International Comparison CCQM-K10.2018.1 - BTEX gas mixtures

T. Macé[1], C. Sutour[1], F. Mary[1], F. Marioni[1], M. Iturrate-Garcia[2], D. Roos[2], T. Bühlmann[2], W. Travnicek[3], V. Petkova-Krasteva[3], S. Schaefer[3], S. Unglert[3], D. Worton[4]

[1]Laboratoire National de métrologie et d'Essais (LNE), 1, rue Gaston Boissier, 75724 Paris Cedex 15, France.
[2]Federal Institute of Metrology (METAS), Lindenweg, 50, 3003 Bern-Wabern, Switzerland.
[3]Federal Environment Agency Germany Umweltbundesamt (UBA), Paul-Ehrlich-Str. 29, 63225 Langen, Germany.
[4]National Physical Laboratory (NPL), Hampton Road, Teddington, Middlesex, TW11 0LW, United Kingdom.

Field

Amount of substance

Project reference

CCQM-K10.2018.1 - BTEX gas mixtures

Subject

Comparison of BTEX in nitrogen (Track C)

Organizing body

CCQM-GAWG

Coordinator

LNE
Tatiana Macé
1, rue Gaston Boissier
75724 Paris Cedex 15
France
Phone +33 1 40 43 38 53
E-mail tatiana.mace@lne.fr

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1 Introduction

Following the CCQM-K10.2018 key comparison [1], the CCQM GAWG (Gas Analysis Working Group of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology) accepted the project proposal for the organization of a follow-up key comparison. LNE operates as coordinator in this comparison.

The objective of this CCQM-K10.2018.1 key comparison is to compare the measurement capabilities of national metrology institutes (NMIs) in measuring amount fractions of BTEX (benzene, toluene, ethylbenzene, p-xylene, m-xylene and o-xylene) in nitrogen as described in the CCQM-K10.2018 comparison. The nominal amount fractions of the gas mixture used for this comparison are 5 $nmol\cdot mol^{-1}$. This key comparison offers an opportunity to the laboratories to improve their CMCs. The link with the results in CCQM-K10.2018 is provided through the use of a comparison gas mixture provided by NPL who participated in CCQM-K10.2018 and had a satisfactory performance. NPL prepared a BTEX gas mixture at 5 $nmol\cdot mol^{-1}$ by the gravimetric method which was analysed by NIST in the CCQM-K10.2018 comparison; NIST determined that the BTEX amount fractions of NPL's gas mixture were stable over time, and that the results were in good agreement with the KCRV for all compounds included in the NPL's gas mixture. In the CCQM-K10.2018.1 comparison the gas mixture provided by NPL contains the same compounds (BTEX) at the same nominal amount fractions than those of NPL's gas mixture used in the last CCQM-K10.2018 comparison. Therefore NPL values used in the CCQM-K10.2018.1 comparison can be considered as equivalent to the KCRVs in CCQM-K10.2018 comparison. The key comparison reference values (KCRV) for this CCQM-K10.2018.1 key comparison are the gravimetric amount fractions of the NPL comparison gas mixture.

2 Design and organisation of the key comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
LNE	FR	Laboratoire National de métrologie et d'Essais, Paris, France
METAS	CH	Federal Institute of Metrology, Bern-Wabern, Switzerland
UBA	DE	Federal Environment Agency Germany Umweltbundesamt, Langen, Germany
NPL	GB	National Physical Laboratory, Teddington, United Kingdom (Link with the results in CCQM-K10.2018 comparison)

2.2 Measurement standard

NPL prepared gravimetrically one gas mixture containing six volatile organic compounds (VOCs), known as BTEX (benzene, toluene, ethylbenzene, p-xylene, m-xylene and o-xylene) in a balance of nitrogen and validated the preparation using gas chromatography (FID). The gas mixture composition and its associated uncertainty were calculated in accordance with ISO 6142-1 [2]. The gas mixture was contained in one cylinder with a water volume of 10 litres, equipped with a valve of type DIN 477 No. 1 and filled at a pressure of 1.04×10^7 Pa.

The NPL's comparison gas mixture was sent to LNE which studied the stability of the comparison gas mixture by performing five measurements during a period of about 2 months before the comparison. It was then circulated successively to the other two participants during six months, and came back to LNE for a final stability study, consisting in a series of five measurements during about 1 month.

The nominal ranges of amount fractions of the targeted components in the comparison gas mixture are given in **Error! Not a valid bookmark self-reference.**.

Table 2: Nominal composition of the comparison gas mixture, given in amount fractions

Component	Amount fraction (x)
benzene	5 nmol·mol^{-1}
toluene	5 nmol·mol^{-1}
ethylbenzene	5 nmol·mol^{-1}
m-xylene	5 nmol·mol^{-1}
p-xylene	5 nmol·mol^{-1}
o-xylene	5 nmol·mol^{-1}
nitrogen	Balance

2.3 Measurement protocol

The measurement protocol requested each laboratory to perform three measurements minimum on the comparison gas mixture on different days, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions [3]. The protocol informed the participants about the nominal amount fraction ranges. The laboratories provided their analyzed amount fractions and associated uncertainties [4] for the BTEX components in the comparison gas mixture. The participants were also requested to submit a description of their method and a full description of the results and the uncertainty evaluation.

2.4 Schedule

The schedule of this key comparison was as follows (Table 3).

Table 3: Key comparison schedule

Date	Event
May 2023	Agreement of protocol
June 2023	Registration of participants
June 2023 to July 2023	First analysis of comparison gas mixture by LNE
July 2023	Shipment of the comparison gas mixture to METAS by LNE
July 2023 to September 2023	Calibration performed by METAS
September 2023	Shipment of the comparison gas mixture to UBA by METAS
September 2023 to December 2023	Calibration performed by UBA
December 2023	Shipment of the comparison gas mixture to LNE by UBA
January 2024 to February 2024	Re-analysis of the comparison gas mixture by LNE
April 2024	Draft A report available

3 Study of the stability of the comparison gas mixture

LNE calibrated five times the gas mixtures according to the method described in the annex B before sending it to the other participants and after the comparison to evaluate if the BTEX amount fractions were stable during the comparison which lasted one year.

The Table 4 show all the analysed amount fractions obtained by LNE during the comparison (2023-2024). The uncertainties obtained in the stability study are similar to those of the finally used KCRV obtained in CCQM-K10.2018 comparison.

Table 4: Analytical amount fractions and the associated uncertainties obtained by LNE on the gas mixture D115803 over time

	Date	benzene		toluene		ethylbenzene	
		x_{LNE} (nmol·mol^{-1})	U_{LNE} (nmol·mol^{-1})	x_{LNE} (nmol·mol^{-1})	U_{LNE} (nmol·mol^{-1})	x_{LNE} (nmol·mol^{-1})	U_{LNE} (nmol·mol^{-1})
Before sending the cylinder to METAS	16/05/2023	4.982	0.130	5.095	0.078	5.433	0.118
	31/05/2023	4.962	0.084	5.090	0.103	5.371	0.131
	15/06/2023	4.963	0.088	5.089	0.090	5.379	0.126
	28/06/2023	4.988	0.099	5.058	0.102	5.364	0.125
	05/07/2023	4.991	0.095	5.089	0.093	5.378	0.130
After receiving the cylinder from UBA	16/01/2024	5.001	0.100	5.108	0.072	5.338	0.142
	23/01/2024	4.990	0.086	5.059	0.075	5.430	0.120
	06/02/2024	4.976	0.101	5.069	0.080	5.347	0.140
	12/02/2024	5.028	0.087	5.106	0.097	5.406	0.115
	26/02/2024	5.039	0.079	5.086	0.074	5.397	0.122

	Date	p-xylene		m-xylene		o-xylene	
		x_{LNE} (nmol·mol^{-1})	U_{LNE} (nmol·mol^{-1})	x_{LNE} (nmol·mol^{-1})	U_{LNE} (nmol·mol^{-1})	x_{LNE} (nmol·mol^{-1})	U_{LNE} (nmol·mol^{-1})
Before sending the cylinder to METAS	16/05/2023	5.211	0.084	5.293	0.075	4.867	0.103
	31/05/2023	5.184	0.112	5.300	0.064	4.885	0.088
	15/06/2023	5.198	0.126	5.320	0.062	4.907	0.094
	28/06/2023	5.214	0.102	5.293	0.075	4.884	0.071
	05/07/2023	5.179	0.090	5.326	0.131	4.919	0.140
After receiving the cylinder from UBA	16/01/2024	5.114	0.156	5.244	0.154	4.872	0.138
	23/01/2024	5.269	0.063	5.374	0.062	4.978	0.056
	06/02/2024	5.168	0.201	5.303	0.120	4.851	0.107
	12/02/2024	5.176	0.114	5.315	0.133	4.886	0.113
	26/02/2024	5.240	0.116	5.381	0.127	4.916	0.154

The analytical amount fractions and the associated uncertainties obtained by LNE on the gas mixture D115803 over time are plotted in **Error! Reference source not found.** to 6.

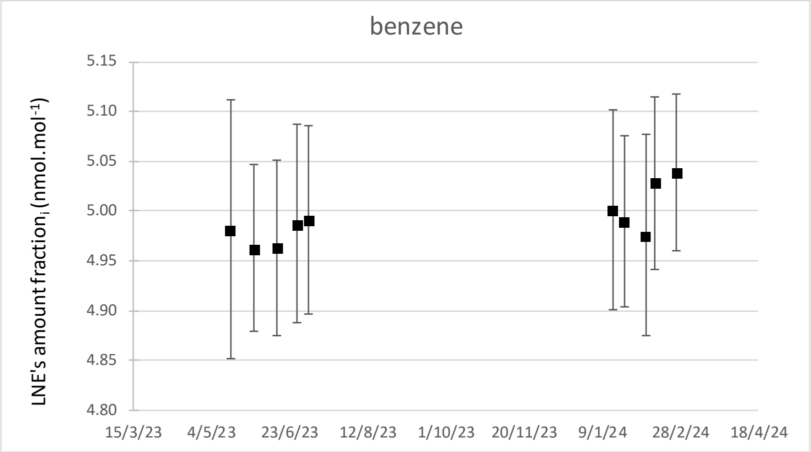


Figure 1: Analytical amount fractions obtained by LNE over time for benzene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence

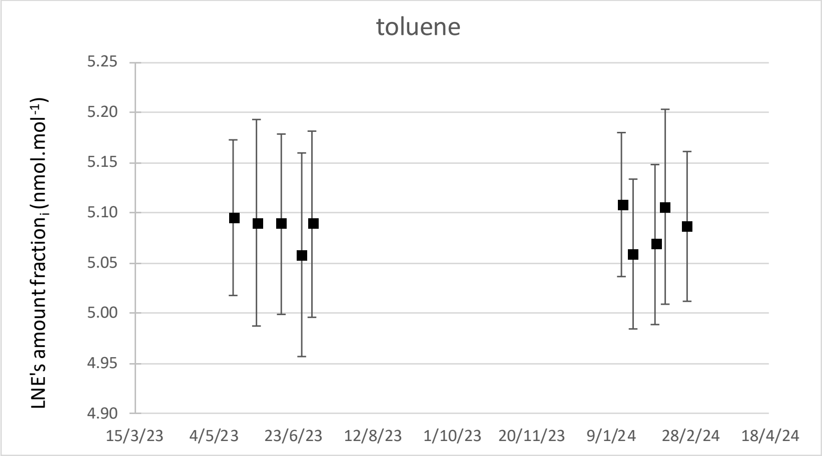


Figure 2: Analytical amount fractions obtained by LNE over time for toluene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence

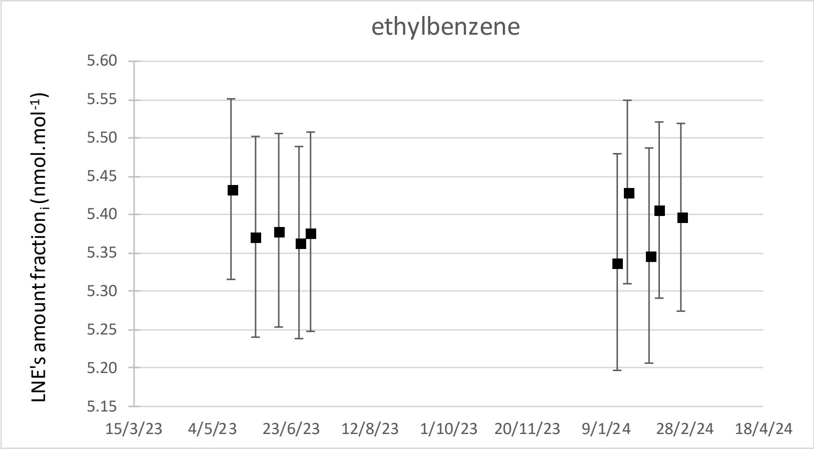


Figure 3: Analytical amount fractions obtained by LNE over time for ethylbenzene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence

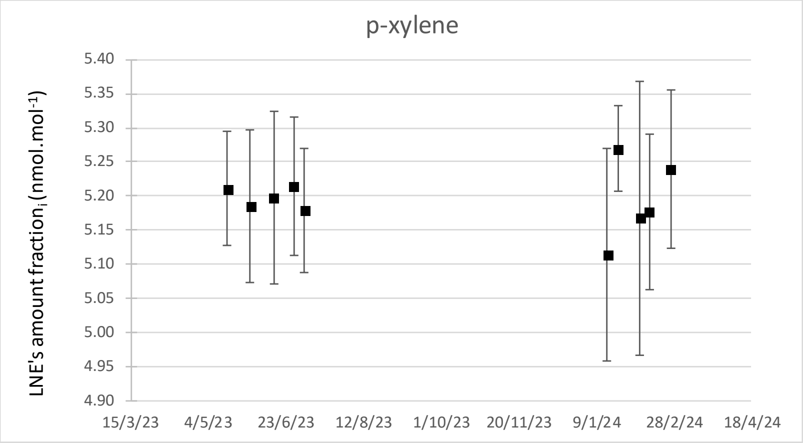


Figure 4: Analytical amount fractions obtained by LNE over time for p-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence

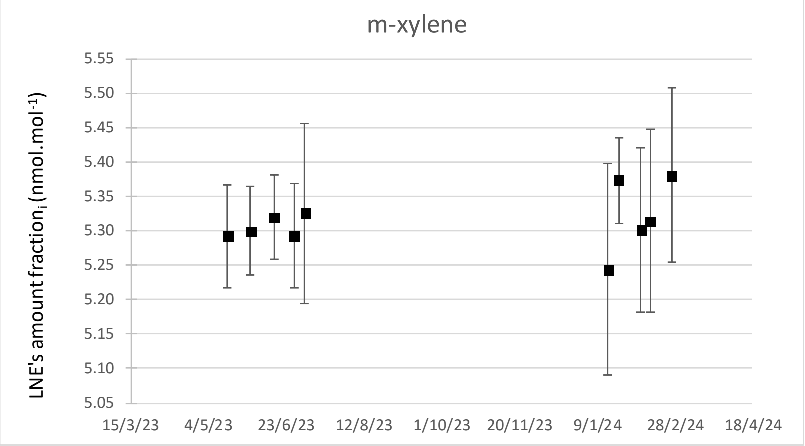


Figure 5: Analytical amount fractions obtained by LNE over time for m-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence

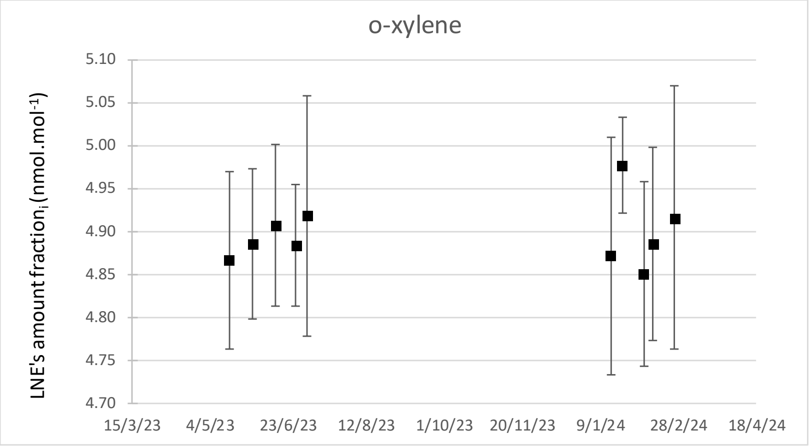


Figure 6: Analytical amount fractions obtained by LNE over time for o-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence

The results show that no drifts are observed for any of the amount fractions of the BTEX components present in the comparison gas mixture. The fluctuations of the amount fractions are due to the reproducibility of the measurements.

4 Participant methods

The methods and procedures used by the participants to analyze the comparison gas mixture are described in their respective reports (see Appendices B to D), and summarized in Table 5. In this key comparison unlike in the CCQM-K10.2018 comparison UBA separates p-xylene and m-xylene, and METAS which separates p-xylene and m-xylene reports individual values for each.

Table 5: Methods used by the participants to analyze the comparison gas mixture

Participant	Analytical method
LNE	Dynamic generation of calibration standards using gravimetric gas mixtures prepared by LNE. Analysis of all components simultaneously using a GC-FID (Compact GC, Interscience) with preconcentration.
METAS	Dynamic generation of calibration standards using permeation units of the components placed in a primary magnetic suspension balance (MSB, TA Instruments). Analysis of all components simultaneously using a GC-FID (8890, Agilent, CA, USA) with preconcentration.
UBA	Static dilution of pure certified reference materials in a mixing chamber for preparing calibration standards (ISO 6144). Analysis of all components individually using a GC-FID (GC Arnel-Clarus 680 GL, PerkinElmer) with preconcentration.

5 Degrees of equivalence

The key comparison reference values i.e. the values for the amount fractions and associated uncertainties are based on the certificate provided by NPL in the certificate of calibration reference 2023020246 from 3 April 2023 (see Annex 1) and are given in the Table 6.

Table 6: Key reference amount fractions of the gas mixture D115803, and the associated uncertainties

Component	**Amount fraction (x) (nmol·mol^{-1})**	**Expanded uncertainty (nmol·mol^{-1})**
Benzene	4.89	0.10
Toluene	5.00	0.11
Ethylbenzene	5.26	0.11
m-Xylene	5.19	0.11
p-Xylene	5.05	0.11
o-Xylene	4.73	0.10

The degree of equivalence D of the participant, for component *i*, is defined as:

$$D = x_\mathrm{i} - x_\mathrm{KCRV} \qquad (1)$$

Where x_i is the result of the laboratory for component *i* and x_KCRV denotes the key comparison reference value for the amount fraction as provided by NPL.

The standard uncertainty of D ($u(D)$) for component *i* can be expressed as:

$$u(D) = \sqrt{u^2(x_\mathrm{i}) + u^2(x_\mathrm{KCRV})} \tag{2}$$

Where $u(x_\mathrm{i})$ is the combined uncertainty on the result x_i of the laboratory for component *i* and $u(x_\mathrm{KCRV})$ is the combined uncertainty on the key comparison reference value for the amount fraction x_KCRV as provided by NPL.

In this section, the results of the key comparison are summarised. In the tables 7 to 12, the following data are presented:

x_KCRV	key comparison reference value for the amount fraction as provided by NPL (nmol·mol^{-1})
U(x_KCRV)	expanded uncertainty of key comparison reference value for the amount fraction as provided by NPL, at 95 % level of confidence [5] (nmol·mol^{-1})
$k_{x\mathrm{KCRV}}$	stated coverage factor for expanded uncertainty of key reference value for the amount fraction as provided by NPL
x_i	result of laboratory for the component *i* (nmol·mol^{-1})
U(x_i)	expanded uncertainty of result of laboratory for the component *i*, at 95 % level of confidence [5] (nmol·mol^{-1})
$k_{x\mathrm{i}}$	stated coverage factor for expanded uncertainty of result of laboratory for the component *i*
D	difference between result of laboratory for the component *i* and the key comparison reference value for the amount fraction as provided by NPL (nmol·mol^{-1})
U(D)	expanded uncertainty of difference *D*, at 95 % level of confidence [5] (nmol·mol^{-1})
k_D	assigned coverage factor for degree of equivalence

Tables 7 to 12 show the results for the BTEX components as reported by METAS and UBA. For LNE the result was obtained by pooling all measurements from the stability study.

The reported expanded uncertainties calculated by the three participants are different in size. For example, in the case of m-xylene and p-xylene, the expanded uncertainties provided by UBA are approximately three times higher than those calculated by METAS.

Table 7: Results and degrees of equivalence for benzene

benzene										
Laboratory	**Cylinder**	x_KCRV	**U(x_KCRV)**	$k_{x\mathrm{KCRV}}$	x_i	**U(x_i)**	$k_{x\mathrm{i}}$	D	**U(D)**	k_D
LNE	D115803	4.89	0.10	2	4.98	0.14	2	0.09	0.17	2
METAS	D115803	4.89	0.10	2	4.91	0.06	2	0.02	0.12	2
UBA	D115803	4.89	0.10	2	4.82	0.11	2	-0.07	0.15	2

Table 8: Results and degrees of equivalence for toluene

toluene										
Laboratory	**Cylinder**	x_KCRV	**U(x_KCRV)**	$k_{x\mathrm{KCRV}}$	x_i	**U(x_i)**	$k_{x\mathrm{i}}$	D	**U(D)**	k_D
LNE	D115803	5.00	0.11	2	5.08	0.13	2	0.08	0.17	2
METAS	D115803	5.00	0.11	2	5.28	0.08	2	0.28	0.14	2
UBA	D115803	5.00	0.11	2	4.77	0.111	2	-0.23	0.16	2

Table 9: Results and degrees of equivalence for ethylbenzene

ethylbenzene										
Laboratory	**Cylinder**	x_{KCRV}	$U(x_{\mathrm{KCRV}})$	$k_{x\mathrm{KCRV}}$	x_{i}	$U(x_{\mathrm{i}})$	$k_{x\mathrm{i}}$	D	$U(D)$	k_D
LNE	D115803	5.26	0.11	2	5.38	0.17	2	0.12	0.20	2
METAS	D115803	5.26	0.11	2	5.42	0.11	2	0.16	0.16	2
UBA	D115803	5.26	0.11	2	5.57	0.207	2	0.31	0.23	2

Table 10: Results and degrees of equivalence for p-xylene

p-xylene										
Laboratory	**Cylinder**	x_{KCRV}	$U(x_{\mathrm{KCRV}})$	$k_{x\mathrm{KCRV}}$	x_{i}	$U(x_{\mathrm{i}})$	$k_{x\mathrm{i}}$	D	$U(D)$	k_D
LNE	D115803	5.05	0.11	2	5.18	0.17	2	0.13	0.20	2
METAS	D115803	5.05	0.11	2	5.56	0.12	2	0.51	0.16	2
UBA	D115803	5.05	0.11	2	4.63	0.33	2	-0.42	0.35	2

Table 11: Results and degrees of equivalence for m-xylene

m-xylene										
Laboratory	**Cylinder**	x_{KCRV}	$U(x_{\mathrm{KCRV}})$	$k_{x\mathrm{KCRV}}$	x_{i}	$U(x_{\mathrm{i}})$	$k_{x\mathrm{i}}$	D	$U(D)$	k_D
LNE	D115803	5.19	0.11	2	5.31	0.16	2	0.12	0.19	2
METAS	D115803	5.19	0.11	2	5.28	0.10	2	0.09	0.15	2
UBA	D115803	5.19	0.11	2	5.88	0.315	2	0.69	0.33	2

Table 12: Results and degrees of equivalence for o-xylene

o-xylene										
Laboratory	**Cylinder**	x_{KCRV}	$U(x_{\mathrm{KCRV}})$	$k_{x\mathrm{KCRV}}$	x_{i}	$U(x_{\mathrm{i}})$	$k_{x\mathrm{i}}$	D	$U(D)$	k_D
LNE	D115803	4.73	0.10	2	4.89	0.15	2	0.16	0.18	2
METAS	D115803	4.73	0.10	2	4.92	0.09	2	0.19	0.13	2
UBA	D115803	4.73	0.10	2	5.24	0.33	2	0.51	0.35	2

The degrees of equivalence and the associated expanded uncertainties obtained for each component are plotted in Figures 7 to 12.

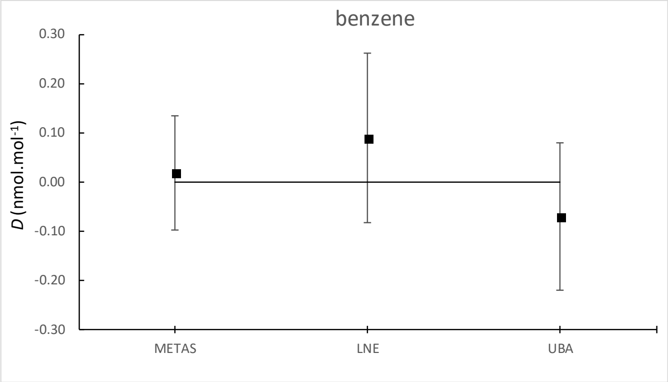


Figure 7: Degrees of equivalence for benzene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

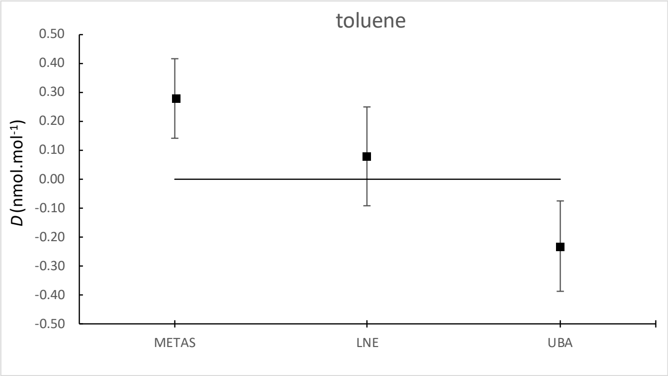


Figure 8: Degrees of equivalence for toluene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

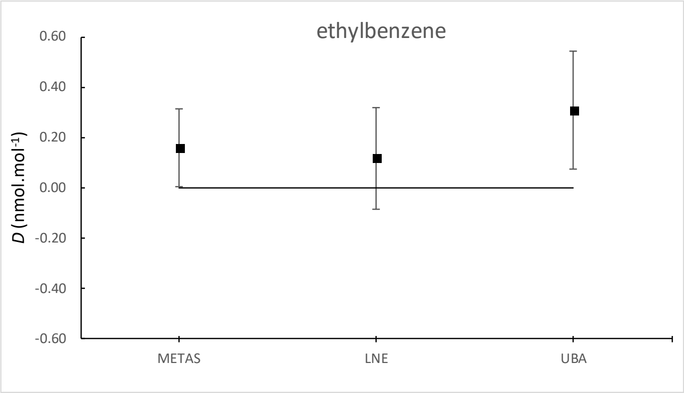


Figure 9: Degrees of equivalence for ethylbenzene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

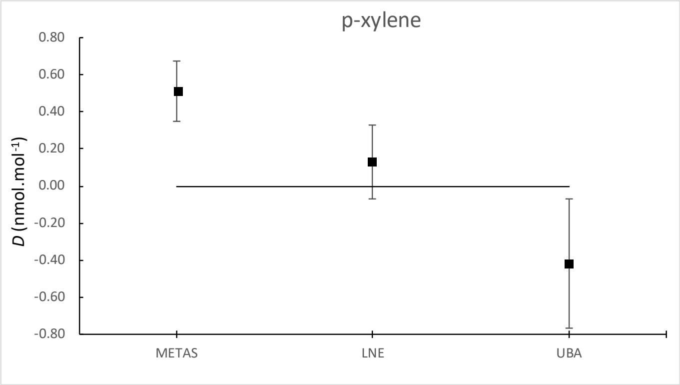


Figure 10: Degrees of equivalence for p-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

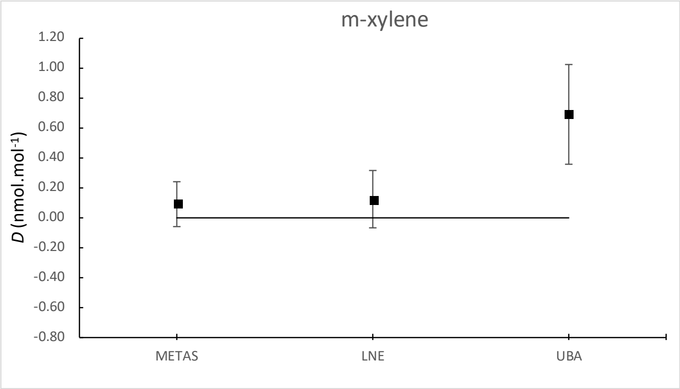


Figure 11: Degrees of equivalence for m-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

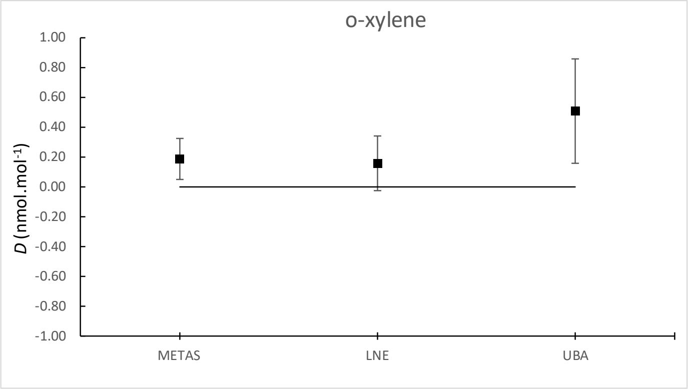


Figure 12: Degrees of equivalence for o-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

For benzene, all results are consistent with the key comparison reference value (KCRV).

For toluene, ethylbenzene, p-xylene and o-xylene, LNE's results are consistent with the key reference amount fractions; the results from METAS and UBA are discrepant with respect to the key reference amount fractions.

For m-xylene, METAS's and LNE's results are consistent with the key reference amount fractions; the result from UBA is discrepant with respect to the key reference amount fraction.

6 Link with CCQM-K10.2018

The link with the results in CCQM-K10.2018 is provided through the key comparison reference value (KCRV) based on a transfer standard from NPL who participated with satisfactory performance in CCQM-K10.2018 comparison. To enable assessing the equivalence between the results in this key comparison and the results in CCQM-K10.2018, the degrees of equivalence have been calculated. Let δ_i denote the difference between the result of participant *i* in this key comparison and the key comparison reference value for the "correction cylinder" in CCQM-K10.2018 [1]. Then,

$$\delta_i = D_i - D_{NPL} \qquad (3)$$

where D_{NPL} denotes the degree of equivalence of NPL in CCQM-K10.2018 and D_i the degree of equivalence in this key comparison (see section 5). The standard uncertainty associated with δ_i

can be readily obtained by applying the law of propagation of uncertainty for correlated input quantities (equation (13) in ISO/IEC Guide 98-3) [4].

The results from NPL, the linking laboratory between the two key comparisons are considered to be correlated. The precision component in the uncertainty budget was deemed uncorrelated, whereas the components due to the calibration standards were correlated. The covariance between the result from the linking laboratory in CCQM-K10.2018 and that on the certificate of the travelling standard in this key comparison was calculated using equation (F.1) in ISO/IEC Guide 98-3 [4].

From the underlying information concerning the uncertainty budget, a correlation coefficient of 0.20 was derived between the pairs of amount fractions for each component. The uncertainty contribution due to the calibration standard was considered to be common to both uncertainty budgets (in CCQM-K10.2018 and in this key comparison). The expression for the squared standard uncertainty associated with δ_i takes the form

$$u^2(\delta_i) = u^2(D_i) + u^2(D_{NPL}) - 2r(D_i, D_{NPL})u(D_i)u(D_{NPL}) \qquad (4)$$

where $r(D_i, D_{NPL})$ denotes the correlation coefficient between the two degrees of equivalence, which is equal to the correlation coefficient between NPL's result in CCQM-K10.2018 and the key comparison reference value in this key comparison. The degrees of equivalence of the linking laboratory in CCQM-K10.2018 are given in table 13. The degrees of equivalence with respect to the KCRV in CCQM-K10.2018 are given in tables 14-19.

Table 13: Degrees of equivalence of the linking laboratory in CCQM-K10.2018 and the correlation coefficients

Component	D_{NPL}	$u(D_{NPL})$	r
benzene	0.020	0.112	0.2
toluene	0.040	0.112	0.2
ethylbenzene	0.000	0.103	0.2
p-xylene	0.050	0.112	0.2
m-xylene	0.060	0.112	0.2
o-xylene	0.060	0.112	0.2

Table 14: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for benzene

Laboratory	Cylinder	x_i	$U(x_i)$	k_{xi}	δ	$U(\delta)$	k_δ
LNE	D115803	4.98	0.14	2	0.11	0.27	2
METAS	D115803	4.91	0.06	2	0.04	0.25	2
UBA	D115803	4.82	0.11	2	-0.05	0.26	2

Table 15: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for toluene

Laboratory	Cylinder	x_i	$U(x_i)$	k_{xi}	δ	$U(\delta)$	k_δ
LNE	D115803	5.08	0.13	2	0.12	0.27	2
METAS	D115803	5.28	0.08	2	0.32	0.25	2
UBA	D115803	4.77	0.111	2	-0.19	0.27	2

Table 16: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for ethylbenzene

Laboratory	Cylinder	x_i	$U(x_i)$	k_{xi}	δ	$U(\delta)$	k_δ
LNE	D115803	5.38	0.17	2	0.12	0.28	2
METAS	D115803	5.42	0.11	2	0.16	0.25	2
UBA	D115803	5.57	0.207	2	0.31	0.30	2

Table 17: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for p-xylene

Laboratory	Cylinder	x_i	$U(x_i)$	k_{xi}	δ	$U(\delta)$	k_δ
LNE	D115803	5.18	0.17	2	0.18	0.29	2
METAS	D115803	5.56	0.12	2	0.56	0.27	2
UBA	D115803	4.63	0.33	2	-0.37	0.41	2

Table 18: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for m-xylene

Laboratory	Cylinder	x_i	$U(x_i)$	k_{xi}	δ	$U(\delta)$	k_δ
LNE	D115803	5.31	0.16	2	0.18	0.29	2
METAS	D115803	5.28	0.10	2	0.15	0.26	2
UBA	D115803	5.88	0.315	2	0.75	0.39	2

Table 19: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for o-xylene

Laboratory	Cylinder	x_i	$U(x_i)$	k_{xi}	δ	$U(\delta)$	k_δ
LNE	D115803	4.89	0.15	2	0.22	0.28	2
METAS	D115803	4.92	0.09	2	0.25	0.25	2
UBA	D115803	5.24	0.33	2	0.57	0.41	2

The degrees of equivalence with respect to the KCRV in CCQM-K10.2018 are represented in figures 13-18.

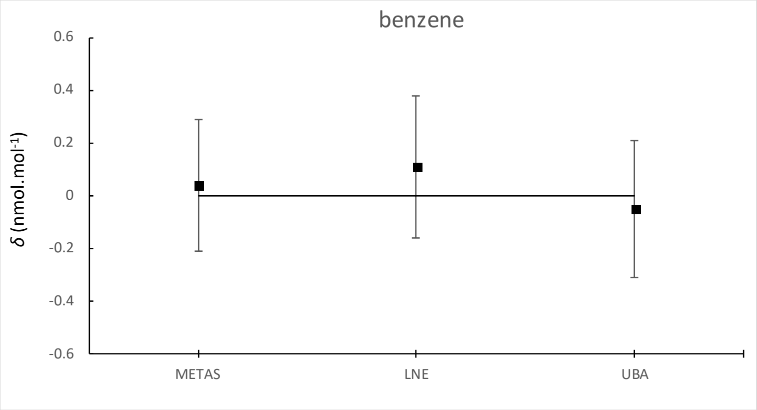


Figure 13: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for benzene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

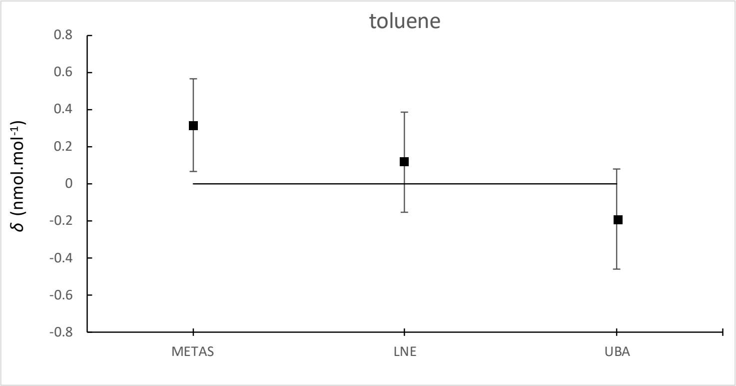


Figure 14: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for toluene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

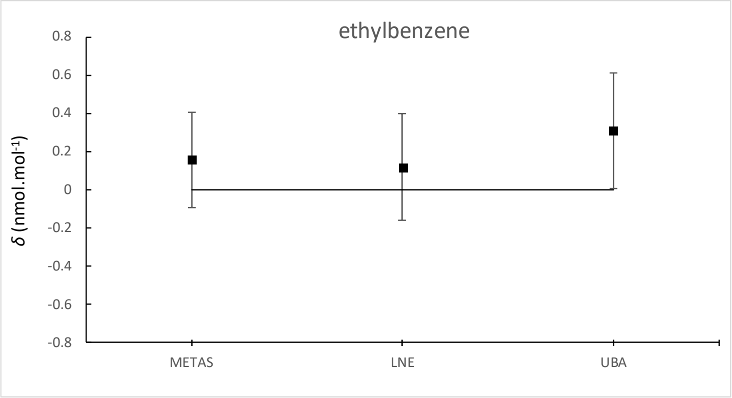


Figure 15: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for ethylbenzene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

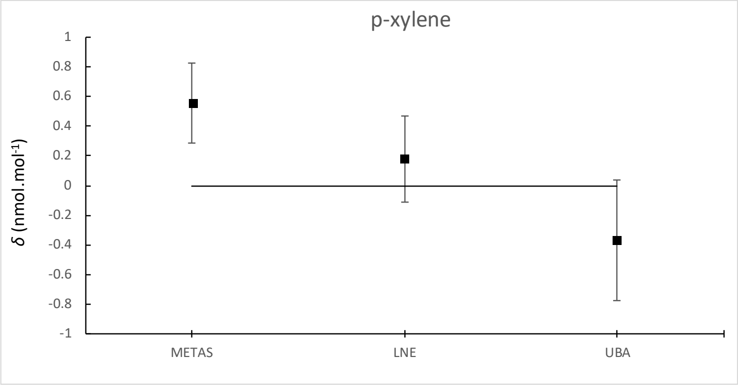


Figure 16: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for p-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

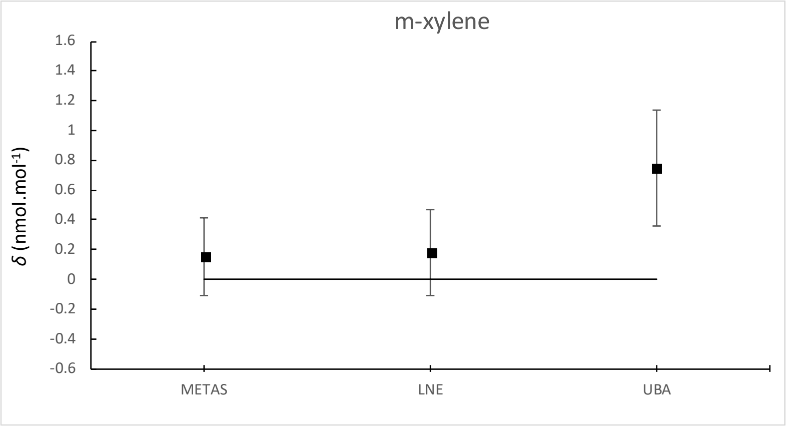


Figure 17: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for m-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

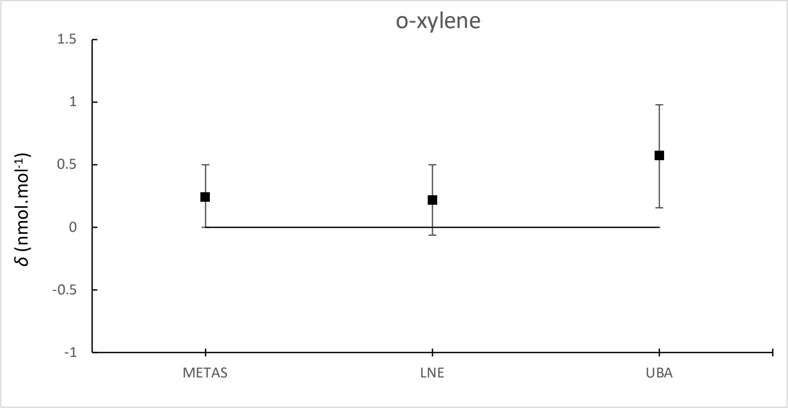


Figure 18: Degrees of equivalence with respect to the KCRV of CCQM-K10.2018 for o-xylene. The uncertainty bars represent the expanded uncertainties (k=2) at 95% level of confidence.

For benzene, all results are consistent with the key comparison reference value (KCRV) of CCQM-K10.2018.

For toluene and p-xylene, LNE's and UBA's results are consistent with the KCRV of CCQM-K10.2018; the results from METAS are discrepant with respect to the KCRV of CCQM-K10.2018.

For ethylbenzene, m-xylene and o-xylene, LNE's and METAS's results are consistent with the KCRV of CCQM-K10.2018; the results from UBA are discrepant with respect to the KCRV of CCQM-K10.2018.

7 Discussion and conclusions

The results obtained in the CCQM-K10.2018 comparison for the gravimetric study, based on the response ratios and reported compositions of the participants' gas mixtures, identified consistently high bias for LNE which could be linked to the measurement method used to validate the preparation of the gravimetric gas mixtures. The results in this key comparison show good agreement for benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene with comparable expanded uncertainties for LNE. The calibration method developed by LNE was improved since the last CCQM-K10.2018 comparison by using a new gas chromatograph (Compact GC (Interscience) equipped with a CP-xylene capillary column) and by increasing the flows for BTEX gas mixtures and dilution gas during the generation of the reference gas mixture to calibrate the gas chromatograph (flow rates are two times higher than those used in the last CCQM-K10.2018 comparison).

As for LNE, CCQM-K10.2018 results for METAS were biased high, which METAS attributed to a potential calibration error of their measurement system. The results in this key comparison show good agreement for benzene, ethylbenzene, m-xylene and o-xylene for METAS. The associated expanded uncertainties stated by METAS in this key comparison are lower than those determined in the CCQM-K10.2018 comparison due to the use of a primary magnetic suspension balance (MSB, TA Instruments. DE. USA) instead of the mobile in-house constructed generator "ReGaS2". The discrepancies for toluene and p-xylene are most likely explained by the age of the permeation devices (>5 years) used for the generation of the calibration standards.

The results obtained for UBA in the CCQM-K10.2018 comparison for the comparative study agreed with the KCRV for all components measured. UBA results in this key comparison show good agreement for benzene, toluene and p-xylene. The deviations for ethylbenzene, m-xylene and o-xylene may be due to a malfunction in the mixing chamber leading to a lack of homogeneity in the reference gas mixture. Moreover, the associated expanded uncertainties calculated by UBA in this key comparison are higher than those obtained in the CCQM-K10.2018 comparison due to a more accurate determination of the standard uncertainties on pressures and temperatures inside the mixing chamber.

8 Supported claims

This key comparison can be used to support CMC claims for gas mixtures of BTEX in nitrogen from 1 nmol·mol^{-1} to 10 $\mu\text{mol·mol}^{-1}$ as described in the final report of CCQM-K10.2018 [1].

9 References

[1] Christina E Cecelski, George C Rhoderick, Antonio M Possolo, Jennifer Carney, Miroslav Vokoun, Jitka Privoznikova, Sangil Lee, Ji Hwan Kang, Yong Doo Kim, Dal Ho Kim, Tatiana Macé, Christophe Sutour, Céline Pascale, Napo Ntsasa, James Tshilongo, Mudalo Jozela, Nompumelelo Leshabane, Goitsemang Lekoto, David R Worton, Paul J Brewer, Fred Farrow-Dunn, Sergi Moreno, Klaus Wirtz, Volker Stummer, L A Konopelko, A V Kolobova, Y A Kustikov, A Y Klimov, O V Efremova, Janneke I T van Wijk and Adriaan M H van der Veen, International Comparison CCQM-K10.2018: BTEX in nitrogen at 5 nmol mol^{-1}, Final Report, 2022

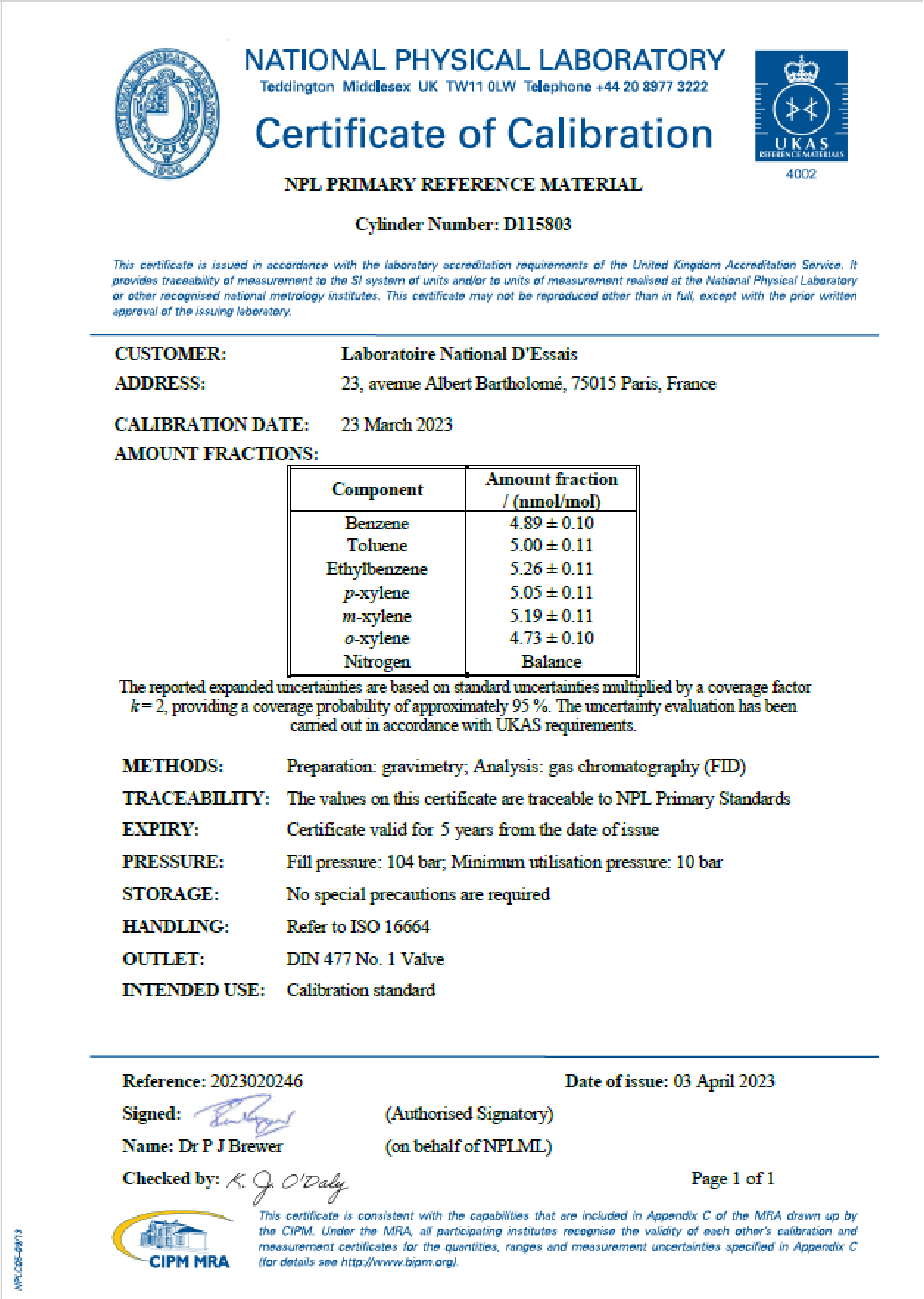
[2] International Organization for Standardization, ISO 6142-1:2015 Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures, 1st edition

[3] International Organization for Standardization, ISO 6143:2001 Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures, 2nd edition

[4] International Organization for Standardization, ISO/IEC Guide 98-3:2008 Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995), 1st edition

[5] CIPM, “Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes”, Sèvres (F), October 1999

Annex A NPL's certificate of calibration reference 2023020246 from 3 April 2023



NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS REFERENCE MATERIALS
4002

NPL PRIMARY REFERENCE MATERIAL

Cylinder Number: D115803

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: **Laboratoire National D'Essais**
ADDRESS: 23, avenue Albert Bartholomé, 75015 Paris, France

CALIBRATION DATE: 23 March 2023
AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Benzene	4.89 ± 0.10
Toluene	5.00 ± 0.11
Ethylbenzene	5.26 ± 0.11
p-xylene	5.05 ± 0.11
m-xylene	5.19 ± 0.11
o-xylene	4.73 ± 0.10
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)
TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards
EXPIRY: Certificate valid for 5 years from the date of issue
PRESSURE: Fill pressure: 104 bar; Minimum utilisation pressure: 10 bar
STORAGE: No special precautions are required
HANDLING: Refer to ISO 16664
OUTLET: DIN 477 No. 1 Valve
INTENDED USE: Calibration standard

Reference: 2023020246 **Date of issue:** 03 April 2023
Signed: (Authorised Signatory)
Name: Dr P J Brewer (on behalf of NPLML)
Checked by: K. J. O'Daly Page 1 of 1

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognise the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

Annex B Measurement report of LNE

CCQM-K10.2018.1 comparison
Key comparison of analytical capabilities for BTEX gas mixtures

Laboratory name: LNE
Pressure before measurements: 105 bar
Pressure after measurements: 65 bar

B.1 Results

B.1.1 Measurement #1

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	16/05/23	4.982	0.94	5
Toluene	16/05/23	5.095	0.28	5
Ethylbenzene	16/05/23	5.433	0.32	5
para-Xylene	16/05/23	5.211	0.35	5
meta-Xylene	16/05/23	5.293	0.25	5
ortho-Xylene	16/05/23	4.867	0.63	5

B.1.2 Measurement #2

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	31/05/23	4.962	0.31	5
Toluene	31/05/23	5.090	0.57	5
Ethylbenzene	31/05/23	5.371	0.41	5
para-Xylene	31/05/23	5.185	0.53	5
meta-Xylene	31/05/23	5.300	0.31	5
ortho-Xylene	31/05/23	4.885	0.42	5

B.1.3 Measurement #3

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	15/06/23	4.963	0.41	5
Toluene	15/06/23	5.089	0.68	5
Ethylbenzene	15/06/23	5.379	0.33	5
para-Xylene	15/06/23	5.198	0.72	5
meta-Xylene	15/06/23	5.320	0.27	5
ortho-Xylene	15/06/23	4.907	0.76	5

B.1.4 Measurement #4

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	28/06/23	4.988	0.64	5
Toluene	28/06/23	5.058	0.73	5
Ethylbenzene	28/06/23	5.364	0.29	5
para-Xylene	28/06/23	5.214	0.59	5
meta-Xylene	28/06/23	5.293	0.48	5
ortho-Xylene	28/06/23	4.884	0.16	5

B.1.5 Measurement #5

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	05/07/23	4.991	0.55	5
Toluene	05/07/23	5.089	0.48	5
Ethylbenzene	05/07/23	5.378	0.40	5
para-Xylene	05/07/23	5.179	0.44	5
meta-Xylene	05/07/23	5.326	0.57	5
ortho-Xylene	05/07/23	4.919	0.99	5

B.1.6 Measurement #6

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	16/01/24	5.001	0.66	5
Toluene	16/01/24	5.108	0.37	5
Ethylbenzene	16/01/24	5.338	0.77	5
para-Xylene	16/01/24	5.114	0.88	5
meta-Xylene	16/01/24	5.244	1.1	5
ortho-Xylene	16/01/24	4.872	0.72	5

B.1.7 Measurement #7

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	23/01/24	4.990	0.33	5
Toluene	23/01/24	5.059	0.41	5
Ethylbenzene	23/01/24	5.429	0.29	5
para-Xylene	23/01/24	5.269	0.27	5
meta-Xylene	23/01/24	5.374	0.23	5
ortho-Xylene	23/01/24	4.978	0.18	5

B.1.8 Measurement #8

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	06/02/24	4.976	0.50	5
Toluene	06/02/24	5.069	0.44	5
Ethylbenzene	06/02/24	5.347	0.68	5
para-Xylene	06/02/24	5.168	1.5	5
meta-Xylene	06/02/24	5.303	0.95	5
ortho-Xylene	06/02/24	4.851	0.47	5

B.1.9 Measurement #9

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	12/02/24	5.028	0.44	5
Toluene	12/02/24	5.106	0.56	5
Ethylbenzene	12/02/24	5.406	0.052	5
para-Xylene	12/02/24	5.176	0.51	5
meta-Xylene	12/02/24	5.315	0.66	5
ortho-Xylene	12/02/24	4.886	0.94	5

B.1.10 Measurement #10

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	26/02/24	5.039	0.25	5
Toluene	26/02/24	5.086	0.31	5
Ethylbenzene	26/02/24	5.397	0.41	5
para-Xylene	26/02/24	5.240	0.83	5
meta-Xylene	26/02/24	5.381	0.89	5
ortho-Xylene	26/02/24	4.916	1.25	5

B.1.11 Results

Component	Date (mm/yy)	Result (nmol·mol^{-1})	Expanded uncertainty (nmol·mol^{-1})	Coverage factor
Benzene	05/23-02/24	4.98	0.14	2
Toluene	05/23-02/24	5.08	0.13	2
Ethylbenzene	05/23-02/24	5.38	0.17	2
para-Xylene	05/23-02/24	5.18	0.17	2
meta-Xylene	05/23-02/24	5.31	0.16	2
ortho-Xylene	05/23-02/24	4.89	0.15	2

B.2 Calibration standards

Four gravimetric gas mixtures (benzene, ethylbenzene, toluene and o,m,p xylenes) at 2 µmol·mol^{-1} in nitrogen are prepared according to the ISO 6142 standard.
For preparing a gravimetric gas mixture, each 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. One successive gravimetric dilution is performed to obtain the final gas mixture at 2 µmol·mol^{-1}.

The dynamic reference gas mixture is generated by diluting dynamically the four gravimetric gas mixtures at 2 µmol·mol^{-1} to obtain a reference gas mixture at 5 nmol·mol^{-1} of BTEX in pure nitrogen. The flowrates are measured with five accurate flowmeters (Molbloc).

The amount fraction of benzene (as an example) in the dynamic gas mixture $x_{\text{benzene,dynamic RGM}}$ is calculated as follows:

$$x_{\text{benzene,dynamic RGM}} = \frac{q_{\text{m,benzene}} \cdot x_{\text{benzene,gravimetric RGM}}}{q_{\text{m,benzene}} \cdot q_{\text{m,toluene}} \cdot q_{\text{m,ethylbenzene}} \cdot q_{\text{m,xylenes}} \cdot q_{\text{m,nitrogen}}}$$

With:

- $x_{\text{benzene,gravimetric RGM}}$	the benzene amount fraction of the benzene gravimetric gas mixture
- $q_{\text{m,benzene}}$	the flow of the benzene gravimetric gas mixture
- $q_{\text{m,toluene}}$	the flow of the toluene gravimetric gas mixture
- $q_{\text{m,ethylbenzene}}$	the flow of the ethylbenzene gravimetric gas mixture
- $q_{\text{m,xylenes}}$	the flow of the xylenes gravimetric gas mixture
- $q_{\text{m,nitrogen}}$	the flow of nitrogen

The uncertainty budget of the benzene amount fraction (and also the other compounds) in the dynamic reference gas mixture is calculated using the standard uncertainties and by applying the law of propagation of uncertainties expressed in the Guide to the Expression of Uncertainty in Measurement (GUM; JCGM, 2008) on the Eq. (1).

The table 1 summarized the uncertainty of the benzene amount fraction in the dynamic reference gas mixture generated by dynamic dilution of gravimetric gas mixtures at 2 µmol·mol^{-1}.

Table1: Uncertainty budget of benzene amount fraction in the dynamic reference gas mixture at 5 nmol·mol^{-1} for measurement #1

Variable	Units	Value	u(Xi)	Sensitivity coefficient C(Xi)	C(Xi).u(Xi)	Contribution
$q_{\mathrm{m,benzene}}$	ml·min^{-1}	20.753	0.060	0.2399	1.44E-02	15.72%
$x_{\mathrm{benzene,gravimetric\ RGM}}$	nmol·mol^{-1}	1999	12	0.0025	3.00E-02	68.12%
$q_{\mathrm{m,toluene}}$	ml·min^{-1}	21.189	0.061	-0.0006	-4.00E-05	0.00%
$q_{\mathrm{m,ethylbenzene}}$	ml·min^{-1}	22.831	0.066	-0.0006	-4.00E-05	0.00%
$q_{\mathrm{m,xylenes}}$	ml·min^{-1}	21.979	0.064	-0.0006	-4.00E-05	0.00%
$q_{\mathrm{m,nitrogen}}$	ml·min^{-1}	8225.3	24.3	-0.0006	-1.46E-02	16.16%

$x_{\mathrm{benzene,dynamic\ RGM}}$ (nmol·mol^{-1})	**4.991**	**0.073**	**(k = 2)**

B.3 Instrumentation

The gas mixture of 5 nmol·mol^{-1} of BTEX was analyzed using a GC-FID with a preconcentration with Module (Tenax). The GC-FID is a Compact GC from Interscience equipped with a CP-xylene capillary column for the separation of the compounds. The chromatographic conditions are listed below.

- Sample flow: 40 ml·min^{-1}
- Sample time: 10 min
- Column pressure: 55 kPa
- Oven temperature: 50°C
- Trap temperature: 5°C
- Desorption temperature: 280°C
- Desorption time: 70 s

B.4 Calibration method and value assignment

The GC is calibrated at 5 nmol·mol^{-1} with a dynamic reference gas mixture obtained by diluting dynamically the gravimetric reference gas mixtures (cf. paragraph B.2). The flowrates are measured with five accurate flowmeters (Molbloc). Five determinations of the chromatographic areas of BTEX peaks are performed to determine the amount fraction of the gas mixture at 5 nmol·mol^{-1}.

The amount fraction of each component (x_{compound}) is calculated as follows:

$$x_{\mathrm{compound}} = x_{\mathrm{compound,dynamic\ RGM}} \cdot \frac{A_{\mathrm{sample}}}{A_{\mathrm{dynamic\ RGM}}} \qquad \text{Eq. (2)}$$

With:

- $x_{\mathrm{compound,dynamic\ RGM}}$ Amount fraction of each component in the dynamic reference gas mixture at 5 nmol·mol^{-1}
- A_{sample} Average area of five chromatographic peaks for each component in the gas mixture to be analysed
- $A_{\mathrm{dynamic\ RGM}}$ Average area of five chromatographic peaks for each component in the dynamic RGM at 5 nmol·mol^{-1}

B.5 Uncertainty evaluation

The uncertainty budget of the benzene amount fraction in the gas mixture to be analysed is calculated using the standard uncertainties and by applying the law of propagation of uncertainties expressed in the Guide to the Expression of Uncertainty in Measurement (GUM; JCGM, 2008) on the Eq. (2).

The table 2 represents the uncertainty budget for one determination (measurement #1) of the benzene amount fraction in the gas mixture to be analysed.

Table 2: Uncertainty budget of benzene amount fraction in the gas mixture to be analysed for the measurement #1

Variable	Units	Values	u(Xi)	Sensib. C(Xi)	C(Xi).u(Xi)	Contribution
$q_{\mathrm{m,benzene}}$	ml·min^{-1}	20.753	0.060	0.239	1.44E-02	4.87%
$x_{\mathrm{benzene,gravimetric\ RGM}}$	nmol·mol^{-1}	1999	12	0.002	2.99E-02	21.10%
$q_{\mathrm{m,toluene}}$	ml·min^{-1}	21.189	0.061	-0.001	-3.70E-05	0.00%
$q_{\mathrm{m,ethylbenzene}}$	ml·min^{-1}	22.831	0.066	-0.001	-4.00E-05	0.00%
$q_{\mathrm{m,xylenes}}$	ml·min^{-1}	21.979	0.064	-0.001	-3.80E-05	0.00%
$q_{\mathrm{m,nitrogen}}$	ml·min^{-1}	8225.3	24.3	-0.001	-1.46E-02	5.01%
A_{sample}	-	0.2720	0.0025	18.316	4.67E-02	51.35%
$A_{\mathrm{dynamic\ RGM}}$	-	0.2725	0.0015	-18.283	-2.74E-02	17.67%

Amount fraction of benzene (measurement #1)	**nmol·mol^{-1}**	**4.982**	**± 0.13**	**(k = 2)**

The final result of the determination of the amount fraction of benzene is calculated as the average of the ten analyses obtained in reproducibility conditions. The uncertainty associated to this result is calculated as the quadratic sum of the standard deviation of the ten measurements and the average uncertainty of the individual measurements:

$$\mathrm{u}(x_{\mathrm{benzene}}) = \sqrt{u(r)^2 + u(m)^2}$$

u(r) : standard deviation of the ten measurements
u(m) : average of the uncertainty of the measurements

$$\mathrm{u}(x_{\mathrm{benzene}}) = \sqrt{u(0.040)^2 + u(0.057)^2}$$

Table 3: Uncertainty budget of the mean benzene amount fraction in the gas mixture to be analysed

Final amount fraction of benzene	**nmol·mol^{-1}**	**4.98**	**± 0.14**	**(k = 2)**

Annex C Measurement report of METAS

CCQM-K10.2018.1 comparison
Key comparison of analytical capabilities for BTEX gas mixtures

Laboratory name:	Federal Institute of Metrology METAS
Pressure before measurements:	85.0 bar
Pressure after measurements:	83.5 bar

C.1 Results

C.1.1 Measurement #1

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	10/08/23	4.88	1.35	5
Toluene	18/08/23	5.28	0.31	5
Ethylbenzene	25/08/23	5.41	0.83	5
para-Xylene	05/09/23	5.66	0.89	5
meta-Xylene	12/09/23	5.31	1.30	5
ortho-Xylene	23/09/23	5.05	0.89	3*

*5 replicates were measured. but due to issues with the analytical instrument. only 3 values were valid.

C.1.2 Measurement #2

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	11/08/23	4.90	1.01	5
Toluene	18/08/23	5.29	1.01	5
Ethylbenzene	26/08/23	5.43	0.83	4*
para-Xylene	06/09/23	5.57	0.34	5
meta-Xylene	13/09/23	5.29	0.63	5
ortho-Xylene	24/09/23	4.95	0.77	5

*5 replicates were measured but due to issues with the analytical instrument only 4 values were valid.

C.1.3 Measurement #3

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	11/08/23	4.94	1.02	5
Toluene	19/08/23	5.27	0.46	5
Ethylbenzene	27/08/23	5.43	0.63	5
para-Xylene	07/09/23	5.45	1.08	5
meta-Xylene	13/09/23	5.25	0.84	5
ortho-Xylene	24/09/23	4.76	0.64	5

C.1.4 Results

Component	Date (dd/mm/yy)	Result (nmol·mol^{-1})	Expanded uncertainty (nmol·mol^{-1})	Coverage factor
Benzene	11/08/23	4.91	0.06	2
Toluene	19/08/23	5.28	0.08	2
Ethylbenzene	27/08/23	5.42	0.11	2
para-Xylene	07/09/23	5.56	0.12	2
meta-Xylene	13/09/23	5.28	0.10	2
ortho-Xylene	24/09/23	4.92	0.09	2

C.2 Calibration standards

Calibration standards were generated dynamically based on the permeation [1] and dilution [2] methods. For that purpose. we placed permeation units (VICI Metronics. WA. USA) of the compounds under study in one of the METAS primary magnetic suspension balance (MSB. TA Instruments. DE. USA). one at each time (Table 1). Pressure. temperature and flow conditions within the MSB permeation chamber were regulated. The chamber pressure was set at 2600 hPa and the flow rate at 300 mL·min^{-1}. The chamber temperature ranged from 38 °C (toluene) to 46 °C (meta-xylene) (Table 1). Nitrogen obtained from liquid nitrogen evaporation (quality liquid nitrogen 5.0; 99.999 % purity) was used as carrier and dilution gas.

Table 1: Set calibration temperature, permeation rate and purity of the permeation units used in the intercomparison, as well as amount fraction of the generated calibration standards for value assignment. U is the expanded uncertainty (coverage factor *k* = 2).

Compound	Calibration temperature ± *U* (°C)	Permeation rate ± *U* (ng·min^{-1})	Purity* (Amount fraction of pure substance in %)	Amount fraction for value assignment ± *U* (nmol·mol^{-1})
benzene	44.95 ± 0.03	351.6 ± 1.0	99.96	4.97 ± 0.03
toluene	37.97 ± 0.03	221.3 ± 2.2	99.90	4.95 ± 0.06
ethylbenzene	44.95 ± 0.03	128.7 ± 2.2	99.9	4.98 ± 0.10
p-xylene	43.95 ± 0.03	183.9 ± 1.5	99.9	4.51 ± 0.05
m-xylene	45.94 ± 0.03	138.6 ± 1.6	99.7	4.86 ± 0.06
o-xylene	44.95 ± 0.03	122.5 ± 1.8	99.7	4.92 ± 0.08

*Purity values provided by manufacturer based on the purity results of the liquid compounds used to fill the permeation units. METAS did not perform a purity analysis.

A two-step dilution system coupled to the MSB [3] was used to dilute the binary gas mixtures to amount-of-substance fractions around 5 nmol·mol^{-1} (Table 1). The elements of the dilution system, mass flow controllers (MFC) and mass flow meter (MFM) were calibrated against METAS secondary flow standard (DryCal® 800. Mesa Labs. CO. USA). MSB and dilution system parts in contact with the gas mixture were coated (SilcoNert® 2000) to avoid surface effects.

Before placing the permeation units in the MSB, they were kept under conditions of temperature. pressure and flow similar to the conditions of the calibration standard generation for several weeks (4 – 11 weeks). Once in the MSB, at least 57 hours were waited before starting the generation of calibration standards to ensure the stability of the permeation units.

C.3 Instrumentation

A gas chromatography-flame ionization detector (GC-FID) system (8890, Agilent, CA, USA) was used as analytical method. Gas sampling was performed through an autosampler (CIA Advantage -xr 14, Markes International, UK) in MFC sampling mode (50 mL·min^{-1} sampling flow) connected to a thermal desorption unit (UNITY-xr, Markes International, UK), which was coupled to the GC-FID. Relative pressure in the used autosampler inlets (calibration standards. comparison standard and dilution gas for blanks) was around 1034 hPa. Samples were transferred to the GC-FID by heating the focusing cold trap (Air Toxics TO-14) in the thermal desorber (from -30 °C up to 250 °C at 40 °C/s). The trap purge flow was set at 50 mL·min^{-1} for 2 minutes. All the instrument lines in contact with the gas to be measured were coated (SilcoNert® 2000) and heated (120 °C) to minimize losses due to adsorption and condensation. The capillary column selected for these measurements was a Stabilwax (60 m (length), 0.25 mm (internal diameter) and 0.5 µm (film thickness); Restek Corporation, PA, USA). The GC-FID oven was held at 55 °C for 5 minutes. Then, it was heated up to 65 °C at 2 °C/min. This temperature was hold for 10 minutes. Afterwards, the temperature was increased to 80 °C at 5 °C/min. The final temperature was 180 °C, which was reached at 30 °C/min.

C.4 Calibration method and value assignment

The GC-FID was calibrated 3 times (one time per measurement) for each compound under study. The calibration was done by generating "fresh" (i.e. generated during the measurements) dynamic calibration standards at specific low amount-of-substance fraction (ca. 5 nmol·mol^{-1}) as described in Section 2. Five different calibration points were obtained by modifying the loaded amounts in the cold trap of the thermal desorption unit instead of by changing the amount-of-substance fraction of the binary gas mixtures. Loading flows remained constant while the loading time was set at 4.5 min, 4.8 min, 5.0 min, 5.3 min and 5.5 min in the autosampler. Each measurement consisted of the following sequence:

- initial blank analysis (3 replicates)
- 4.5 min calibration standard (5 replicates)
- 4.8 min calibration standard (5 replicates)
- 5.0 min calibration standard (5 replicates)
- 5.3 min calibration standard (5 replicates)
- 5.5 min calibration standard (5 replicates)
- comparison standard (5 replicates)
- blank analysis (5 replicates)

Loading time for blanks and comparison standard was 5 minutes. Sampling flow was set at 50 mL·min^{-1} in all cases (blanks, calibration standards and comparison standard).

The first step of the value assignment was to determine the permeation rate of each permeation unit at the calibration temperature. The permeation rate was calculated as the mass loss (in ng) during the calibration period (in minutes). Mass values of the permeation units were drift and air buoyancy corrected using two reference weights of same volume but different masses. The reference weights were measured periodically (every 3 permeation unit measurements (each measurement lasting 3 minutes) for the drift correction and every 18 measurements for the buoyancy correction). Then, the generated amount-of-substance fraction was estimated following a modified version of Eq. (1). Because residual amount-of-substance fractions of the compounds under study in the used dilution gas were not observed, this term (x_{Res_i}) was removed from Eq. (1) (i.e. modified version of Eq. (1)).

$$x_{cal\_i} = \left(\frac{q_{m\_i} \cdot p_i \cdot V_{m\_N2}}{M_i \cdot q_{v\_dil1}} + x_{Res\_i} \right) \cdot \frac{q_{v\_cal}}{q_{v\_dil2}} + x_{Res\_i} \cdot \left(1 - \frac{q_{v\_cal}}{q_{v\_dil2}} \right) \quad (1)$$

where,

x_{cal_i}: amount fraction of compound *i* in the calibration standard (in nmol·mol^{-1})

q_{m_i}: permeation rate of compound *i* permeation unit (in ng·min^{-1})

p_i: purity of compound *i* permeation unit (ratio)

V_{m_N2}: molar volume of the carrier/dilution gas (nitrogen) (in mL·mol^{-1})

M_i: molar mass of compound *i* (in g·mol^{-1})

q_{v_dil1}: first dilution total gas flow (in mL·min^{-1})

x_{Res_i}: residual amount-of-substance fraction of compound *i* in the dilution gas (in nmol·mol^{-1})

q_{v_cal}: calibration standard gas flow (in mL·min^{-1})

q_{v_dil2}: second dilution total gas flow (in mL·min^{-1})

Loaded amounts in the cold trap for each compound and calibration standard were calculated by multiplying the amount-of-substance fraction estimated according Eq. (1) by the loading time of each calibration standard (4.5 min, 4.8 min, 5.0 min, 5.3 min and 5.5 min). Calibration curves of the GC-FID were obtained by linear regression using the least square method for each compound. For that purpose, response peak areas of the calibration standard measurements were integrated using the software ChromSpace® 1D (SepSolve Analytical, UK). For the compounds under study, blank peak areas were not removed from the compound areas because they were below detection limit and therefore considered negligible. For each calibration standard, peak areas of the replicates were averaged. Amount fractions in the comparison standard were calculated for each measurement using Eq. (2).

$$x_{cs\_ij} = \left(\frac{A_{cs\_ij} - a_{ij}}{b_{ij}}\right) \cdot \frac{1}{t_{cs\_j}} \qquad (2)$$

where,

x_{cs_ij}: amount fraction of compound *i* in the comparison standard estimated during measurement *j* (in nmol·mol^{-1})

A_{ts_ij}: average peak area of compound *i* obtained during measurement *j* of the comparison standard (in area units (AU))

a_{ij}: intercept of the calibration linear regression for compound *i* and measurement *j* (in AU)

b_{ij}: slope of the calibration linear regression for compound *i* and measurement *j* (in AU/(min · nmol·mol^{-1}))

t_{cs_j}: sampling time of the comparison standard during measurement *j* (in min)

The assigned value was the average amount fraction estimated following Eq. (2) of the three intercomparison measurements for each compound.

C.5 Uncertainty evaluation

The main contributors to the overall uncertainty of the assigned values were the uncertainty of the calibration process, which included uncertainties of the magnetic suspension balance and of the dilution system, and the uncertainty of the analytical method that included uncertainties of the sampling and of the identification and integration of response peaks (i.e. peak resolution). The uncertainty associated to the method repeatability was also considered through replicates (5 replicates per standard and compound) and measurement repetition (3 measurements per compound). The model equations used are the ones described in the section above. Uncertainties were estimated using the software GUM Workbench Pro (version 2.4.1.406, Metrodata GmbH).

In the example shown in Table 1 (third measurement of benzene), the uncertainty sources indicated corresponds to:

- uncertainty of the permeation rate of the benzene permeation unit ($q_{m\_benzene}$)
- uncertainty sources of the amount fraction of the generated calibration standards:
    - molar volume of the dilution gas (V_{m_N2})
    - molar mass of the compound ($M_{m\_benzene}$)
    - total gas flow of the first-step dilution (q_{v_dil1})
    - gas flow of the calibration standard from the first-step dilution (q_{v_cal})
    - gas flow of the second-step dilution (q_{v_dil2})
    - purity of the permeation unit ($p_{benzene}$)
    - response peak areas of the five calibration standards ($A_{cal1\_benzene3}$..... $A_{cal5\_benzene3}$); each response considers the experimental standard deviation of the five replicates analyzed for each calibration standard
    - sampling time of the calibration standards ($t_{cal1\_benzene3}$..... $t_{cal5\_benzene3}$)

- response peak area of the comparison standard indicated as the average of the five replicates analyzed for each measurement ($\bar{A}_{cs\_benzene3}$); the response peak area considers the experimental standard deviation of the five replicates
- sampling time of the comparison standard ($t_{cs\_benzene}$).

Table 2: Example of uncertainty evaluation for benzene (measurement 3). The combined uncertainty (coverage factor k = 1) and expanded uncertainty (k = 2) of the assigned value is given by $u(x_{cs\_benzene3})$ and $U(x_{cs\_benzene3})$, respectively.

	unit	value	standard uncertainty	uncert. type	distribution	sensitivity coefficient	uncertainty contribution (nmol·mol^{-1})
$q_{m\_benzene}$	ng·min^{-1}	351.58	0.458	B	normal	0.014	0.0064
V_{m_N2}	mL·mol^{-1}	22409.18	1.84	B	normal	0.00022	0.00041
$M_{benzene}$	g·mol^{-1}	78.1114	0.0035	B	normal	-0.063	-0.00022
q_{v_dil1}	mL·min^{-1}	2269.98	2.27	B	normal	-0.0022	-0.0050
q_{v_cal}	mL·min^{-1}	73.004	0.11	B	normal	0.06	0.0066
q_{v_dil2}	mL·min^{-1}	580.145	0.723	B	normal	-0.0076	-0.0055
$p_{benzene}$	no units	0.995	0.0029	B	rectangular	5.0	0.014
$A_{cal1\_benzene3}$	area units	5024152	26000	A	normal	$-210\cdot10^{-9}$	-0.0056
$A_{cal2\_benzene3}$	area units	5318580	16400	A	normal	$-200\cdot10^{-9}$	-0.0032
$A_{cal3\_benzene3}$	area units	5508398	19800	A	normal	$-180\cdot10^{-9}$	-0.0036
$A_{cal4\_benzene3}$	area units	5895490	22800	A	normal	$-170\cdot10^{-9}$	-0.0038
$A_{cal5\_benzene3}$	area units	6097058	34400	A	normal	$-150\cdot10^{-9}$	-0.0053
$t_{cal1\_benzene3}$	min	4.5	0.00577	B	rectangular	0.23	0.0014
$t_{cal2\_benzene3}$	min	4.8	0.00577	B	rectangular	0.21	0.0012
$t_{cal3\_benzene3}$	min	5.0	0.00577	B	rectangular	0.20	0.0011
$t_{cal4\_benzene3}$	min	5.3	0.00577	B	rectangular	0.18	0.0010
$t_{cal5\_benzene3}$	min	5.5	0.00577	B	rectangular	0.17	0.00097
$\bar{A}_{cs\_benzene3}$	area units	5523100	24700	A	normal	$910\cdot10^{-9}$	0.023
$t_{cs\_benzene3}$	min	5.0	0.00577	B	rectangular	-0.99	-0.0057
$x_{cs\_benzene3}$	nmol·mol^{-1}	**4.943**					
$u(x_{cs\_benzene3})$	nmol·mol^{-1}	0.028			assumed normal		
$U(x_{cs\_benzene3})$	nmol·mol^{-1}	**0.056**			assumed normal		

For each compound, the final result was estimated as the average of the three measurements performed. The expanded uncertainty of each final result takes into account the uncertainties associated to each of the measurements, as well as the correlation between the three measurements of each compound. A correlation coefficient of 0.9 between the measurement results was evaluated because, despite using the same permeator unit and instrument set up. individual reference amount fractions were calculated for each instrument calibration. Table 3 shows an example of final result and its uncertainty for benzene.

Table 3: Example for benzene of final assigned amount fraction value in the comparison standard. Results of each measurement (3 measurements) are represented by $x_{cs\_benzene1}$ (measurement 1), $x_{cs\_benzene2}$ (measurement 2) and $x_{cs\_benzene3}$ (measurement 3). The final value is the average of the 3 measurements. The combined uncertainty (coverage factor k = 1) and expanded uncertainty (k = 2) of the assigned value is given by $u(x_{cs\_benzene})$ and $U(x_{cs\_benzene})$, respectively.

	unit	value	standard uncertainty	uncert. type	distribution	sensitivity coefficient	uncertainty contribution
$x_{cs\_benzene1}$	nmol·mol^{-1}	4.883	0.034	B	normal	0.33	0.011
$x_{cs\_benzene2}$	nmol·mol^{-1}	4.898	0.031	B	normal	0.33	0.010
$x_{cs\_benzene3}$	nmol·mol^{-1}	4.943	0.028	B	normal	0.33	0.0093
$\boldsymbol{x_{cs\_benzene}}$	nmol·mol^{-1}	**4.908**					
$u(x_{cs\_benzene})$	nmol·mol^{-1}	0.030			assumed normal		
$\boldsymbol{U(x_{cs\_benzene})}$	nmol·mol^{-1}	**0.060***			assumed normal		

*a correlation coefficient of 0.9 between measurement results was applied

C.6 References

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

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

[3] Van der Veen, A.M.H., van Wijk, J.I.T., Harris, K., Goodman, C., Hodges, J., Uehara, S., Kang, J.H., Kim, Y.D., Lee, S., Worton, D.R., Bartlett, S., van Aswegen, S., Brewer, P.J., Efremova, O.V., Zhang, T., Wang, D., Han, Q., Zeyi, Z., Iturrate-Garcia, M., Pascale, C. and Niederhauser, B. (2021). International comparison CCQM-K117 ammonia. *Metrology,* 58, 08017.

Annex D Measurement report of UBA

CCQM-K10.2018.1 comparison
Key comparison of analytical capabilities for BTEX gas mixtures

Laboratory name: UBA

D.1 Results

D.1.1 MEASUREMENTS WITH PERKIN ELMER GC

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	31/10/2023	0.00486	0.61	8
Toluene	31/10/2023	0.00481	1.37	8
Ethylbenzene	31/10/2023	0.00565	2.97	8
Sum para/meta-Xylene	31/10/2023	0.01041	2.24	8
meta-Xylene	-	-	-	-
ortho-Xylene	31/10/2023	0.00539	5.91	8

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	07/11/2023	0.00482	0.59	8
Toluene	07/11/2023	0.00479	1.30	8
Ethylbenzene	07/11/2023	0.00560	2.43	8
Sum para/meta-Xylene	07/11/2023	0.01032	1.75	8
meta-Xylene	-	-	-	-
ortho-Xylene	07/11/2023	0.00528	4.59	8

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene	20/12/2023	0.0048	0.35	9
Toluene	20/12/2023	0.0047	0.90	9
Ethylbenzene	20/12/2023	0.0055	1.85	9
Sum para/meta-Xylene	20/12/2023	0.0102	1.35	9
meta-Xylene	-	-	-	-
ortho-Xylene	20/12/2023	0.0051	3.70	9

Results

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Expanded uncertainty (µmol·mol^{-1})	Coverage factor
Benzene	31/10-20/12/2024	0.00482	0.000111	2
Toluene	31/10-20/12/2024	0.00477	0.000111	2
Ethylbenzene	31/10-20/12/2024	0.00557	0.000207	2
Sum para/meta-Xylene	31/10-20/12/2024	0.01029	0.000278	2
meta-Xylene	-	-	-	-
ortho-Xylene	31/10-20/12/2024	0.00524	0.000333	2

D.1.2 ADDITIONAL MEASUREMENTS WITH AMA GC IN ORDER TO SEPARATE M- AND P-XYLENE

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene				
Toluene				
Ethylbenzene				
para-Xylene	31/10/2023	0.00445	1.64	10
meta-Xylene	31/10/2023	0.00605	2.02	10
ortho-Xylene				

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene				
Toluene				
Ethylbenzene				
para-Xylene	07/11/2023	0.00470	1.44	10
meta-Xylene	07/11/2023	0.00579	1.29	10
ortho-Xylene				

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Standard deviation (% relative)	Number of replicates
Benzene				
Toluene				
Ethylbenzene				
para-Xylene	20/12/2023	0.00474	0.84	10
meta-Xylene	20/12/2023	0.00581	1.50	10
ortho-Xylene				

Results

Component	Date (dd/mm/yy)	Result (µmol·mol^{-1})	Expanded uncertainty (µmol/mol)	Coverage factor
Benzene				
Toluene				
Ethylbenzene				
para-Xylene	31/10-20/12/2024	0.00463	0.000330	2
meta-Xylene	31/10-20/12/2024	0.00588	0.000315	2
ortho-Xylene				

D.2 Calibration standards

The calibration gas was prepared by static dilution (DIN EN ISO 6144:2006). Pure certified reference material (CRM) certified by National Institute of Japan (NMIJ) was used for the injection into mixing chamber.

Table 1: List of pure certified reference material (CRM) used to calibrate the instruments at UBA.

	CAS No.	Amount fraction (mol·mol^{-1})	Expanded uncertainty (mol·mol^{-1})
Benzene	71-43-2	0.99992	0.00003
Toluene	108-88-3	0.9997	0.00030
Ethylbenzene	100-41-4	0.9988	0.00030
meta-Xylene	108-38-3	0.9980	0.00020
para-Xylene	106-42-3	0.99865	0.00010
ortho-Xylene	95-47-6	0.9993	0.00010

D.3 Instrumentation

The test gas was measured by PerkinElmer GC Arnel-Clarus 680 GL and Turbomatrix Thermal Desorber 300 TD applying DIN EN ISO 14662-3:2016.

Separation column: DB-1 (60 m, ID 530 µm)

Additionally, the test gas was measured by AMA GC 5000.

Separation column: AMAsep WAX (30 m, ID 0.32 mm, film thickness 0.25 µm)

D.4 Calibration method and value assignment

The calibration gas is prepared by static dilution (DIN EN ISO 6144:2006). Several independent prepared calibration points in the measuring range (0-100 ppb) are applied according DIN EN ISO 14662-3:2016. This procedure is repeated for every single compound. This is part of the annual ground calibration that was verified by a bracketing procedure by preparing two concentrations in an interval of ca. ± 10 % of the expected value of the cylinder for Perkin Elmer GC.

The calibration of AMA GC relies only on the bracketing method.

The injection method is modified. The syringes are substituted by capillary tubes and the pure liquid substance is sucked in by a gas flow induced by low pressure and filled-up with air simultaneously. The capillary is weighed before and after filling up with pure substance. The filled-up capillary is weighed 5 times. This mixture is diluted 3-times by pressurizing and relaxing the mixture. See GUM Workbench Budget. Pressure and temperature are measured exactly.

With Perkin Elmer we could not separate meta- and para-Xylene from each other. Only the sum of both is reported here. With AMA we could separate meta- and para-Xylene. Each value is reported.

D.5 Uncertainty evaluation

Example for Benzene

$$u_c{}^2 = u_1{}^2 + u_R{}^2 + u_M{}^2 \tag{1}$$

u_c = Combined uncertainty

u_1 = Combined uncertainty given by static dilution method valid for the calibration

u_R = Reproducibility of the static dilution method at UBA

u_M = standard uncertainty of measurements

Calculation of u_1 according to JCGM 100:2008 [2] supported by GUM Workbench software.

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

Standard deviation of all calibration points is included in the reproducibility of the static dilution method.

u_1 = 0.96 % rel.

u_R = 0.64 % rel.

u_M = 0.02 % rel.

This results for benzene in the combined uncertainty of:

$$u_c = \sqrt{0.962\ \%^2 + 0.640\ \%^2 + 0.019\ \%^2} = \sqrt{1.34}\ \% = 1{,}16\ \%\ rel$$

Coverage factor: 2

$$U = 2 * u_c = 2.31\ \%$$

$$U_{xi} = \frac{x_{xi} \times 2.31\ \%}{100} = \frac{4{,}82\ \frac{nmol}{mol} \times 2.31\ \%}{100} = 0{,}11\ \frac{nmol}{mol}$$

Uncertainty Budget for Calibration gas Benzene as example.

The budgets for the other Components are similar and shown in table 2 and table 3.

Table 2: List of uncertainties for device Perkin Elmer CG.

	u_M / %	u_R / %	u_1 / %	u_c / %	U / %	*Expanded uncertainty (nmol·mol^{-1})*
Benzene	0.96	0.64	0.02	1.34	2.31	0,111
Toluene	1.11	0.36	0.13	1.37	2.34	0,112
Ethylbenzene	1.78	0.36	0.39	3.44	3.71	0,207
m+p-Xylene	1.27	0.44	0.11	1.82	2.70	0,278
o-Xylene	3.13	0.54	0.13	10.07	6.35	0,333

Table 3: List of uncertainties for device AMA GC.

	u_1 / %	u_R / %	u_M / %	u_c / %	U / %	*Expanded uncertainty (nmol·mol^{-1})*
meta-Xylene	2,52	0,11	0,89	2,68	5,35	0,315
para-Xylene	3,45	0,11	0,89	3,56	7,13	0,330

Model Equation:

For the mass concentration of component *i* the following calculation is used under consideration variable temperature and pressure conditions.

$$\beta_k = \beta * \prod_{i=1}^{n} \frac{p_{i1}\,T_{i2}}{p_{i2}T_{i1}} \tag{2}$$

Model Equation for capillary injection:

$$\beta = \frac{m_i * F_i * T_K * p_R}{V_K * T_R * p_K} \tag{3}$$

with the mass of component *i*

$$m_i = W1 - W2 \tag{4}$$

This results in the following equation.

$$\beta_k = \frac{(W1-W2)*10^6 * F_i * T_K * p_R}{V_K * T_R * p_K} * \frac{p_{11}\,T_{12}}{p_{12}T_{11}} * \frac{p_{21}\,T_{22}}{p_{22}T_{21}} \tag{5}$$

Example for benzene approximately 15 µg·m^{-3} ≈ 5 nmol·mol^{-1} :

List of Quantities:

Quantity	Unit	Definition
β_k	µg·m^{-3}	Concentration at reference conditions
$W1$	mg	Weight of filled capillary
$W2$	mg	Weight of empty capillary
F_i	mol·mol^{-1}	Amount fraction (mol·mol^{-1})
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

Uncertainty Budgets:

β_k: Concentration at reference conditions

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$W1$	13866.72000 mg	2.24·10^{-3} mg	15	0.034 µg·m^{-3}	23.3 %	20.5 %
$W2$	13865.81600 mg	4.02·10^{-3} mg	-15	-0.061 µg·m^{-3}	75.6 %	66.5 %
F_i	0.99992000 mol·mol^{-1}	9.81·10^{-6} mol·mol^{-1}	14	130·10^{-6} µg·m^{-3}	0.0 %	0.0 %
T_K	295.14000 K	6.93·10^{-3} K	0.046	320·10^{-6} µg·m^{-3}	0.0 %	0.0 %
p_R	101.325 kPa					
V_K	0.1124400 m^3	57.7·10^{-6} m^3	-120	-7.0·10^{-6} µg·m^{-3}	1.0 %	7.2 %
T_R	293.15 K					
p_K	159.650000 kPa	577·10^{-6} kPa	-0.086	-50·10^{-6} µg·m^{-3}	0.0 %	0.0 %

Quantity	**Value**	**Standard Uncertainty**	**Distribution**	**Sensitivity Coefficient**	**Uncertainty Contribution**	**Index**
p_{11}	9.144000 kPa	$577\cdot10^{-6}$ kPa	1.5	$860\cdot10^{-6}$ μg·m^{-3}	0.0 %	3.2 %
T_{12}	295.43000 K	$6.93\cdot10^{-3}$ K	0.046	$320\cdot10^{-6}$ μg·m^{-3}	0.0 %	0.0 %
p_{12}	158.965000 kPa	$577\cdot10^{-6}$ kPa	-0.086	$-50\cdot10^{-6}$ μg·m^{-3}	0.0 %	0.0 %
T_{11}	294.80000 K	$6.93\cdot10^{-3}$ K	-0.046	$-320\cdot10^{-6}$ μg·m^{-3}	0.0 %	0.0 %
p_{21}	9.003000 kPa	$577\cdot10^{-6}$ kPa	1.5	$880\cdot10^{-6}$ μg·m^{-3}	0.0 %	2.5 %
T_{22}	295.57000 K	$6.93\cdot10^{-3}$ K	0.046	$320\cdot10^{-6}$ μg·m^{-3}	0.0 %	0.0 %
p_{22}	159.255000 kPa	$577\cdot10^{-6}$ kPa	-0.086	$-50\cdot10^{-6}$ μg·m^{-3}	0.0 %	0.0 %
T_{21}	295.20000 K	$6.93\cdot10^{-3}$ K	-0.046	$-320\cdot10^{-6}$ μg·m^{-3}	0.0 %	0.0 %
β_k	15.1713 μg·m^{-3}	0.0830 μg·m^{-3}				

Results:

Quantity	**Value**	**Expanded Uncertainty** $u_{\mathrm{R,Benzene,15}}$	**Coverage factor**	**Coverage**
β_k	15.171 μg·m^{-3}	0.55 % (relative)	1.00	manual

The expanded uncertainty u_{R} is calculated for the mass concentration range β_k between 0–45 μg·m^{-3}. For further calculations the highest u_{R} (worst case scenario) is taken per default. In this case $u_{\mathrm{R,Benzene}}$ amounts to 0,64 % rel.

D.6 References

[1] DIN EN ISO 6144:2006-11: Gas analysis – Preparation of calibration gas mixtures - Static volumetric method

[2] JCGM 100:2008, Evaluation of measurement data – Guide to the expression of uncertainty in measurement

[3] DIN EN 14662-3:2016: Außenluft –Messverfahren zur Bestimmung von Benzolkonzentrationen –Teil 3: Automatische Probenahme mit einer Pumpe und gaschromatographische In-situ-Bestimmung