdot 10^{-3}$ |
| | N ₂ | 565.28819039 g | A,B | Normal | |
| *Weighing final mixture | 2 pre-mixture | 11.12334016 g | A,B | Normal | $9.7 \cdot 10^{-4}$ |
| | N ₂ | 666.09328308 g | A,B | Normal | |
| Verification | | 5.080 nmol/mol | A | Normal | 0.102 |
| Combined standard uncertainty | | | | | 0.102 |
| Expanded uncertainty k=2 | | | | | 0.20 |

3.6 ortho -Xylene

| Uncertainty source X_i | | Estimate x_i | Evaluation type (A or B) | Distribution | Contribution $u_i(y)$ nmol/mol |
|--|----------------------------------|-------------------------------|--------------------------------|--------------|--------------------------------------|
| Purity of Nitrogen | | 999998.67 $\mu\text{mol/mol}$ | B | Normal | $3.6 \cdot 10^{-7}$ |
| Purity of ortho-Xylene | | 99.24 % | B | Normal | $4.1 \cdot 10^{-4}$ |
| Impurity of ortho-Xylene in the other BTEX components | | - | B | Normal | $1.4 \cdot 10^{-4}$ |
| *Weighing 1 stage premixture (≈ 20 ppm) | ortho -Xylene | 0.04373000 g | A,B | Normal | $3.4 \cdot 10^{-3}$ |
| | Other BTEX components summary | - | A,B | Normal | |
| | N ₂ | 573.34546102 g | A,B | Normal | |
| *Weighing 2 stage premixture (300 nmol/mol ⁻¹) | 1 pre-mixture | 8.65898284 g | A,B | Normal | $1.4 \cdot 10^{-3}$ |
| | N ₂ | 565.28819039 g | A,B | Normal | |
| *Weighing final mixture | 2 pre-mixture | 11.12334016 g | A,B | Normal | $9.5 \cdot 10^{-4}$ |
| | N ₂ | 666.09328308 g | A,B | Normal | |
| Verification | | 4.961 nmol/mol | A | Normal | 0.101 |
| Combined standard uncertainty | | | | | 0.101 |
| Expanded uncertainty k=2 | | | | | 0.20 |

*Uncertainty due to weighing includes constituents related to accuracy of balance, buoyancy effect resulting from change of cylinder volume during filling, mass pierces used, drift of balance, residual gas in cylinder.

4. COMPLEMENTARY INFORMATION

4.1 Purity tables

Benzene

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|------------------------------------|------------------|-----------------------------------|
| Benzene | 99.99 | — |
| Toluene | 0.00070 | 0.00004 |
| non BTEX hydrocarbons (as pentane) | 0.0080 | 0.0004 |

Toluene

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|------------------------------------|------------------|-----------------------------------|
| Toluene | 99.79 | — |
| Benzene | 0.00300 | 0.00015 |
| Ethylbenzene | 0.00300 | 0.00015 |
| para-Xylene | 0.00060 | 0.00003 |
| meta-Xylene | 0.00200 | 0.00010 |
| ortho -Xylene | 0.00090 | 0.00005 |
| non BTEX hydrocarbons (as pentane) | 0.20 | 0.010 |

Ethylbenzene

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|--------------|------------------|-----------------------------------|
| Ethylbenzene | 99.73 | — |

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|------------------------------------|------------------|-----------------------------------|
| Benzene | 0.150 | 0.008 |
| Toluene | 0.0300 | 0.0015 |
| meta-Xylene | 0.0120 | 0.0006 |
| ortho -Xylene | 0.00090 | 0.00005 |
| non BTEX hydrocarbons (as pentane) | 0.075 | 0.004 |

para-Xylene

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|------------------------------------|------------------|-----------------------------------|
| para-Xylene | 99.72 | — |
| Toluene | 0.0090 | 0.0005 |
| Ethylbenzene | 0.180 | 0.009 |
| meta-Xylene | 0.06 | 0.003 |
| ortho -Xylene | 0.024 | 0.0013 |
| non BTEX hydrocarbons (as pentane) | 0.00500 | 0.00025 |

meta -Xylene

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|------------------------------------|------------------|-----------------------------------|
| meta-Xylene | 99.66 | — |
| Benzene | 0.0009 | 0.00005 |
| Toluene | 0.008 | 0.0005 |
| Ethylbenzene | 0.0210 | 0.0010 |
| para-Xylene | 0.120 | 0.006 |
| ortho -Xylene | 0.170 | 0.009 |
| non BTEX hydrocarbons (as pentane) | 0.0220 | 0.0011 |

ortho -Xylene

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|------------------------------------|------------------|-----------------------------------|
| ortho -Xylene | 99.24 | — |
| Ethylbenzene | 0.0090 | 0.0005 |
| meta -Xylene | 0.0160 | 0.0008 |
| para -Xylene | 0.470 | 0.023 |
| non BTEX hydrocarbons (as pentane) | 0.27 | 0.014 |

Nitrogen

| Component | Mole fraction, % | Expanded uncertainty (k=2), % mol |
|------------------|------------------|-----------------------------------|
| Nitrogen | 999998.672 | 0.200 |
| Ar | 0.916 | 0.011 |
| CH ₄ | 0.0025 | 0.0014 |
| CO | 0.0025 | 0.0014 |
| CO ₂ | 0.0025 | 0.0014 |
| H ₂ | 0.0025 | 0.0014 |
| H ₂ O | 0.40 | 0.20 |
| O ₂ | 0.0015 | 0.0009 |

4.2 Dilution series to produce final standard mixture

Preparation of final mixtures was carried out from pure substances in accordance with ISO 6142 in 3 stages:

1-st stage – 3 mixtures BTEX/N₂ –level 20 µmol/mol;

2-nd stage –3 mixtures BTEX/N₂– level 300 nmol/mol;

3-nd stage –5 target mixtures BTEX/N₂ - 5 nmol/mol.

All the mixtures were prepared in Luxfer cylinders with Aculife III + IV coating (V= 5 L)

4.3 Verification procedure applied to final mixture

Verification for the final mixtures was carried out on Chromato-mass-spectrometer «Chromatec- crystal 5000» (Russia) by checking consistency between 3 similar prepared target mixtures.

2 verifications were performed (with 1 week interval), each including 10 measurements in repeatability conditions.

u_{ver} was within (1-2) % for different BTEX components.

Operating mode

| | |
|-------------------------|--|
| Chromatographic column | Restek Stabilwax Cat.№ 10623 (30m x 0,25mmID x 0,25µm) |
| Carrier gas | High purity Helium 99,9999% |
| Carrier gas flow rate | 2,5 ml/min |
| Split | 1:2 |
| Column oven temperature | 80°C |
| SIM | m/z=78 + 91 |
| Ionization energy | 70 eV |
| Sample volume | 0,1 ml |
| Analysis time | 2,7 min |

4.4 Stability testing of mixture

Short-term stability testing (within 1 week interval) did not show instability within the accuracy of the measurement method.

4.5 Cylinder (№ 5603810) pressure - 10.5 MPa.

Date: 24/07/2018

B.7 VSL

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : VSL

Laboratory code :

Cylinder number : VSL136606

NOMINAL COMPOSITION: 5×10^{-9} (nmol/mol; ppb)

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|----------------|------------|---|---|--|
| Benzene | 2018-04-03 | 5.008 | 0.050 | 0.100 |
| Toluene | 2018-04-03 | 5.023 | 0.050 | 0.100 |
| Ethylbenzene | 2018-04-03 | 5.100 | 0.076 | 0.153 |
| meta-Xylene | 2018-04-03 | 4.894 | 0.098 | 0.196 |
| para-Xylene | 2018-04-03 | 4.870 | 0.097 | 0.195 |
| ortho-Xylene | 2018-04-03 | 5.044 | 0.101 | 0.202 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES.

Gravimetric method, according to ISO 6142-1:2015.

The mixtures were obtained by serial dilution independently prepared parent mixtures, prepared by injection of a weighed liquid BTEX mixture into a stainless-steel transfer line heated and brought in the evacuated cylinder by means of a BIP nitrogen stream.

3. UNCERTAINTY BUDGET.

Please provide a complete uncertainty budget.

The uncertainty associated with the amount-of-substance fractions is determined in accordance with ISO 6142-1:2015 and ISO 19229:2015. The measurement model of ISO 6142-1 is used for this purpose. 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). An extra allowance is made for the consistency of the Primary Standard gas Mixtures used in the verification measurement (see below).

Complementary information.

Please include information on:

- 1) a purity table with uncertainties for the benzene, toluene, ethylbenzene, meta-para-ortho-xylenes, and balance nitrogen used to prepare your standard mixture
- a purity table with uncertainties for the benzene, toluene, ethylbenzene, meta-para-ortho-xylenes.

Table 1-- Purity table o-xylene

| Component | o-xylene | |
|------------------------|----------|----------|
| | x | u(x) |
| o-xylene | 0.990798 | 0.016909 |
| m-xylene | 0.000236 | 0.000133 |
| p-xylene | 0.002640 | 0.001893 |
| Ethylbenzene | 0.000166 | 0.000125 |
| Toluene | 0.000046 | 0.000003 |
| Benzene | | |
| Water | 0.000156 | 0.000000 |
| Hydrocarbons nos | 0.005959 | 0.016802 |
| 1,3,5-Trimethylbenzene | | |

Table 2 -- Purity table m-xylene

| Component | m-xylene | |
|------------------------|----------|----------|
| | x | u(x) |
| o-xylene | 0.001416 | 0.000271 |
| m-xylene | 0.997163 | 0.000321 |
| p-xylene | 0.000729 | 0.000067 |
| Ethylbenzene | 0.000126 | 0.000026 |
| Toluene | 0.000118 | 0.000026 |
| Benzene | | |
| Water | 0.000065 | 0.000001 |
| Hydrocarbons nos | 0.000381 | 0.000153 |
| 1,3,5-Trimethylbenzene | | |

Table 3 – Purity table p-xylene

| Component | p-xylene | |
|------------------------|----------|----------|
| | x | u(x) |
| o-xylene | 0.000198 | 0.000013 |
| m-xylene | | |
| p-xylene | 0.998012 | 0.000390 |
| ethylbenzene | 0.001171 | 0.000128 |
| toluene | 0.000200 | 0.000013 |
| benzene | | |
| Water | 0.000063 | 0.000000 |
| Hydrocarbons nos | 0.000356 | 0.000368 |
| 1,3,5-Trimethylbenzene | | |

Table 4 – Purity table of ethylbenzene

| Component | ethylbenzene | |
|------------------------|--------------|----------|
| | x | u(x) |
| o-xylene | | |
| m-xylene | | |
| p-xylene | | |
| ethylbenzene | 0.997132 | 0.001376 |
| toluene | 0.000311 | 0.000014 |
| benzene | 0.002239 | 0.001376 |
| water | 0.000095 | 0.000001 |
| Hydrocarbons nos | 0.000172 | 0.000019 |
| 1,3,5-Trimethylbenzene | 0.000051 | 0.000018 |

Table 5 -- Purity table of toluene

| Component | toluene | |
|------------------------|----------|----------|
| | x | u(x) |
| o-xylene | | |
| m-xylene | 0.000032 | 0.000013 |
| p-xylene | | |
| ethylbenzene | 0.000069 | 0.000031 |
| toluene | 0.999741 | 0.000034 |
| benzene | | |
| water | 0.000128 | 0.000000 |
| Hydrocarbons nos | 0.000030 | 0.000001 |
| 1,3,5-Trimethylbenzene | | |

Table 6 – Purity table of benzene

| Component | benzene | |
|------------------------|----------|----------|
| | x | u(x) |
| o-xylene | | |
| m-xylene | | |
| p-xylene | | |
| ethylbenzene | | |
| toluene | | |
| benzene | 0.999889 | 0.000033 |
| water | 0.000043 | 0.000000 |
| Hydrocarbons nos | 0.000067 | 0.000033 |
| 1,3,5-Trimethylbenzene | | |

Table 7 Purity table of liquid mixture (LM0062) for preparation of BTEX

| Component | Amount fraction (mol/mol) | standard uncertainty (mol/mol) |
|------------------------|---------------------------|--------------------------------|
| Hydrocarbons | 0.0011763 | 0.0028423 |
| Water | 0.0000923 | 0.0000003 |
| Benzene | 0.1670434 | 0.0006106 |
| Toluene | 0.1675711 | 0.0005535 |
| ortho-Xylene | 0.1682679 | 0.0014084 |
| Ethylbenzene | 0.1701164 | 0.0005797 |
| meta-Xylene | 0.1632663 | 0.0005407 |
| Para-Xylene | 0.1624576 | 0.0006451 |
| 1,3,5 Trimethylbenzene | 0.0000086 | 0.0000031 |

- a purity table with uncertainties for Nitrogen gas.

Table 8 – Purity table of nitrogen (APN26B)

| Component | Amount fraction (mol/mol) | standard uncertainty (mol/mol) |
|-----------------|---------------------------|--------------------------------|
| Argon | 0.000005000 | 0.000003000 |
| Methane | 0.000000008 | 0.000000005 |
| Carbon monoxide | 0.000000015 | 0.000000009 |
| Carbon dioxide | 0.000000010 | 0.000000006 |
| Hydrogen | 0.000000025 | 0.000000015 |
| Water | 0.000000010 | 0.000000006 |
| Nitrogen | 0.999994832 | 0.000006000 |
| Oxygen | 0.000000100 | 0.000000030 |

Table 9 – Purity table of the final mixture, including gravimetric uncertainties.

| Component | Amount fraction (mol/mol) | standard uncertainty (mol/mol) |
|-----------|---------------------------|--------------------------------|
| Argon | 0.0000050000409 | 0.0000027133437 |

| Component | Amount fraction (mol/mol) | standard uncertainty (mol/mol) |
|------------------------|---------------------------|-----------------------------------|
| Methane | 0.000000080000 | 0.000000045222 |
| Carbon monoxide | 0.000000150002 | 0.000000081400 |
| Carbon dioxide | 0.000000100001 | 0.000000054267 |
| Hydrocarbons | 0.000000000353 | 0.000000000852 |
| Hydrogen | 0.000000249993 | 0.000000135667 |
| Water | 0.000000100028 | 0.000000054267 |
| Nitrogen | 0.9999948019814 | 0.0000054266872 |
| Oxygen | 0.000000100008 | 0.000000271334 |
| Benzene | 0.000000050075 | 0.000000000197 |
| Toluene | 0.000000050233 | 0.000000000182 |
| ortho-Xylene | 0.000000050442 | 0.000000000358 |
| Ethylbenzene | 0.000000050996 | 0.000000000184 |
| meta-Xylene | 0.000000048943 | 0.000000000175 |
| para-Xylene | 0.000000048700 | 0.000000000194 |
| 1,3,5-Trimethylbenzene | 0.000000000003 | 0.000000000001 |

2) outline of dilution series to produce final standard mixture.

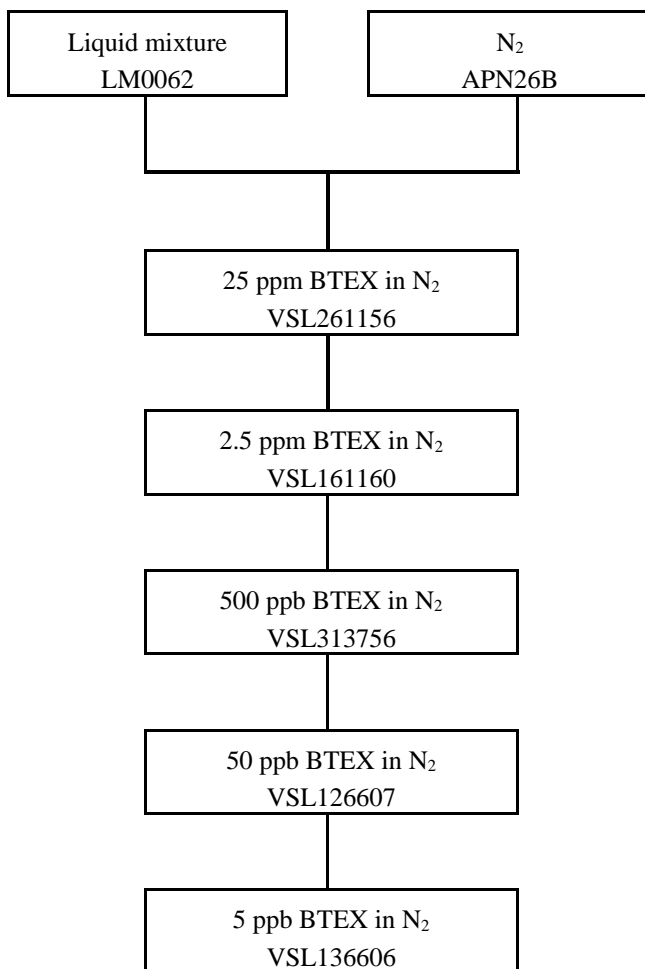


Figure 1 – Schematic overview of the dilution series

- 3) outline/discussion of the verification procedure applied to final mixture

Verification procedure applied to final mixture

The measurement cylinder was newly prepared from a newly mother mixture and analysed two times on different days in two different sets with 5 VSL calibration standards from 2 ppb - 10 ppb. In addition, also extra mixtures were measured for the verification of the calibration of the GC/FID. All mixtures were injected 7 times, of which the first 2 were discarded. The mean and standard deviation of the 5 remaining injections was then used for the calculations.

The data treatment was done in accordance with ISO 6143 [1]. The PSMs used are prepared and validated in accordance with ISO 6142-1 [2]. The data treatment is done with in-house developed software [3]. Based on an analysis of the response factors of the PSMs, an uncertainty contribution was developed to account for, e.g., adsorption effects in cylinders as well as in the transfer lines during preparation. These uncertainty contributions are given in table ...

The calibration curve obtained for each series of measurements was a weighted linear regression of y in x , where y is the mean response (peak area) of the five sub-measurements of the calibration standard and the x its concentration expressed in ppb ($\mu\text{mol/mol}$). The value for amount of fraction was obtained by reverse use of the calibration curve. The associated uncertainty was obtained using the law of propagation of uncertainty. All curves have been calculated using linear regression of first order.

Measurement procedure

The regulators used for connecting the gas mixtures are flushed several times the day before the measurements are taken. The cylinders are connected to the GC equipment with 1/16 inch silconert coated sampling lines and set to 1 bar(g) for analysis.

The equipment used was a Trace GC with a FID, equipped with a Series 2 UNITY-Air Server systems and CIA 8. The sample gas passes through the cold trap (Ozone Precursors/Freon), kept at -15°C , and it is trapped. The gas flow is controlled by a mass flow controller located in the CIA8. By fast heating of the trap, the concentrated sample is desorbed and injected on a capillary column in the GC.

The Unity software controls the sampling, focussing and injection in the GC part, while the Trace workstation (EZChrom software) is used for the GC data acquisition. After the measurement the data can be re-integrated.

Table 10 – Sampling and analytical conditions

| UNITY | | Trace –GC | |
|--|---|------------|--|
| Instrument | Thermal desorber (from Markes) Series 2 UNITY-Air Server systems and CIA 8 | Instrument | GC with FID |
| Cold trap | Ozone Precursors/Freon | Column | Left detector: CPWAX 52CB, part no. CP8853, (60m* 0.32mm*0.25 μm). |
| UNITY 2 Method for VOC (2-50ppb) | Method : VOC.mtd Flow Path Temp: 140 Minimum Carrier Pressure 5.0 GC Cycle Time : 40.5 min. Pre-Sampling Prepurge Time 1.0 min Cmb Flow: 20 ml/min Sampling Sample Time 15 minutes Post sampling Line Purge 1 minute Post Sampling Trap Purge 1 minute | Method | Deans1_v2.met Initial 40°C, Hold 2 minutes. Ramp with 7°C/min to 200°C and hold 11 minutes. |

| UNITY | | Trace –GC | |
|-------|---|-----------|--|
| | Trap Flow, Split Flow: 20 ml/min Trap Settings Pre-Trap Fire Purge : 1 min. Trap Low -15 °C Trap High 300 °C Trap Hold 5.0 min. | | |

The Verification of the results are discussed below.

Verification results

An initial evaluation of the verification results demonstrated that the uncertainty assigned to the PSMs was too small to account for, e.g., adsorption effects during preparation and sampling. An analysis was conducted of measurements performed in the past two years using the response factors. Based on this statistical analysis, the extra dispersion in the PSMs was identified. Table

Table 11: Excess relative standard deviation for the amount-of-substance fractions of the components in the PSMs

| | Benzene | Toluene | Ethylbenzene | p-Xylene | m-Xylene | o-Xylene |
|----------|----------------|----------------|---------------------|-----------------|-----------------|-----------------|
| pooled | 1.02% | 1.09% | 1.57% | 1.65% | 2.37% | 1.98% |
| pooled | 0.90% | 0.94% | 1.48% | 1.48% | 2.69% | 2.15% |
| assigned | 1.0% | 1.0% | 1.5% | 2.0% | 2.0% | 2.0% |

With the assigned uncertainties, the verification results were reprocessed. Now the residuals met the requirements of ISO 6143. The results for benzene, p-xylene, m-xylene and o-xylene are shown in figures 2-5. These assigned uncertainties have also been assigned to the amount-of-substance fractions of the components in the transfer standard for this key comparison.

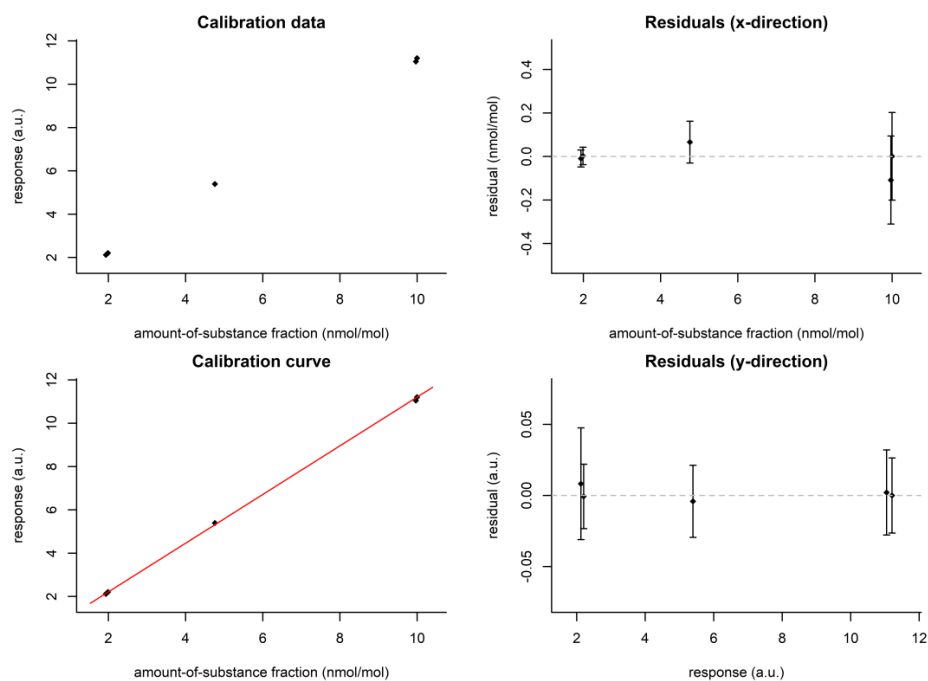


Figure 2 -- Calibration function and residuals for benzene

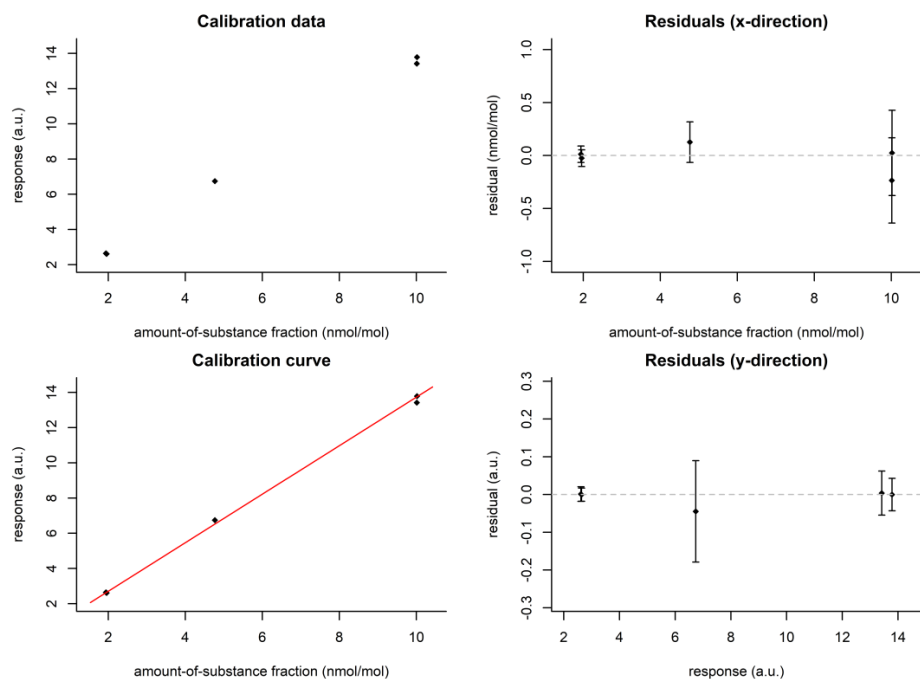


Figure 3 -- Calibration function and residuals for p-xylene

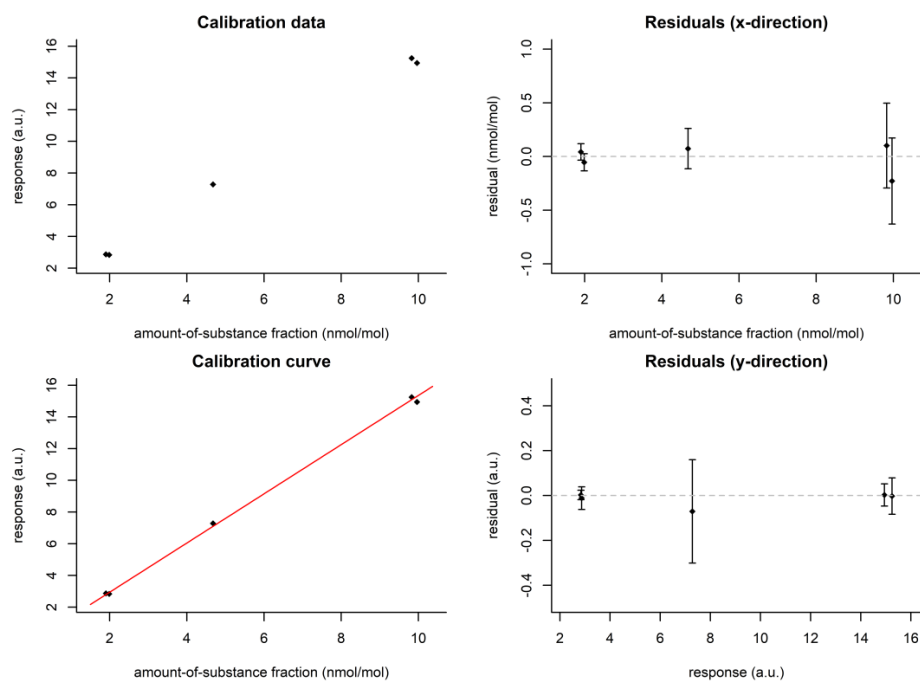


Figure 4 -- Calibration function and residuals for m-xylene

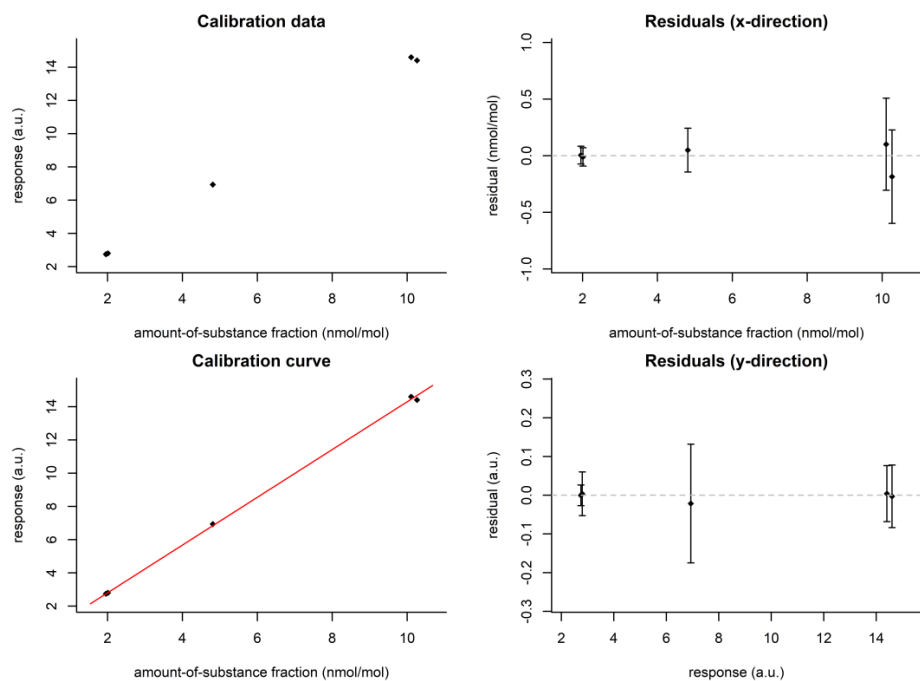


Figure 5 -- Calibration function and residuals for o-xylene

The results of one of the verification measurements are summarised in table 12.

Table 12 – Results first verification measurement; y denotes response and x amount-of-substance fraction (nmol mol⁻¹)

| Mixture | y | u(y) | x(n) | x | u(x) | u(x)/x | Δx | $\Delta x/u(x)$ | $\Delta x/x$ |
|-----------|---------|--------|---------|--------|--------|--------|------------|-----------------|--------------|
| VSL136647 | 5.5707 | 0.0053 | 5.0031 | 4.9857 | 0.0259 | 0.52% | -0.0173 | -0.67 | -0.35% |
| VSL136606 | 5.5582 | 0.0127 | 5.0075 | 4.9746 | 0.0278 | 0.56% | -0.0329 | -1.19 | -0.66% |
| PRM267456 | 5.5210 | 0.0053 | 5.0037 | 4.9415 | 0.0256 | 0.52% | -0.0621 | -2.43 | -1.24% |
| VSL136615 | 5.5562 | 0.0042 | 5.0047 | 4.9728 | 0.0256 | 0.52% | -0.0319 | -1.24 | -0.64% |
| VSL230725 | 11.0306 | 0.0066 | 10.0144 | 9.8422 | 0.0636 | 0.65% | -0.1722 | -2.71 | -1.72% |

4) Outline of any stability testing of mixture

Stability testing of these type of mixtures in similar cylinders has been performed. Evidence is found that no significant instability can be expected within the time frame of this key comparison. This experience is evidenced by the results of the second verification, which are concordant with those obtained in the first verification.

5) Cylinder pressure

The cylinder pressure in the cylinder before shipment to was 125 bar.

References

- [1] International Organization for Standardization, "ISO 6143 – Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures", ISO Geneva, 2001
- [2] International Organization for Standardization, "ISO 6142-1 – Gas analysis -- Preparation of calibration gas mixtures -- Part 1: Gravimetric method for Class I mixtures", ISO Geneva, 2015
- [3] Van der Veen A.M.H., "CurveFit 2.14 – User's guide", VSL, Delft, the Netherlands, S-CH.14.02

You may provide additional data, such as raw measurement data, information on your measurement procedure, etc.

C Comparative participant reports

C.1 METAS

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : METAS

Laboratory code :

Cylinder number : APE1228493

NOMINAL COMPOSITION: 5×10^{-9} (nmol/mol; ppb)

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|----------------|-------------------|---|---|--|
| Benzene | 27.08.18-04.09.18 | 6.21 | 0.36 | 0.72 |
| Toluene | 31.08.18-04.09.18 | 5.49 | 0.08 | 0.15 |
| Ethylbenzene | 27-28.08.18 | 5.15 | 0.07 | 0.14 |
| meta-Xylene | 27.08.18-04.09.18 | 5.38 | 0.07 | 0.14 |
| para-Xylene | 27.08.18-04.09.18 | 5.62 | 0.04 | 0.08 |
| ortho-Xylene | 27.08.18-04.09.18 | 5.38 | 0.10 | 0.19 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES.

The reference gas mixtures were prepared by permeation and dynamic dilution at nmol/mol level in nitrogen. Six permeation units (one per compounds, from Fine Metrology or VICI) were used in a mobile in-house constructed generator "ReGaS2" at defined pressure and temperature conditions. The permeation units were calibrated in a magnetic suspension balance (Rubotherm) before and after the preparation to obtain a calibration curve in function of the temperature.

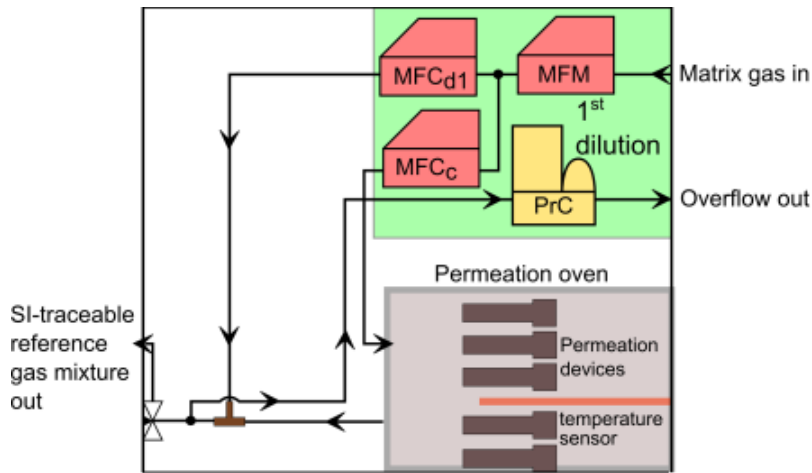


Figure 1: Scheme of ReGaS2 ("Reactive Gas Standard2") to produce reference gas mixture of up to 5 compounds at the same time

The generated amount fractions were sampled for 4 different loading times on adsorption tubes (Tenax) with a controlled flow of 50 ml/min per tubes (Thermal Mass Flow Controller, Vögtlin). It resulted in a 4-points calibration curve for the measuring instrument.

The measurement of BTEX was done with ATD-GC-FID (Clarus 500, Perkin-Elmer and column Stabilwax, Restek).

The cylinder was measured in the same way, with the same sampling equipment and the same measurement method.

3. UNCERTAINTY BUDGET.

The software GUM Workbench V2.4 was used for the uncertainty estimation. Here below an example for the ethylbenzene concentration in the gas cylinder.

Equation:

$$E1 = T_{XE} \cdot P_E \cdot t1 \cdot v/V - E_N;$$

$$E2 = T_{XE} \cdot P_E \cdot t2 \cdot v/V - E_N;$$

$$E3 = T_{XE} \cdot P_E \cdot t3 \cdot v/V - E_N;$$

$$E4 = T_{XE} \cdot P_E \cdot t4 \cdot v/V - E_N;$$

$$EA = (E1 + E2 + E3 + E4)/4;$$

$$EAnz_{mean} = (EAnz_1 + EAnz_2 + EAnz_3 + EAnz_4)/4;$$

$$b_E = p_E/q_E;$$

$$p_E = (E1 - EA) \cdot (EAnz_1 - EAnz_{mean}) + (E2 - EA) \cdot (EAnz_2 - EAnz_{mean}) + (E3 - EA) \cdot (EAnz_3 - EAnz_{mean}) + (E4 - EA) \cdot (EAnz_4 - EAnz_{mean});$$

$$q_E = (E1 - EA)^2 + (E2 - EA)^2 + (E3 - EA)^2 + (E4 - EA)^2;$$

$$a_E = EAnz_{mean} - b_E \cdot EA;$$

$$ERes2 = (EAnz_{Res2} - a_E)/b_E;$$

$$E_{bout2} = (ERes2 \cdot F_E)/(t_{asp2} \cdot v);$$

List of quantities:

| | | |
|----------------------|-----------------|---|
| t1 | min | Loading time 1 |
| v | ml/min | Aspiration flow |
| V | ml/min | Total flow ReGaS2 |
| t2 | min | Loading time 2 |
| t3 | min | Loading time 3 |
| t4 | min | Loading time 4 |
| t _{asp2} | min | Loading time2 for cylinder |
| E1 | ng | Ethylbenzene mass into tube after t1 |
| T _{xE} | ng/min | Ethylbenzene permeation rate |
| P _E | mol/mol | Purity Ethylbenzene in permeator |
| E _N | ng | Rest Ethylbenzene in carrier gas |
| E2 | ng | Ethylbenzene mass into tube after t2 |
| E3 | ng | Ethylbenzene mass into tube after t3 |
| E4 | ng | Ethylbenzene mass into tube after t4 |
| EA | ng | Ethylbenzene mass average |
| EAnz _{mean} | arb. units | Ethylbenzene area average |
| EAnz ₁ | arb units | Ethylbenzene area after t1 |
| EAnz ₂ | arb units | Ethylbenzene area after t2 |
| EAnz ₃ | arb units | Ethylbenzene area after t3 |
| EAnz ₄ | arb units | Ethylbenzene area after t4 |
| b _E | arb units/ng | Slope of Ethylbenzene calibration |
| p _E | ng*arb. unit | Numerator slope of Ethylbenzene calibration |
| q _E | ng ² | Denominator slope of Ethylbenzene calibration |
| a _E | arb. unit | y-intercept of Ethylbenzene calibration |
| ERes2 | ng | Ethylbenzene mass for tasp2 from cylinder |
| EAnzRes2 | arb. unit | Ethylbenzene area for tasp2 from cylinder |
| F _E | m3/L | conversion factor Ethylbenzene |
| Ebout2 | ppb | Cylinder concentration for tasp2 |

| Quantity | Value | Standard Uncertainty | Distribution | Sensitivity Coefficient | Uncertainty Contribution | Index |
|-------------------|----------------|----------------------|--------------|-------------------------|---------------------------|--------|
| t1 | 5.000 min | 0.150 min | normal | 0.061 | 9.1·10 ⁻³ ppb | 1.7 % |
| v | 50.400 ml/min | 0.750 ml/min | normal | not valid! | 0.0 ppb | 0.0 % |
| V | 5044.00 ml/min | 5.04 ml/min | normal | -1.0·10 ⁻³ | -5.2·10 ⁻³ ppb | 0.5 % |
| t2 | 15.000 min | 0.150 min | normal | 0.059 | 8.9·10 ⁻³ ppb | 1.6 % |
| t3 | 30.000 min | 0.150 min | normal | 0.057 | 8.6·10 ⁻³ ppb | 1.5 % |
| t4 | 40.000 min | 0.150 min | normal | 0.056 | 8.4·10 ⁻³ ppb | 1.4 % |
| t _{asp2} | 30.000 min | 0.150 min | normal | -0.17 | -0.026 ppb | 13.7 % |
| T _{xE} | 172.49 ng/min | 1.81 ng/min | normal | 0.030 | 0.054 ppb | 60.2 % |
| P _E | 0.97 mol/mol | | | | | |

| Quantity | Value | Standard Uncertainty | Distribution | Sensitivity Coefficient | Uncertainty Contribution | Index |
|----------------------|------------------------------------|----------------------|--------------|-------------------------|---------------------------|--------|
| E _N | 0.0 ng | 0.0 ng | triangular | 0.0 | 0.0 ppb | 0.0 % |
| EA | 37.615 ng | 0.697 ng | | | | |
| EAnz _{mean} | 17732 arb. units | 103 arb. units | | | | |
| EAnz ₁ | 3958.7 arb units | 21.1 arb units | normal | -77·10 ⁻⁶ | -1.6·10 ⁻³ ppb | 0.0 % |
| EAnz ₂ | 11778.3 arb units | 96.9 arb units | normal | -75·10 ⁻⁶ | -7.3·10 ⁻³ ppb | 1.1 % |
| EAnz ₃ | 23742 arb units | 152 arb units | normal | -73·10 ⁻⁶ | -0.011 ppb | 2.5 % |
| EAnz ₄ | 31447 arb units | 369 arb units | normal | -71·10 ⁻⁶ | -0.026 ppb | 14.2 % |
| b _E | 470.9 arb units/ng | 10.5 arb units/ng | | | | |
| p _E | 954.2·10 ³ ng*arb. unit | 21300 ng*arb. unit | | | | |
| q _E | 2026.3 ng ² | 77.3 ng ² | | | | |
| a _E | 18 arb. unit | 166 arb. unit | | | | |
| ERes2 | 36.910 ng | 0.719 ng | | | | |
| EAnzRes2 | 17399.3 arb. unit | 28.3 arb. unit | normal | 300·10 ⁻⁶ | 8.4·10 ⁻³ ppb | 1.4 % |
| F _E | 211.0 m3/L | | | | | |
| Ebout2 | 5.1507 ppb | 0.0697 ppb | | | | |

Note: in the uncertainty of the permeation rate (T_{xE}) contributions from weighing process with magnetic suspension balance, long-term stability of permeation rate, purity of substance as well as influence of temperature variability are included.

4. COMPLEMENTARY INFORMATION.

- 1) The purities of the pure permeation units are listed here below as well as the purity of the matrix gas, nitrogen. These values are given by the manufacturer.

| | Producer | Purity declared |
|--------------|----------------|-----------------|
| Benzene | VICI | 99.5% |
| Ethylbenzene | Fine Metrology | 99.5% |
| Toluene | VICI | 99.9% |
| M_Xylene | VICI | 99% |
| O-Xylene | VICI | 99.5% |
| p-Xylene | VICI | 99.5% |
| N2 | Carbagas | 99.9999% |

Prior to the comparison, each gas compound was generated alone (in nitrogen) as well as nitrogen only and measured with the same setup (sampling/analysis) to check for impurities. For Ethylbenzene and o-Xylene, a purity of 97% was observed and taken into account.

| | Purity after analysis | Standard uncertainty |
|--------------|-----------------------|----------------------|
| Benzene | 0.995 | 0.0021 |
| Ethylbenzene | 0.97 | 0.009 |
| Toluene | 0.999 | 0.00041 |
| M_Xylene | 0.99 | 0.0041 |
| O-Xylene | 0.97 | 0.009 |
| p-Xylene | 0.995 | 0.0021 |

- 2) The dilution flow in the mobile generator was constant. The total flow (carrier and dilution flows) used for the generation of the reference gas mixture was ~5045 ml/min. The time of absorption in the tubes was changed in order to make a calibration curve for the GC-FID (5 to 40 minutes = quantities from 7 to 630 ng).
- 3) Several series of samples on adsorption tubes were measured with 5 different compounds (Benzene, Ethylbenzene, m/p/o-Xylene or Benzene, Toluene, m/p/o-Xylene produced at the same time) with 3 replicates for each sampling.
- 4) There is no stability check of reference gas cylinder. This point is not applicable for dynamic mixtures. Stability check for the transfer standard is done by the coordinator.
- 5) The cylinder pressure was 90 bars after use

C.2 UBA

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : German Environment Agency (D)
Laboratory code : UBA (D)

Cylinder number : APE 1228493

Nominal Composition: 5×10^{-9} (nmol/mol; ppb) within ± 0.2 nmol/mol

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|---------------------|------------|---|---|--|
| Benzene | 18.10.2018 | 5.09 | 0.02 | 0.04 |
| Toluene | 25.10.2018 | 4.92 | 0.02 | 0.05 |
| Ethylbenzene | 31.10.2018 | 4.48 | 0.02 | 0.04 |
| meta- + para-Xylene | 08.11.2018 | 9.80 | 0.07 | 0.14 |
| ortho-Xylene | 31.10.2018 | 4.60 | 0.03 | 0.06 |

Briefly describe your preparation procedures

The calibration gas is prepared by static dilution method ISO 6144 and used the bracketing procedure by preparing two concentrations in an interval of ca. $\pm 5\%$ of a test measurement. The testgas was measured by GC Clarus 680 GL and Turbomatrix 300 apply DIN EN 14662 (2005).

The ISO 6144 was modified by the injection method. The syringes was substituted by capillary tubes and the pure liquid substance was sucked in by a gas flow induced by low pressure and fill up air simultaneously. The capillary was weighed before and after filling up with pure substance. The filled up capillary was weighed 5 times. This mixture was diluted 3-times by pressurize and relax the mixture. See GUM Workbench Budget. Pressure and temperature was measured exactly. We could not separate meta- und para-xylene from each other. Only the sum of both is reported here.

Uncertainty budget.

Example for Benzene

$$u_c^2 = u_l^2 + u_R^2 + u_M \quad (1)$$

u_c = Combined uncertainty

u_l = Combined uncertainty given by static dilution method valid for both bracketing points

u_R = Reproducibility of the static dilution method in UBA laboratory

u_M = standard uncertainty of measurements:.

Calculation of u_l according to ISO Guide GUM supported by GUM Workbench software.

In this calculation is shown the route of traceability to SI.

Standard deviation of the 3 calibrations is included in the reproducibility of the static dilution method.

$$u_l = 0.19 \% \text{ rel.}$$

$$u_R = 0.23 \% \text{ rel.}$$

$$u_M = 0.13 \% \text{ rel.}$$

$$u_c = \mathbf{0.33 \% \text{ rel}} \quad (1)$$

Coverage factor: 2

$$U = 0.66 \%$$

UNCERTAINTY BUDGET FOR CALIBRATION GAS BENZENE AS EXAMPLE

THE BUDGETS FOR THE OTHER COMPONENTS ARE SIMILAR.

Model Equation:

$$\beta_k = (W1 - W2) * 1000 * F_i * T_K * p_R / V_K / T_R / p_K * p_{11} * T_{12} / p_{12} / T_{11} * p_{21} * T_{22} / p_{22} / T_{21}$$

List of Quantities:

| Quantity | Unit | Definition |
|-----------|--------------------------|--|
| β_k | $\mu\text{g}/\text{m}^3$ | Concentration at reference conditions |
| W1 | mg | Weight of filled capillary |
| W2 | mg | Weight of empty capillary |
| F_i | mol/mol | Amount of substance fraction (mol/mol) |
| T_K | K | Vessel temperature |
| p_R | kPa | Reference pressure |
| V_K | m^3 | Volume of the Vessel |
| T_R | K | Reference Pressure |
| p_K | kPa | Vessel pressure high |
| p_{11} | kPa | 1. Pressure |
| T_{12} | K | Temperature 1. filling |
| p_{12} | kPa | Pressure 1. filling |
| T_{11} | K | Temperature after 1. pump down |
| p_{21} | kPa | Pressure after 2. pump down |
| T_{22} | K | Temperature after 2. filling up |
| p_{22} | kPa | Pressure after 2. filling up |
| T_{21} | K | Temperature after 2. pump down |

W1:

Type A summarized

Mean: 13869.744 mg

Experimental standard deviation: 0.005 mg

Number of observations: 5

accurate scales MSE 225P-100-DA

W2:

Type A summarized

Mean: 13867.156 mg

Experimental standard deviation: 0.009 mg

Number of observations: 5

F_i :

Type B rectangular distribution

Value: 0.99992 mol/mol

Halfwidth of limits: 0.000017 mol/mol

T_K:

Type B rectangular distribution

Value: 298.75 K

Halfwidth of limits: 0.003 K

p_R:

Constant

Value: 101.325 kPa

V_K:

Type B rectangular distribution

Value: 0.11244 m³

Halfwidth of limits: 0.0001 m³

Estimation of Volume by filling the Vessel with graduated cylinders

T_R:

Constant

Value: 293.15 K

p_K:

Type B rectangular distribution

Value: 159.731 kPa

Halfwidth of limits: 0.004 kPa

Mensor Calibration Line

p₁₁:

Type B rectangular distribution

Value: 5.0837 kPa

Halfwidth of limits: 0.003 kPa

MKS Instruments

T₁₂:

Type B rectangular distribution

Value: 298.87 K

Halfwidth of limits: 0.003 K

Fluke Model 1529-R

p₁₂:

Type B rectangular distribution

Value: 160.768 kPa

Halfwidth of limits: 0.004 kPa

T₁₁:

Type B rectangular distribution

Value: 297.98 K

Halfwidth of limits: 0.003 K

p₂₁:

Type B rectangular distribution

Value: 5.75 kPa

Halfwidth of Limits: 0.003 kPa

T₂₂:

Type B rectangular distribution

Value: 298.71 K

Halfwidth of limits: 0.003 K

p₂₂:

Type B rectangular distribution

Value: 159.8 kPa

Halfwidth of limits: 0.004 kPa

T₂₁:

Type B rectangular distribution

Value: 297.61 K

Halfwidth of limits: 0.003 K

Uncertainty Budgets:

β_k: Concentration at reference conditions

| Quantity | Value | Standard Uncertainty | Distribution | Sensitivity Coefficient | Uncertainty Contribution | Index |
|-----------------|-------------------------|----------------------------------|--------------|-------------------------|---|--------|
| W1 | 13869.74400 mg | $2.24 \cdot 10^{-3}$ mg | normal | 6.6 | $0.015 \mu\text{g}/\text{m}^3$ | 20.5 % |
| W2 | 13867.15600 mg | $4.02 \cdot 10^{-3}$ mg | normal | -6.6 | $-0.027 \mu\text{g}/\text{m}^3$ | 66.5 % |
| F _i | 0.99992000 mol/mol | $9.81 \cdot 10^{-6}$ mol/mol | rectangular | 17 | $170 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |
| T _K | 298.75000 K | $1.73 \cdot 10^{-3}$ K | rectangular | 0.057 | $99 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |
| p _R | 101.325 kPa | | | | | |
| V _K | 0.1124400 m^3 | $57.7 \cdot 10^{-6} \text{ m}^3$ | rectangular | -150 | $-8.8 \cdot 10^{-3} \mu\text{g}/\text{m}^3$ | 7.2 % |
| T _R | 293.15 K | | | | | |
| p _K | 159.73100 kPa | $2.31 \cdot 10^{-3}$ kPa | rectangular | -0.11 | $-250 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |
| p ₁₁ | 5.08370 kPa | $1.73 \cdot 10^{-3}$ kPa | rectangular | 3.4 | $5.8 \cdot 10^{-3} \mu\text{g}/\text{m}^3$ | 3.2 % |
| T ₁₂ | 298.87000 K | $1.73 \cdot 10^{-3}$ K | rectangular | 0.057 | $99 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |
| p ₁₂ | 160.76800 kPa | $2.31 \cdot 10^{-3}$ kPa | rectangular | -0.11 | $-240 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |
| T ₁₁ | 297.98000 K | $1.73 \cdot 10^{-3}$ K | rectangular | -0.057 | $-99 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |
| p ₂₁ | 5.75000 kPa | $1.73 \cdot 10^{-3}$ kPa | rectangular | 3.0 | $5.1 \cdot 10^{-3} \mu\text{g}/\text{m}^3$ | 2.5 % |
| T ₂₂ | 298.71000 K | $1.73 \cdot 10^{-3}$ K | rectangular | 0.057 | $99 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |
| p ₂₂ | 159.80000 kPa | $2.31 \cdot 10^{-3}$ kPa | rectangular | -0.11 | $-250 \cdot 10^{-6} \mu\text{g}/\text{m}^3$ | 0.0 % |

| Quantity | Value | Standard Uncertainty | Distribution | Sensitivity Coefficient | Uncertainty Contribution | Index |
|-----------------|---------------------------|--------------------------|--------------|-------------------------|--|-------|
| | | | | | | |
| T ₂₁ | 297.61000 K | 1.73·10 ⁻³ K | rectangular | -0.057 | -99·10 ⁻⁶ µg/m ³ | 0.0 % |
| β _k | 17.0421 µg/m ³ | 0.0325 µg/m ³ | | | | |

Results:

| Quantity | Value | Expanded Uncertainty | Coverage factor | Coverage |
|----------------|--------------------------|----------------------|-----------------|----------|
| β _k | 17.042 µg/m ³ | 0.19 % (relative) | 1.00 | manual |
| | | | | |

2. COMPLEMENTARY INFORMATION.

Please include information on:

- 1) A purity table with uncertainties for benzene, toluene, ethylbenzene, meta-, para-, ortho-xylenes, and balance nitrogen used to prepare your standard mixture.

CRM was certified by National Metrology Institute of Japan

| | Purity mol/mol | Expanded uncertainty |
|--------------|-------------------|-------------------------|
| Benzene | 0.99992 | 0.00003 |
| Toluene | 0.9997 | 0.0003 |
| Ethylbenzene | 0.9988 | 0.0003 |
| meta-Xylene | 0.9980 | 0.0002 |
| ortho-Xylene | 0.9993 | 0.0001 |
| | | |

- 2) Outline of dilution series to produce final standard mixture – see GUM Budget
- 3) Outline/discussion of the verification procedure applied to final mixture
- 4) Outline of any stability testing of mixture
- 5) Cylinder pressure

Optional

You may provide additional data, such as raw measurement data, information on your measurement procedure, etc.

C.3 CHMI

CCQM KEY COMPARISON-K10.2018: BTEX in Nitrogen

Comparability study of laboratories' preparation capabilities for BTEX in nitrogen

Laboratory : Czech Hydrometeorological Institute
Ambient Air Quality Calibration Laboratory
Na Šabatce 2050/17
143 06 Prague 4
Czech Republic

Laboratory code : 2284

Cylinder number : APE1228493 (D569767), pressure 11,0-10,4 MPa

NOMINAL COMPOSITION: 5×10^{-9} (nmol/mol; ppb)

1. RESULTS

| BTEX Component | Date | Gravimetric amount-of-substance fraction (nmol/mol) | Standard uncertainty ($k=1$) (nmol/mol) | Expanded uncertainty (95 %) (nmol/mol) |
|---------------------|------------|---|---|--|
| Benzene | | 5,15 | 0,157 | 0,31 |
| Toluene | 14.12.2018 | 5,14 | 0,120 | 0,24 |
| Ethylbenzene | 10.1.2019 | 4,85 | 0,126 | 0,25 |
| meta+para-Xylene *) | 12.3.2019 | 10,05 | 0,267 | 0,53 |
| ortho-Xylene | | 4,95 | 0,145 | 0,29 |

2. BRIEFLY DESCRIBE YOUR PREPARATION PROCEDURES.

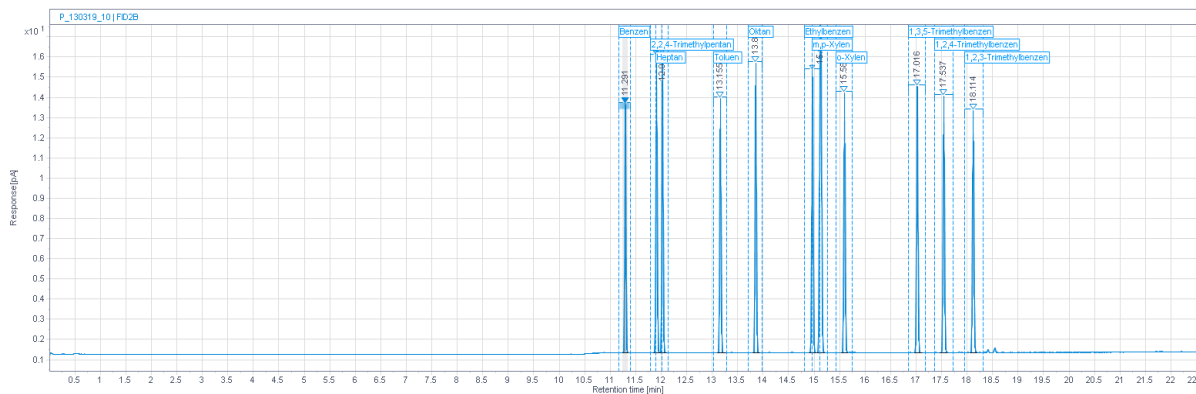
- A cylinder is connected to an analytical system.
- The first step is an inject helium (volume 200 ml) for controlling clean of the analytical system.
- The second step is twice inject of primary reference material (cylinder number D860586R), volume 100 ml.
- The third step is three times inject of sample APE1228493 (D569767), volume 100 ml.
- Last step is inject of primary reference material (cylinder number D860586R), volume 100 ml.
- The PRM which was measured three times we used for created a calibration curve. The PRM is used for direct comparison.

Calibration standard: NPL Primary reference material, cylinder number D860586R
 Certificate D860586R, date of issue 20 December 2017
 calibration date 13 December 2017
 pressure regulator: CONCOA silcosteel 4222301-01-000R, s/n 06C06AF4

Amount fraction

| Component | Amount fraction / (nmol/mol) |
|--------------------------|---------------------------------|
| Benzene | 10,07 ± 0,21 |
| Toluene | 9,79 ± 0,25 |
| Ethylbenzene | 10,59 ± 0,27 |
| <i>meta+para</i> -Xylene | 20,60 ± 0,52 |
| <i>ortho</i> -Xylene | 10,13 ± 0,26 |

Chromatogram of PRM:



Preconcentration: preconcentrator 7200 Entech Instruments

| Temperatures | Zones | Trap temp | M1 preheat | M1>M2 | M3 precool | M2 preheat | M1>M2 | Inject | Bakeout |
|--------------|--------------------|-----------|------------|---------|------------|------------|----------|--------|---------|
| | Mod 1 | - 40 °C | 10 °C | 10 °C | -- | -- | -- | -- | 150 °C |
| | Mod 1 Bulkhead | 40 °C | -- | 60 °C | -- | -- | -- | -- | 150 °C |
| | Mod 2 | - 50 °C | -- | - 50 °C | -- | - 50 °C | 220 °C | -- | 220 °C |
| | Mod 2 Bulkhead | 40 °C | -- | | -- | 40 °C | -- | -- | 150 °C |
| | Mod 3 | -- | -- | | - 175 °C | -- | - 150 °C | 80 °C | -- |
| | Rotary valve plate | 80 °C | -- | -- | -- | -- | -- | -- | 80 °C |

Sample transfer line: 80 °C

GC transfer line: 100 °C

Volume of sample: 100 ml

Analytical system: Agilent technologies 7890B GC system

| | |
|-----------------|--|
| COLUMN | AGILENT 123-1063; DB-1 (60m × 320µm × 1 µm); flow 4 mL/min AGILENT 19091P-315; HP-Plot Al2O3S (50m × 320µm × 8 µm); flow 3 mL/min |
| OVEN | temperature on 50 °C, maximum oven temperature 200 °C |
| DETECTOR | FID FRONT: heater 200 °C; air flow 400 mL/min; He fuel flow 30 mL/min; makeup flow 25 ml/min |
| | FID BACK: heater 200 °C; air flow 400 mL/min; He fuel flow 30 mL/min; makeup flow 25 ml/min |

3. UNCERTAINTY BUDGET.

BENZENE

| Parameter | Unit | Value | Exp.unc. | Std.unc. | Δ rel.unc. | | Δ rel.exp.un |
|---|-------------|--------------|-------------|------------|------------|------------|--------------|
| PE-A (WE-A) work etalon - analyzer (GC) HP7890B | | | | abs.term x | | rel.term y | |
| PRM certificate D86 0586R | | | | | | | |
| Benzene | nmol/mol | 10,07 | 0,21 | 0,105 | 0,010427 | | 2,09 |
| | | | | | | | |
| Calibration PE-A traceability to PRM | | | | | | | |
| different of input pressure | % | 2 | 0,02 | 0,01 | 0,01 | | 2,00 |
| PE-A abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPE-A(PRM) | 0,04 | 0,02 | | 0,016 | 3,20 |
| number of PRM analysis, std.unc.of DPEA(PRM) | | 3 | | 0,09515 | 0,009449 | | 1,89 |
| Value of PE-A for PRM | nmol/mol | 10,07 | 0,35 | 0,17384 | | | 3,45 |
| calibration coef. $f_{kal, PE-A(PRM)}$ (~ 1) | 1 | 1 | 0,03453 | 0,01726 | | | 3,45 |
| Calibration of calibration gas source | | | | | | | |
| standard deviation of individual measurements | 1 | 4 | 0,046 | 0,023 | 0,023 | | 4,60 |
| source - abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPEA(source) | 0,04 | 0,02 | | 0,016 | 3,20 |
| number of source analysis, std.unc.of DPEA(source) | | 3 | | 0,05161 | 0,010021 | | 2,00 |
| Concentration of calibration gas source | nmol/mol | 5,150 | 0,31 | 0,15684 | 0,030453 | | 6,02 |

TOLUENE

| Parameter | Unit | Value | Exp.unc. | Std.unc. | Δ rel.unc. | | Δ rel.exp.un |
|---|-------------|--------------|-------------|------------|------------|------------|--------------|
| PE-A (WE-A) work etalon - analyzer (GC) HP7890B | | | | abs.term x | | rel.term y | |
| PRM certificate D86 0586R | | | | | | | |
| Toluene | nmol/mol | 9,79 | 0,25 | 0,125 | 0,012768 | | 2,55 |
| | | | | | | | |
| Calibration PE-A traceability to PRM | | | | | | | |
| different of input pressure | % | 2 | 0,02 | 0,01 | 0,01 | | 2,00 |
| PE-A abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPE-A(PRM) | 0,04 | 0,02 | | 0,019 | 3,80 |
| number of PRM analysis, std.unc.of DPEA(PRM) | | 3 | | 0,10924 | 0,011158 | | 2,23 |
| Value of PE-A for PRM | nmol/mol | 9,79 | 0,39 | 0,19272 | | | 3,94 |
| calibration coef. $f_{kal, PE-A(PRM)}$ (~ 1) | 1 | 1 | 0,03937 | 0,01969 | | | 3,94 |
| Calibration of calibration gas source | | | | | | | |
| standard deviation of individual measurements | 1 | 4 | 0,0098 | 0,0049 | 0,0049 | | 0,98 |
| source - abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPEA(source) | 0,04 | 0,02 | | 0,019 | 3,80 |
| number of source analysis, std.unc.of DPEA(source) | | 3 | | 0,05983 | 0,011639 | | 2,33 |
| Concentration of calibration gas source | nmol/mol | 5,140 | 0,24 | 0,12022 | 0,023388 | | 4,67 |

ETHYLBENZENE

| Parameter | Unit | Value | Exp.unc. | Std.unc. | Δ rel.unc. | Δ rel.exp.un |
|---|-------------|--------------|----------|------------|------------|--------------|
| PE-A (WE-A) work etalon - analyzer (GC) HP7890B | | | | abs.term x | rel.term y | |
| PRM certificate D86 0586R | | | | | | |
| Etylbenzene | nmol/mol | 10,59 | 0,27 | 0,135 | 0,012748 | 2,55 |
| | | | | | | |
| Calibration PE-A traceability to PRM | | | | | | |
| different of input pressure | % | 2 | 0,02 | 0,01 | 0,01 | 2,00 |
| PE-A abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPE-A(PRM) | 0,04 | 0,02 | 0,022 | 4,40 |
| number of PRM analysis, std.unc.of $D_{PEA}(PRM)$ | | 3 | | 0,13599 | 0,012841 | 2,57 |
| Value of PE-A for PRM | nmol/mol | 10,59 | 0,44 | 0,21894 | | 4,13 |
| calibration coef. $f_{kal,PE-A}(PRM)$ (~ 1) | 1 | 1 | 0,04135 | 0,02067 | | 4,13 |
| Calibration of calibration gas source | | | | | | |
| standard deviation of individual measurements | 1 | 4 | 0,0164 | 0,0082 | 0,0082 | 1,64 |
| source - abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPEA(source) | 0,04 | 0,02 | 0,022 | 4,40 |
| number of source analysis, std.unc.of $D_{PEA}(source)$ | | 3 | | 0,06477 | 0,013354 | 2,67 |
| Concentration of calibration gas source | nmol/mol | 4,850 | 0,25 | 0,12582 | 0,025942 | 5,15 |

META+PARA-XYLENE

| Parameter | Unit | Value | Exp.unc. | Std.unc. | Δ rel.unc. | Δ rel.exp.un |
|---|-------------|--------------|----------|------------|------------|--------------|
| PE-A (WE-A) work etalon - analyzer (GC) HP7890B | | | | abs.term x | rel.term y | |
| PRM certificate D86 0586R | | | | | | |
| m+p-Xylene | nmol/mol | 20,60 | 0,52 | 0,26 | 0,012621 | 2,52 |
| | | | | | | |
| Calibration PE-A traceability to PRM | | | | | | |
| different of input pressure | % | 2 | 0,02 | 0,01 | 0,01 | 2,00 |
| PE-A abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPE-A(PRM) | 0,04 | 0,02 | 0,018 | 3,60 |
| number of PRM analysis, std.unc.of $D_{PEA}(PRM)$ | | 3 | | 0,21501 | 0,010438 | 2,09 |
| Value of PE-A for PRM | nmol/mol | 20,6 | 0,79 | 0,39531 | | 3,84 |
| calibration coef. $f_{kal,PE-A}(PRM)$ (~ 1) | 1 | 1 | 0,03838 | 0,01919 | | 3,84 |
| Calibration of calibration gas source | | | | | | |
| standard deviation of individual measurements | 1 | 4 | 0,03 | 0,015 | 0,015 | 3,00 |
| source - abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPEA(source) | 0,04 | 0,02 | 0,018 | 3,60 |
| number of source analysis, std.unc.of $D_{PEA}(source)$ | | 3 | | 0,10634 | 0,010581 | 2,12 |
| Concentration of calibration gas source | nmol/mol | 10,050 | 0,53 | 0,26688 | 0,026556 | 5,27 |

ORTHO-XYLENE

| Parameter | Unit | Value | Exp.unc. | Std.unc. | Δ rel.unc. | Δ rel.exp.un |
|---|-------------|--------------|----------|------------|------------|--------------|
| PE-A (WE-A) work etalon - analyzer (GC) HP7890B | | | | abs.term x | rel.term y | |
| PRM certificate D86 0586R | | | | | | |
| o-Xylene | nmol/mol | 10,13 | 0,26 | 0,13 | 0,012833 | 2,57 |
| | | | | | | |
| Calibration PE-A traceability to PRM | | | | | | |
| different of input pressure | % | 2 | 0,02 | 0,01 | 0,01 | 2,00 |
| PE-A abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPE-A(PRM) | 0,04 | 0,02 | 0,018 | 3,60 |
| number of PRM analysis, std.unc.of $D_{PEA}(PRM)$ | | 3 | | 0,10716 | 0,010578 | 2,12 |
| Value of PE-A for PRM | nmol/mol | 10,13 | 0,39 | 0,19658 | | 3,88 |
| calibration coef. $f_{kal,PE-A}(PRM)$ (~ 1) | 1 | 1 | 0,03881 | 0,01941 | | 3,88 |
| Calibration of calibration gas source | | | | | | |
| standard deviation of individual measurements | 1 | 4 | 0,038 | 0,019 | 0,019 | 3,80 |
| source - abs. and rel. term x, y (reproducibility) | nmol/mol, 1 | DPEA(source) | 0,04 | 0,02 | 0,018 | 3,60 |
| number of source analysis, std.unc.of $D_{PEA}(source)$ | | 3 | | 0,05514 | 0,011152 | 2,23 |
| Concentration of calibration gas source | nmol/mol | 4,945 | 0,29 | 0,14518 | 0,029359 | 5,86 |