Final Report for Supplementary Comparison APMP.QM-S12: BTEX in Nitrogen at 100 nmol/mol

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1. Field

Amount of substance.

2. Subject

Comparison of primary gas mixture standards containing 100 nmol mol⁻¹ benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and styrene in nitrogen.

3. Participants

A total of four laboratories participated in this supplementary comparison. The participants are listed in the following.

Acronym	Country	Institute
CERI	JP	Chemicals Evaluation and Research Institute, Saitama, Japan
NIM	CR	National Institute of Metrology, Beijing, China
NMISA	ZA	National Metrology Institute of South Africa, Pretoria, South Africa
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea

4. Organization body

APMP TCQM.

5. Introduction

Benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and styrene (subsequently referred to gas BTEX) are volatile organic compounds emitted from gasoline, fossil fuel combustion, paints, rubber products, and adhesives. Exposure to BTEX can make adverse health effects on humans. Therefore, BTEX in both ambient and indoor air is regulated and monitored to protect public health.

For this supplementary comparison, a multicomponent mixture of BTEX 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 new buildings and construction materials. The supplementary comparison is designed to underpin calibration capabilities using BTEX gas mixtures that are prepared gravimetrically as transfer standards.

6. Measurement schedule

Event	Deadline
Draft protocol	April 2016
Final protocol	June 2016
Registration	September 2016
Mixture preparation	July 2016 – January 2017
Shipment of mixtures	February 2017
Submission of results	August 2018
Return of mixtures	April 2017 – November 2018
Draft A report	February 2019
Draft B report	July 2019

7. Measurement standards

A suite of primary standard gas mixtures (PSMs) was prepared gravimetrically by KRISS according to ISO 6142-1. Liquid raw materials for BTEX 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 dm³. 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 fraction of BTEX was 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 in mixture *i*, can be expressed as

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

where $x_{i,grav}$ is the amount-of-substance fraction of a target component in mixture *i* 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

$$u_{i,prep}^{2} = u_{i,grav}^{2} + u_{i,purity}^{2} + u_{i,stab}^{2}$$
⁽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 stability. Results from both short- and long-term stability studies show that analytically determined values agree with their gravimetric preparation values within the analytical uncertainties. Therefore, the prepared values were not corrected due to stability (i.e., $\Delta x_{i,stab} = 0$).

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

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

where $x_{i,ver}$ and $u_{i,ver}$ are the measurement result from verification and its standard uncertainty, respectively. Assuming that both preparation and verification are unbiased, the uncertainty associated with the verification relies on the measurement capability and experimental design. Returning to the definition on the reference value, the reference value of mixture *i* in a key comparison can be expressed as

$$x_{i,ref} = \langle x_{i,ref} \rangle + \delta x_{i,ref} \tag{4}$$

where
$$x_{i,ref} = x_{i,prep} + \Delta x_{i,ver}$$
 (5)

where $\Delta x_{i,ver}$ is the correction result from the verification.

Thus, equation (5) can be expressed as

$$x_{i,ref} = \langle x_{i,prep} \rangle + \langle \Delta x_{i,ver} \rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver}$$
(6)

where $\delta x_{i,prep}$ and $\delta \Delta x_{i,ver}$ are the error for the gravimetric preparation and verification, respectively. The verification experiments demonstrated that the verification values agreed with the preparation values within the preparation uncertainties. Thus, the expectation of the correction, $\langle \Delta x_{i,ver} \rangle$, was set as zero, which means that there is no correction due to the verification. Therefore, the reference value of mixture *i* is expressed as

$$x_{i,ref} = \langle x_{i,prep} \rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver}$$
⁽⁷⁾

As far as the verification experiments have demonstrated that the gravimetric values of the key comparison mixtures agreed with analytical values within the uncertainty of these measurements, the reference value in equation (7) becomes the preparation value. As a result, the standard uncertainty of the reference value is expressed as

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2$$
(8)

To verify the sample gas mixtures prepared by KRISS, each cylinder was analyzed against the reference cylinder before their dispatch and after their return. Results from the verification showed that all gas mixtures were consistent within their measurement uncertainties (Figure 1). 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.

GC-FID					
Column		CP-chirasil (2	25 m × 250 μm ×	0.25 μm)	
		Flow	0.5 mL/min (He	2)	
Oven		70 °C (is	sothermal, 19.1 1	nin)	
Detector	250 °C (isothern	mal), H ₂ : 35 mL/	min, Air: 300 m	L/min, Makeup:	15 mL/min
	Trap	$M1 \rightarrow M2$	M2→M3	Inject	Bake out
	temperature,	temperature,	temperature,	temperature,	temperature,
	°C	°C	°C	°C	°C
Mod 1 Trap	40	40			40
Mod 2 Trap	-100	-100	220		200
Mod 3 Trap	-170 110				
Trapping sample					
Sample flow		90 mL/min			
Sample volume		80 mL			

All gas mixtures at 100 nmol mol⁻¹ were analyzed using a GC-FID with a cryogenic preconcentrator. The detailed analytical conditions are summarized in the following.

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.

Laboratory	Cylinder	Measurement period	Calibration standards	Instrument calibration	Measurement technique
CERI	D929219	Jan 2018	Own standards	multiple point calibration	GC-FID
KRISS	D731952	Aug 2018	Own standards	one point calibration	GC-FID with pre- concentrator
NIM	D929214	Apr 2018	Own standards	one point calibration	GC-MSD
NMISA	D929234	May 2018	Own standards	two point calibration	GC-FID with pre- concentrator

Table 1. Summary of the measurement methods of the participants



Figure 1. Results from verification of gravimetrically prepared gas mixtures

10. Degree of equivalence (DoE)

A degree of equivalence for each participating laboratory was calculated as

$$D_i = x_{i,lab} - x_{i,SCRV}$$

where $x_{i,lab}$ and $x_{i,KCRV}$ 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.

$$x_{i,SCRV} = x_{i,ref}$$

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

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The use of squares in the legend to dates is a bit confusing, since there being used to represent cylinder D

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(9)

(10)

7

Therefore, the standard uncertainty of D_i can be expressed as

$$u^{2}(D_{i}) = u_{i,lab}^{2} + u_{i,SCRV}^{2}$$
(12)

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 key comparison are summarized in Table 2 and Figure 2.

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
CERI – D517567								
Benzene	106.34	0.20	2.37	2.38	107.4	0.4	1.1	4.8
Toluene	105.61	0.12	2.45	2.45	107.3	0.7	1.7	5.1
Ethylbenzene	105.06	0.22	2.26	2.27	108.5	2.0	3.4	6.0
m-xylene	103.69	0.30	2.77	2.79	107.6	2.0	3.9	6.9
Styrene	105.86	0.16	2.39	2.40	110.7	1.9	4.8	6.1
o-xylene	106.53	0.32	2.75	2.77	110.3	1.4	3.8	6.2
NIM – D254193								
Benzene	106.09	0.19	2.37	2.38	108.1	1.1	2.0	5.2
Toluene	105.35	0.12	2.45	2.45	108.0	1.1	2.7	5.4
Ethylbenzene	104.81	0.22	2.25	2.26	111.1	1.1	6.3	5.0
m-xylene	103.44	0.30	2.76	2.78	109.1	1.6	5.7	6.4
Styrene	105.60	0.16	2.34	2.35	112.7	1.7	7.1	5.8
o-xylene	106.27	0.31	2.74	2.76	113.1	1.7	6.8	6.5
NMISA – D517607								
Benzene	106.88	0.20	2.38	2.39	72.48	4.33	-34.40	9.89
Toluene	106.14	0.12	2.47	2.47	74.48	4.86	-31.66	10.91
Ethylbenzene	105.59	0.22	2.27	2.28	94.43	4.91	-11.16	10.83
m-xylene	104.21	0.30	2.79	2.81	102.03	5.15	-2.18	11.73
Styrene	106.39	0.16	2.39	2.40	107.43	5.74	1.04	12.44
o-xylene	107.07	0.32	2.76	2.78	95.05	4.92	-12.02	11.30
KRISS – D517566								
Benzene	107.08	0.20	2.39	2.40	106.55	1.49	-0.53	5.65
Toluene	106.34	0.12	2.48	2.48	105.53	1.51	-0.81	5.81
Ethylbenzene	105.79	0.22	2.28	2.29	104.56	1.49	-1.23	5.47
m-xylene	104.41	0.30	2.80	2.82	103.13	1.78	-1.28	6.66
Styrene	106.59	0.16	2.35	2.36	104.80	1.52	-1.79	5.61
o-xylene	107.27	0.32	2.77	2.79	105.79	1.80	-1.48	6.64

Table 2. Summarized results for APMP.QM-S12 (nmol mol⁻¹)

(11)



Figure 2. Degrees of equivalence for APMP.QM-S12

12. Conclusions

The comparison has been successfully conducted to evaluate the participants' measurement capabilities for BTEX in nitrogen. Both CERI and KRISS results are consistent with their SCRVs for all analytes. NIM results are not consistent with their SCRVs for three analytes such as ethylbenzene, o-xylene, and styrene while NMISA results are not consistent with their SCRVs for four analytes such as benzene, toluene, ethylbenzene, o-xylene.

13. Supported CMC claims

This supplementary comparison underpins core skills and competencies required in gravimetric preparation, analytical verification and purity analysis of BTEX. 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, *o*-xylene, *m*-xylene, and styrene in nitrogen at the range of 50 nmol mol⁻¹ to 10 μ mol mol⁻¹.

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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.

Amount fraction (nmol mol ⁻¹)	Amount fraction (nmol mol ⁻¹)	Uncertainty (%)	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 104.81 nmol mol⁻¹, and D is 6.3 nmol mol⁻¹, its HFTLS statements are in the following.

Amount fraction	Amount fraction	Uncertainty	Uncertainty
(nmol mol ⁻¹)	(nmol mol ⁻¹)	(%)	(%)
12.8	100	100	12.2
100	10 000	12.2	12.2

Annex B: Measurement reports Laboratory name: Chemicals Evaluation and Research Institute, Japan Cylinder number: D517567

Measurement #2	1			
Component	Date	Result	Standard deviation	Number of
	(dd/mm/yy)	(nmol/mol)	(% relative)	replicates
Benzene	22/01/18	107.4	0.80	2
Toluene	22/01/18	106.6	0.72	2
Ethylbenzene	22/01/18	109.0	3.27	2
o-xylene	22/01/18	109.1	1.50	2
m-xylene	22/01/18	109.6	3.64	2
Styrene	22/01/18	110.6	0.63	2
Measurement #2	2			
Component	Date	Result	Standard deviation	Number of
	(dd/mm/yy)	(nmol/mol)	(% relative)	replicates
Benzene	23/01/18	107.2	0.53	2
Toluene	23/01/18	107.3	0.86	2
Ethylbenzene	23/01/18	107.1	1.08	2
o-xylene	23/01/18	110.9	0.12	2
m-xylene	23/01/18	106.9	1.02	2
Styrene	23/01/18	110.9	3.01	2
Measurement #3	3			
Component	Date	Result	Standard deviation	Number of
	(dd/mm/yy)	(nmol/mol)	(% relative)	replicates
Benzene	25/01/18	107.6	0.12	2
Toluene	25/01/18	106.7	0.30	2
Ethylbenzene	25/01/18	107.2	2.13	2
o-xylene	25/01/18	109.8	1.34	2
m-xylene	25/01/18	105.9	0.02	2
Styrene	25/01/18	110.7	1.95	2

Measurement #4	1			
Component	Date	Result	Standard deviation	Number of
	(dd/mm/yy)	(nmol/mol)	(% relative)	replicates
Benzene	26/01/18	107.4	0.21	2
Toluene	26/01/18	107.7	0.26	2
Ethylbenzene	26/01/18	110.1	0.61	2
o-xylene	26/01/18	109.8	0.15	2
m-xylene	26/01/18	108.7	1.33	2
Styrene	26/01/18	112.2	1.90	2
Measurement #5	5			
Component	Date	Result	Standard deviation	Number of
	(dd/mm/yy)	(nmol/mol)	(% relative)	replicates
Benzene	29/01/18	107.2	0.06	2
Toluene	29/01/18	107.4	0.15	2
Ethylbenzene	29/01/18	109.2	1.75	2
o-xylene	29/01/18	111.4	2.32	2
m-xylene	29/01/18	107.2	1.88	2
Styrene	29/01/18	108.8	1.60	2
Measurement #6	3			
Component	Date	Result	Standard deviation	Number of
	(dd/mm/yy)	(nmol/mol)	(% relative)	replicates
Benzene	30/01/18	107.5	0.20	2
Toluene	30/01/18	108.1	0.19	2
Ethylbenzene	30/01/18	108.2	1.78	2
o-xylene	30/01/18	110.8	1.22	2
m-xylene	30/01/18	107.2	0.65	2
Styrene	30/01/18	111.0	0.30	2
Results				
Component	Result (nmol/mol)	Expa	inded uncertainty (nmol/mol)	Coverage factor
Benzene	107.4		0.8	2
Toluene	107.1		1 4	2
Ethylbenzene	108.5		3.9	2
o-xvlene	110.3		2.8	2
m-xvlene	107.6		4.0	2
Styrene	110.7		3.7	$\overline{2}$
·····	•			

Calibration Standards		
Serial number	Component	Mole fraction
of cylinder	component	nmol/mol
CPB25958	Benzene	110.60
	Toluene	126.67
	Ethylbenzene	106.13
	o-xylene	114.01
	m-xylene	99.94
	Styrene	119.42
Serial number	Component	Note traction
of cylinder	D I	nmol/mol
CPB23440	Benzene	114.20
	Toluene	114.90
	Ethylbenzene	109.59
	o-xylene	117.72
	m-xylene	90.65
	Styrene	108.32
Serial number		Mole fraction
of cylinder	Component	nmol/mol
CPB20800	Benzene	99.77
	Toluene	106.74
	Ethylbenzene	95.74
	o-xylene	102.85
	m-xylene	84.21
	Styrene	100.63

Calibration standards were prepared by gravimetric dilution of pure Benzene, Toluene, Ethylbenzene, o-xylene, m-xylene and Styrene. That procedure is as follows,



Fig. Procedure of preparation

Purity table of BTEX

/			
	Component	Purity (certified value)	Expanded uncertainty
		mol/mol	mol/mol

Benzene	99.992	0.003(<i>k</i> =2.57)
Toluene	99.984	0.013(<i>k</i> =4.30)
Ethylbenzene	99.88	0.03(<i>k</i> =2.04)
o-xylene	99.933	0.002(<i>k</i> =1.96)
m-xylene	99.80	0.02(<i>k</i> =2.57)
Styrene	99.8	0.3 (<i>k</i> =2)

Purity table of dilution gas (N_2)

Component	Analytical value µmol/mol
O ₂	≤ 0.1
Ar	≤ 1
СО	≤ 0.01
CO ₂	≤ 0.01
Total hydro carbon (THC)	≤ 0.01
SO ₂	≤ 0.005
NOx	≤ 0.005
Benzene	≤ 0.0006
Toluene	≤ 0.0005
Ethylbenzene	≤ 0.0004
o- xylene	≤ 0.0004
m- xylene	≤ 0.0004
Styrene	≤ 0.0004

Analytical method

Calibration method: Multipoint calibration Traceability: Own standards Instrument: Agilent Technologies 7890A Detector: Flame Ionization Detector Column: Bentone34 + SP-1200 (1.75+5)(80/100) (GL Sciences Inc.) in stainless column(5 m, 3 mm i.d.)

Comparisons were made by the following sequence:

 $H_i \rightarrow M_i \rightarrow K_i \rightarrow L_i$

Where,

 H_i : measurement of standard (Serial number of cylinder : CPB25958) (*i*=1,2) M_i : measurement of standard (Serial number of cylinder : CPB23440) (*i*=1,2) L_i : measurement of standard (Serial number of cylinder : CPB20800) (*i*=1,2) K_i : measurement of the APMP.QM-S12 gas mixture (*i*=1,2)

Configuration of analysis system:

Gas cylinder \rightarrow Regulator \rightarrow Auto 6-way valve \rightarrow Instrument (Column \rightarrow Detector)

The mole fractions of BTEX in the APMP.QM-S12 gas mixture were calculated as follows:

The instrument was calibrated using gravimetrically prepared standards. Each calibration curve was linear given by least squares method :

 $y = ax_s + b$

Where,

y: APMP.QM-S12 sample concentration n: Gas standards number xs: Indication of sample xi: Indication of standard material i yi: Concentration of standard material i \overline{x} : Average of indication of standard materials \overline{y} : Average of concentration of standard materials

$$a = \frac{S(xy)}{S(xx)} \qquad b = \overline{y} - a \times \overline{x}$$

$$S(xx) = \sum_{n=1}^{n} (x_i - \overline{x})^2 \qquad S(xy) = \sum_{n=1}^{n} (x_i - \overline{x})(y_i - \overline{y})$$

Uncertainty evaluation

Benzene

Source	Estimate	Distribution	Divisor	Standard uncertainty
Repeatability of	0.3537	Normal	1	0.3537
measurement	nmol/mol	Normai	T	nmol/mol
Gas standards	0.1858	Normal	1	0.1858
	nmol/mol	normai	L	nmol/mol
	Combi	0.3995		
	Expanded uncertainty (<i>k</i> =2)			0.8

Toluene

Source	Estimate	Distribution	Divisor	Standard uncertainty
Repeatability of	0.6750	Normal	1	0.6750
measurement	nmol/mol	normai	1	nmol/mol
Caa standarda	0.1682	Normal	1	0.1682
Gas standards	nmol/mol	normai	Ţ	nmol/mol
	Combi	0.6956		
		1.4		

Ethylbenzene

Source	Estimate	Distribution	Divisor	Standard uncertainty
Repeatability of	1.9360	Normal	1	1.9360
measurement	nmol/mol			nmol/mol
Gas standards	0.2754	Normal	1	0.2754
	nmol/mol	Normai	L	nmol/mol
	Combi	1.955		
	Expanded uncertainty (<i>k</i> =2)			3.9

o- xylene				
Source	Estimate	Distribution	Divisor	Standard uncertainty
Repeatability of	1.3783	Normal	1	1.3783
measurement	nmol/mol	normai	1	nmol/mol
Casatandarda	0.1891	Normal	1	0.1891
Gas stanuarus	nmol/mol	normai	1	nmol/mol
	Combi	1.391		
	Expanded uncertainty (<i>k</i> =2)			2.8

m- xylene				
Source	Estimate	Distribution	Divisor	Standard uncertainty
Repeatability of	1.9570	Normal	1	1.9570
measurement	nmol/mol	roman	L	nmol/mol
Gas standards	0.2872	Normal	1	0.2872
Gas stanuarus	nmol/mol	Normai	1	nmol/mol
	Combi	1.997		
	Expanded uncertainty (<i>k</i> =2)			4.0

Styrene				
Source	Estimate	Distribution	Divisor	Standard uncertainty
Repeatability of	1.8025	Normal	1	1.8025
measurement	nmol/mol	rtormai	-	nmol/mol
Gas standarda	0.3329	Normal	1	0.3329
Gas stanuarus	nmol/mol	Normai	T	nmol/mol
	Combi	1.832		
	Expanded uncertainty ($k=2$)			3.7

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Report form

Laboratory name: National Institute of Metrology, China Cylinder number: D254193

Measurement 1[#]

Component	Data	Result	Standard	Number of
	(dd/mm/yy)	(nmol/mol)	Deviation	replicates
			(%relative)	
Benzene	11/04/2018	107.8	0.19%	4
Toluene	11/04/2018	107.5	0.24%	4
Ethylbenzene	11/04/2018	110.3	0.19%	4
o-xylene	11/04/2018	112.0	0.18%	4
m-xylene	11/04/2018	108.1	0.24%	4
Styrene	11/04/2018	111.5	0.19%	4

Measurement 2[#]

Component	Data	Result	Standard	Number of
	(dd/mm/yy)	(nmol/mol)	Deviation	replicates
			(%relative)	
Benzene	20/04/2018	107.8	0.34%	4
Toluene	20/04/2018	107.9	0.20%	4
Ethylbenzene	20/04/2018	111.4	0.23%	4
o-xylene	20/04/2018	114.5	0.23%	4
m-xylene	20/04/2018	110.2	0.16%	4
Styrene	20/04/2018	114.5	0.17%	4

Measurement 3[#]

Component	Data	Result	Standard	Number of
	(dd/mm/yy)	(nmol/mol)	Deviation	replicates
			(%relative)	
Benzene	27/04/2018	108.7	0.17%	4
Toluene	27/04/2018	108.4	0.23%	4
Ethylbenzene	27/04/2018	111.6	0.44%	4
o-xylene	27/04/2018	114.1	0.45%	4
m-xylene	27/04/2018	110.2	0.24%	4
Styrene	27/04/2018	113.5	0.21%	4

Results

Component	Result	Expanded	Coverage
_	(nmol/mol)	uncertainty	factor
		(nmol/mol)	
Benzene	108.1	2.2	2
Toluene	108.0	2.2	2
Ethylbenzene	111.1	2.2	2
o-xylene	113.1	3.4	2
m-xylene	109.1	3.2	2
Styrene	112.7	3.3	2

Calibration standards

Please provide a brief description of the calibration standards used.



Analytical method

Please provide a brief description of the instrumentation and method used for analysis. Instrument: GC-MS (Aglient GCMS 7890A-5975C)

Method: Column DB-WAX 60m×0.32µm×1.0µm

20:1

Split ratio

Carrier gas Helium

Temperature 70°C for 5min, 7 °C/min ramp up to 120 °C, 120 °C for 10min.

Uncertainty evaluation

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

Component	Result (nmol/mol)	Uncertainty budget (nmol/mol)			Combined uncertainty
		Repeatability and reproducibility	Weighing/Purity	Adsorption	(nmol/mol) <i>k</i> =1
Benzene	108.1	0.62	0.87	0.11	1.1
Toluene	108.0	0.63	0.86	0.11	1.1
Ethylbenzene	111.1	0.63	0.88	0.11	1.1
o-xylene	109.1	0.62	1.46	0.11	1.6
m-xylene	113.1	0.62	1.53	0.11	1.7
Styrene	112.7	0.15	1.56	0.56	1.6

Report form Laboratory name: National Metrology Institute of South Africa Measurement 1[#]

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Benzene	19/10/2017	71.94	7.01	3
Toluene	19/10/2017	74.18	7.96	3
Ethylbenzene	19/10/2017	91.17	5.36	3
o-xylene	19/10/2017	104.68	4.30	3
m-xylene	19/10/2017	94.01	5.43	3
Styrene	19/10/2017	112.03	4.38	3
Measurement 2 [#]	ŧ			
Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Benzene	19/10/2017	72.38	5.34	3
Toluene	19/10/2017	74.38	6.03	3
Ethylbenzene	19/10/2017	95.36	4.79	3
o-xylene	19/10/2017	102.30	4.41	3
m-xylene	19/10/2017	94.91	5.15	3
Styrene	19/10/2017	108.59	4.86	3

Measurement 3[#]

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Benzene	20/10/2017	73.14	5.36	3
Toluene	20/10/2017	74.90	5.31	3
Ethylbenzene	20/10/2017	96.77	4.52	3
o-xylene	20/10/2017	99.14	5.64	3
m-xylene	20/10/2017	96.26	4.79	3
Styrene	20/10/2017	101.69	4.30	3

Results

Component	Result	Expanded uncertainty	Coverage Factor
	(nmol/mol)	(nmol/mol)	
Benzene	72.48	8.65	2
Toluene	74.48	9.72	2
Ethylbenzene	94.43	9.82	2
o-xylene	95.05	9.83	2
m-xylene	102.03	10.30	2
Styrene	107.43	11.48	2

Calibration Standards

The analysis of the comparison sample was performed using two standards of the similar mole fraction prepared using the gravimetric method, diluted from a premix of 10 μ mol/mol.

The calibration standards and the comparison sample were store under the same conditions during the comparison period.

Analytical method

The analysis was performed on the Agilent 7890B gas chromatograph equipped with flame ionisation detector. The analysis method is stated below:

Parameter	Condition
Carrier gas	Nitrogen BIP
Split ratio	Split-less mode through the cryogenic pre-
	concentrator
Column	HP-INNOWax, (60 m x 320 μm x 0.5 μm)
Column flow	3.4 ml/min
Oven programming	40 °C hold for 5 min, ramp at 2 °C/min to
	60 °C hold for 2 min, ramp at 4°C/min to
	75°C hold for 1 min, ramp at 20 4°C/min to
	120°C hold for 2 min.
Detector	FID at 350 °C

The Entech 7200 cryogenic pre-concentrator was used to trap the samples with conditions shown below:

Parameter	Condition
Trap 1 (Empty tube), operated at -40 °C	Removal of CO ₂ and H ₂ O
Trap 2 (Tenax TA) operated at -40 °C	Trapping of VOC
Cry focuser operated at -150 °C	Focusing of VOC prior to injection into the
	column

Uncertainty evaluation

The uncertainty contributions included are the following

- Gravimetric uncertainty of the standards
- Repeatability of the measurement
- Analysis stability of the standards

Report Laboratory name: Korea Research Institute of Standards and Science Cylinder number: D517566 Authorship: Ji Hwang KANG, Yong Doo KIM, Sangil LEE, Dal Ho KIM

Measurement 1[#]

Component	Date	Result	Standard	Number of
	(dd/mm/yy)	(nmol/mol)	deviation	replicates
			(% relative)	
Benzene	28/08/18	106.88	0.15	3
Toluene	28/08/18	105.83	0.22	3
Ethylbenzene	28/08/18	104.92	0.19	3
o-xylene	28/08/18	106.20	0.15	3
m-xylene	28/08/18	103.48	0.18	3
Styrene	28/08/18	105.09	0.28	3

Measurement 2[#]

Component	Date	Result	Standard	Number of
	(dd/mm/yy)	(nmol/mol)	deviation	replicates
			(% relative)	
Benzene	29/08/18	106.81	0.20	3
Toluene	29/08/18	105.83	0.17	3
Ethylbenzene	29/08/18	104.89	0.15	3
o-xylene	29/08/18	106.14	0.15	3
m-xylene	29/08/18	103.44	0.16	3
Styrene	29/08/18	105.23	0.13	3

Measurement 3[#]

Component	Date	Result	Standard	Number of
	(dd/mm/yy)	(nmol/mol)	deviation	replicates
			(% relative)	
Benzene	01/09/18	105.96	0.09	3
Toluene	01/09/18	104.95	0.20	3
Ethylbenzene	01/09/18	103.86	0.32	3
o-xylene	01/09/18	105.03	0.38	3
m-xylene	01/09/18	102.46	0.24	3
Styrene	01/09/18	104.08	0.54	3

Results

Component	Result	Expanded uncertainty	Coverage factor
	(nmol/mol)	(nmol/mol)	
Benzene	106.55	3.04	2
Toluene	105.53	3.10	2
Ethylbenzene	104.56	3.05	2
o-xylene	105.79	3.66	2
m-xylene	103.13	3.61	2
Styrene	104.80	3.12	2

Calibration standards

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 μ mol/mol. The PSMs were further diluted with nitrogen to 100 nmol/mol (Figure 1). The PSMs 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	CP-chirasil $(25m \times 250 \ \mu m \times 0.25 \ \mu m)$		
	Flow 0.5 mL/min (He)		
Oven	70 °C (isothermal, 19.1 min)		
Detector	250 °C (isothermal), H ₂ : 35 mL/min, Air: 300 mL/min, Makeup: 15 mL/min		

	Trap	$M1 \rightarrow M2$	M2→M3	Inject	Bake out		
	temperature,	temperature,	temperature,	temperature,	temperature,		
	°C	°C	°C	°C	°C		
Mod 1 Trap	40	40			40		
Mod 2 Trap	-100	-100	220		200		
Mod 3 Trap			-170	110			
Trapping sample							
Sample flow	90 mL/min						
Sample volume	80 mL						

Table 2. Method parameters for the cryogenic concentrator

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., $PSM_{ref} - PSM_{sample} - PSM_{ref} - PSM_{ref} - PSM_{ref} - PSM_{sample} - PSM_{ref}$). 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 PSM 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.

$$x_{sample} = x_{ref} \times R_{avg}$$

(1)

where x_{sample} is the amount mole fraction of the sample, x_{ref} is the amount mole fraction of KRISS PSM, and R_{avg} is the average of GC peak area ratios (i.e., peak area of the sample to peak area of the KRISS PSM) 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 Xt	Estimate <i>xi</i>	Assumed distribution	Standard uncertainty <i>u(xi)</i>	Sensitivity coefficient cı	Contribution to standard uncertainty u1(y), nmol mol ⁻¹
Gravimetric preparation (x_{ref})	107.930 nmol mol ⁻¹	Normal distribution	1.305 nmol mol ⁻¹	x_{sample}/x_{ref}	$0.012 imes x_{sample}$
Response ratio	0.987	Normal distribution	0.008	x_{sample}/R_{ref}	$0.008 imes x_{sample}$

Coverage factor: 2

Expanded uncertainty: 3.04 nmol mol⁻¹

 Table 4. Uncertainty budget for toluene

Uncertainty source X _I	Estimate <i>xi</i>	Assumed distribution	Standard uncertainty <i>u(x_i)</i>	Sensitivity coefficient c1	Contribution to standard uncertainty u1(y), nmol mol ⁻¹
Gravimetric preparation (x_{ref})	107.182 nmol mol ⁻¹	Normal distribution	1.368 nmol mol ⁻¹	x_{sample}/x_{ref}	$0.013 \times x_{sample}$
Response ratio	0.985	Normal distribution	0.007	x_{sample}/R_{ref}	$0.007 imes x_{sample}$

Coverage factor: 2

Expanded uncertainty: 3.10 nmol mol⁻¹

 Table 5. Uncertainty budget for ethylbenzene

Uncertainty source Xt	Estimate <i>x_i</i>	Assumed distribution	Standard uncertainty <i>u(xi)</i>	Sensitivity coefficient cı	Contribution to standard uncertainty u1(y), nmol mol ⁻¹
Gravimetric preparation (x_{ref})	106.629 nmol mol ⁻¹	Normal distribution	1.292 nmol mol ⁻¹	x_{sample}/x_{ref}	$0.012 imes x_{sample}$
Response ratio	0.981	Normal distribution	0.008	x_{sample}/R_{ref}	$0.008 imes x_{sample}$

Coverage factor: 2

Expanded uncertainty: 3.05 nmol mol⁻¹

Table 6. Uncertainty budget for o-xylene

Uncertainty source Xt	Estimate <i>xi</i>	Assumed distribution	Standard uncertainty <i>u(x_i)</i>	Sensitivity coefficient c1	Contribution to standard uncertainty u1(y), nmol mol ⁻¹
Gravimetric preparation (x_{ref})	108.119 nmol mol ⁻¹	Normal distribution	1.625 nmol mol ⁻¹	x_{sample}/x_{ref}	$0.015 imes x_{sample}$
Response ratio	0.978	Normal distribution	0.009	x_{sample}/R_{ref}	$0.008 imes x_{sample}$

Coverage factor: 2

Expanded uncertainty: 3.66 nmol mol⁻¹

 Table 7. Uncertainty budget for m-xylene

Uncertainty source X _l	Estimate <i>xi</i>	Assumed distribution	Standard uncertainty <i>u(x_i)</i>	Sensitivity coefficient cı	Contribution to standard uncertainty u1(y), nmol mol ⁻¹
Gravimetric preparation (x_{ref})	105.238 nmol mol ⁻¹	Normal distribution	1.622 nmol mol ⁻¹	x_{sample}/x_{ref}	$0.015 \times x_{sample}$
Response ratio	0.980	Normal distribution	0.008	x_{sample}/R_{ref}	$0.008 \times x_{sample}$

Coverage factor: 2

Expanded uncertainty: 3.61 nmol mol⁻¹

 Table 8. Uncertainty budget for styrene

Uncertainty source Xt	Estimate <i>x_i</i>	Assumed distribution	Standard uncertainty <i>u(xi)</i>	Sensitivity coefficient c1	Contribution to standard uncertainty u ₁ (y), nmol mol ⁻¹
Gravimetric preparation (x_{ref})	107.437 nmol mol ⁻¹	Normal distribution	1.306 nmol mol ⁻¹	x_{sample}/x_{ref}	$0.012 imes x_{sample}$
Response ratio	0.975	Normal distribution	0.009	x_{sample}/R_{ref}	$0.008 imes x_{sample}$

Coverage factor: 2

Expanded uncertainty: 3.12 nmol mol⁻¹