# Final report for supplementary comparison APMP.QM-S14: Hazardous air pollutants in nitrogen at 100 nmol mol$^{-1}$

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**1. Field**
Amount of substance.

**2. Subject**
Comparison of primary reference gas mixtures containing 100 nmol $mol^{-1}$ benzene, toluene, ethylbenzene, *m*-xylene, styrene, *o*-xylene, chloroform, 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, 1,1-dichloroethane, carbon tetrachloride, 1,3-butadiene and dichloromethane in nitrogen.

**3. Participants**
A total of three laboratories participate in this supplementary comparison. The participants are listed in the following.

| Acronym | Country | Institute |
|---|---|---|
| KRISS | KR | Korea Research Institute of Standards and Science, Daejeon, Republic of Korea |
| NIM | CN | National Institute of Metrology, Beijing, China |
| NMISA | ZA | National Metrology Institute of South Africa, Pretoria, South Africa |

**4. Organization body**
APMP TCQM.

**5. Introduction**
Hazardous air pollutants (HAPs) are toxic air pollutants that are mainly emitted from man-made sources such as chemical processes, automobiles, power plants, and refineries, building materials, and cleaning solvents. Some HAPs are emitted from wildfires and chemical leak. HAPs are regulated and monitored to protect public health and the environment because they cause severe health effects such as cancer, damages to the immune system, reproductive and respiratory health problems.
For this supplementary comparison, a multicomponent mixture of HAPs in nitrogen has been chosen at an amount-of-substance fraction level of 100 nmol $mol^{-1}$ that is more close to their emission levels from their sources. The supplementary comparison is designed to underpin calibration capabilities using HAPs gas mixtures that are prepared gravimetrically as transfer standards.

**6. Measurement schedule**

| Event | Deadline |
|---|---|
| Draft protocol | Apr 2016 |
| Final protocol | Dec 2017 |
| Registration | Jan 2018 |
| Mixture preparation | May 2018 |

| | |
|---|---|
| Shipment of mixtures | June 2018 |
| Submission of results | Feb 2020 (NIM), Sept 2020 (NMISA) |
| Return of mixtures | Dec 2019 |
| Draft A report | Oct 2020 |
| Draft B report | Nov 2020 |
| Final report | April 2021 |

**7. Measurement standards**

A suite of primary reference gas mixtures (PRMs) was prepared gravimetrically by KRISS according to ISO 6142-1[1]. Liquid raw materials for HAPs were analyzed for their purity. The diluent gases, nitrogen, were checked for their impurities. The prepared mixtures were compared against a reference gas mixture (at about 100 nmol $mol^{-1}$ in nitrogen) for verification. All gas mixtures were prepared in aluminum cylinders (Air Products) with Experis treatment and an internal volume of 10 $dm^3$. The final filling pressure was approximately 10 MPa. The amount-of-substance fractions were determined based on gravimetry and purity analysis. The nominal amount-of-substance fractions were about 100 nmol $mol^{-1}$.

To assign an amount-of-substance fraction to a gravimetrically prepared gas mixture, the following three groups of uncertainty components have been considered:

1. gravimetric preparation (weighing process) ($x_{i,grav}$)
2. purity of the parent gases ($x_{i,purity}$)
3. stability of the gas mixture ($x_{i,stab}$)

The amount-of-substance fraction, $x_{i,prep}$, of a target component *i* in mixture, can be expressed as

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} \quad (1)$$

where $x_{i,grav}$ is the amount-of-substance fraction of a target component $i$ in mixture gravimetrically prepared, $\Delta x_{i,purity}$ is the correction based on purity analysis, and $\Delta x_{i,stab}$ is the correction due to stability. The uncertainty of the amount-of-substance fraction, $u_{i,prep}$, can be estimated as

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 + u_{i,stab}^2 \quad (2)$$

where $u_{i,grav}$ is the uncertainty from weighing process, $u_{i,purity}$ is the uncertainty from purity analysis, and $u_{i,stab}$ is the uncertainty due to short-term stability (i.e., due to physical adsorption loss onto cylinder internal surface). Physical adsorption loss for each analyte has been evaluated by applying cylinder-to-cylinder division method [2] for one of prepared gas mixtures. Results from the division method show that response ratios of mother to daughter cylinder for each analyte are not different from one statistically, indicating little physical adsorption loss for all analytes (Figure 1). The results describe that analytically determined values agree with their gravimetric values within the analytical uncertainties. Therefore, the

prepared values were not corrected due to physical adsorption loss (i.e., $\Delta x_{i,stab} = 0$). However, the differences have been used to estimate $u_{i,stab}$ and then combined into $u_{i,prep}$.

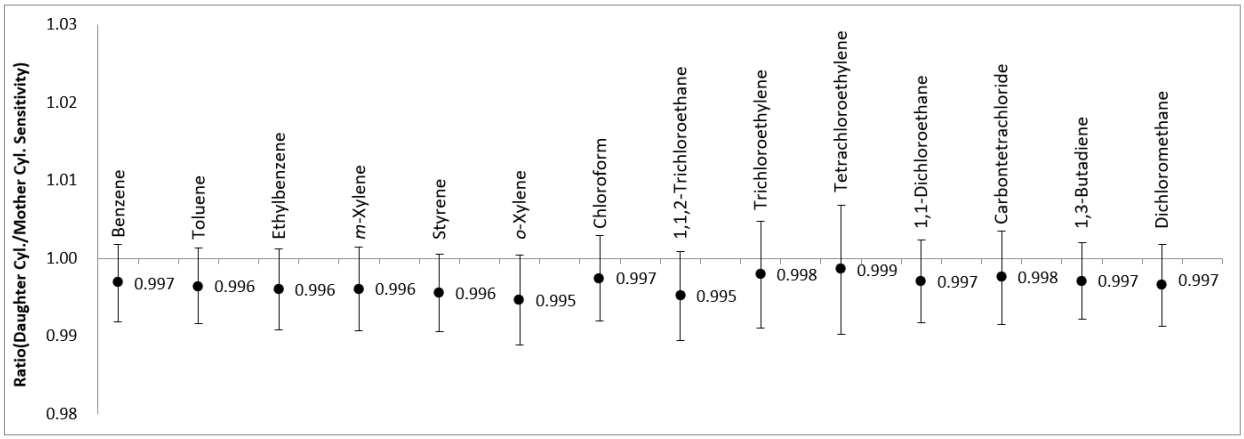


**Figure 1**. Results of evaluation of physical adsorption loss onto cylinder internal surface. Error bars represent expanded uncertainties ($k = 2$)

The gravimetrically prepared mixtures have been verified by comparing the gravimetric value with its analytical measurement value as shown in the following conditions.

$$\left|x_{i,prep} - x_{i,ver}\right| \leq 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2} \tag{3}$$

where $x_{i,ver}$ and $u_{i,ver}$ are the measurement result from verification and its standard uncertainty, respectively.
The verification experiments demonstrated that the verification values agreed with the preparation values within the preparation uncertainties (Figure 2). As far as the verification experiments have demonstrated that the gravimetric values of the supplementary comparison mixtures agreed with analytical values within the uncertainty of these measurements, the reference value ($x_{i,ref}$) becomes the preparation value. As a result, the standard uncertainty of the reference value is expressed as

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2 \tag{4}$$

To verify the sample gas mixtures prepared by KRISS throughout this comparison, each sample gas mixture was analyzed against the reference gas mixture, which was prepared with the sample gas mixtures, before their dispatch and after their return. Results from the verification showed that all gas mixtures were consistent within their measurement uncertainties (Figure 3). Although the gas mixtures agree within their uncertainties, an excess uncertainty for long-term stability was added into the verification uncertainties (Table 2). The maximum difference in the verification results for each component was added as the excess uncertainty. The excess standard uncertainty was estimated by dividing the maximum difference by $2\sqrt{3}$ assuming rectangular distribution.

All gas mixtures at 100 nmol mol$^{-1}$ were analyzed using a GC-FID with a cryogenic pre-concentrator. The detailed analytical conditions are summarized in the following.

| GC-FID |
|---|

| | |
|---|---|
| Column | VOCOL (60 m × 320 μm × 1.8 μm) |
| | Flow 2 mL/min (He) |
| Oven | 105 °C (isothermal, 34.5 min) |
| Detector | 250 °C (isothermal), $H_2$: 35 mL/min, Air: 300 mL/min |

| | Trap temperature, °C | M1→ M2 temperature, °C | M2→M3 temperature, °C | Inject temperature, °C | Bake out temperature, °C |
|---|---|---|---|---|---|
| Mod 1 Trap | 40 | 40 | | | 40 |
| Mod 2 Trap | -95 | -95 | 220 | | 200 |
| Mod 3 Trap | | | -170 | 110 | |
| Trapping sample | | | | | |
| Sample flow | 90 mL/min | | | | |
| Sample volume | 270 mL | | | | |

## 8. Measurement protocols

Each laboratory was requested to perform at least 3 measurements with independent calibrations. All laboratories were also asked to provide detailed information regarding their calibration standards, analytical method, and uncertainty evaluation.

## 9. Measurement method

The details on the measurement methods used by the participants are described in the individual participant reports. A summary of the calibration method, date of measurement, and the way in which metrological traceability is established is given in Table 1.

**Table 1**. Summary of the measurement methods of the participants

| Laboratory | Cylinder | Measurement period | Calibration standards | Instrument calibration | Measurement technique |
|---|---|---|---|---|---|
| KRISS | APEX1218423 | Aug 2018 | Own standards | one point calibration | GC-FID with pre-concentrator |
| NIM | APE1218317 | Apr 2018 | Own standards | one point calibration | GC-MSD |
| NMISA | APE1218321 | May 2018 | Own standards | one point calibration | GC-FID with pre-concentrator |

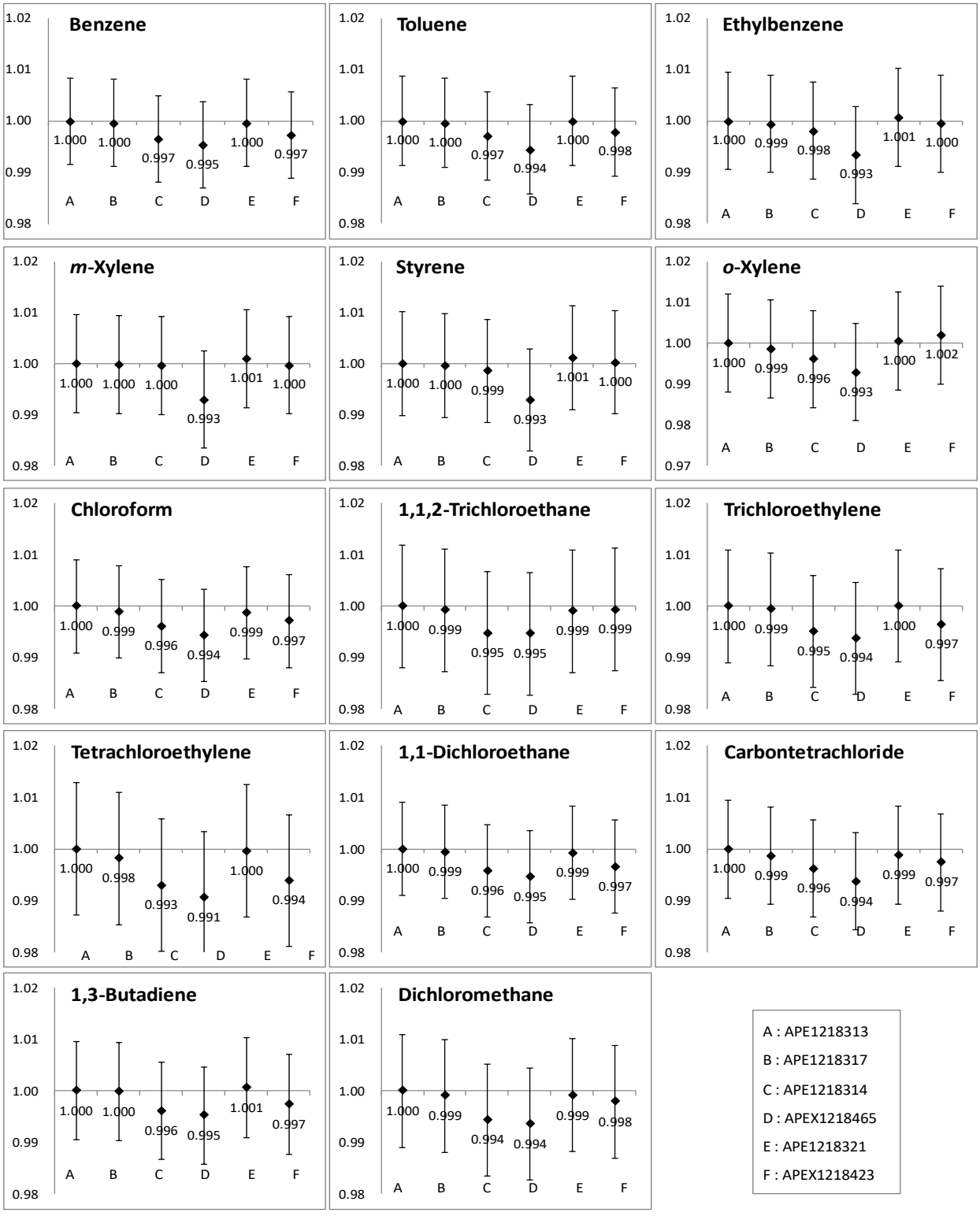


**Figure 2.** Results from verification of gravimetrically prepared gas mixtures. Error bars represent expanded uncertainties ($k = 2$) and y-axis is for the sensitivity ratio of sample to reference gas mixture

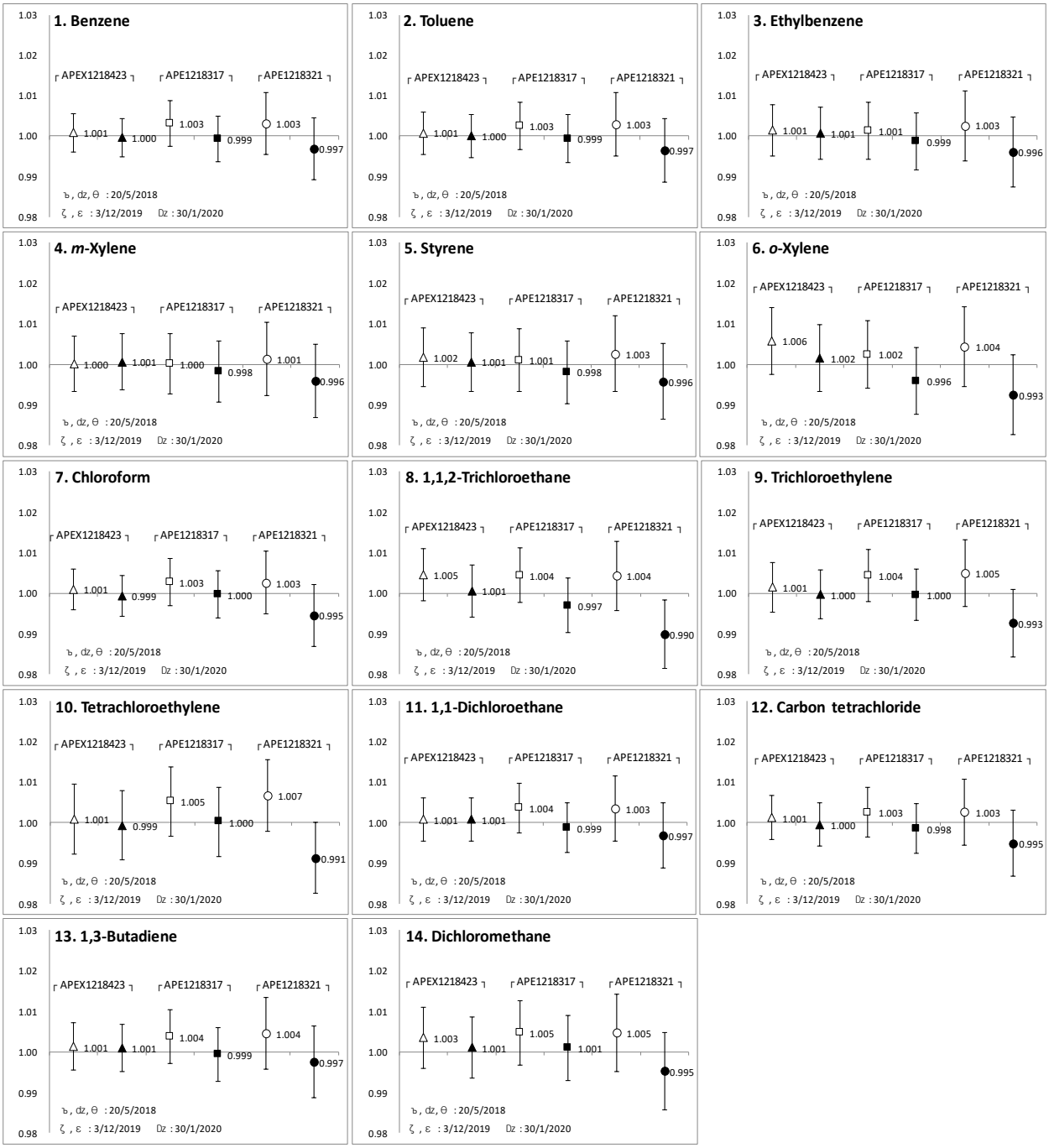


**Figure 3.** Results of verification before and after dispatching sample cylinders. Error bars represent expanded uncertainties ($k = 2$) and y-axis is for the sensitivity ratio of sample to reference gas mixture.

## 10. Degree of equivalence (DoE)

A degree of equivalence for each participating laboratory was calculated as

$$D_i = x_{i,lab} - x_{i,SCRV} \tag{5}$$

where $x_{i,lab}$ and $x_{i,SCRV}$ are the value reported by each participant and the supplementary comparison reference value (SCRV), respectively. In this comparison, the preparation value is set to the SCRV value as expressed in the following.

$$x_{i,SCRV} = x_{i,ref} \quad (6)$$

Thus, the uncertainty of the SCRV values can be expressed as

$$u_{i,SCRV} = u_{i,ref} \quad (7)$$

Therefore, the standard uncertainty of $D_i$ can be expressed as

$$u^2(D_i) = u_{i,lab}^2 + u_{i,SCRV}^2 \quad (8)$$

where $u_{i,lab}$ and $u_{i,SCRV}$ are the standard uncertainties of $x_{i,lab}$ and $x_{i,SCRV}$, respectively

## 11. Results and Discussion

A complete set of results from each participant is described in annex A of this report. The results of the supplementary comparison are summarized in Table 2 and Figure 4.

**Table 2.** Summarized results for APMP.QM-S14 (nmol mol$^{-1}$)

| Laboratory Cylinder | $x_{i,ref}$ | $u_{i,prep}$ | $u_{i,ver}$ | $u_{i,ref}$ | $x_{i,lab}$ | $u_{i,lab}$ | $D_i$ | U($D_i$) $k = 2$ |
|---|---|---|---|---|---|---|---|---|
| **NIM – APE1218317** | | | | | | | | |
| benzene | 104.20 | 0.11 | 0.43 | 0.44 | 105.2 | 1.1 | 1.0 | 2.3 |
| toluene | 104.73 | 0.12 | 0.44 | 0.45 | 105.2 | 1.1 | 0.5 | 2.3 |
| ethylbenzene | 103.94 | 0.15 | 0.47 | 0.49 | 104.3 | 1.0 | 0.4 | 2.3 |
| m-xylene | 103.10 | 0.16 | 0.47 | 0.49 | 103.3 | 1.5 | 0.2 | 3.3 |
| styrene | 102.73 | 0.18 | 0.49 | 0.52 | 102.5 | 1.5 | -0.2 | 3.2 |
| o-xylene | 103.59 | 0.19 | 0.59 | 0.62 | 102.0 | 1.5 | -1.6 | 3.3 |
| chloroform | 106.11 | 0.13 | 0.46 | 0.48 | 108.6 | 1.1 | 2.5 | 2.4 |
| 1,1,2-trichloroethane | 101.56 | 0.17 | 0.58 | 0.61 | 101.7 | 1.5 | 0.1 | 3.3 |
| trichloroethylene | 104.13 | 0.07 | 0.56 | 0.57 | 105.3 | 1.6 | 1.2 | 3.4 |
| tetrachloroethylene | 101.53 | 0.07 | 0.65 | 0.65 | 101.9 | 1.0 | 0.4 | 2.4 |
| 1,1-dichloroethane | 103.54 | 0.13 | 0.45 | 0.47 | 103.9 | 1.0 | 0.4 | 2.3 |
| carbon tetrachloride | 102.99 | 0.16 | 0.46 | 0.49 | 102.2 | 1.0 | -0.8 | 2.3 |
| 1,3-butadiene | 102.86 | 0.17 | 0.46 | 0.49 | 102.8 | 1.0 | -0.1 | 2.3 |
| dichloromethane | 102.69 | 0.24 | 0.51 | 0.51 | 102.1 | 1.0 | -0.6 | 2.3 |
| **NMISA – APE1218321** | | | | | | | | |
| benzene | 105.42 | 0.11 | 0.43 | 0.44 | 118.6 | 3.5 | 13.2 | 7.0 |
| toluene | 105.96 | 0.12 | 0.44 | 0.46 | 108.3 | 3.4 | 2.3 | 6.9 |
| ethylbenzene | 105.16 | 0.15 | 0.47 | 0.50 | 112.6 | 3.0 | 7.4 | 6.0 |
| m-xylene | 104.31 | 0.16 | 0.47 | 0.50 | 116.4 | 2.8 | 12.1 | 5.6 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| styrene | 103.93 | 0.18 | 0.49 | 0.53 | * | * | | |
| o-xylene | 104.81 | 0.19 | 0.60 | 0.63 | 93.8 | 2.5 | -11.0 | 5.1 |
| chloroform | 106.78 | 0.13 | 0.46 | 0.48 | 109.1 | 2.2 | 2.3 | 4.4 |
| 1,1,2-trichloroethane | 102.20 | 0.18 | 0.58 | 0.61 | * | * | | |
| trichloroethylene | 104.79 | 0.07 | 0.57 | 0.57 | 103.3 | 2.9 | -1.5 | 5.8 |
| tetrachloroethylene | 102.17 | 0.07 | 0.65 | 0.66 | 128.0 | 6.0 | 25.8 | 12.1 |
| 1,1-dichloroethane | 104.20 | 0.13 | 0.45 | 0.47 | * | * | | |
| carbon tetrachloride | 103.64 | 0.16 | 0.46 | 0.49 | * | * | | |
| 1,3-butadiene | 104.27 | 0.19 | 0.47 | 0.50 | 106.1 | 0.7 | 1.8 | 1.6 |
| dichloromethane | 107.85 | 0.25 | 0.54 | 0.59 | 103.2 | 2.9 | -4.6 | 5.9 |
| **KRISS – APEX1218423** | | | | | | | | |
| benzene | 104.68 | 0.11 | 0.43 | 0.44 | 104.61 | 0.47 | -0.07 | 1.29 |
| toluene | 105.21 | 0.12 | 0.44 | 0.46 | 105.20 | 0.49 | -0.01 | 1.33 |
| ethylbenzene | 104.42 | 0.15 | 0.47 | 0.49 | 104.53 | 0.52 | 0.11 | 1.44 |
| m-xylene | 103.58 | 0.16 | 0.47 | 0.50 | 103.66 | 0.55 | 0.08 | 1.47 |
| styrene | 103.20 | 0.18 | 0.49 | 0.52 | 103.30 | 0.57 | 0.10 | 1.55 |
| o-xylene | 104.07 | 0.19 | 0.59 | 0.62 | 104.39 | 0.69 | 0.32 | 1.86 |
| chloroform | 106.03 | 0.13 | 0.46 | 0.48 | 105.93 | 0.51 | -0.10 | 1.39 |
| 1,1,2-trichloroethane | 101.48 | 0.17 | 0.58 | 0.61 | 101.56 | 0.64 | 0.07 | 1.76 |
| trichloroethylene | 104.06 | 0.07 | 0.56 | 0.57 | 103.99 | 0.59 | -0.07 | 1.64 |
| tetrachloroethylene | 101.45 | 0.07 | 0.65 | 0.63 | 101.41 | 0.67 | -0.05 | 1.88 |
| 1,1-dichloroethane | 103.46 | 0.13 | 0.45 | 0.47 | 103.51 | 0.51 | 0.05 | 1.38 |
| carbon tetrachloride | 102.91 | 0.16 | 0.46 | 0.49 | 102.80 | 0.54 | -0.11 | 1.46 |
| 1,3-butadiene | 103.53 | 0.19 | 0.46 | 0.50 | 103.58 | 0.51 | 0.04 | 1.44 |
| dichloromethane | 107.09 | 0.25 | 0.53 | 0.59 | 107.17 | 0.61 | 0.08 | 1.69 |

* Note: the analytes were not measured by NMISA

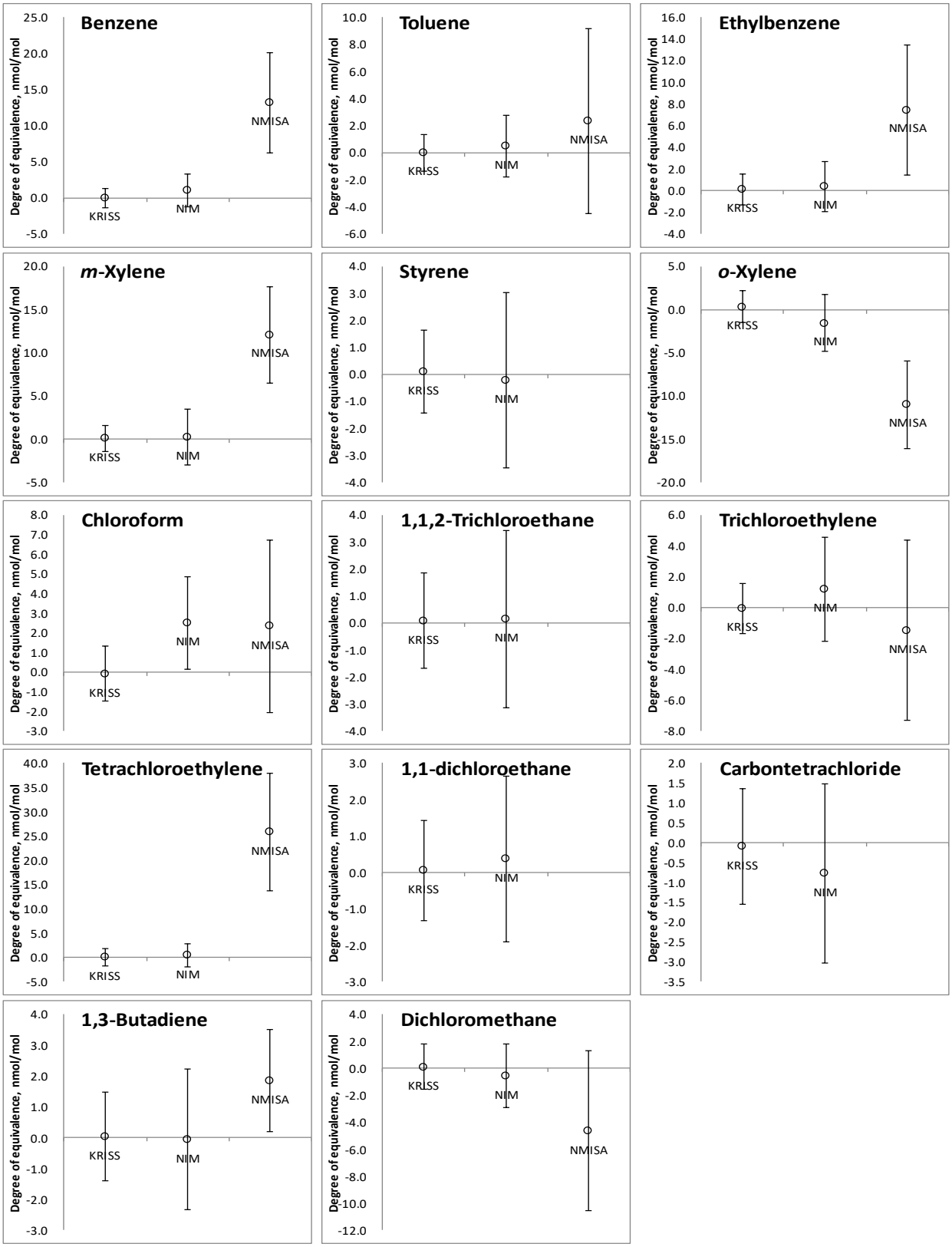


**Figure 4**. Degrees of equivalence for APMP.QM-S14. Error bars represent expanded uncertainties ($k$ = 2)

## 12. Conclusions

The comparison has been successfully conducted to evaluate the participants' measurement capabilities for HAPs in nitrogen at 100 nmol $mol^{-1}$. Both NIM and KRISS results are consistent with their SCRVs for all analytes except chloroform from NIM. NMISA results are consistent with their SCRVs for toluene, styrene, chloroform, 1,1,2-trichloroethane, trichloroethylene, 1,1-dichloroethane, carbon tetrachloride, and dichloromethane while NMISA results are not consistent with their SCRVs for benzene, ethylbenzene, m-xylene, o-xylene, tetrachloroethylene, 1,3-butadiene.

## 13. Supported CMC claims

This supplementary comparison underpins core skills and competencies required in gravimetric preparation, analytical verification and purity analysis of HAPs. It is considered as a Track C comparison due to its nature with the stability challenges. The results of this supplementary comparison can be used to support CMC claims for benzene, toluene, ethylbenzene, *m*-xylene, styrene, *o*-xylene, chloroform, 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, carbon tetrachloride, 1,3-butadiene and dichloromethane in nitrogen as explained in the Annex A.

## 14. References

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

[2] Lee S, Kim M E, Oh S H, Kim J S 2017 Determination of physical adsorption loss of primary standard gas mixtures in cylinders using cylinder-to-cylinder division *Metrologia* **54** L26.

## Coordinator and Correspondence

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Gas Metrology Group
Korea Research Institute of Standards and Science

**Annex A: Examples for HFTLS statements for CMC claims**

1. Participant's results are consistent with SCRVs

When a participant reported standard uncertainty is 0.4 nmol $mol^{-1}$ and its SCRV is 106.34 nmol $mol^{-1}$, its HFTLS statements are in the following.

| Lower limit of amount fraction (nmol $mol^{-1}$) | Upper limit of amount fraction (nmol $mol^{-1}$) | Lower limit of expanded uncertainty (%) | Upper limit of expanded uncertainty (%) |
|---|---|---|---|
| 0.8 | 100 | 100 | 0.8 |
| 100 | 10 000 | 0.8 | 0.8 |

2. Participant's results are not consistent with SCRVs

When a participant reported standard uncertainty is 1.1 nmol $mol^{-1}$, its SCRV is 104.8 nmol $mol^{-1}$, and D is 6.3 nmol $mol^{-1}$, its HFTLS statements are in the following.

| Lower limit of amount fraction (nmol $mol^{-1}$) | Upper limit of amount fraction (nmol $mol^{-1}$) | Lower limit of expanded uncertainty (%) | Upper limit of expanded uncertainty (%) |
|---|---|---|---|
| 12.8 | 100 | 100 | 12.2 |
| 100 | 10 000 | 12.2 | 12.2 |

**Annex B: Measurement reports**

**Report form**
Laboratory name: National Institute of Metrology, China
Cylinder number: APE1218317

Measurement 1#

| Component | Date (dd/mm/yy) | Result (nmol $mol^{-1}$) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| Benzene | 15/08/2019 | 104.6 | 0.10% | 6 |
| Toluene | 15/08/2019 | 104.6 | 0.17% | 6 |
| Ethylbenzene | 15/08/2019 | 103.6 | 0.12% | 6 |
| o-xylene | 15/08/2019 | 101.5 | 0.18% | 6 |
| m-xylene | 15/08/2019 | 102.8 | 0.22% | 6 |
| Styrene | 15/08/2019 | 100.1 | 0.24% | 6 |
| 1,3-butadiene | 15/08/2019 | 102.6 | 0.15% | 6 |
| Tetrachloroethylene | 15/08/2019 | 101.4 | 0.30% | 6 |
| Trichloroethylene | 15/08/2019 | 106.1 | 0.23% | 6 |
| 1,1,2-trichloroethane | 15/08/2019 | 100.9 | 0.21% | 6 |
| 1,1-dichloroethane | 15/08/2019 | 103.4 | 0.29% | 6 |
| Carbon tetrachloride | 15/08/2019 | 102.2 | 0.32% | 6 |
| Chloroform | 15/08/2019 | 108.6 | 0.34% | 6 |
| Dichloromethane | 15/08/2019 | 102.0 | 0.34% | 6 |

Measurement 2#

| Component | Date (dd/mm/yy) | Result (nmol mol-1) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| Benzene | 21/08/2019 | 105.5 | 0.36% | 6 |
| Toluene | 21/08/2019 | 105.3 | 0.28% | 6 |
| Ethylbenzene | 21/08/2019 | 103.8 | 0.47% | 6 |
| o-xylene | 21/08/2019 | 100.5 | 0.29% | 6 |
| m-xylene | 21/08/2019 | 104.0 | 0.35% | 6 |
| Styrene | 21/08/2019 | 103.8 | 0.26% | 6 |
| 1,3-butadiene | 21/08/2019 | 103.0 | 0.43% | 6 |
| Tetrachloroethylene | 21/08/2019 | 101.8 | 0.33% | 6 |
| Trichloroethylene | 21/08/2019 | 104.2 | 0.23% | 6 |
| 1,1,2-trichloroethane | 21/08/2019 | 101.6 | 0.26% | 6 |
| 1,1-dichloroethane | 21/08/2019 | 103.9 | 0.29% | 6 |
| Carbon tetrachloride | 21/08/2019 | 101.8 | 0.25% | 6 |
| Chloroform | 21/08/2019 | 108.1 | 0.20% | 6 |
| Dichloromethane | 21/08/2019 | 102.0 | 0.39% | 6 |

Measurement 3#

| Component | Date (dd/mm/yy) | Result (nmol mol$^{-1}$) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| Benzene | 25/08/2019 | 106.0 | 0.28% | 6 |
| Toluene | 25/08/2019 | 105.8 | 0.09% | 6 |
| Ethylbenzene | 25/08/2019 | 104.8 | 0.24% | 6 |
| o-xylene | 25/08/2019 | 103.2 | 0.08% | 6 |
| m-xylene | 25/08/2019 | 103.6 | 0.23% | 6 |
| Styrene | 25/08/2019 | 103.5 | 0.26% | 6 |
| 1,3-butadiene | 25/08/2019 | 102.1 | 0.06% | 6 |
| Tetrachloroethylene | 25/08/2019 | 102.2 | 0.16% | 6 |
| Trichloroethylene | 25/08/2019 | 104.4 | 0.15% | 6 |
| 1,1,2-trichloroethane | 25/08/2019 | 102.2 | 0.19% | 6 |
| 1,1-dichloroethane | 25/08/2019 | 104.2 | 0.14% | 6 |
| Carbon tetrachloride | 25/08/2019 | 101.8 | 0.19% | 6 |
| Chloroform | 25/08/2019 | 108.8 | 0.12% | 6 |
| Dichloromethane | 25/08/2019 | 102.1 | 0.25% | 6 |

Measurement 4

| Component | Date (dd/mm/yy) | Result (nmol mol$^{-1}$) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| Benzene | 16/09/2019 | 104.7 | 0.23% | 6 |
| Toluene | 16/09/2019 | 105.1 | 0.30% | 6 |
| Ethylbenzene | 16/09/2019 | 104.8 | 0.31% | 6 |
| o-xylene | 16/09/2019 | 102.7 | 0.27% | 6 |
| m-xylene | 16/09/2019 | 102.9 | 0.16% | 6 |
| Styrene | 16/09/2019 | 102.4 | 0.80% | 6 |
| 1,3-butadiene | 16/09/2019 | 103.6 | 0.47% | 6 |
| Tetrachloroethylene | 16/09/2019 | 102.1 | 0.56% | 6 |
| Trichloroethylene | 16/09/2019 | 106.3 | 0.41% | 6 |
| 1,1,2-trichloroethane | 16/09/2019 | 102.0 | 0.39% | 6 |
| 1,1-dichloroethane | 16/09/2019 | 103.9 | 0.53% | 6 |
| Carbon tetrachloride | 16/09/2019 | 102.9 | 0.59% | 6 |
| Chloroform | 16/09/2019 | 108.7 | 0.53% | 6 |
| Dichloromethane | 16/09/2019 | 102.4 | 0.53% | 6 |

Results

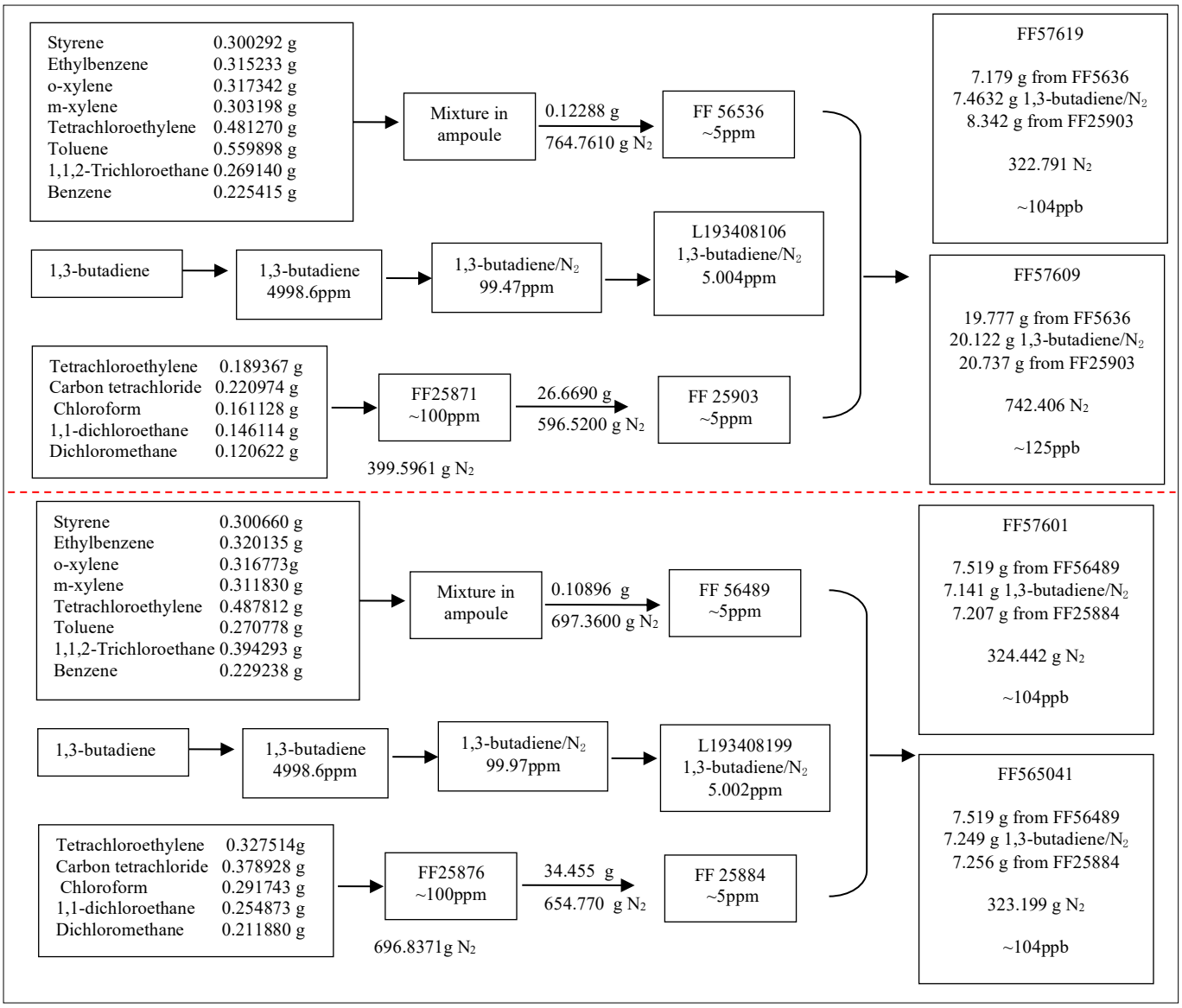
| Component | Result (nmol mol$^{-1}$) | Expanded uncertainty (nmol mol$^{-1}$) | Coverage factor |
|---|---|---|---|
| Benzene | 105.2 | 2% | 2 |
| Toluene | 105.2 | 2% | 2 |
| Ethylbenzene | 104.3 | 2% | 2 |
| o-xylene | 102.0 | 3% | 2 |

| | | | |
|---|---|---|---|
| m-xylene | 103.3 | 3% | 2 |
| Styrene | 102.5 | 3% | 2 |
| 1,3-butadiene | 102.8 | 2% | 2 |
| Tetrachloroethylene | 101.9 | 2% | 2 |
| Trichloroethylene | 105.3 | 3% | 2 |
| 1,1,2-trichloroethane | 101.7 | 3% | 2 |
| 1,1-dichloroethane | 103.9 | 2% | 2 |
| Carbon tetrachloride | 102.2 | 2% | 2 |
| Chloroform | 108.6 | 2% | 2 |
| Dichloromethane | 102.1 | 2% | 2 |

## Calibration standards

Please provide a brief description of the calibration standards used.

The following chart shows a brief outline of the dilution series undertaken to produce the final mixtures. The dilution series were designed based on the saturated vapor pressure of the target components. The components with similar saturated vapor pressure were mixed together so that the evaporation loss was minimized. The components were either directly injected into the cylinder or mixed in ampoule prior to the injection. The calibration standards were measured against each other and the consistency of different cylinder was within 0.1%-0.7%.




## Analytical method

Please provide a brief description of the instrumentation and method used for analysis

The calibration standard and sample were directly injected into GCMS system without preconcentration. An A-B-A sequence were repeated several times so that the instrument reading was stabilized to an acceptable level. The chromatographic condition is listed as below:

| System | Injection volume | Split ratio | Oven temperature | Colum | Ion mode |
|---|---|---|---|---|---|
| GCMS | 5mL | 30:1 | 40°C 5min<br>5°C/min to 180 °C | DB624UI<br>60m*0.32mm*1.8μm | SIM |

## Uncertainty evaluation

Please provide a brief description of the evaluation of measurement uncertainty.

The major uncertainty came from the following parts: the purity of materials, the weighing, the atomic weight as well as the consistency of verification. The effect of adsorption was also evaluated.

**a) Purity table for the nominally pure Benzene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00170 | 0.00017 |
| Others | GCMS | Normal | 0.00220 | 0.00022 |
| Benzene | / | / | 0.99610 | 0.00028 |

**b) Purity table for the nominally pure Toluene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00080 | 0.00008 |
| Others | GCMS | Normal | 0.00140 | 0.00014 |
| Toluene | / | / | 0.99860 | 0.00016 |

**c) Purity table for the nominally pure Ethylbenzene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Toluene | GCMS | Normal | 0.00230 | 0.00023 |
| Water | Karl Fischer | Normal | 0.00179 | 0.00018 |
| Benzene | GCMS | Normal | 0.00160 | 0.00016 |
| Others | GCMS | Normal | 0.00530 | 0.00053 |
| Ethylbenzene | / | / | 0.98901 | 0.00063 |

**d) Purity table for the nominally pure o-xylene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00100 | 0.00010 |
| m-xylene | GCMS | Normal | 0.01260 | 0.00126 |
| Others | GCMS | Normal | 0.00430 | 0.00043 |
| o-xylene | / | / | 0.98210 | 0.00134 |

**e) Purity table for the nominally pure m-xylene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | GCMS | Normal | 0.00100 | 0.00010 |
| p-xylene | Karl Fischer | Normal | 0.01260 | 0.00126 |
| Others | GCMS | Normal | 0.00430 | 0.00043 |
| o-xylene | GCMS | Normal | 0.98210 | 0.00134 |

**f) Purity table for the nominally pure Styrene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.23320 | 0.02332 |
| Others | GCMS | Normal | 0.05000 | 0.00500 |
| Styrene | / | / | 0.99717 | 0.00024 |

**g) Purity table for the nominally pure 1,3-butadiene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| $N_2$ | PDHID | Normal | 0.00005 | 0.00001 |
| Others | GCMS | Normal | 0.00015 | 0.00002 |
| 1,3-butadiene | / | / | 0.99980 | 0.00002 |

**h) Purity table for the nominally pure Tetrachloroethylene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00088 | 0.00009 |
| Others | GCMS | Normal | 0.00040 | 0.00004 |
| Tetrachloroethylene | / | / | 0.99872 | 0.00010 |

**i) Purity table for the nominally pure Trichloroethylene**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00106 | 0.00011 |
| Others | GCMS | Normal | 0.00280 | 0.00028 |
| Tetrachloroethylene | / | / | 0.99614 | 0.00030 |

**j) Purity table for the nominally pure 1,1,2-trichloroethane**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00354 | 0.00035 |
| Others | GCMS | Normal | 0.01240 | 0.00124 |
| 1,1,2-trichloroethane | / | / | 0.98406 | 0.03545 |

**k) Purity table for the nominally pure 1,1-dichloroethane**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00148 | 0.00015 |
| Others | GCMS | Normal | 0.01790 | 0.00179 |
| 1,1-dichloroethane | / | / | 0.98062 | 0.0018 |

**l) Purity table for the nominally pure Carbon tetrachloride**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00072 | 0.00007 |
| Others | GCMS | Normal | 0.00520 | 0.00052 |
| $CCl_4$ | / | / | 0.99408 | 0.00052 |

**m) Purity table for the nominally pure Chloroform**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00106 | 0.00011 |
| Others | GCMS | Normal | 0.00280 | 0.00028 |
| Chloroform | / | / | 0.99614 | 0.00030 |

**n) Purity table for the nominally pure Dichloromethane**

| Compounds | Instrument | Distribution | Concentration mol/mol | Standard uncertainty |
|---|---|---|---|---|
| Water | Karl Fischer | Normal | 0.00191 | 0.00019 |
| Others | GCMS | Normal | 0.00020 | 0.00002 |
| Dichloromethane | / | / | 0.99789 | 0.00019 |

**o) Purity table for the Nitrogen**

| Compounds | Amount fraction ($10^{-6}$mol/mol) | Standard uncertainty ($10^{-6}$mol/mol) | Assumed distribution |
|---|---|---|---|
| $CH_4$ | 0.001 | 0.0005 | Rectangular |
| Ar | 48.3 | 4.8 | Normal |
| $O_2$ | 0.02 | 0.006 | Normal |
| $CO_2$ | 0.010 | 0.003 | Normal |
| $H_2O$ | 0.10 | 0.04 | Normal |
| $N_2O$ | 0.0001 | 0.0004 | Rectangular |
| $N_2$ | 999952.1 | 4.8 | Normal |

**p) Purity table for the final mixture**

**(Standard 1)** Cylinder Identification Number: FF 56504

| Component | Mole fraction Value | Unit | Expanded Uncertainty | Unit | Coverage Factor |
|---|---|---|---|---|---|
| CH4 | 9.9894E-10 | mol/mol | 9.376E-10 | mol/mol | 2 |
| Ar | 4.8249E-05 | mol/mol | 9.001E-06 | mol/mol | 2 |
| O2 | 1.9979E-08 | mol/mol | 1.125E-08 | mol/mol | 2 |
| CO2 | 9.9894E-09 | mol/mol | 5.626E-09 | mol/mol | 2 |
| H2O | 1.0189E-07 | mol/mol | 7.501E-08 | mol/mol | 2 |

| | | | | | |
|---|---|---|---|---|---|
| N2O | 9.9894E-12 | mol/mol | 5.438E-12 | mol/mol | 2 |
| N2 | 9.9995E-01 | mol/mol | 2.115E-04 | mol/mol | 2 |
| other | 1.3953E-09 | mol/mol | 1.525E-10 | mol/mol | 2 |
| C4H6 | 1.0511E-07 | mol/mol | 2.113E-04 | mol/mol | 2 |
| C2HCl3 | 1.0482E-07 | mol/mol | 1.567E-10 | mol/mol | 2 |
| CCl4 | 1.0368E-07 | mol/mol | 1.816E-10 | mol/mol | 2 |
| CHCl3 | 1.0271E-07 | mol/mol | 1.608E-10 | mol/mol | 2 |
| C2H4Cl2 | 1.0666E-07 | mol/mol | 4.155E-10 | mol/mol | 2 |
| CH2Cl2 | 1.0518E-07 | mol/mol | 1.614E-10 | mol/mol | 2 |
| C8H8 | 1.0074E-07 | mol/mol | 9.184E-10 | mol/mol | 2 |
| C7H8 | 1.0263E-07 | mol/mol | 9.355E-10 | mol/mol | 2 |
| C6H6 | 1.0219E-07 | mol/mol | 9.531E-10 | mol/mol | 2 |
| C8H10(ethylbenzene) | 1.0416E-07 | mol/mol | 9.849E-10 | mol/mol | 2 |
| C8H10(m) | 1.0363E-07 | mol/mol | 9.701E-10 | mol/mol | 2 |
| C8H10(0) | 1.0225E-07 | mol/mol | 9.638E-10 | mol/mol | 2 |
| C8H10(p) | 2.1566E-10 | mol/mol | 4.310E-11 | mol/mol | 2 |
| C2Cl4 | 1.0269E-07 | mol/mol | 8.663E-10 | mol/mol | 2 |
| C2H3Cl3 | 1.0174E-07 | mol/mol | 9.937E-10 | mol/mol | 2 |

**(Standard 2)** Cylinder Identification Number: FF 57601

| Component | Mole fraction Value | Unit | Expanded Uncertainty | Unit | Coverage Factor |
|---|---|---|---|---|---|
| CH4 | 9.990E-10 | mol/mol | 9.375E-10 | mol/mol | 2 |
| Ar | 4.825E-05 | mol/mol | 9.000E-06 | mol/mol | 2 |
| O2 | 1.998E-08 | mol/mol | 1.125E-08 | mol/mol | 2 |
| CO2 | 9.990E-09 | mol/mol | 5.625E-09 | mol/mol | 2 |
| H2O | 1.019E-07 | mol/mol | 7.500E-08 | mol/mol | 2 |
| N2O | 9.990E-12 | mol/mol | 5.438E-12 | mol/mol | 2 |
| N2 | 1.000E+00 | mol/mol | 2.076E-04 | mol/mol | 2 |
| other | 1.031E-07 | mol/mol | 2.073E-04 | mol/mol | 2 |
| C4H6 | 1.443E-09 | mol/mol | 1.577E-10 | mol/mol | 2 |
| C2HCl3 | 1.037E-07 | mol/mol | 1.554E-10 | mol/mol | 2 |
| CCl4 | 1.026E-07 | mol/mol | 1.799E-10 | mol/mol | 2 |
| CHCl3 | 1.016E-07 | mol/mol | 1.593E-10 | mol/mol | 2 |
| C2H4Cl2 | 1.055E-07 | mol/mol | 4.112E-10 | mol/mol | 2 |
| CH2Cl2 | 1.041E-07 | mol/mol | 1.600E-10 | mol/mol | 2 |
| C8H8 | 1.041E-07 | mol/mol | 9.490E-10 | mol/mol | 2 |
| C7H8 | 1.061E-07 | mol/mol | 9.666E-10 | mol/mol | 2 |
| C6H6 | 1.057E-07 | mol/mol | 9.849E-10 | mol/mol | 2 |
| C8H10 | 1.077E-07 | mol/mol | 1.018E-09 | mol/mol | 2 |
| C8H10 | 1.071E-07 | mol/mol | 1.002E-09 | mol/mol | 2 |
| C8H10 | 1.057E-07 | mol/mol | 9.959E-10 | mol/mol | 2 |

| | | | | | |
|---|---|---|---|---|---|
| C8H10 | 2.230E-10 | mol/mol | 4.456E-11 | mol/mol | 2 |
| C2Cl4 | 1.062E-07 | mol/mol | 8.951E-10 | mol/mol | 2 |
| C2H3Cl3 | 1.052E-07 | mol/mol | 1.027E-09 | mol/mol | 2 |

**(Standard 3)** Cylinder Identification Number: FF 57619

| Component | Mole fraction Value | Unit | Expanded Uncertainty | Unit | Coverage Factor |
|---|---|---|---|---|---|
| CH4 | 9.989E-10 | mol/mol | 9.343E-10 | mol/mol | 2 |
| Ar | 4.825E-05 | mol/mol | 8.969E-06 | mol/mol | 2 |
| O2 | 1.998E-08 | mol/mol | 1.121E-08 | mol/mol | 2 |
| CO2 | 9.989E-09 | mol/mol | 5.606E-09 | mol/mol | 2 |
| H2O | 1.019E-07 | mol/mol | 7.474E-08 | mol/mol | 2 |
| N2O | 9.989E-12 | mol/mol | 5.419E-12 | mol/mol | 2 |
| N2 | 1.000E+00 | mol/mol | 2.172E-04 | mol/mol | 2 |
| other | 1.079E-07 | mol/mol | 2.169E-04 | mol/mol | 2 |
| C4H6 | 1.422E-09 | mol/mol | 1.554E-10 | mol/mol | 2 |
| C2HCl3 | 1.038E-07 | mol/mol | 1.716E-10 | mol/mol | 2 |
| CCl4 | 1.035E-07 | mol/mol | 1.889E-10 | mol/mol | 2 |
| CHCl3 | 9.713E-08 | mol/mol | 1.758E-10 | mol/mol | 2 |
| C2H4Cl2 | 1.047E-07 | mol/mol | 4.212E-10 | mol/mol | 2 |
| CH2Cl2 | 1.025E-07 | mol/mol | 2.043E-10 | mol/mol | 2 |
| C8H8 | 1.035E-07 | mol/mol | 9.375E-10 | mol/mol | 2 |
| C7H8 | 1.049E-07 | mol/mol | 9.509E-10 | mol/mol | 2 |
| C6H6 | 1.034E-07 | mol/mol | 9.597E-10 | mol/mol | 2 |
| C8H10 | 1.055E-07 | mol/mol | 9.932E-10 | mol/mol | 2 |
| C8H10 | 1.037E-07 | mol/mol | 9.697E-10 | mol/mol | 2 |
| C8H10 | 1.054E-07 | mol/mol | 9.865E-10 | mol/mol | 2 |
| C8H10 | 2.157E-10 | mol/mol | 4.310E-11 | mol/mol | 2 |
| C2Cl4 | 1.042E-07 | mol/mol | 8.744E-10 | mol/mol | 2 |
| C2H3Cl3 | 1.033E-07 | mol/mol | 1.005E-09 | mol/mol | 2 |

**(Standard 4)** Cylinder Identification Number: FF 57609

| Component | Mole fraction Value | Unit | Expanded Uncertainty | Unit | Coverage Factor |
|---|---|---|---|---|---|
| CH4 | 9.987E-10 | mol/mol | 9.221E-10 | mol/mol | 2 |
| Ar | 4.824E-05 | mol/mol | 8.852E-06 | mol/mol | 2 |
| O2 | 1.997E-08 | mol/mol | 1.107E-08 | mol/mol | 2 |
| CO2 | 9.987E-09 | mol/mol | 5.533E-09 | mol/mol | 2 |
| H2O | 1.023E-07 | mol/mol | 7.377E-08 | mol/mol | 2 |
| N2O | 9.987E-12 | mol/mol | 5.348E-12 | mol/mol | 2 |
| N2 | 1.000E+00 | mol/mol | 2.511E-04 | mol/mol | 2 |
| other | 1.248E-07 | mol/mol | 2.509E-04 | mol/mol | 2 |
| C4H6 | 1.680E-09 | mol/mol | 1.837E-10 | mol/mol | 2 |

| | | | | | |
|---|---|---|---|---|---|
| C2HCl3 | 1.267E-07 | mol/mol | 1.808E-10 | mol/mol | 2 |
| CCl4 | 1.263E-07 | mol/mol | 2.051E-10 | mol/mol | 2 |
| CHCl3 | 1.186E-07 | mol/mol | 1.904E-10 | mol/mol | 2 |
| C2H4Cl2 | 1.278E-07 | mol/mol | 5.030E-10 | mol/mol | 2 |
| CH2Cl2 | 1.251E-07 | mol/mol | 2.264E-10 | mol/mol | 2 |
| C8H8 | 1.223E-07 | mol/mol | 1.101E-09 | mol/mol | 2 |
| C7H8 | 1.240E-07 | mol/mol | 1.117E-09 | mol/mol | 2 |
| C6H6 | 1.221E-07 | mol/mol | 1.128E-09 | mol/mol | 2 |
| C8H10 | 1.247E-07 | mol/mol | 1.167E-09 | mol/mol | 2 |
| C8H10 | 1.225E-07 | mol/mol | 1.140E-09 | mol/mol | 2 |
| C8H10 | 1.245E-07 | mol/mol | 1.159E-09 | mol/mol | 2 |
| C8H10 | 2.549E-10 | mol/mol | 5.093E-11 | mol/mol | 2 |
| C2Cl4 | 1.232E-07 | mol/mol | 1.026E-09 | mol/mol | 2 |
| C2H3Cl3 | 1.221E-07 | mol/mol | 1.181E-09 | mol/mol | 2 |

**q) The repeatability and consistency of verification**

Repeatability check

One sample was injected 6 times to verify the repeatability of analytical method.

| Compound | Diff.-1 | Diff.-2 | Diff.-3 | Diff.-4 | Diff.-5 | Diff.-6 |
|---|---|---|---|---|---|---|
| 1,3-butadiene | 0.39% | 0.34% | 0.14% | -0.09% | -0.21% | -0.36% |
| Dichloromethane | 0.45% | -0.05% | -0.01% | -0.22% | -0.27% | -0.44% |
| 1,1-dichloroethane | 0.23% | -0.01% | 0.19% | 0.11% | 0.23% | -0.04% |
| Chloroform | 0.47% | 0.10% | 0.08% | -0.11% | -0.18% | -0.33% |
| Carbon tetrachloride | 0.25% | -0.22% | 0.17% | 0.12% | -0.06% | -0.35% |
| Benzene | 0.26% | 0.16% | 0.34% | 0.07% | -0.10% | -0.27% |
| Trichloroethylene | -0.01% | -0.02% | 0.19% | 0.02% | -0.05% | -0.22% |
| Toluene | -0.41% | -0.42% | 0.21% | 0.23% | -0.04% | -0.33% |
| 1,1,2-trichloroethane | 0.26% | -0.01% | 0.29% | 0.06% | -0.19% | -0.31% |
| Tetrachloroethylene | 0.13% | -0.01% | 0.26% | 0.09% | -0.12% | -0.29% |
| Ethylbenzene | 0.04% | -0.28% | 0.26% | 0.12% | -0.22% | -0.44% |
| m-xylene | 0.24% | -0.21% | 0.41% | 0.25% | -0.14% | -0.36% |
| o-xylene | 0.01% | -0.22% | 0.37% | 0.07% | -0.39% | -0.43% |
| Styrene | 0.13% | -0.53% | 0.01% | 0.08% | -0.43% | -0.69% |

Consistency verification

Two cylinders were measured against each other to verify the consistency of the prepared standards. These cylinders are FF57601 and FF565041, of which parent gas was from different mixture.

| Compound | Diff.-1 | Diff.-2 | Diff.-3 | Diff.-4 | Diff.-5 | Diff.-6 |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| 1,3-butadiene | -0.19% | -0.29% | -0.20% | -0.20% | -0.20% | -0.19% |
| Dichloromethane | -1.18% | -1.23% | -0.93% | -0.95% | -0.84% | -0.73% |
| 1,1-dichloroethane | -0.10% | -0.12% | -0.08% | -0.09% | -0.11% | -0.10% |
| Chloroform | -0.92% | -0.83% | -1.07% | -0.66% | -0.91% | -0.52% |
| Carbon tetrachloride | -0.89% | -1.12% | -1.46% | -0.76% | -0.39% | -0.52% |
| Benzene | 0.38% | 0.56% | 0.40% | 0.45% | 0.33% | 0.31% |
| Trichloroethylene | -1.31% | -1.30% | -1.31% | -1.30% | -1.26% | -1.22% |
| Toluene | 0.10% | 0.10% | 0.10% | 0.15% | 0.10% | 0.10% |
| 1,1,2-trichloroethane | 0.01% | -0.08% | -0.35% | -0.51% | -0.46% | -0.40% |
| Tetrachloroethylene | -0.10% | -0.11% | -0.07% | -0.08% | -0.07% | -0.07% |
| Ethylbenzene | 0.10% | 0.08% | 0.12% | 0.15% | 0.18% | 0.19% |
| m-xylene | 0.19% | 0.16% | 0.16% | 0.20% | 0.24% | 0.14% |
| o-xylene | 1.01% | 0.75% | 0.56% | 0.43% | 0.37% | 0.21% |
| Styrene | -1.06% | -1.26% | -1.10% | -0.71% | -0.54% | -0.36% |

**r) Adsorption loss**

The adsorption loss was determined by the following method: about 60 L gases was decanted to the target cylinder (C.A. 10 bar). The daughter cylinder was measured against mother cylinder after 30 days of stabilization.

| Compound | 1 | 2 | 3 | 4 | AVE |
|---|---|---|---|---|---|
| 1,3-butadiene | 0.07% | 0.27% | -0.13% | -0.16% | 0.01% |
| Dichloromethane | -0.31% | 0.00% | 0.17% | -0.24% | -0.09% |
| 1,1-dichloroethane | 0.33% | 0.35% | -0.15% | -0.56% | -0.01% |
| Chloroform | -0.23% | -0.16% | -0.14% | -0.38% | -0.23% |
| Carbon tetrachloride | -0.66% | -0.47% | -0.48% | -0.50% | -0.53% |
| Benzene | -0.32% | -0.07% | 0.01% | -0.13% | -0.13% |
| Trichloroethylene | -0.65% | -0.31% | -0.20% | -0.33% | -0.37% |
| Toluene | -0.40% | -0.16% | -0.15% | -0.28% | -0.25% |
| 1,1,2-trichloroethane | -0.82% | -0.59% | -0.80% | -0.88% | -0.77% |
| Tetrachloroethylene | -0.51% | -0.10% | -0.03% | -0.37% | -0.25% |
| Ethylbenzene | -0.53% | -0.24% | -0.31% | -0.51% | -0.40% |
| m-xylene | -0.49% | -0.22% | -0.34% | -0.72% | -0.44% |
| o-xylene | -0.90% | -0.63% | -0.57% | -0.76% | -0.71% |
| Styrene | -1.78% | -1.60% | -1.56% | -1.54% | -1.62% |

Report form
Laboratory name: National Metrology Institute of South Africa
Cylinder number: D51 7565

Table 1: Measurement 1#

| Component | Date (25/10/19) | Result (μmol/mol) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| 1,3-butadiene | 0,10699 | 0,00053 | 0,49191 | Five |
| Dichloromethane | 0,0963 | 0,0028 | 2,9250 | Five |
| Chloroform | 0,1138 | 0,0018 | 1,6150 | Five |
| Benzene | 0,1168 | 0,0024 | 2,0742 | Five |
| Trichloroethylene | 0,0996 | 0,0025 | 2,4969 | Five |
| Toluene | 0,1175 | 0,0029 | 2,4443 | Five |
| Tetrachloroethylene | 0,1284 | 0,0046 | 3,5904 | Five |
| Ethylbenzene | 0,1137 | 0,0020 | 1,7624 | Five |
| m-xylene | 0,1177 | 0,0019 | 1,600 | Five |
| o-xylene | 0,0942 | 0,0019 | 1,9806 | Five |

Table 2: Measurement 2#

| Component | Date (12/11/19) | Result (μmol/mol) | Standard Uncertainty (% relative) | Number of replicates |
|---|---|---|---|---|
| 1,3-butadiene | 0,10486 | 0,00083 | 0,79308 | Five |
| Dichloromethane | 0,1058 | 0,0030 | 2,8664 | Five |
| Chloroform | 0,1042 | 0,0026 | 2,5452 | Five |
| Benzene | 0,1166 | 0,0043 | 3,6727 | Five |
| Trichloroethylene | 0,1057 | 0,0034 | 3,2035 | Five |
| Toluene | 0,1044 | 0,0044 | 4,1928 | Five |
| Tetrachloroethylene | 0,1310 | 0,0082 | 6,2756 | Five |
| Ethylbenzene | 0,1116 | 0,0038 | 3,3508 | Five |
| m-xylene | 0,1152 | 0,0034 | 2,9599 | Five |
| o-xylene | 0,0945 | 0,0030 | 3,1637 | Five |

Table 3: Measurement 3#

| Component | Date (12/11/19) | Result (μmol/mol) | Standard Uncertainty (% relative) | Number of replicates |
|---|---|---|---|---|
| 1,3-butadiene | 0,10628 | 0,00050 | 0,47155 | Five |
| Dichloromethane | 0,1076 | 0,0028 | 2,5819 | Five |
| Chloroform | 0,1094 | 0,0019 | 1,7198 | Five |
| Benzene | 0,1225 | 0,0034 | 2,7852 | Five |
| Trichloroethylene | 0,1045 | 0,0026 | 2,5161 | Five |
| Toluene | 0,1030 | 0,0027 | 2,6589 | Five |
| Tetrachloroethylene | 0,1251 | 0,0038 | 3,0631 | Five |
| Ethylbenzene | 0,1124 | 0,0028 | 2,4887 | Five |
| m-xylene | 0,1164 | 0,0027 | 2,3182 | Five |
| o-xylene | 0,0928 | 0,0023 | 2,4635 | Five |

Table 4: Comparison sample results

| Component | Result (μmol/mol) | Expanded uncertainty (μmol/mol) | Coverage factor |
|---|---|---|---|
| 1,3-butadiene | 0,1061 | 0,0013 | 2 |
| Dichloromethane | 0,1032 | 0,0058 | 2 |
| Chloroform | 0,1091 | 0,0043 | 2 |
| Benzene | 0,1186 | 0,0069 | 2 |
| Trichloroethylene | 0,1033 | 0,0057 | 2 |
| Toluene | 0,1083 | 0,0068 | 2 |
| Tetrachloroethylene | 0,128 | 0,012 | 2 |
| Ethylbenzene | 0,1126 | 0,0059 | 2 |
| m-xylene | 0,1164 | 0,0055 | 2 |
| o-xylene | 0,0938 | 0,0049 | 2 |

## Calibration standards

Please provide a brief description of the calibration standards used.

The calibration standards were prepared in two dilution steps from high pure chemicals of HAPs and BIP nitrogen gas. The high pure chemicals were purchased from Sigma Aldrich SA and the BIP nitrogen from Air Products SA. The first dilution step of HAPs was prepared using the syringe method whereby liquids were directly introduced into the cylinder with nitrogen as a diluent gas to the mole-fraction of 10 μmol/mol. The 100 nmol/mol calibration standards were therefore diluted from the verified 10 μmol/mol gas standard mixtures.

## Analytical method

Please provide a brief description of the instrumentation and method used for analysis

The analysis of HAPs was done using gas chromatography (GC) with two channels of Mass Spectrometer detector (MSD) and Flame Ionisation Detector (FID) connected to the Nutech pre-concentrator. The determination of HAPs in nitrogen was done using a single point calibration with a 100 µmol/mol HAPs in nitrogen PSGM. The comparison sample and the calibration standard were connected on the multi-position sampler box to the pre-concentrator which is connected to the GC. The column parameters for GC-MS are Restek (60 m x 320 µm x 1 µm) and for GC-FID are DB-624 column (30 m x 250 µm x 1,4 µm). The analytical conditions for FID are 60 $^0$C holding time of 8 min, 80$^0$C holding time of 13 min at the rate of 5$^0$C/min, 150 $^0$C holding time of 2min at the rate of 10 $^0$C/min.

The Nutech pre-concentrator conditions were as follows;

Table 4: Cryogenic pre-concentration steps

| | |
|---|---|
| CryoTrap 1 | Glass beads trap operated at -100°C |
| CryoTrap 2 | Tenax® trap operated at -20°C |
| CryoFocuser | Cryo focuser operated at -165°C |
| Volume pre-concentrated | 200ml |

The mole fraction for the sample was calculated using the following model equation

$$c_{unknown} = \frac{c_{known}}{Area_{known}} Area_{unknown}$$

## Uncertainty evaluation

Please provide a brief description of the evaluation of measurement uncertainty,

Considered uncertainty budget for the comparison sample is as follows;

$$u_{combined} = \sqrt{({u_{Meas1}}^2 + {u_{Meas2}}^2 + {u_{Meas3}}^2)/3}$$

Table 1: Uncertainty budget associated with HAPs comparison sample values

| Uncertainty budget | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Uncertainty contribution** | 1,3-butadiene | Dichloro methane | Chloroform | Benzene | Trichloro ethylene | Toluene | Tetrachloro ethylene | Ethylbenzene | Xylene (p,m) | o-xylene |
| **Value** | | | | | | | | | | |
| Combined standard uncertainty (k=1) | 0,00064 | 0,0029 | 0,0022 | 0,0035 | 0,0029 | 0,0034 | 0,0059 | 0,0029 | 0,0027 | 0,0024 |
| Expanded uncertainty (k=2) | 0,00128 | 0,0058 | 0,0043 | 0,0069 | 0,0057 | 0,0068 | 0,0117 | 0,0059 | 0,0055 | 0,0049 |
| %REU | 1,2 | 5,6 | 4,0 | 5,8 | 5,6 | 6,3 | 9,2 | 4,7 | 5,3 | 5,2 |

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Report
Laboratory name: Korea Research Institute of Standards and Science
Cylinder number: APEX1218423
Authorship: Ji Hwan KANG, Yong Doo KIM, Sangil LEE, Dal Ho KIM

Measurement 1[#]

| Component | Date (dd/mm/yy) | Result (nmol/mol) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| Benzene | 05/11/19 | 104.59 | 0.01 | 3 |
| Toluene | 05/11/19 | 105.19 | 0.02 | 3 |
| Ethylbenzene | 05/11/19 | 104.53 | 0.01 | 3 |
| m-Xylene | 05/11/19 | 103.70 | 0.01 | 3 |
| Styrene | 05/11/19 | 103.34 | 0.02 | 3 |
| o-Xylene | 05/11/19 | 104.46 | 0.09 | 3 |
| Chloroform | 05/11/19 | 105.93 | 0.03 | 3 |
| 1,1,2-Trichloroethane | 05/11/19 | 101.66 | 0.16 | 3 |
| Trichloroethylene | 05/11/19 | 103.97 | 0.03 | 3 |
| Tetrachloroethylene | 05/11/19 | 101.38 | 0.01 | 3 |
| 1,1-dichloroethane | 05/11/19 | 103.54 | 0.02 | 3 |
| Carbontetrachloride | 05/11/19 | 102.81 | 0.03 | 3 |
| 1,3-Butadiene | 05/11/19 | 103.54 | 0.01 | 3 |
| Dichloromethane | 05/11/19 | 107.18 | 0.03 | 3 |

Measurement 2[#]

| Component | Date (dd/mm/yy) | Result (nmol/mol) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| Benzene | 06/11/19 | 104.65 | 0.08 | 3 |
| Toluene | 06/11/19 | 105.25 | 0.06 | 3 |
| Ethylbenzene | 06/11/19 | 104.62 | 0.06 | 3 |
| m-Xylene | 06/11/19 | 103.68 | 0.14 | 3 |
| Styrene | 06/11/19 | 103.34 | 0.12 | 3 |
| o-Xylene | 06/11/19 | 104.49 | 0.14 | 3 |
| Chloroform | 06/11/19 | 105.96 | 0.07 | 3 |
| 1,1,2-Trichloroethane | 06/11/19 | 101.55 | 0.05 | 3 |
| Trichloroethylene | 06/11/19 | 104.02 | 0.05 | 3 |
| Tetrachloroethylene | 06/11/19 | 101.48 | 0.05 | 3 |
| 1,1-dichloroethane | 06/11/19 | 103.50 | 0.23 | 3 |
| Carbontetrachloride | 06/11/19 | 102.82 | 0.08 | 3 |
| 1,3-Butadiene | 06/11/19 | 103.61 | 0.08 | 3 |
| Dichloromethane | 06/11/19 | 107.18 | 0.10 | 3 |

Measurement 3[#]

| Component | Date (dd/mm/yy) | Result (nmol/mol) | Standard deviation (% relative) | Number of replicates |
|---|---|---|---|---|
| Benzene | 25/11/19 | 104.61 | 0.07 | 3 |
| Toluene | 25/11/19 | 105.17 | 0.07 | 3 |
| Ethylbenzene | 25/11/19 | 104.44 | 0.06 | 3 |
| m-Xylene | 25/11/19 | 103.60 | 0.06 | 3 |
| Styrene | 25/11/19 | 103.21 | 0.07 | 3 |
| o-Xylene | 25/11/19 | 104.21 | 0.03 | 3 |
| Chloroform | 25/11/19 | 105.91 | 0.063 | 3 |
| 1,1,2-Trichloroethane | 25/11/19 | 101.46 | 0.09 | 3 |
| Trichloroethylene | 25/11/19 | 103.97 | 0.08 | 3 |
| Tetrachloroethylene | 25/11/19 | 101.36 | 0.06 | 3 |
| 1,1-dichloroethane | 25/11/19 | 103.49 | 0.07 | 3 |
| Carbontetrachloride | 25/11/19 | 102.76 | 0.09 | 3 |
| 1,3-Butadiene | 25/11/19 | 103.58 | 0.07 | 3 |
| Dichloromethane | 25/11/19 | 107.15 | 0.06 | 3 |

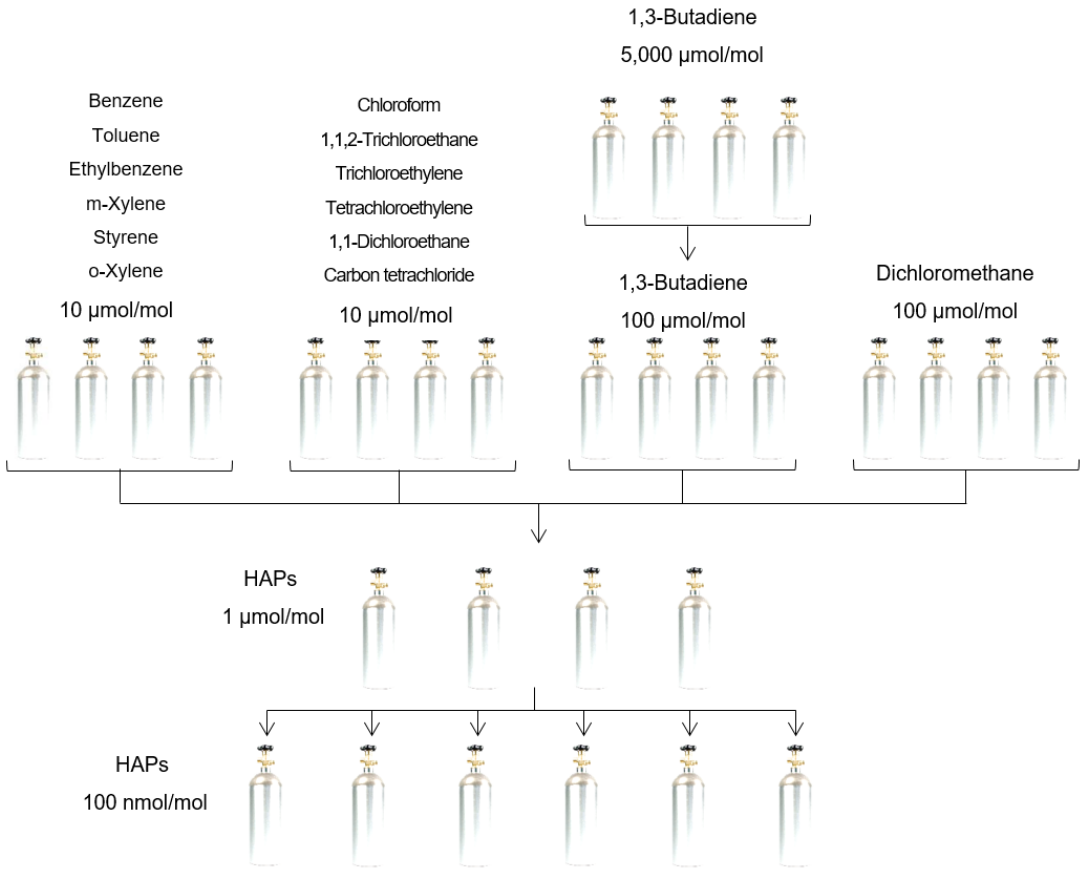
Results

| Component | Result (nmol/mol) | Expanded uncertainty (nmol/mol) | Coverage factor |
|---|---|---|---|
| Benzene | 104.61 | 0.95 | 2 |
| Toluene | 105.20 | 0.97 | 2 |
| Ethylbenzene | 104.53 | 1.05 | 2 |
| m-Xylene | 103.66 | 1.09 | 2 |
| Styrene | 103.30 | 1.14 | 2 |
| o-Xylene | 104.39 | 1.38 | 2 |
| Chloroform | 105.93 | 1.02 | 2 |
| 1,1,2-Trichloroethane | 101.56 | 1.28 | 2 |
| Trichloroethylene | 103.99 | 1.19 | 2 |
| Tetrachloroethylene | 101.41 | 1.35 | 2 |
| 1,1-dichloroethane | 103.51 | 1.01 | 2 |
| Carbontetrachloride | 102.80 | 1.09 | 2 |
| 1,3-Butadiene | 103.58 | 1.03 | 2 |
| Dichloromethane | 107.17 | 1.22 | 2 |

Calibration standards

A set of primary reference gas mixtures (PRMs) 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 PRMs at 10 µmol/mol. The PRMs were further diluted with

nitrogen to 100 nmol/mol (Figure 1). The PRMs at each step were analyzed against each other for verification.




Analytical method
All analysis was carried out using GC-FID (6890, Agilent Technologies) with a cryogenic concentrator (7200 Preconcentrator, Entech Instruments). Table 1 and 2 describe the method parameters of the GC-FID and the cryogenic concentrator, respectively.

**Table 1. Method parameters for the GC-FID system**

| GC-FID (Agilent 6890) | |
|---|---|
| Column | VOCOL (60m × 320 µm × 1.8 µm) |
| | Flow 2 mL/min (He) |
| Oven | 105 °C (isothermal, 34.5 min) |
| Detector | 250 °C (isothermal), $H_2$: 35 mL/min, Air: 300 mL/min, Makeup: 15 mL/min |

**Table 2. Method parameters for the cryogenic concentrator**

| | Trap temperature, °C | M1→ M2 temperature, °C | M2→M3 temperature, °C | Inject temperature, °C | Bake out temperature, °C |
|---|---|---|---|---|---|
| Mod 1 Trap | 40 | 40 | | | 40 |

| | | | | | |
|---|---|---|---|---|---|
| Mod 2 Trap | -95 | -95 | 220 | | 200 |
| Mod 3 Trap | | | -170 | 110 | |
| Trapping sample | | | | | |
| Sample flow | 90 mL/min | | | | |
| Sample volume | 270 mL | | | | |

The KRISS and the sample mixture were analyzed using a GC-FID with a cryogenic concentrator. The analysis method consisted of six sample injections by alternating between the two cylinders (i.e., $PRM_{ref}$ – $PRM_{sample}$ – $PRM_{ref}$ – $PRM_{sample}$ – $PRM_{ref}$ – $PRM_{sample}$ – $PRM_{ref}$). Please provide a brief description of the instrumentation and method used for analysis

Uncertainty evaluation
The measurement uncertainty consists of uncertainties from two sources such as the gravimetric preparation of the KRISS PRM and the comparison analysis. The gravimetric preparation uncertainty includes uncertainties from impurity analysis, molecular weight, weighing process, short-term stability (i.e., absorption on the internal surface of a cylinder), and internal consistency (i.e., the reproducibility of the gravimetric preparation). The analytical uncertainty is comprised of reproducibility, repeatability, and drift of GC measurements.
The amount mole fractions of the sample cylinder are determined by the following equation.

$$x_{sample} = x_{ref} \times R_{avg} \quad (1)$$

where $x_{sample}$ is the amount mole fraction of the sample, $x_{ref}$ is the amount mole fraction of KRISS PRM, and $R_{avg}$ is the average of GC peak area ratios (i.e., peak area of the sample to peak area of the KRISS PRM) for nine measurements during three days.

The combined standard uncertainty is estimated as

$$\left(\frac{u(x_{sample})}{x_{sample}}\right)^2 = \left(\frac{u(x_{ref})}{x_{ref}}\right)^2 + \left(\frac{u(R_{avg})}{R_{avg}}\right)^2$$

**Table 3. Uncertainty budget for Benzene**

| **Uncertainty source** $X_I$ | **Estimate** $x_I$ | **Assumed distribution** | **Standard uncertainty** $u(x_i)$ | **Sensitivity coefficient** $c_I$ | **Contribution to standard uncertainty** $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 105.020 nmol mol$^{-1}$ | Normal distribution | 0.442 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.004 \times x_{sample}$ |
| Response ratio | 0.996 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 0.95 nmol mol$^{-1}$

**Table 4. Uncertainty budget for Toluene**

| **Uncertainty source $X_I$** | **Estimate $x_I$** | **Assumed distribution** | **Standard uncertainty $u(x_i)$** | **Sensitivity coefficient $c_I$** | **Contribution to standard uncertainty $u_I(y)$,** nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 105.551 nmol mol$^{-1}$ | Normal distribution | 0.458 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.004 \times x_{sample}$ |
| Response ratio | 0.997 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 0.97 nmol mol$^{-1}$

**Table 5. Uncertainty budget for Ethylbenzene**

| **Uncertainty source $X_I$** | **Estimate $x_I$** | **Assumed distribution** | **Standard uncertainty $u(x_i)$** | **Sensitivity coefficient $c_I$** | **Contribution to standard uncertainty $u_I(y)$,** nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 104.757 nmol mol$^{-1}$ | Normal distribution | 0.496 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.998 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.05 nmol mol$^{-1}$

**Table 6. Uncertainty budget for m-Xylene**

| **Uncertainty source $X_I$** | **Estimate $x_I$** | **Assumed distribution** | **Standard uncertainty $u(x_i)$** | **Sensitivity coefficient $c_I$** | **Contribution to standard uncertainty $u_I(y)$,** nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 103.915 nmol mol$^{-1}$ | Normal distribution | 0.497 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |

| | | | | | |
|---|---|---|---|---|---|
| Response ratio | 0.998 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.09 nmol mol$^{-1}$

**Table 7. Uncertainty budget for Styrene**

| **Uncertainty source $X_I$** | **Estimate $x_I$** | **Assumed distribution** | **Standard uncertainty $u(x_i)$** | **Sensitivity coefficient $c_I$** | **Contribution to standard uncertainty $u_I(y)$**, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 103.535 nmol mol$^{-1}$ | Normal distribution | 0.525 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.998 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.14 nmol mol$^{-1}$

**Table 8. Uncertainty budget for o-Xylene**

| **Uncertainty source $X_I$** | **Estimate $x_I$** | **Assumed distribution** | **Standard uncertainty $u(x_i)$** | **Sensitivity coefficient $c_I$** | **Contribution to standard uncertainty $u_I(y)$**, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 104.407 nmol mol$^{-1}$ | Normal distribution | 0.624 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.006 \times x_{sample}$ |
| Response ratio | 1.000 | Normal distribution | 0.003 | $x_{sample}/R_{ref}$ | $0.003 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.38 nmol mol$^{-1}$

**Table 9. Uncertainty budget for Chloroform**

| **Uncertainty source $X_I$** | **Estimate $x_I$** | **Assumed distribution** | **Standard uncertainty $u(x_i)$** | **Sensitivity coefficient $c_I$** | **Contribution to standard uncertainty $u_I(y)$**, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 107.217 nmol mol$^{-1}$ | Normal distribution | 0.483 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.988 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.02 nmol mol$^{-1}$

**Table 10. Uncertainty budget for 1,1,2-Trichloroethane**

| **Uncertainty source** $X_I$ | **Estimate** $x_I$ | **Assumed distribution** | **Standard uncertainty** $u(x_i)$ | **Sensitivity coefficient** $c_I$ | **Contribution to standard uncertainty** $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 102.621 nmol mol$^{-1}$ | Normal distribution | 0.613 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.006 \times x_{sample}$ |
| Response ratio | 0.990 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.28 nmol mol$^{-1}$

**Table 11. Uncertainty budget for Trichloroethylene**

| **Uncertainty source** $X_I$ | **Estimate** $x_I$ | **Assumed distribution** | **Standard uncertainty** $u(x_i)$ | **Sensitivity coefficient** $c_I$ | **Contribution to standard uncertainty** $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 105.221 nmol mol$^{-1}$ | Normal distribution | 0.574 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.988 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.19 nmol mol$^{-1}$

**Table 12. Uncertainty budget for Tetrachloroethylene**

| **Uncertainty source** $X_I$ | **Estimate** $x_I$ | **Assumed distribution** | **Standard uncertainty** $u(x_i)$ | **Sensitivity coefficient** $c_I$ | **Contribution to standard uncertainty** $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 102.587 nmol mol$^{-1}$ | Normal distribution | 0.660 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.006 \times x_{sample}$ |
| Response ratio | 0.988 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.35 nmol mol$^{-1}$

**Table 13. Uncertainty budget for 1,1-Dichloroethane**

| Uncertainty source $X_I$ | Estimate $x_I$ | Assumed distribution | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $c_I$ | Contribution to standard uncertainty $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 104.622 nmol mol$^{-1}$ | Normal distribution | 0.471 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.989 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.01 nmol mol$^{-1}$

**Table 14. Uncertainty budget for Carbontetrachloride**

| Uncertainty source $X_I$ | Estimate $x_I$ | Assumed distribution | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $c_I$ | Contribution to standard uncertainty $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 104.059 nmol mol$^{-1}$ | Normal distribution | 0.493 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.988 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.09 nmol mol$^{-1}$

**Table 15. Uncertainty budget for 1,3-Butadiene**

| Uncertainty source $X_I$ | Estimate $x_I$ | Assumed distribution | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $c_I$ | Contribution to standard uncertainty $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 109.896 nmol mol$^{-1}$ | Normal distribution | 0.523 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.942 | Normal distribution | 0.001 | $x_{sample}/R_{ref}$ | $0.001 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.03 nmol mol$^{-1}$

**Table 16. Uncertainty budget for Dichloromethane**

| Uncertainty source | Estimate $x_I$ | Assumed distribution | Standard uncertainty | Sensitivity coefficient | Contribution to standard |
|---|---|---|---|---|---|

| $X_I$ | | | $u(x_i)$ | $c_I$ | **uncertainty** $u_I(y)$, nmol mol$^{-1}$ |
|---|---|---|---|---|---|
| Gravimetric preparation ($x_{ref}$) | 107.906 nmol mol$^{-1}$ | Normal distribution | 0.589 nmol mol$^{-1}$ | $x_{sample}/x_{ref}$ | $0.005 \times x_{sample}$ |
| Response ratio | 0.993 | Normal distribution | 0.002 | $x_{sample}/R_{ref}$ | $0.002 \times x_{sample}$ |

Coverage factor: 2
Expanded uncertainty: 1.22 nmol mol$^{-1}$