

Final Draft Report - 25/10/2005

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Field

Amount of substance : Gas standards

Subject

Comparison of primary standards of VOCs containing Benzene, chloroform, dichloromethane, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,3-butadiene, and vinyl chloride in nitrogen

Participants

Rep. of Korea (KRISS), Japan (NMIJ, CERI), Netherlands (NMi), Russia (VNIIM), United Kingdom (NPL), United States of America (NIST)

Organized by

CCQM Gas Analysis Working Group

Rationale

Benzene, chloroform, dichloromethane, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,3-butadiene, and vinyl chloride are Volatile Organic Compounds (VOCs) and are called as HAPs (Hazardous Air Pollutants). These VOCs are priority hazardous substances and the Air Pollution Control Law in some countries regulates them. At the CCQM Gas Analysis Working Group meeting held in April of 2001 (Paris), it was agreed to organize a key comparison on the VOCs.

At the CCQM gas analysis working group meeting in April 2003, it was agreed that CCQM organize this pilot study (CCQM-P71) for institutes that are participated as study level on CCQM-K22. Therefore, CCQM-P71 was run in parallel to CCQM-K22. The CCQM-P71 was reported as a separated report.

Conduct of the comparison

CERI prepared primary standards of VOCs in Nitrogen for distribution to each participating laboratory. Aluminium cylinders of 10 L (dm³) nominal were used and the initial pressure in the cylinders was approximately 10 MPa. The nominal concentrations of the each component are 100

nmol/mol and are in the range from 90 nmol/mol to 110 nmol/mol in nitrogen. Concentrations of each VOC in the cylinders and the stability were checked before the shipment to the participants.

Protocol of the comparison was circulated before the comparison. According to the protocol, the participants measured the concentration of VOCs in the cylinder received with respect to their own standards of VOCs at least three times with independent calibrations, obtained under repeatability conditions. The methods reported are given in **Table 1**. After the completion of the comparison, the standards were returned to CERI where they were re-analysed by comparison with primary standards that had not been distributed. These measurements showed no significant change in the VOCs amount fraction within the estimated uncertainty of the measurements except for 1,2-dichloroethane. Concentrations of 1,2-dichloroethane showed 0.6% to 2% decrease.

Table 1. Conditions of CCQM-K22: comparison of VOCs in nitrogen standards

Laboratory	Cylinder number	Analytical method	Standards	Sample volume	Total num. of sub-measurements	Remarks
KRISS	CPB-27161	GC-FID with cryogenic concentrator	Gravimetric one point	50 mL	25	-
NIST	CPB-27162	GC-FID with cryogenic preconcentrator	Gravimetric 3-4PSMs	50 mL – 500 mL	9-18	-
NMi	CPB-26346	GC-FID with thermal desorption (cold trap)	Dynamic volumetric	0.5 L – 2 L	15	-
NMIJ/CERI	CPB-28005	GC-FID with cold-trap concentrator	Gravimetric one point	300 mL	15	-
NPL	CPB-28006	GC-FID with cold-trap concentrator	Gravimetric two point (Two sets)	60 mL	8	-
VNIIM	CPB-28010	GC-FID	Gravimetric one point	1 mL	16	7 components without 1,3-butadiene

Concentration and Uncertainty of the distributed standards

Each distributed standard materials were prepared using gravimetric method. Benzene and 1,2-dichloroethane are certified reference materials (NMIJ CRM 4002-a and NIMC CRM 4004a). Chloroform, dichloromethane, trichloroethylene and tetrachloroethylene are not certified now, but they are candidates for NMIJ CRMs. Their purities have been measured by the same manner as NMIJ CRMs by NMIJ. Purities of 1,3-butadiene and Vinyl chloride were measured by CERI. These high purity materials were put in evacuated small vessels (0.25 L) and expand into 10 L cylinders. The masses of each component were obtained by weighing the small vessels before and after the expansion. Then a balance of nitrogen was added in the cylinders. The mass of nitrogen was measured by weighing the cylinder. The nitrogen was analysed for VOCs and found to have less than 0.1 nmol/mol for each component. The 10 L cylinders were manufactured from aluminium, with a passivated inner surface that minimises the reactivity of the cylinder walls with contents.

The uncertainties of the standard gases were estimated by combining the uncertainty of gravimetric preparation and instability. The former was including uncertainties of weighing including the expansion of a gas cylinder by pressure, purity analysis of the component materials and reproducibility of preparation. The uncertainty caused by the instability was evaluated from deviations of concentration in each cylinder between before and after the analysis by the participants. The reference values of each VOC components and their expanded uncertainties estimated from gravimetric values and stability test by NMIJ and CERI are summarized in **Tables 2-9**. These deviations are considered to be enough small compared to differences between reported values from the participants and reference values. The deviations and the differences are summarized in Annex-1.

Table 2. The concentration and its standard uncertainty of distributed standards for Benzene

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	92.90	0.15	0.30	0.13	0.36
CPB-27162	95.77	0.15	0.30	0.13	0.36
CPB-26346	93.63	0.15	0.30	0.13	0.36
CPB-28005	93.76	0.15	0.30	0.13	0.36
CPB-28006	96.33	0.15	0.30	0.13	0.36
CPB-28010	92.90	0.15	0.30	0.13	0.36

Table 3. The concentration and its standard uncertainty of distributed standards for Chloroform

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	99.10	0.15	0.23	0.14	0.31
CPB-27162	102.15	0.15	0.23	0.14	0.31
CPB-26346	99.87	0.15	0.23	0.14	0.31
CPB-28005	100.00	0.15	0.23	0.14	0.31
CPB-28006	102.75	0.15	0.23	0.14	0.31
CPB-28010	99.09	0.15	0.23	0.14	0.31

Table 4. The concentration and its standard uncertainty of distributed standards for Dichloromethane

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	102.06	0.15	0.25	0.33	0.44
CPB-27162	101.70	0.15	0.25	0.33	0.44
CPB-26346	101.61	0.15	0.25	0.33	0.44
CPB-28005	102.52	0.15	0.25	0.33	0.44
CPB-28006	103.82	0.15	0.25	0.33	0.44
CPB-28010	103.99	0.15	0.25	0.33	0.44

Table 5. The concentration and its standard uncertainty of distributed standards for Trichloroethylene

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	104.11	0.15	0.35	0.21	0.43
CPB-27162	107.32	0.15	0.35	0.21	0.43
CPB-26346	104.92	0.15	0.35	0.21	0.43
CPB-28005	105.07	0.15	0.35	0.21	0.43
CPB-28006	107.95	0.15	0.35	0.21	0.43
CPB-28010	104.11	0.15	0.35	0.21	0.43

Table 6. The concentration and its standard uncertainty of distributed standards for Tetrachloroethylene

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	95.22	0.15	0.15	0.40	0.45
CPB-27162	98.16	0.15	0.15	0.40	0.45
CPB-26346	95.96	0.15	0.15	0.40	0.45
CPB-28005	96.09	0.15	0.15	0.40	0.45
CPB-28006	98.73	0.15	0.15	0.40	0.45
CPB-28010	95.21	0.15	0.15	0.40	0.45

Table 7. The concentration and its standard uncertainty of distributed standards for 1,2-dichloroethane

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	98.21	0.15	0.66	0.92	1.14
CPB-27162	101.24	0.15	0.66	0.92	1.14
CPB-26346	98.98	0.15	0.66	0.92	1.14
CPB-28005	99.12	0.15	0.66	0.92	1.14
CPB-28006	101.84	0.15	0.66	0.92	1.14
CPB-28010	98.21	0.15	0.66	0.92	1.14

Table 8. The concentration and its standard uncertainty of distributed standards for 1,3-butadiene

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	99.13	0.15	0.16	0.29	0.36
CPB-27162	98.78	0.15	0.16	0.29	0.36
CPB-26346	98.70	0.15	0.16	0.29	0.36
CPB-28005	99.58	0.15	0.16	0.29	0.36
CPB-28006	100.85	0.15	0.16	0.29	0.36
CPB-28010	101.01	0.15	0.16	0.29	0.36

Table 9. The concentration and its standard uncertainty of distributed standards for Vinyl chloride

	Concentration (nmol/mol)	Uncertainty of gravimetric preparation		Uncertainty of stability (nmol/mol)	Combined uncertainty (nmol/mol)
		Uncertainty of weighing and purities (nmol/mol)	Uncertainty of reproducibility (verification) (nmol/mol)		
CPB-27161	98.55	0.15	0.16	0.20	0.30
CPB-27162	98.20	0.15	0.16	0.20	0.30
CPB-26346	98.12	0.15	0.16	0.20	0.30
CPB-28005	99.00	0.15	0.16	0.20	0.30
CPB-28006	100.25	0.15	0.16	0.20	0.30
CPB-28010	100.42	0.15	0.16	0.20	0.30

Results

The results submitted by the seven participants are shown in **Tables 10 to 17** and **Figures 1 to 8**. In **Figure 1 to 8**, the results are plotted in terms of their deviation from the gravimetric value. Expanded uncertainties are calculated using a coverage factor $k = 2$, as an approximation of 95% confidence intervals.

Four of the five participants submitted results that were within 1% of the relevant reference value. In these cases, the estimated uncertainty was larger than the deviation from the reference value

Table 10. Results of key comparison CCQM-K22 Benzene in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of Benzene in nitrogen

Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

x_{igrav} : gravimetric value of the benzene amount-of-substance fraction in the cylinder received by laboratory i

u_{igrav} : combined standard uncertainty of x_{igrav}

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement	100*relative difference
KRISS	92.07	0.74	92.9	0.4	Sep-2003	-0.89
NIST	96.4	0.85	95.8	0.4	Nov-2003	0.63
NMi	92.7	2.0	93.6	0.4	Oct-2003	-0.96
NMIJ/CERI	94.1	0.4	93.8	0.4	Aug-2003	0.32
NPL	97.1	0.9	96.3	0.4	<Sep-2003	0.83
VNIIM	90.4	0.4	92.9	0.4	Dec-2003	-2.69

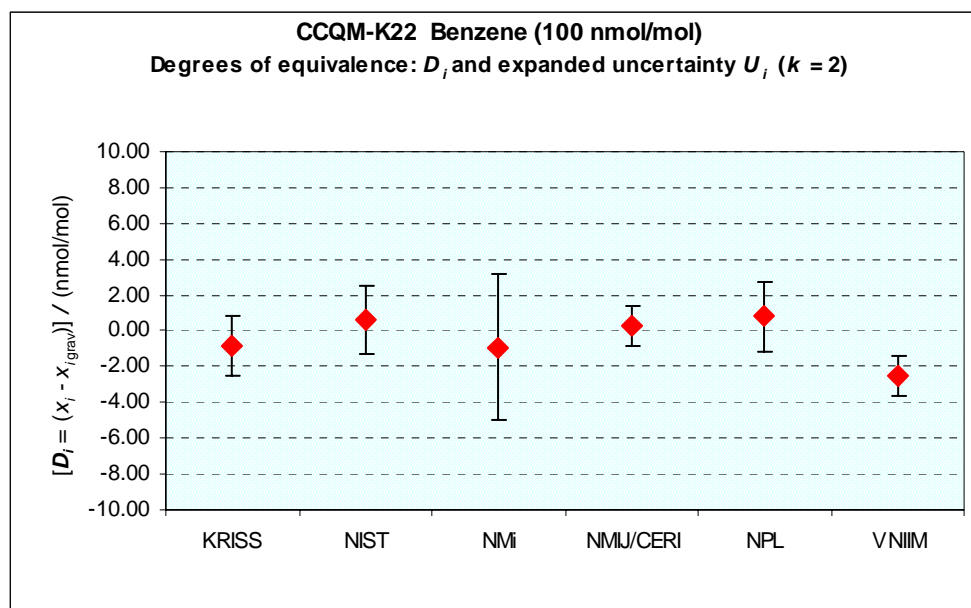


Figure 1. Results of key comparison CCQM-K22 Benzene in nitrogen

Table 11. Results of key comparison CCQM-K22 Chloroform in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of Chloroform in nitrogen

Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

x_{igrav} : gravimetric value of the chloroform amount-of-substance fraction in the cylinder received by laboratory i

u_{igrav} : combined standard uncertainty of x_{igrav}

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement	100*relative difference
KRISS	97.82	0.78	99.1	0.3	Sep-2003	-1.29
NIST	103.8	1.45	102.2	0.3	Nov-2003	1.57
NMi	98.3	1.82	99.9	0.3	Oct-2003	-1.60
NMIJ/CERI	99.8	0.30	100.0	0.3	Aug-2003	-0.20
NPL	101.8	1.10	102.8	0.3	<Sep-2003	-0.97
VNIIM	99.0	1.02	99.1	0.3	Dec-2003	-0.10

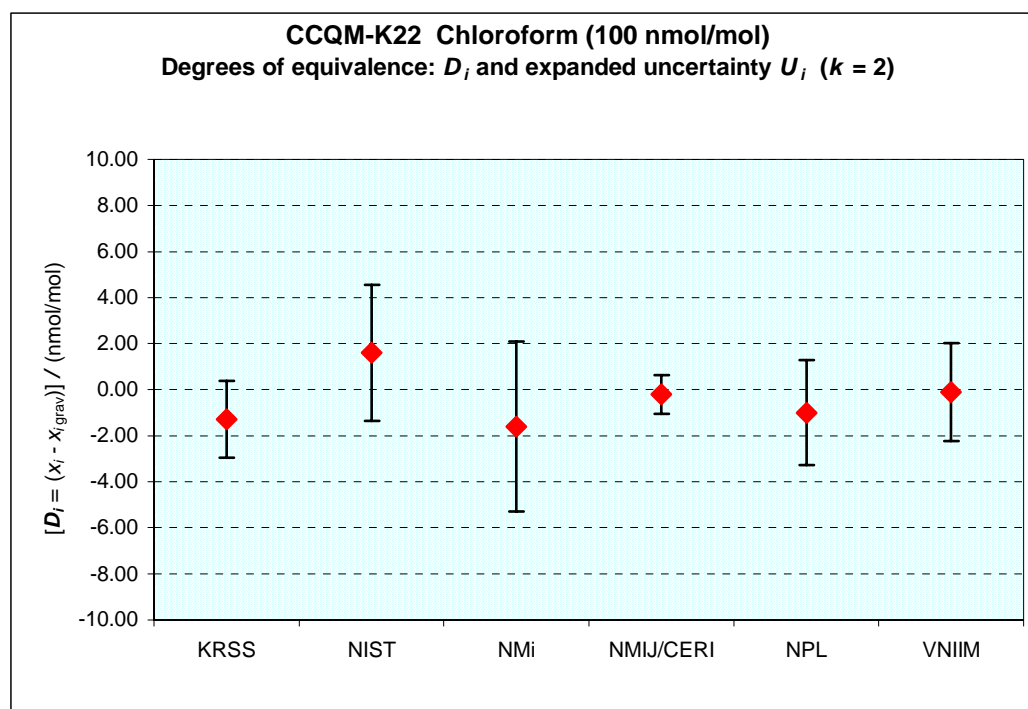


Figure 2. Results of key comparison CCQM-K22 Chloroform in nitrogen

Table 12. Results of key comparison CCQM-K22 Dichloromethane in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of Dichloromethane in nitrogen
 Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

x_{igrav} : gravimetric value of the dichloromethane amount-of-substance fraction in the cylinder received by laboratory i

u_{igrav} : combined standard uncertainty of x_{igrav}

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement	100*relative difference
KRISS	101.75	0.82	102.1	0.5	Sep-2003	-0.34
NIST	103.6	0.85	101.7	0.5	Nov-2003	1.87
NMi	102.0	1.84	101.6	0.5	Oct-2003	0.39
NMIJ/CERI	102.7	0.3	102.5	0.5	Aug-2003	0.20
NPL	106.2	1.55	103.8	0.5	<Sep-2003	2.31
VNIIM	103.5	1.1	104.0	0.5	Dec-2003	-0.48

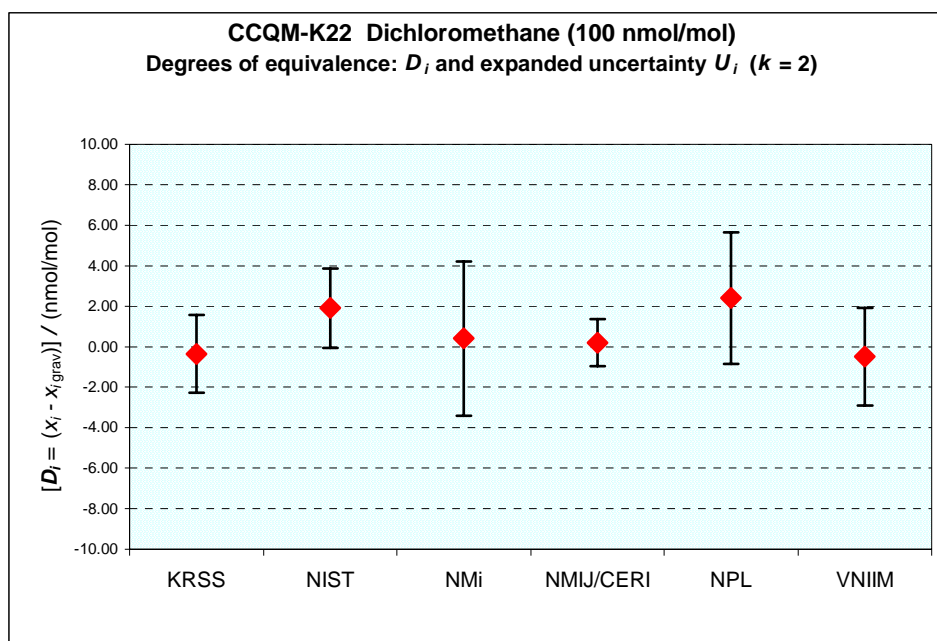


Figure 3. Results of key comparison CCQM-K22 Dichloromethane in nitrogen

Table 13. Results of key comparison CCQM-K22 Trichloroethylene in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of Trichloroethylene in nitrogen
 Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

$x_{i\text{grav}}$: gravimetric value of the trichloroethylene amount-of-substance fraction in the cylinder received by laboratory i

$u_{i\text{grav}}$: combined standard uncertainty of $x_{i\text{grav}}$

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	$x_{i\text{grav}}$ nmol/mol	$u_{i\text{grav}}$ nmol/mol	Date of measurement	100*relative difference
KRISS	103.90	0.83	104.1	0.5	Sep-2003	-0.19
NIST	111.7	1.25	107.3	0.5	Nov-2003	4.10
NMi	104.7	2.09	104.9	0.5	Oct-2003	-0.19
NMIJ/CERI	105.2	0.40	105.1	0.5	Aug-2003	0.10
NPL	109.0	1.30	108.0	0.5	<Sep-2003	0.93
VNIIM	103.7	0.56	104.1	0.5	Dec-2003	-0.38

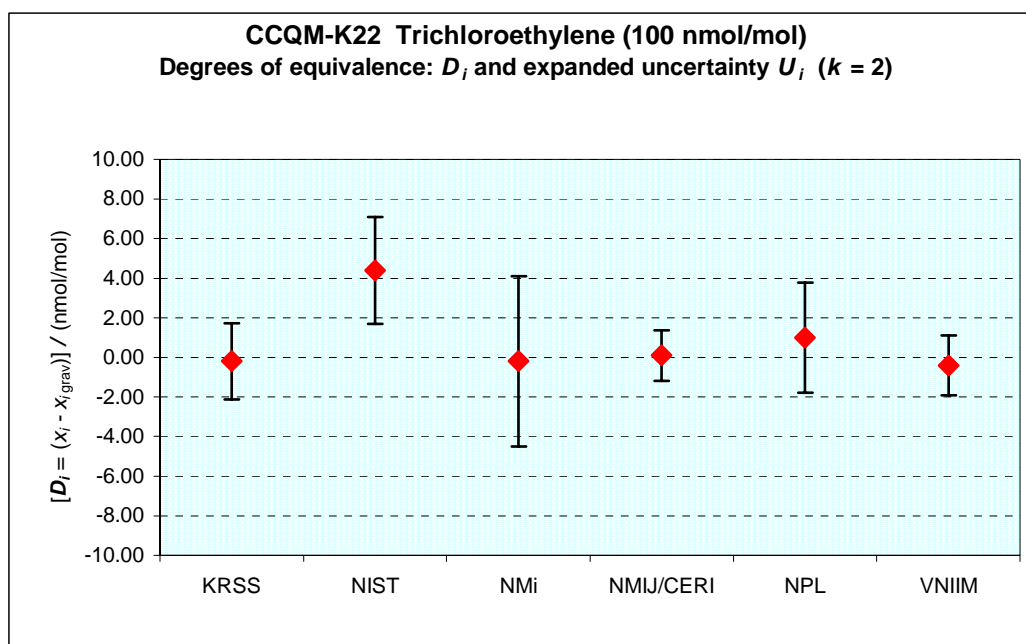


Figure 4. Results of key comparison CCQM-K22 Trichloroethylene in nitrogen

Table 14. Results of key comparison CCQM-K22 Tetrachloroethylene in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of Tetrachloroethylene in nitrogen
 Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

x_{igrav} : gravimetric value of the tetrachloroethylene amount-of-substance fraction in the cylinder received by laboratory i

u_{igrav} : combined standard uncertainty of x_{igrav}

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement	100*relative difference
KRISS	95.42	0.77	95.2	0.5	Sep-2003	0.23
NIST	100.4	0.85	98.2	0.5	Nov-2003	2.24
NMi	96.8	2.18	96.0	0.5	Oct-2003	0.83
NMIJ/CERI	96.3	0.25	96.1	0.5	Aug-2003	0.21
NPL	99.0	0.95	98.7	0.5	<Sep-2003	0.30
VNIIM	94.0	0.8	95.2	0.5	Dec-2003	-1.26

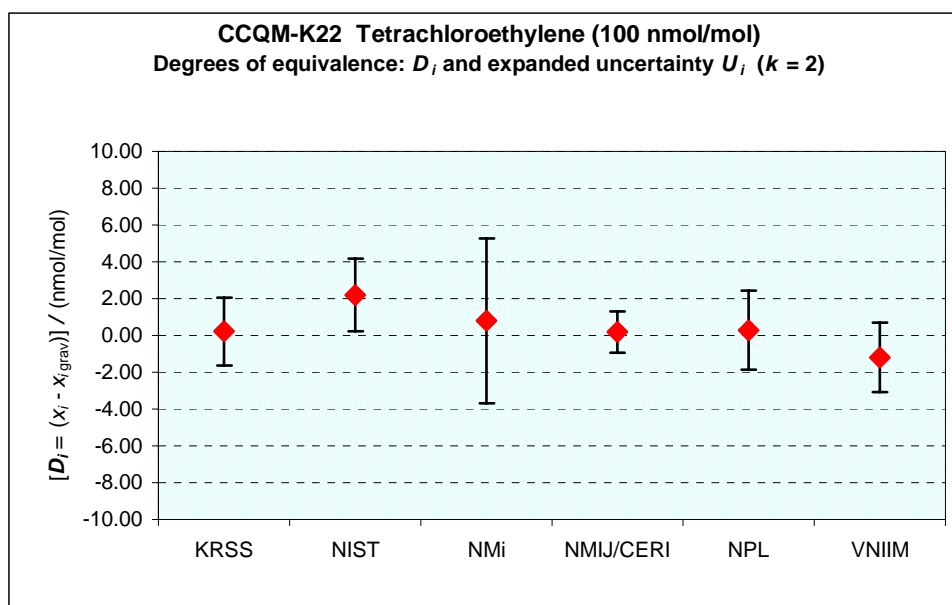


Figure 5. Results of key comparison CCQM-K22 Tetrachloroethylene in nitrogen

Table 15. Results of key comparison CCQM-K22 1,2-dichloroethane in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of 1,2-dichloroethane in nitrogen
 Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

$x_{i\text{grav}}$: gravimetric value of the 1,2-dichloroethane amount-of-substance fraction in the cylinder received by laboratory i

$u_{i\text{grav}}$: combined standard uncertainty of $x_{i\text{grav}}$

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	$x_{i\text{grav}}$ nmol/mol	$u_{i\text{grav}}$ nmol/mol	Date of measurement	100*relative difference
KRISS	100.83	0.80	98.2	1.2	Sep-2003	2.68
NIST	102.2	1.1	101.2	1.2	Nov-2003	0.99
NMi	94.4	3.3	99.0	1.2	Oct-2003	-4.65
NMIJ/CERI	97.4	0.70	99.1	1.2	Aug-2003	-1.72
NPL	101.9	1.20	101.8	1.2	<Sep-2003	0.10
VNIIM	96.4	0.6	98.2	1.2	Dec-2003	-1.83

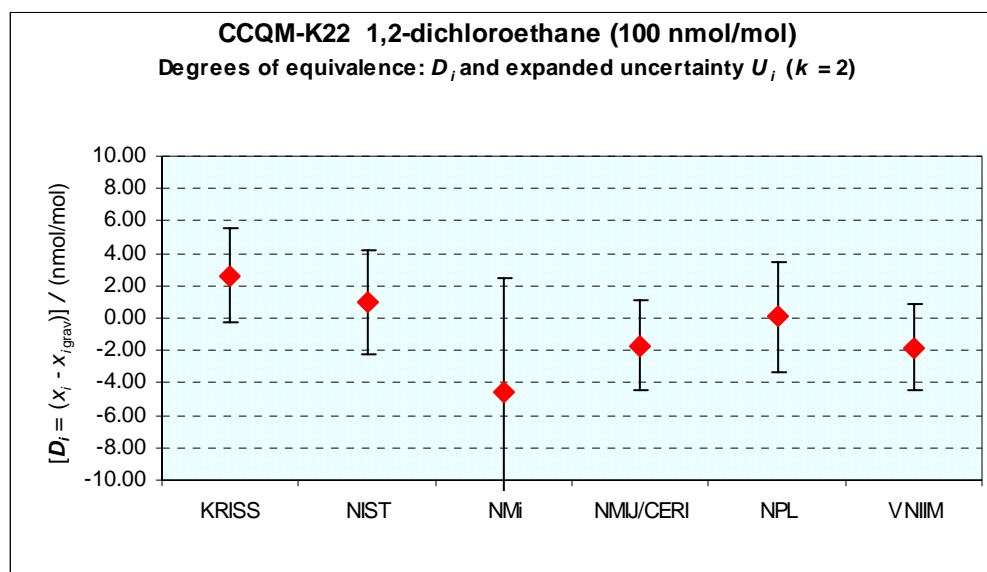


Figure 6. Results of key comparison CCQM-K22 1,2-dichloroethane in nitrogen

Table 16. Results of key comparison CCQM-K22 1,3-butadiene in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of 1,3-butadiene in nitrogen
 Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

x_{igrav} : gravimetric value of the 1,3-butadiene amount-of-substance fraction in the cylinder received by laboratory i

u_{igrav} : combined standard uncertainty of x_{igrav}

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement	100*relative difference
KRISS	100.21	0.68	99.1	0.4	Sep-2003	1.12
NIST	98.1	1.8	98.8	0.4	Nov-2003	-0.71
NMi	99.1	1.34	98.7	0.4	Oct-2003	0.41
NMIJ/CERI	99.5	0.25	99.6	0.4	Aug-2003	-0.10
NPL	102.9	0.95	100.8	0.4	<Sep-2003	2.08
VNIIM	-	-	101.0	0.4	-	-

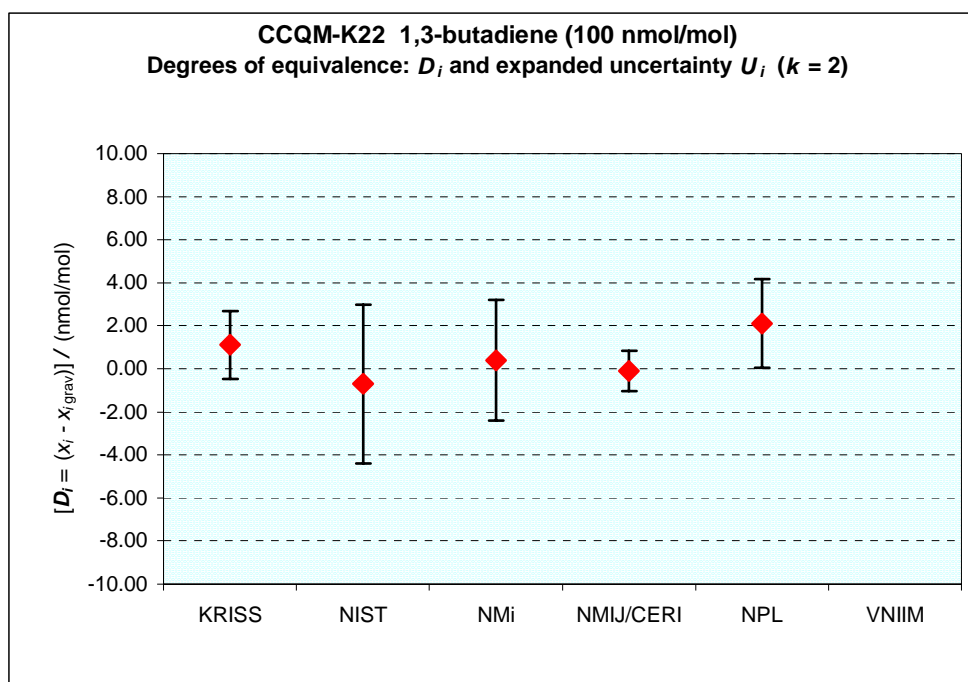


Figure 7. Results of key comparison CCQM-K22 1,3-butadiene in nitrogen

Table 17. Results of key comparison CCQM-K22 Vinyl chloride in nitrogen

Key comparison CCQM-K22

Measurand : Amount-of-substance fraction of Vinyl chloride in nitrogen
 Nominal Value : 100 nmol/mol

x_i : result of measurement carried out by laboratory i

u_i : combined standard uncertainty of x_i

x_{igrav} : gravimetric value of the vinyl chloride amount-of-substance fraction in the cylinder received by laboratory i

u_{igrav} : combined standard uncertainty of x_{igrav}

The column 100*relative difference is not for MRA Appendix B.

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement	100*relative difference
KRISS	98.64	0.66	98.6	0.3	Sep-2003	0.04
NIST	99.2	1.1	98.2	0.3	Nov-2003	1.02
NMi	101.2	2.38	98.1	0.3	Oct-2003	3.16
NMIJ/CERI	99.2	0.25	99.0	0.3	Aug-2003	0.20
NPL	101.7	0.95	100.2	0.3	<Sep-2003	1.50
VNIIM	100.1	0.54	100.4	0.3	Dec-2003	-0.30

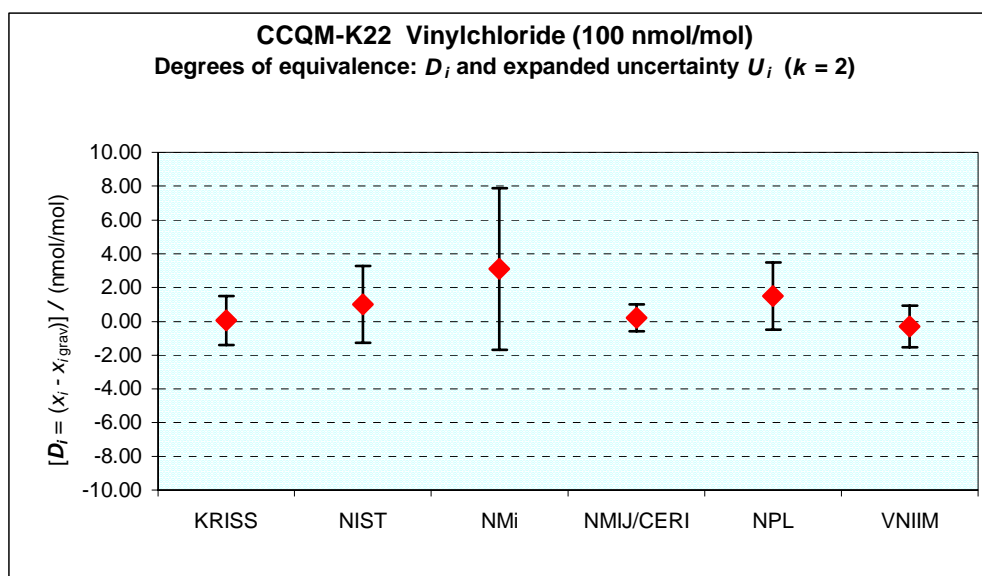


Figure 8. Results of key comparison CCQM-K22 Vinyl chloride in nitrogen

Conclusions

This key comparison demonstrates that the level of comparability between 6 participants is adequate to meet the requirement for 8 VOCs at concentration range from 10nmol/mol to 100µmol/mol.

In the GAWG meeting held at CENAM, Mexico on Oct 2005 GAWG member agreed about the “How Far does The Light Shine statement” for this key comparison and the statement is as follows;

This comparison will cover the comparability of gas mixtures containing benzene, chloroform, dichloromethane, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,3-butadiene, vinyl chloride, toluene, carbon tetrachloride, 1,1,1-trichloroethane, o-xylene, m-xylene, p-xylene, 1,1-dichloroethylene, cis-1,2-dichloroethylene, 1,1,2-trichloroethane, trans-1,3-dichloropropane, cis-1,3-dichloropropane, and ethyl benzene with concentration region from 10nmol/mol to 100µmol/mol.

References

Gas analysis -- Preparation of calibration gas mixtures -- Gravimetric Method, ISO/DIS 6142, 1998.

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Completion Date

December 31, 2003

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Annex 1

In the case of international comparison, it takes long period to complete all of the process. Instabilities of the samples may cause error in the results of the comparison. Therefore the instabilities should be as small as possible. In the CCQM-K22 and CCQM-P71 which was carried out in parallel with CCQM-K22, All samples showed some deviations during the comparison. These deviations were evaluated and are considered for the uncertainty of the sample.

The uncertainty caused by the instability was evaluated from deviations of the concentration in each cylinder between $x_{i,bef}$, the analytical values before the shipment to the participants and $x_{i,aft}$, those after the return from the participants. The deviations in concentration during the comparison, and x_i , reported values from participants are tabulated in Tables 1-8. In addition, the differences in concentration between $x_{i,ver}$, the verified values after preparation and $x_{i,grv}$, gravimetric values, differences in concentration between $x_{i,bef}$, the analyzed values before shipment to the participants and $x_{i,grv}$, gravimetric values, differences in concentration between $x_{i,aft}$, the analyzed values after shipment to the participants and $x_{i,grv}$, gravimetric values are tabulated in Tables 1-8. These concentration changes versus $x_i - x_{i,grv}$, differences between the reported values from participants and the gravimetric values are plotted in Figure 1. As shown in the figure, these deviations are considered to be small enough compared to differences between reported values from the participants and reference values.

Table 1. The concentration changes during the comparison versus x_i , reported values from participants for Benzene.

Benzene					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	-0.83	0.52	0.48	0.27	-0.21
NIST	0.60	0.68	0.25	0.26	0.01
NMi	-0.90	0.56	0.55	0.33	-0.22
NMIJ/CERI	0.30	0.05	0.40	0.47	0.07
NPL	0.80	0.14	0.44	0.42	-0.02
VNIIM	7.90	0.40	0.47	0.36	-0.11
NRCCRM	-2.50	0.50	0.30	0.20	-0.10

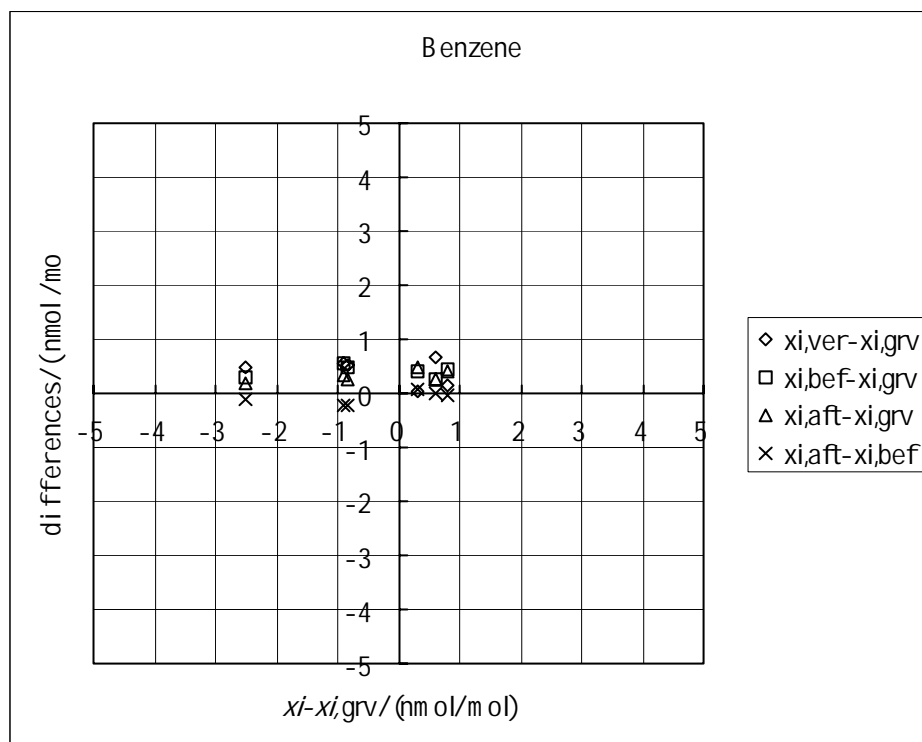


Figure 1. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for Benzene.

Table 2. The concentration changes during the comparison versus x_i , reported values from participants for Chloroform.

Chloroform					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	-1.28	0.16	-0.10	-0.17	-0.07
NIST	1.60	0.11	-0.31	-0.37	-0.06
NMi	-1.60	0.17	-0.04	-0.14	-0.10
NMIJ/CERI	-0.20	-0.20	-0.13	-0.24	-0.11
NPL	-1.00	-0.16	0.09	-0.15	-0.24
VNIIM	-0.10	0.25	0.03	-0.28	-0.31

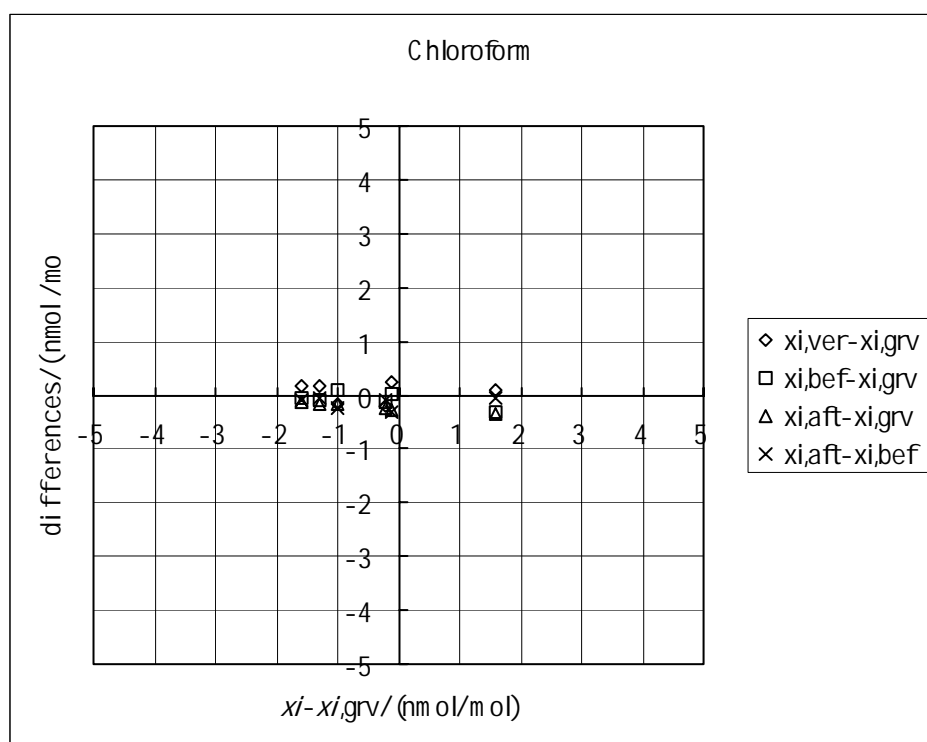


Figure 2. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for Chloroform.

Table 3. The concentration changes during the comparison versus x_i , reported values from participants for Dichloromethane.

Dichloromethane					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	-0.35	0.02	-0.03	0.18	0.21
NIST	1.90	0.27	0.14	0.21	0.07
NMi	0.40	0.21	0.16	0.40	0.24
NMIJ/CERI	0.20	0.51	0.14	0.03	-0.11
NPL	2.40	0.67	0.06	0.33	0.27
VNIIM	-0.50	0.48	0.44	-0.20	-0.64

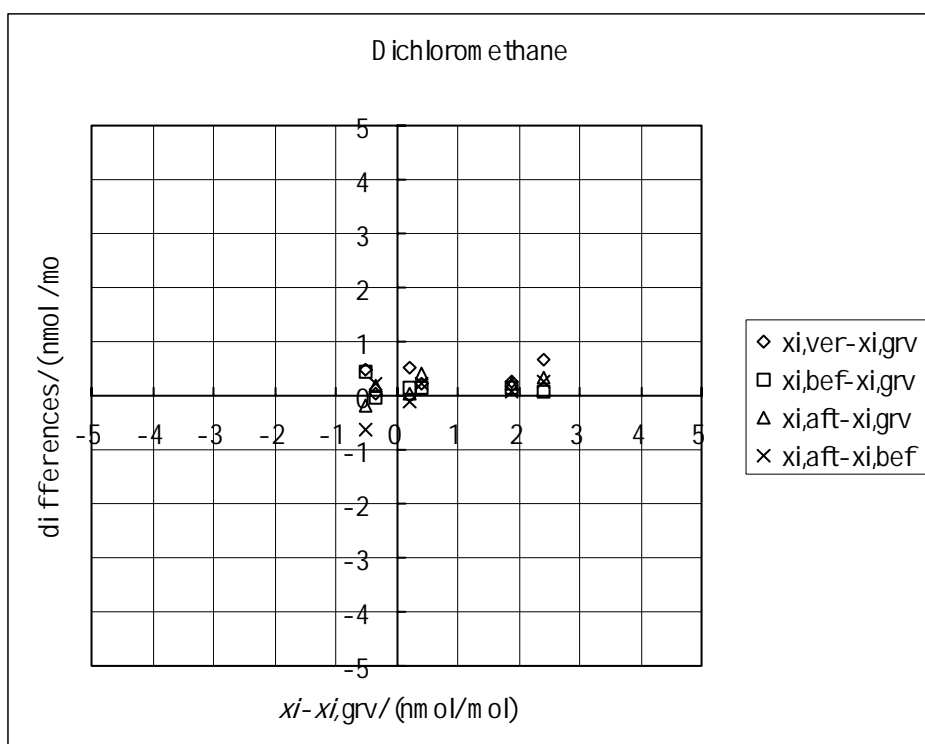


Figure 3. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for Dichloromethane.

Table 4. The concentration changes during the comparison versus x_i , reported values from participants for Trichloroethylene.

Trichloroethylene					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	-0.20	0.43	-0.03	0.10	0.13
NIST	4.40	0.72	-0.19	-0.17	0.02
NMi	-0.20	0.64	0.25	0.05	-0.20
NMIJ/CERI	0.10	-0.07	0.34	0.19	-0.15
NPL	1.00	0.01	0.34	-0.13	-0.47
VNIIM	-0.40	0.30	-0.08	0.02	0.10

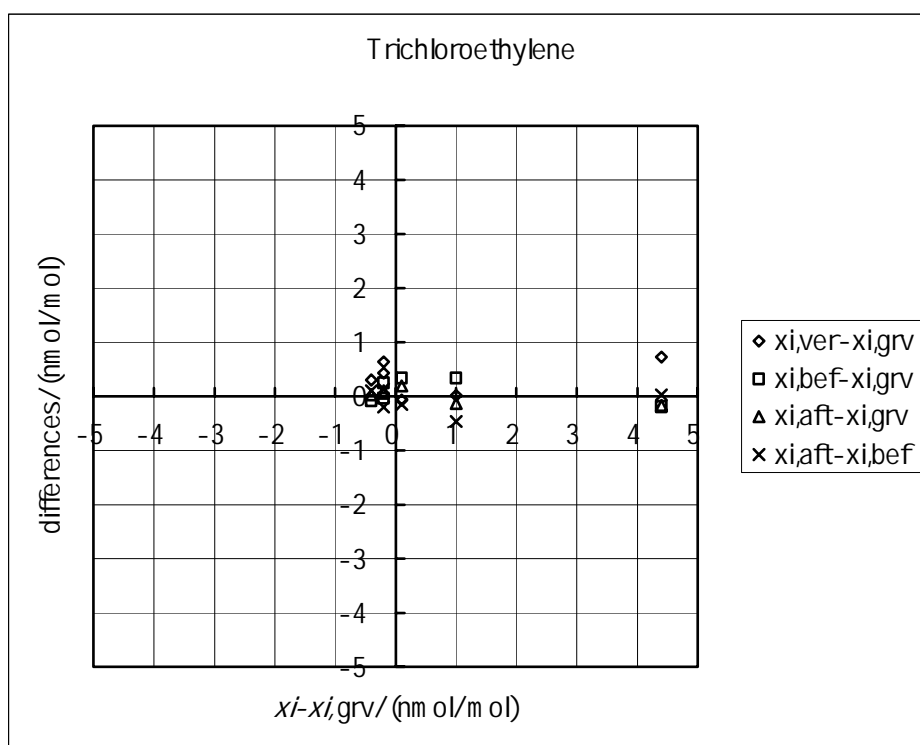


Figure 4. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for Trichloroethylene.

Table 5. The concentration changes during the comparison versus x_i , reported values from participants for Tetrachloroethylene.

Tetrachloroethylene					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	0.22	0.20	0.14	0.40	0.26
NIST	2.20	0.11	0.09	0.55	0.46
NMi	0.80	0.28	0.35	0.22	-0.13
NMIJ/CERI	0.20	0.13	0.18	0.37	0.19
NPL	0.30	0.15	0.34	0.64	0.30
VNIIM	-1.20	0.16	0.51	-0.11	-0.62

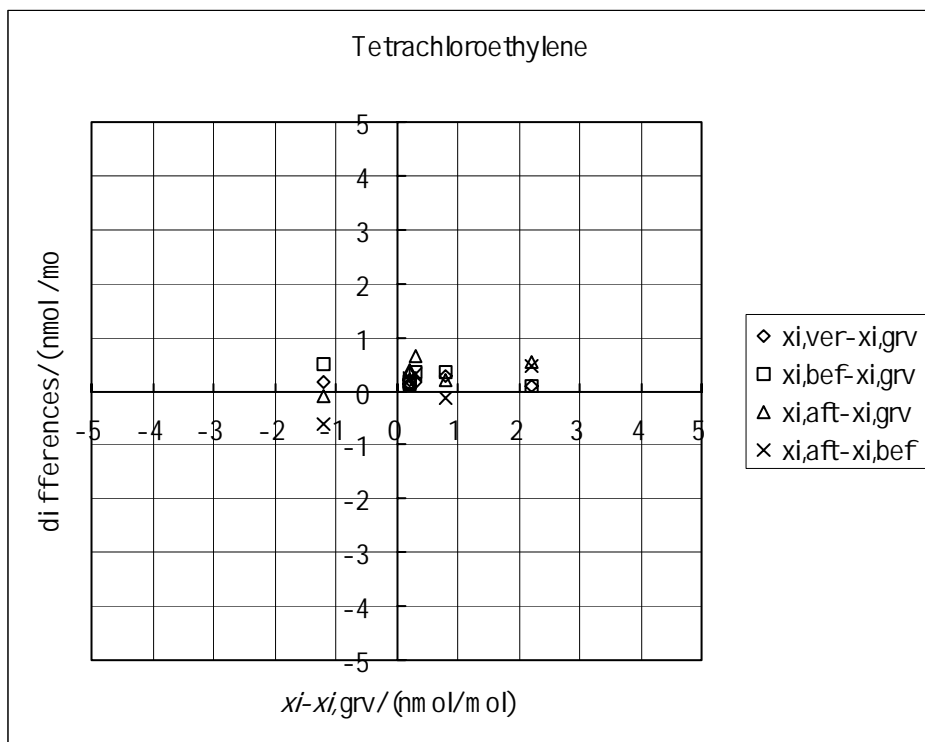


Figure 5. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for Tetrachloroethylene.

Table 6. The concentration changes during the comparison versus x_i , reported values from participants for 1,2-dichloroethane.

1,2-dichloroethane					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	2.63	1.67	1.32	-0.05	-1.37
NIST	1.00	1.46	0.30	-0.77	-1.07
NMi	-4.60	1.21	0.92	-0.14	-1.06
NMIJ/CERI	-1.70	0.21	-0.74	-2.74	-2.00
NPL	0.10	0.63	0.11	-0.57	-0.68
VNIIM	-1.80	1.51	0.95	0.19	-0.76

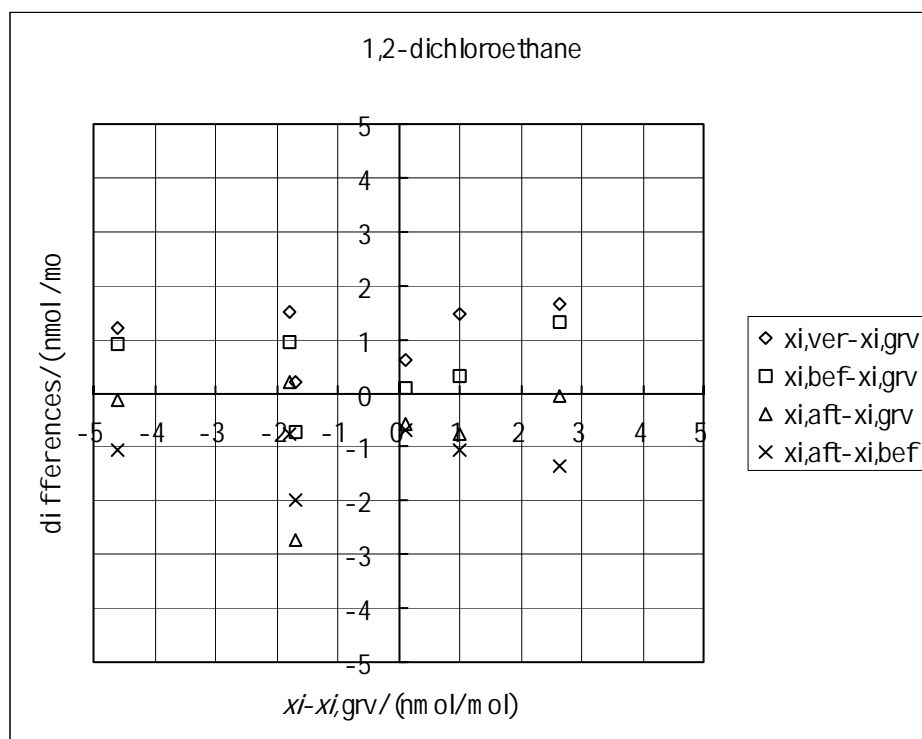


Figure 6. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for 1,2-dichloroethane.

Table 7. The concentration changes during the comparison versus x_i , reported values from participants for 1,3-butadiene.

1,3-butadiene					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	1.11	-0.01	0.22	-0.21	-0.43
NIST	-0.70	0.08	0.25	-0.13	-0.38
NMi	0.40	-0.12	-0.05	0.14	0.19
NMIJ/CERI	-0.10	0.06	-0.13	-0.23	-0.10
NPL	2.10	0.14	-0.15	-0.17	-0.02

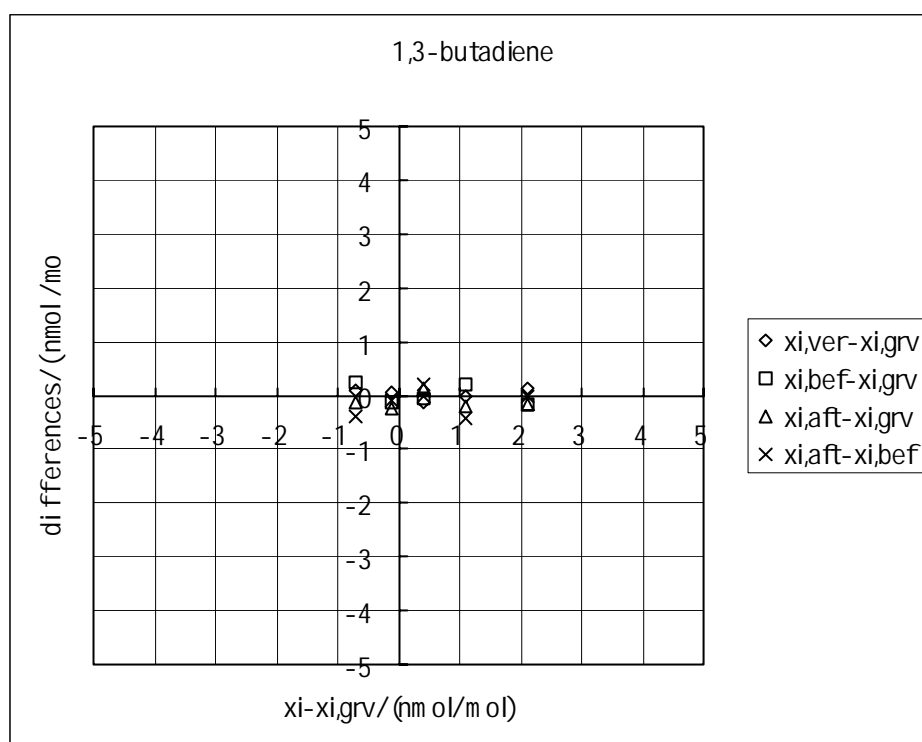


Figure 7. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for 1,3-butadiene.

Table 8. The concentration changes during the comparison versus x_i , reported values from participants for Vinyl chloride.

Vinylchloride					
Lab i	$x_i - x_{i,grv}$ nmol/mol	$x_{i,ver} - x_{i,grv}$ nmol/mol	$x_{i,bef} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,grv}$ nmol/mol	$x_{i,aft} - x_{i,bef}$ nmol/mol
KRISS	0.04	-0.05	0.24	-0.08	-0.32
NIST	1.00	-0.01	0.19	0.10	-0.09
NMi	3.10	-0.14	-0.05	0.01	0.06
NMIJ/CERI	0.20	0.04	0.03	0.19	0.16
NPL	1.50	0.08	-0.10	0.06	0.16
VNIIM	-0.30	-0.16	0.02	-0.26	-0.28

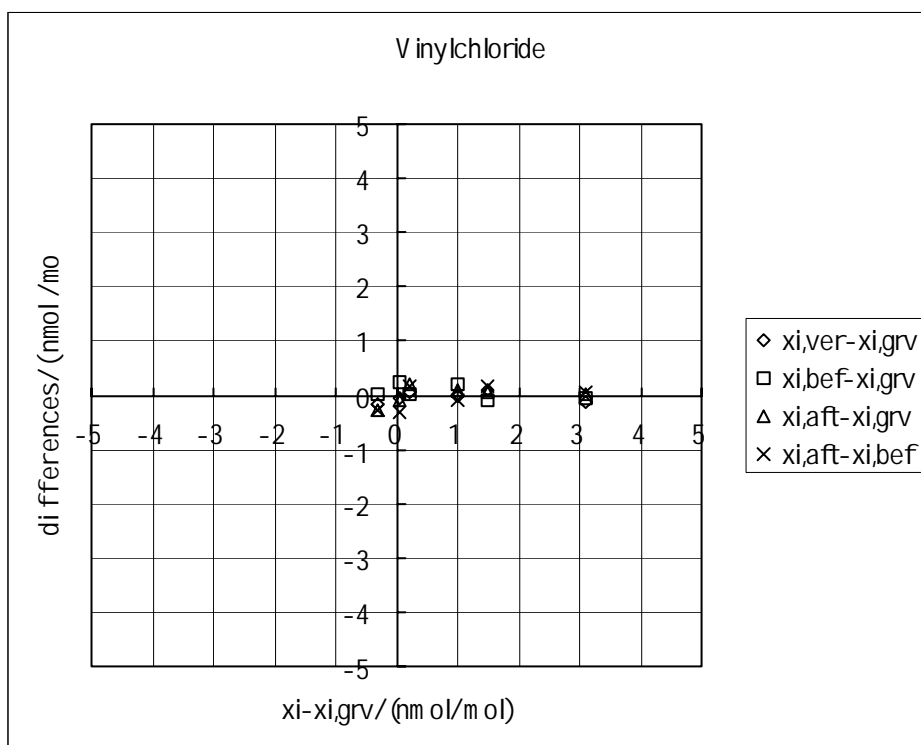


Figure 8. The Plots of concentration changes during the comparison versus differences between reported values from participants and gravimetric values for Vinyl chloride.

Measurement report of KRISS

Laboratory : KRISS

Cylinder number : CPB 27161 (3-01)

NOMINAL COMPOSITION : $90 \cdot 10^{-9}$ – $110 \cdot 10^{-9}$ mol/mol

Measurement No. 1	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	03-09-26	92.05	0.1	5
Chloroform		97.79	0.4	5
Dichloromethane		97.03	0.1	5
Trichloroethylene		103.94	0.1	5
Tetrachloroethylene		95.37	0.1	5
1,2-dichloroethane		100.79	0.6	5
1,3-butadene		100.27	0.2	5
Vinyl chloride		98.72	0.2	5

Measurement No. 2	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	03-09-29	91.42	0.6	5
Chloroform		97.11	0.8	5
Dichloromethane		101.07	0.6	5
Trichloroethylene		103.14	0.7	5
Tetrachloroethylene		94.72	0.7	5
1,2-dichloroethane		100.40	0.7	5
1,3-butadene		99.60	0.6	5
Vinyl chloride		98.04	0.6	5

Measurement No. 3	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	03-09-29	91.93	0.7	5
Chloroform		97.65	0.7	5
Dichloromethane		101.60	0.8	5
Trichloroethylene		103.75	0.7	5
Tetrachloroethylene		95.35	0.8	5
1,2-dichloroethane		100.87	0.7	5
1,3-butadene		99.89	0.6	5
Vinyl chloride		98.36	0.6	5

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Measurement No. 4	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	03-09-30	92.84	0.7	5
Chloroform		98.56	0.8	5
Dichloromethane		102.69	0.5	5
Trichloroethylene		104.72	0.7	5
Tetrachloroethylene		96.23	0.6	5
1,2-dichloroethane		101.59	0.7	5
1,3-butadene		101.03	0.6	5
Vinyl chloride		99.41	0.7	5

Measurement No. 5	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	03-09-30	92.13	0.7	5
Chloroform		97.99	0.7	5
Dichloromethane		101.70	0.6	5
Trichloroethylene		103.97	0.6	5
Tetrachloroethylene		95.42	0.6	5
1,2-dichloroethane		100.49	0.7	5
1,3-butadene		100.24	0.7	5
Vinyl chloride		98.67	0.7	5

Note: Please copy this table as many times as needed for reporting additional measurements

Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Benzene	92.07 nmol/mol	1.98	1.46 nmol/mol
Chloroform	97.82 nmo/mol	1.98	1.54 nmol/mol
Dichloromethane	101.75 nmol/mol	1.98	1.62 nmol/mol
Trichloroethylene	103.90 nmol/mol	1.98	1.64 nmol/mol
Tetrachloroethylene	95.42 nmol/mol	1.98	1.51 nmol/mol
1,2-dichloroethane	100.83 nmol/mol	1.98	1.58 nmol/mol
1,3-butadene	100.21 nmol/mol	1.99	1.34 nmol/mol
Vinyl chloride	98.64 nmol/mol	1.99	1.30 nmol/mol

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

Entech 7100 Cryogenic concentrator(Entech, USA) and HP6890 GC-FID(Agilent, USA) were used for analysis. The ppb VOC sample was concentrated at glass-bead-filled U-trap at -50°C and focused at -150°C with LN_2 . Each steps used desorption temp of 70°C . After connecting the sample gas cylinder, leak in the sample-line was checked, and the line was evacuated by vacuum and purged with sample gas. Sample gas was supplied to 7100 concentrator at 10 psi, and at every analysis, sample transfer-line has been purged with 40 mL of sample before cryoconcentration. 50 mL of sample gas was used for the analysis and transferred at 50 mL/min for 1 min. The cryotrapped sample at glass-bead was transferred to focusing trap for 3.5 min, and the focused sample was injected to GC column for 3 min. The glass-bead trap was baked at 140°C after injection of sample to column. Helium was used as carrier gas.

GC column : CP-SIL 5CB(Varian), 60 m x 0.32 mm id x 1 μm thickness with dimethylsilicon. GC oven temperature was set as temp of 40°C (4 min) and raised to 200°C with rate of $15^{\circ}\text{C}/\text{min}$. FID temp was set 250°C . Column flow was 2 mL/min and EPC used for constant column flow. High purity hydrogen used for FID with EPC controlled flow of 30 mL/min. High purity air was used also as FID fuel gas and supplied with EPC control at 300 mL/min. FID signal was acquired by Agilent Chemstation and GC-FID data was processed using Chemstation software.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

Purities of vinyl chloride, 1,3-butadiene, dichloromethane, 1,2-dichloroethane, benzene, tetrachloroethylene (from Aldrich), chloroform (from Burdick & Jackson), and trichloroethylene (from Fluka) were checked by GC-MS and GC-FID(for organic impurities). Water content of each chemical was estimated from the reagent specification of the producer. Estimated purity for each chemical was as follow: vinyl chloride(99.9%), 1,3-butadiene(99.9%), dichloromethane(99.9%), 1,2-dichloroethane(99.9%), benzene(99.9%), tetrachloroethylene(99.9%), chloroform (99.9%), and trichloroethylene (99.8%).

For vinyl chloride and 1,3-butadiene, KRISS primary reference gases with 0.6% concentrations had been prepared by gravimetry and diluted to 100 ppm which used to make 5 ppm concentration of 8 composition of VOC gas standard. The amounts of nitrogen used for balance gas were measured by gravimetry using high precision gas balance (Mettler, Switzerland) with readability of 2 mg and capacity of 15 kg.

For other VOCs, liquid mix had been prepared by gravimetry, and the portion of liquid mix was taken to make 50 ppm level of gas standards. Chemical balance with readability of 0.01 mg(capacity 200 g, Mettler) was used for measuring weight of liquid. Part of 50 ppm standard was transferred and combined to make 5 ppm level of 8 component mix of VOC standards. The 5 ppm standard gas was diluted to 100 ppb level of gas standards, one of which was selected as KRISS reference standard gas for K-22 intercomparison work.

Luxfer cylinder (Australia) with fine-polished internal surface with stainless steel(SS) valve was used for the preparation of ppm level of VOC gas standards. For 100 ppb level of VOC gas standard, Acculife cylinder from Scott(Netherlands) cylinders were used.

High purity nitrogen was used as balance gas(VOC impurities in the high purity nitrogen were checked using the cryogenic concentration GC-FID) and The chemical balance and gas balance was calibrated by E_2 grade calibration weight before starting measurement. Tare cylinder was used for buoyancy correction of gas weight measurement.

Homogeneity of the ppm level VOC gas standards has been checked by GC-FID (GC column used, 30 m x 0.53mm x 2.65 μm , 0.25 mL of injection loop used for gas switching injection valve, 100°C , oven temp of 40°C (4 min) to 150°C with rate of $15^{\circ}\text{C}/\text{min}$, FID detector temp 250°C , column flow 3.5 mL/min, sample gas flowrate of 50mL/min)

One cylinder of the 5 ppm VOC standard was selected for preparation of 100 ppb level of VOC standard gas. Acculife treated aluminum cylinders (Scott, Netherlands) used for the preparation of 100ppb level of BTX standard. Dilution system for making 5 ppb level BTX standard gases had been checked for its cleanliness (VOC

contamination free) with flushing the system with N₂ and collecting and analyzing the flushed N₂ which was collected in 6 L of Silco canister with pressure of 15 psig.

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.):

One primary reference gas prepared as above was selected as standard for CCQM-K22 work, and one point calibration was used for the analysis since the prepared concentrations are very close to CCQM-K22 sample's concentration. At the same time, linearities of each VOC components were checked to make sure good linearities of analytical condition, and it gave good linearity with passing origin always.

KRISS VOC CRM	conc.(nmol/mol)	k	Uexp(nmol/mol)	Rel U(%)
benzene	98.42	1.98	1.47	1.5
Chloroform	99.36	1.98	1.48	1.5
Dichloromethane	97.03	1.98	1.45	1.5
Trichloroethylene	98.61	1.98	1.47	1.5
Tetrachloroethylene	101.44	1.98	1.51	1.5
1,2-dichloroethane	101.72	1.98	1.52	1.5
1,3-butadiene	99.20	1.98	1.22	1.2
Vinyl chloride	102.17	1.98	1.24	1.2

Analysis of KRISS primary reference gases and CCQM sample were repeated 4 times each, and these are counted as one set of measurement. Total of 5 sets of measurements had been repeated. Lab temperature were kept 24 °C ± 1 °C and atmospheric pressure were between 1000 ~ 1015 hPa. Since no appreciable change in temp and pressure were noticed, no correction for the temperature and pressure were made for the measurement.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument. (automatic, high pressure, mass-flow controller, dilution etc.):

After receiving sample cylinder, box carton was opened, and cylinder was stored at room temperature before analysis (for 2 months). The sample cylinder was connected to cryofocusing-GC-FID analysis system. The sample gas was transferred (with flowrate of 50 mL/min for 1 min) to the 7100 system under 10 psig of cylinder pressure. The 7100 system has MFC after concentrating trap, and measure flowrate and amount of flow of sample gas.

Uncertainty:

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

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

In support of this action, a list of potential uncertainty sources is given. This list may not be complete and is compiled from ISO-Standards, ISO-6142 and ISO-6143.

- a. Uncertainty related to the balance and mass pieces
 - Readability of balance. 1 mg for gas balance, 0.01 mg for chemical balance

Accuracy of balance including linearity. 10 mg for gas balance, 0.04 mg for chemical balance

Incorrect zero point. Negligible

Drift (thermal and time effects). Negligible

Instability due to draught. Negligible

Location of cylinder on the balance pan: Negligible

Always keep the cylinder positioned at the center of weighing pan. Balance has automatic centering function

Errors in the mass pieces used. Not used

Buoyancy effects on the weights used:

Buoyancy was corrected using tare cylinder at each weighing procedure

b. Uncertainties related to the gas cylinder

Mechanical handling of cylinder due to:

loss of metal, paints or labels from surface of cylinder; Negligible

loss of metal from threads of valve/fitting; Negligible

dirt on cylinder, valves or associated fitting. Negligible

Adsorption/desorption effects on the external cylinder surface. Negligible

Weighing room was well air conditioned and kept temperature and humidity constant so that no absorption/desorption effects on the external cylinder surface.

Buoyancy effects resulted from:

the cylinder itself;

differences in temperature of the cylinder from surrounding air due to e.g. filling with gas;

After filling the cylinder with N₂, the cylinder was stood at room temp until it cool down to room temp, and also kept at the weighing room for more than 4 hours before weighing

change of cylinder volume during filling; Negligible

Change of cylinder volume was checked by measuring the diameter of cylinder, but very little change was observed.

change of density of air due to changes in temperature, air pressure, humidity, and carbon dioxide content.

Temperature and humidity were constant during the weighing of cylinder. Buoyancy effect by air pressure change was corrected by using tare cylinder with same shape and weight. CO₂ content of weighing room was also analyzed, and CO₂ effect was negligible.

Uncertainty in determination of external cylinder volume. Negligible

c. Uncertainties related to the component gases

Residual gas in cylinder.

Cylinder used for KRISS CRMs for VOC were evacuated under oil-less high vacuum system (consisting turbo-molecular pump with diaphragm pump backup).

Leakage resulting from;

leakage of air into the cylinder after evacuation; Negligible

Leakage of the cylinder was check by reweighing the cylinder after evacuation (one day later). No leak was noticed

leakage of gas from the cylinder valve during filling; Negligible

Leakage of cylinder also was check by pressurizing the filling system and monitoring pressure change for a day. No pressure change was observed.

escape of gas from cylinder into transport lines. Negligible

Gas remaining in transfer system when weight loss method is used

Gas remaining in transfer system when weight loss method is used.

Weight loss method does not used.

Absorption/reaction of components on internal cylinder surface.

Loss of 100 ppb level of VOCs by adsorption or reaction on the surface of cylinder has been checked by filling to new evacuated cylinder with same specification. Absorption less than 0.5% could not be checked by analysis.

Therefore, 0.5% uncertainty was counted as a loss due to absorption.

Reaction between components. : Negligible

Reaction between VOCs never reported

Impurities in the gases used. Less than 0.1 ppb of VOC

High purity nitrogen with 99.9999% purity was obtained from gas company, and the purity was checked by KRIS. Moisture, CO₂, O₂, Ar, CH₄ were analyzed. Using the same analysis system for VOC analysis, VOC impurities was check down to below ppb level.

Impurities in the parent gases. 0.2%

Insufficient homogenization. Negligible

KRIS CRMs were sufficiently mixed after preparation using rolling mixer, then stood for a day at room temp before use.

Uncertainty of molecular mass. Negligible

d. Uncertainties related to the analysis

Repeatability and selectivity of the analyzer.

Repeatability of GC-FID for ppm level of VOC analysis was < 0.5 %.

Repeatability of Cryogenic GC-FID for 100 ppb level of VOC was < 1 %

Appropriateness of the calibration curve: Negligible

response model and its residuals; Negligible

mismatch of the sample gas and the calibration gas. Negligible

Uncertainty related the corrections for the sampling: 0.1%

change in atmospheric pressure, temperature, sample flow rate, and sampling time. 0.1%

Uncertainty sources with small contribution are not listed on following tables although the sources had been counted for uncertainty budget calculations.

Uncertainty table: Benzene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to liquid injection to cylinder, f_{evp}	1	normal	0.001	92.0	0.092
Factor related to purity of pure VOC chemical, f_{imp}	1	normal	0.002	92.0	0.184
Factor related to liquid mix preparation, f_{mix}	1	normal	0.005	92.0	0.460
Factor related to pressure difference between sample and standard gas, f_{press}	1	normal	0.001	92.1	0.092
Factor related to adsorption loss in preparation of ppm standard gas, f_{ads1}	1	normal	0.001	92.1	0.092
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1	normal	0.005	92.1	0.460
Weighing uncertainty of liquid mix in preparation of 50ppm mixed std gas, W_{50ppm}	0.0981 g	normal	50×10^{-6} g	938	0.047
Uncertainty related to chemical balance, δW_c	0 mg	normal	0.04 mg	0.938	0.038
Uncertainty related to gas balance, δW_g	0 mg	normal	10 mg	4.98×10^{-3}	0.050
Uncertainty related to handling of syringe in weighing of liquid mix, δW_{h1}	0 mg	normal	0.05 mg	0.938	0.047
Uncertainty related to handling of cylinder in weighing of std gas cylinder, δW_{h2}	0 mg	normal	5 mg	4.98×10^{-3}	0.025
Uncertainty of analysis, A_{ratio}	0.9355	normal	2.31×10^{-3}	98.4	0.227

Coverage factor or degree of freedom: $k=1.98$ or $dof=118$

Expanded uncertainty: 1.46 nmol/mol

Uncertainty table: Chloroform

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to liquid injection to cylinder, f_{evp}	1		0.001	97.7	0.098
Factor related to purity of pure VOC chemical, f_{imp}	1		0.002	97.7	0.195
Factor related to liquid mix preparation, f_{mix}	1		0.005	97.7	0.488
Factor related to pressure difference between sample and standard gas, f_{press}	1		0.001	97.8	0.098
Factor related to adsorption loss in preparation of ppm standard	1		0.001	97.8	0.098

gas, f_{ads1}					
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1		0.005	97.8	0.489
Weighing uncertainty of liquid mix in preparation of 50ppm mixed std gas, W_{50ppm}	0.1507 g		50×10^{-6} g	649	0.032
Uncertainty related to chemical balance, δW_c	0 mg		0.04 mg	0.938	0.026
Uncertainty related to gas balance, δW_g	0 mg		10 mg	5.29×10^{-3}	0.053
Uncertainty related to handling of syringe in weighing of liquid mix, δW_{h1}	0 mg		0.05 mg	0.648	0.032
Uncertainty related to handling of cylinder in weighing of std gas cylinder, δW_{h2}	0 mg		5 mg	5.29×10^{-3}	0.027
Uncertainty of analysis, A_{ratio}	0.9845		2.37×10^{-3}	99.4	0.235 l

Coverage factor or degree of freedom: $k=1.98$ or $dof=119$
Expanded uncertainty: 1.54 nmol/mol

Uncertainty table: Dichloromethane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to liquid injection to cylinder, f_{evp}	1		0.001	102	0.102
Factor related to purity of pure VOC chemical, f_{imp}	1		0.002	102	0.203
Factor related to liquid mix preparation, f_{mix}	1		0.005	102	0.508
Factor related to pressure difference between sample and standard gas, f_{press}	1		0.001	102	0.102
Factor related to adsorption loss in preparation of ppm standard gas, f_{ads1}	1		0.001	102	0.102
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1		0.005	102	0.509
Weighing uncertainty of liquid mix in preparation of 50ppm mixed std gas, W_{50ppm}	0.1047 g		50×10^{-6} g	972	0.049
Uncertainty related to chemical balance, δW_c	0 mg		0.04 mg	0.971	0.039 l
Uncertainty related to gas balance, δW_g	0 mg		10 mg	5.50×10^{-3}	0.055
Uncertainty related to handling of syringe in weighing of liquid mix, δW_{h1}	0 mg		0.05 mg	0.971	0.049
Uncertainty related to handling of cylinder in weighing of std gas	0 mg		5 mg	5.50×10^{-3}	0.028

cylinder, δW_{h2}					
Uncertainty of analysis, A_{ratio}	1.0487		2.70×10^{-3}	97.0	0.262

Coverage factor or degree of freedom: $k=1.98$ or $dof=114$
Expanded uncertainty: 1.62 nmol/mol

Uncertainty table: Trichloroethylene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to liquid injection to cylinder, f_{evp}	1		0.001	104	0.104
Factor related to purity of pure VOC chemical, f_{imp}	1		0.002	104	0.208
Factor related to liquid mix preparation, f_{mix}	1		0.005	104	0.519
Factor related to pressure difference between sample and standard gas, f_{press}	1		0.001	104	0.104
Factor related to adsorption loss in preparation of ppm standard gas, f_{ads1}	1		0.001	104	0.104
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1		0.005	104	0.520
Weighing uncertainty of liquid mix in preparation of 50ppm mixed std gas, W_{50ppm}	0.1646 g		50×10^{-6} g	631	0.032
Uncertainty related to chemical balance, δW_c	0 mg		0.04 mg	0.630	0.025
Uncertainty related to gas balance, δW_g	0 mg		10 mg	5.62×10^{-3}	0.056
Uncertainty related to handling of syringe in weighing of liquid mix, δW_{h1}	0 mg		0.05 mg	0.630	0.032
Uncertainty related to handling of cylinder in weighing of std gas cylinder, δW_{h2}	0 mg		5 mg	5.62×10^{-3}	0.028
Uncertainty of analysis, A_{ratio}	1.0537		2.57×10^{-3}	98.6	0.253

Coverage factor or degree of freedom: $k=1.98$ or $dof=118$
Expanded uncertainty: 1.64 nmol/mol

Uncertainty table: Tetrachloroethylene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to liquid injection to cylinder, f_{evp}	1		0.001	95.3	0.095

Factor related to purity of pure VOC chemical, f_{imp}	1		0.002	95.3	0.191 l
Factor related to liquid mix preparation, f_{mix}	1		0.005	95.3	0.477
Factor related to pressure difference between sample and standard gas, f_{press}	1		0.001	95.4	0.095
Factor related to adsorption loss in preparation of ppm standard gas, f_{ads1}	1		0.001	95.4	0.095
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1		0.005	95.4	0.477
Weighing uncertainty of liquid mix in preparation of 50ppm mixed std gas, W_{50ppm}	0.2138 g		50×10^{-6} g	446	0.022
Uncertainty related to chemical balance, δW_c	0 mg		0.04 mg	0.446	0.018
Uncertainty related to gas balance, δW_g	0 mg		10 mg	5.16×10^{-3}	0.052
Uncertainty related to handling of syringe in weighing of liquid mix, δW_{h1}	0 mg		0.05 mg	0.446	0.022
Uncertainty related to handling of cylinder in weighing of std gas cylinder, δW_{h2}	0 mg		5 mg	5.16×10^{-3}	0.026
Uncertainty of analysis, A_{ratio}	0.9407		2.37×10^{-3}	101	0.240

Coverage factor or degree of freedom: $k=1.98$ or $dof=115$
Expanded uncertainty: 1.51 nmol/mol

Uncertainty table: 1,2-dichloroethane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to liquid injection to cylinder f_{evp}	1		0.001	101	0.101
Factor related to purity of pure VOC chemical, f_{imp}	1		0.002	101	0.201
Factor related to liquid mix preparation, f_{mix}	1		0.005	101	0.503
Factor related to pressure difference between sample and standard gas, f_{press}	1		0.001	101	0.101
Factor related to adsorption loss in preparation of ppm standard gas, f_{ads1}	1		0.001	101	0.101
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1		0.005	101	0.504
Weighing uncertainty of liquid mix in preparation of 50ppm mixed std gas, W_{50ppm}	0.1255 g		50×10^{-6} g	804	0.040
Uncertainty related to chemical	0 mg		0.04 mg	0.803	0.032

balance, δW_c					
Uncertainty related to gas balance, δW_g	0 mg		10 mg	9.07×10^{-3}	0.091
Uncertainty related to handling of syringe in weighing of liquid mix, δW_{h1}	0 mg		0.05 mg	0.803	0.040
Uncertainty related to handling of cylinder in weighing of std gas cylinder, δW_{h2}	0 mg		5 mg	9.07×10^{-3}	0.045
Uncertainty of analysis, A_{ratio}	0.9912		2.08×10^{-3}	102	0.212

Coverage factor or degree of freedom: $k=1.98$ or $dof=130$
Expanded uncertainty: 1.58 nmol/mol

Uncertainty table: 1,3-butadene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to purity of pure VOC chemical, f_{imp}	1		0.002	97.6	0.195
Factor related to pressure difference between sample and standard gas, f_{press}	1		0.001	100	0.100
Factor related to adsorption loss in preparation of ppm standard gas, f_{ads1}	1		0.001	100	0.100
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1		0.005	100	0.501
Uncertainty related to gas balance, δW_g	0 mg		10 mg	0.0267	0.267
Uncertainty related to handling of cylinder in weighing of std gas cylinder, δW_{h2}	0 mg		5 mg	0.0267	0.133
Uncertainty of analysis, A_{ratio}	1.0101		2.43×10^{-3}	99.2	0.241

Coverage factor or degree of freedom: $k=1.99$ or $dof=92$
Expanded uncertainty: 1.34 nmol/mol

Uncertainty table: Vinyl chloride

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$ nmol/mol
Factor related to purity of pure VOC chemical, f_{imp}	1		0.002	96.1	0.192
Factor related to pressure difference between sample and standard gas, f_{press}	1		0.001	98.6	0.099
Factor related to adsorption loss in preparation of ppm standard	1		0.001	98.6	0.099

gas, f_{ads1}					
Factor related to adsorption loss in preparation of ppb standard gas, f_{ads2}	1		0.005	98.6	0.493
Uncertainty related to gas balance, δW_g	0 mg		10 mg	0.0244	0.244
Uncertainty related to handling of cylinder in weighing of std gas cylinder, δW_{h2}	0 mg		5 mg	0.0244	0.122
Uncertainty of analysis, A_{ratio}	0.9655		2.25×10^{-3}	102	0.230

Coverage factor or degree of freedom: $k=1.99$ or $dof=92$

Expanded uncertainty: 1.30 nmol/mol

Optional

You may provide additional data like the raw measurement data, information on your measurement procedure etc:

Preparation of 100 ppb level vinylchloride CRM and Analysis of K-22 sample.

Model equation for CRM preparation and analysis

$$C_{sample1} = (A_{Ratio} * x_1) * f_{press};$$

$$x_1 = (n_1 / n_{tot} * 100000000) * (f_{ads2});$$

$$n_{tot} = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 + n_{nt};$$

$$n_1 = m_1 / M_{tot1} * (x_{15} / 1000000);$$

$$n_2 = m_1 / M_{tot1} * (x_{25} / 1000000);$$

$$n_3 = m_1 / M_{tot1} * (x_{35} / 1000000);$$

$$n_4 = m_1 / M_{tot1} * (x_{45} / 1000000);$$

$$n_5 = m_1 / M_{tot1} * (x_{55} / 1000000);$$

$$n_6 = m_1 / M_{tot1} * (x_{65} / 1000000);$$

$$n_7 = m_1 / M_{tot1} * (x_{75} / 1000000);$$

$$n_8 = m_1 / M_{tot1} * (x_{85} / 1000000);$$

$$n_{nt} = n_{n1} + n_{n2};$$

$$n_{n1} = m_1 / M_{tot1} * (x_{n5} / 1000000);$$

$$n_{n2} = m_n / M_n;$$

$$M_{tot1} = M_1 * (x_{15} / 1000000) + M_2 * (x_{25} / 1000000) + M_3 * (x_{35} / 1000000) + M_4 * (x_{45} / 1000000) + M_5 * (x_{55} / 1000000) + M_6 * (x_{65} / 1000000) + M_7 * (x_{75} / 1000000) + M_8 * (x_{85} / 1000000) + M_n * (x_{n5} / 1000000);$$

$$m_1 = (W_{ball} + \square W_g / 1000 + \square W_{had2} / 1000);$$

$$m_n = (W_{baln} + \square W_g / 1000 + \square W_{had2} / 1000);$$

$$x_{15} = (n_{15} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{25} = (n_{25} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{35} = (n_{35} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{45} = (n_{45} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{55} = (n_{55} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{65} = (n_{65} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{75} = (n_{75} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{85} = (n_{85} / n_{tot5} * 1000000) * f_{ads1};$$

$$x_{n5} = (n_{nt5} / n_{tot5} * 1000000);$$

$$n_{tot5} = n_{15} + n_{25} + n_{35} + n_{45} + n_{55} + n_{65} + n_{75} + n_{85} + n_{nt5};$$

$$n_{15} = m_{15} / M_{tot15} * (x_{1100} / 1000000);$$

$$\begin{aligned}
n_{25} &= m_{15} / M_{tot15} * (x_{2100} / 1000000) ; \\
n_{35} &= m_{25} / M_{tot25} * (x_{350} / 1000000) ; \\
n_{45} &= m_{25} / M_{tot25} * (x_{450} / 1000000) ; \\
n_{55} &= m_{25} / M_{tot25} * (x_{550} / 1000000) ; \\
n_{65} &= m_{25} / M_{tot25} * (x_{650} / 1000000) ; \\
n_{75} &= m_{25} / M_{tot25} * (x_{750} / 1000000) ; \\
n_{85} &= m_{25} / M_{tot25} * (x_{850} / 1000000) ; \\
n_{nt5} &= n_{n15} + n_{n25} + n_{n35} ; \\
n_{n15} &= (m_{15} / M_{tot15}) * (x_{n100} / 1000000) ; \\
n_{n25} &= (m_{25} / M_{tot25}) * (x_{n50} / 1000000) ; \\
n_{n35} &= m_{n5} / M_n ; \\
M_{tot15} &= M_1 * (x_{1100} / 1000000) + M_2 * (x_{2100} / 1000000) + M_n * (x_{n100} / 1000000) ; \\
M_{tot25} &= M_3 * (x_{350} / 1000000) + M_4 * (x_{450} / 1000000) + M_5 * (x_{550} / 1000000) + M_6 * (x_{650} / 1000000) + M_7 \\
&* (x_{750} / 1000000) + M_8 * (x_{850} / 1000000) + M_n * (x_{n50} / 1000000) ; \\
m_{15} &= (W_{bal15} + \square W_g / 1000 + \square W_{had2} / 1000) ; \\
m_{25} &= (W_{bal25} + \square W_g / 1000 + \square W_{had2} / 1000) ; \\
m_{n5} &= (W_{baln5} + \square W_g / 1000 + \square W_{had2} / 1000) ;
\end{aligned}$$

$$\begin{aligned}
x_{1100} &= (n_{1100} / n_{tot100} * 1000000) ; \\
x_{2100} &= (n_{2100} / n_{tot100} * 1000000) ; \\
x_{n100} &= (n_{nt100} / n_{tot100} * 1000000) ; \\
n_{tot100} &= n_{1100} + n_{2100} + n_{nt100} ; \\
n_{1100} &= (m_{1100} / M_{tot1100}) * (x_{106} / 100) ; \\
n_{2100} &= (m_{1100} / M_{tot1100}) * (x_{206} / 100) ; \\
n_{nt100} &= n_{n1100} + n_{n2100} ; \\
n_{n1100} &= (m_{1100} / M_{tot1100}) * (x_{n06} / 100) ; \\
n_{n2100} &= m_{n100} / M_n ; \\
M_{tot1100} &= M_1 * (x_{106} / 100) + M_2 * (x_{206} / 100) + M_n * (x_{n06} / 100) ; \\
m_{1100} &= (W_{bal1100} + \square W_g / 1000 + \square W_{had2} / 1000) ; \\
m_{n100} &= (W_{baln100} + \square W_g / 1000 + \square W_{had2} / 1000) ;
\end{aligned}$$

$$\begin{aligned}
x_{350} &= (n_{350} / n_{tot50} * 1000000) * f_{evp} * f_{imp} * f_{mix} ; \\
x_{450} &= (n_{450} / n_{tot50} * 1000000) * f_{evp} * f_{imp} * f_{mix} ; \\
x_{550} &= (n_{550} / n_{tot50} * 1000000) * f_{evp} * f_{imp} * f_{mix} ; \\
x_{650} &= (n_{650} / n_{tot50} * 1000000) * f_{evp} * f_{imp} * f_{mix} ; \\
x_{750} &= (n_{750} / n_{tot50} * 1000000) * f_{evp} * f_{imp} * f_{mix} ; \\
x_{850} &= (n_{850} / n_{tot50} * 1000000) * f_{evp} * f_{imp} * f_{mix} ; \\
x_{n50} &= (n_{n50} / n_{tot50} * 1000000) ; \\
n_{tot50} &= n_{350} + n_{450} + n_{550} + n_{650} + n_{750} + n_{850} + n_{n50} ; \\
n_{350} &= m_{350} / M_3 ; \\
n_{450} &= m_{450} / M_4 ; \\
n_{550} &= m_{550} / M_5 ; \\
n_{650} &= m_{650} / M_6 ; \\
n_{750} &= m_{750} / M_7 ; \\
n_{850} &= m_{850} / M_8 ; \\
n_{n50} &= m_{n50} / M_n ; \\
m_{350} &= (W_{bal350} + \square W / 1000 + \square W_{had1} / 1000) ; \\
m_{450} &= (W_{bal450} + \square W / 1000 + \square W_{had1} / 1000) ; \\
m_{550} &= (W_{bal550} + \square W / 1000 + \square W_{had1} / 1000) ; \\
m_{650} &= (W_{bal650} + \square W / 1000 + \square W_{had1} / 1000) ; \\
m_{750} &= (W_{bal750} + \square W / 1000 + \square W_{had1} / 1000) ; \\
m_{850} &= (W_{bal850} + \square W / 1000 + \square W_{had1} / 1000) ;
\end{aligned}$$

$$\begin{aligned}
x_{106} &= (n_{106} / n_{tot06} * 100) * f_{imp} ; \\
x_{206} &= (n_{206} / n_{tot06} * 100) * f_{imp} ; \\
x_{n06} &= (n_{n06} / n_{tot06} * 100) ; \\
n_{tot06} &= n_{106} + n_{206} + n_{n06} ; \\
n_{106} &= m_{106} / M_1 ; \\
n_{206} &= m_{206} / M_2 ;
\end{aligned}$$

$$n_{n06} = m_{n06} / M_n ;$$

$$m_{106} = (W_{bal106} + \square W_g / 1000 + \square W_{had2} / 1000) ;$$

$$m_{206} = (W_{bal206} + \square W_g / 1000 + \square W_{had2} / 1000) ;$$

List of quantities:

Quantity	Unit	Definition
x_1	ppb	concentration of component STD 1(vinyl chloride) in the mixture (100 ppb)
n_1	mol	the number of moles of component 1 (100 ppb)
m_1	g	weight value measured (gas taken from 5 ppm cyl.)
M_1	g/mol	Molar mass of the component 1
$\square W$	mg	uncertainty related to chemical balance measurement
f_{evp}		factor related to incomplete transfer of liquid sample to cylinder (due to poor evaporation)
f_{imp}		impurity factor in component 1
f_{mix}		factor related to preparation of liquid mix of 6-HAP
x_{15}	ppm	concentration of component 1 in the mixture (5 ppm)
n_{15}	mol	the number of moles of component 1 (5 ppm)
n_{tot}	mol	the total number of moles of 100 ppb cyl.
m_{15}	g	weight value measured (about gas taken from 100 ppm cyl.)
x_{1100}	ppm	concentration of component 1 in the mixture (100 ppm)
n_{1100}	mol	the number of moles of component 1
m_{1100}	g	weight value measured (about gas taken from 0.6 % cyl.)
n_2	mol	the number of moles of component 2 (100 ppb)
n_3	mol	the number of moles of component 3 (100 ppb)
n_4	mol	the number of moles of component 4 (100 ppb)
n_5	mol	the number of moles of component 5 (100 ppb)
n_6	mol	the number of moles of component 6 (100 ppb)
n_7	mol	the number of moles of component 7 (100 ppb)
n_8	mol	the number of moles of component 8 (100 ppb)
n_{nt}	mol	the number of moles of component N_2 (100 ppb)
M_{tot1}	g/mol	total Molar mass of the component (about gas taken from 5 ppm cyl.)
x_{25}	ppm	concentration of component 1 in the mixture (5 ppm)
x_{35}	ppm	concentration of component 1 in the mixture (5 ppm)
x_{45}	ppm	concentration of component 1 in the mixture (5 ppm)
x_{55}	ppm	concentration of component 1 in the mixture (5 ppm)
x_{65}	ppm	concentration of component 1 in the mixture (5 ppm)
x_{75}	ppm	concentration of component 1 in the mixture (5 ppm)
x_{85}	ppm	concentration of component 1 in the mixture (5 ppm)
n_{n1}	mol	the number of moles of component N_2 (about gas taken from 5 ppm cyl.)
n_{n2}	mol	the number of moles of component N_2 (100 ppb)
x_{n5}	ppm	concentration of component N_2 in the mixture (5 ppm)
m_n	g	weight value measured for component N_2 (100 ppb)

Quantity	Unit	Definition
M_n	g/mol	Molar mass of the component N_2
M_2	g/mol	Molar mass of the component 2
M_3	g/mol	Molar mass of the component 3
M_4	g/mol	Molar mass of the component 4
M_5	g/mol	Molar mass of the component 5
M_6	g/mol	Molar mass of the component 6
M_7	g/mol	Molar mass of the component 7
M_8	g/mol	Molar mass of the component 8
n_{tot5}	mol	the total number of moles of 5 ppm cyl.
n_{25}	mol	the number of moles of component 2 (5 ppm)
n_{35}	mol	the number of moles of component 3 (5 ppm)
n_{45}	mol	the number of moles of component 4 (5 ppm)
n_{55}	mol	the number of moles of component 5 (5 ppm)
n_{65}	mol	the number of moles of component 6 (5 ppm)
n_{75}	mol	the number of moles of component 7 (5 ppm)
n_{85}	mol	the number of moles of component 8 (5 ppm)
n_{nt5}	mol	the number of moles of component N_2 (5 ppm)
M_{tot15}	g/mol	total Molar mass of the component (about gas taken from 100 ppm cyl.)
x_{2100}	ppm	concentration of component 2 in the mixture (100 ppm)
m_{25}	g	weight value measured (gas taken from 100 ppm cyl.)
M_{tot25}	g/mol	total Molar mass of the component (about gas taken from 50 ppm cyl.)
x_{350}	ppm	concentration of component 3 in the mixture (50 ppm)
x_{450}	ppm	concentration of component 3 in the mixture (50 ppm)
x_{550}	ppm	concentration of component 3 in the mixture (50 ppm)
x_{650}	ppm	concentration of component 3 in the mixture (50 ppm)
x_{750}	ppm	concentration of component 3 in the mixture (50 ppm)
x_{850}	ppm	concentration of component 3 in the mixture (50 ppm)
n_{n15}	mol	the number of moles of component N_2 (about gas taken from 100 ppm cyl.)
n_{n25}	mol	the number of moles of component N_2 (about gas taken from 50 ppm cyl.)
n_{n35}	mol	the number of moles of component N_2 (5 ppm)
x_{n100}	ppm	concentration of component N_2 in the mixture (100 ppm)
x_{n50}	ppm	concentration of component N_2 in the mixture (50 ppm)
m_{n5}	g	weight value measured for component N_2 (5 ppm)
n_{tot100}	mol	the total number of moles of 100 ppm cyl.
n_{2100}	mol	the number of moles of component 2 (100 ppm)
n_{nt100}	mol	the number of moles of component N_2 (100 ppm)
$M_{tot1100}$	g/mol	total Molar mass of the component (about gas taken from 0.6 % cyl.)
x_{106}	%	concentration of component 1 in the mixture (0.6 %)
x_{206}	%	concentration of component 2 in the mixture (0.6 %)
n_{n1100}	mol	the number of moles of component 1 (100 ppm)
n_{n2100}	mol	the number of moles of component 2 (100 ppm)

Quantity	Unit	Definition
x_{n06}	%	concentration of component N_2 in the mixture (0.6 %)
n_{350}	mol	the number of moles of component 3 (50 ppm)
n_{tot50}	mol	the total number of moles of 50 ppm cyl.
n_{450}	mol	the number of moles of component 4 (50 ppm)
n_{550}	mol	the number of moles of component 5 (50 ppm)
n_{650}	mol	the number of moles of component 6 (50 ppm)
n_{750}	mol	the number of moles of component 7 (50 ppm)
n_{850}	mol	the number of moles of component 8 (50 ppm)
n_{n50}	mol	the number of moles of component N_2 (50 ppm)
m_{350}	g	the mass of component 3 for 50 ppm cyl.
m_{450}	g	the mass of measured component 4 for 50 ppm cyl.
m_{550}	g	the mass of measured component 5 for 50 ppm cyl.
m_{650}	g	the mass of measured component 6 for 50 ppm cyl.
m_{750}	g	the mass of measured component 7 for 50 ppm cyl.
m_{850}	g	the mass of measured component 8 for 50 ppm cyl.
m_{n50}	g	weight value measured for component N_2 for 50 ppm cyl.
n_{106}	mol	the number of moles of component 1 (0.6 %)
n_{tot06}	mol	the total number of moles of 0.6 % cyl.
n_{206}	mol	the number of moles of component 1 (0.6 %)
n_{n06}	mol	the number of moles of component N_2 (0.6 %)
m_{106}	g	the mass of measured component 1 for 0.6 % cyl.
m_{206}	g	the mass of measured component 1 for 0.6 % cyl.
m_{n06}	g	weight value measured for component N_2 for 0.6 % cyl.
W_{bal1}	g	weight value measured (gas taken from 5 ppm cyl.)
m_{n100}	g	weight value measured for component N_2 for 100 ppm cyl.
A_{Ratio}		GC peak area ratio ($A_{sample}/A_{standard}$) - Each reading value is average of 4 analysis
f_{press}		related to pressure difference of sample and standard
f_{ads2}		factor for adsorption loss of gas composition in cylinder (for 100ppb cyl.)
f_{ads1}		factor for adsorption loss of gas composition in cylinder
$C_{sample1}$	ppb	Sample(vinyl chloride) concentration in ppb
$\square W_g$	mg	uncertainty related to chemical balance measurement
W_{bal15}	g	weight value measured (gas taken from 100 ppm cyl.)
W_{bal25}	g	weight value measured (gas taken from 50 ppm cyl.)
W_{baln5}	g	weight value measured (used N_2 of prep. 5 ppm cyl.)
$W_{bal1100}$	g	weight value measured (gas taken from 0.6% cyl.)
$W_{baln100}$	g	weight value measured (used N_2 of prep. 100 ppm cyl.)
W_{baln}	g	weight value measured (used N_2 of prep. 100 ppb cyl.)
W_{bal350}	g	weight value measured of component 3 (for 50 ppm cyl.)
W_{bal450}	g	weight value measured of component 4 (for 50 ppm cyl.)
W_{bal550}	g	weight value measured of component 5 (for 50 ppm cyl.)

Quantity	Unit	Definition
W_{bal650}	g	weight value measured of component 6 (for 50 ppm cyl.)
W_{bal750}	g	weight value measured of component 7 (for 50 ppm cyl.)
W_{bal850}	g	weight value measured of component 8 (for 50 ppm cyl.)
W_{bal106}	g	weight value measured of component 1 (for 0.6 % cyl.)
W_{bal206}	g	weight value measured of component 2 (for 0.6 % cyl.)
$\square W_{\text{had1}}$	mg	
$\square W_{\text{had2}}$	mg	

Uncertainty budget:

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr.-coeff.	Index
x_1	102.165 ppb	0.625 ppb					
n_1	$3.9805 \cdot 10^{-6}$ mol	$14.1 \cdot 10^{-9}$ mol					
m_1	21.8296 g	0.0116 g					
M_1	62.497920 g/mol	$925 \cdot 10^{-6}$ g/mol	50	-1.58	$-1.46 \cdot 10^{-3}$ ppb	0.00	0.000
$\square W$	0.0 mg	0.0400 mg	50	0.0	0.0 ppb	0.0	0.0
f_{evp}	1.00000	$1.00 \cdot 10^{-3}$	50	0.0	0.0 ppb	0.0	0.0
f_{imp}	1.00000	$2.00 \cdot 10^{-3}$	50	96.1	0.192 ppb	0.29	0.087
f_{mix}	1.00000	$5.00 \cdot 10^{-3}$	50	$179 \cdot 10^{-6}$	$894 \cdot 10^{-9}$ ppb	0.00	0.000
x_{15}	5.1087 ppm	0.0161 ppm					
n_{15}	$129.617 \cdot 10^{-6}$ mol	$392 \cdot 10^{-9}$ mol					
n_{tot}	38.961674 mol	$812 \cdot 10^{-6}$ mol					
m_{15}	35.2251 g	0.0112 g					
x_{1100}	103.103 ppm	0.288 ppm					
n_{1100}	$2.65263 \cdot 10^{-3}$ mol	$7.47 \cdot 10^{-6}$ mol					
m_{1100}	11.9165 g	0.0112 g					
n_2	$3.8650 \cdot 10^{-6}$ mol	$14.4 \cdot 10^{-9}$ mol					
n_3	$3.7805 \cdot 10^{-6}$ mol	$21.4 \cdot 10^{-9}$ mol					
n_4	$3.8711 \cdot 10^{-6}$ mol	$21.8 \cdot 10^{-9}$ mol					
n_5	$3.8965 \cdot 10^{-6}$ mol	$22.0 \cdot 10^{-9}$ mol					
n_6	$3.8345 \cdot 10^{-6}$ mol	$21.7 \cdot 10^{-9}$ mol					
n_7	$3.8418 \cdot 10^{-6}$ mol	$21.6 \cdot 10^{-9}$ mol					
n_8	$3.9521 \cdot 10^{-6}$ mol	$22.2 \cdot 10^{-9}$ mol					
n_{nt}	38.961643 mol	$812 \cdot 10^{-6}$ mol					
M_{tot1}	28.0163273 g/mol	$15.6 \cdot 10^{-6}$ g/mol					
x_{25}	4.9604 ppm	0.0164 ppm					
x_{35}	4.8520 ppm	0.0273 ppm					

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr.-coeff.	Index
x ₄₅	4.9683 ppm	0.0278 ppm					
x ₅₅	5.0008 ppm	0.0280 ppm					
x ₆₅	4.9213 ppm	0.0277 ppm					
x ₇₅	4.9307 ppm	0.0275 ppm					
x ₈₅	5.0722 ppm	0.0283 ppm					
n _{n1}	0.779143 mol	413·10 ⁻⁶ mol					
n _{n2}	38.182500 mol	413·10 ⁻⁶ mol					
x _{n5}	999.960186·10 ³ ppm	0.174 ppm					
m _n	1069.6247 g	0.0116 g					
M _n	28.01348000 g/mol	5.00·10 ⁻⁶ g/mol	50	3.52	17.6·10 ⁻⁶ ppb	0.00	0.000
M ₂	54.09044 g/mol	1.62·10 ⁻³ g/mol	50	0.0	0.0 ppb	0.0	0.0
M ₃	84.932000 g/mol	976·10 ⁻⁶ g/mol	50	0.0	0.0 ppb	0.0	0.0
M ₄	119.37670 g/mol	1.39·10 ⁻³ g/mol	50	0.0	0.0 ppb	0.0	0.0
M ₅	98.95860 g/mol	1.21·10 ⁻³ g/mol	50	0.0	0.0 ppb	0.0	0.0
M ₆	78.44840 g/mol	2.42·10 ⁻³ g/mol	50	0.0	0.0 ppb	0.0	0.0
M ₇	131.38740 g/mol	1.55·10 ⁻³ g/mol	50	0.0	0.0 ppb	0.0	0.0
M ₈	165.83220 g/mol	1.95·10 ⁻³ g/mol	50	0.0	0.0 ppb	0.0	0.0
n _{tot5}	25.37192 mol	1.20·10 ⁻³ mol					
n ₂₅	125.854·10 ⁻⁶ mol	402·10 ⁻⁹ mol					
n ₃₅	123.104·10 ⁻⁶ mol	680·10 ⁻⁹ mol					
n ₄₅	126.054·10 ⁻⁶ mol	693·10 ⁻⁹ mol					
n ₅₅	126.881·10 ⁻⁶ mol	699·10 ⁻⁹ mol					
n ₆₅	124.862·10 ⁻⁶ mol	691·10 ⁻⁹ mol					
n ₇₅	125.100·10 ⁻⁶ mol	687·10 ⁻⁹ mol					
n ₈₅	128.692·10 ⁻⁶ mol	706·10 ⁻⁹ mol					
n _{nt5}	25.37091 mol	1.20·10 ⁻³ mol					
M _{tot15}	28.0196460 g/mol	18.3·10 ⁻⁶ g/mol					
x ₂₁₀₀	100.110 ppm	0.295 ppm					
m ₂₅	69.7287 g	0.0112 g					
M _{tot25}	28.039413	189·10 ⁻⁶ g/mol					

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr.-coeff.	Index
	g/mol						
x ₃₅₀	49.503 ppm	0.274 ppm					
x ₄₅₀	50.689 ppm	0.279 ppm					
x ₅₅₀	51.022 ppm	0.281 ppm					
x ₆₅₀	50.210 ppm	0.278 ppm					
x ₇₅₀	50.305 ppm	0.277 ppm					
x ₈₅₀	51.750 ppm	0.284 ppm					
n _{n15}	1.256901 mol	398·10 ⁻⁶ mol					
n _{n25}	2.486056 mol	399·10 ⁻⁶ mol					
n _{n35}	21.627951 mol	399·10 ⁻⁶ mol					
x _{n100}	999.796787·10 ³ ppm	0.583 ppm					
x _{n50}	999.696522·10 ³ ppm	0.153 ppm					
m _{n5}	605.8742 g	0.0112 g					
n _{tot100}	25.728005 mol	786·10 ⁻⁶ mol					
n ₂₁₀₀	2.57563·10 ⁻³ mol	7.66·10 ⁻⁶ mol					
n _{nt100}	25.722777 mol	775·10 ⁻⁶ mol					
M _{tot1100}	28.39144 g/mol	1.52·10 ⁻³ g/mol					
x ₁₀₆	0.63200 %	1.45·10 ⁻³ %					
x ₂₀₆	0.61365 %	1.47·10 ⁻³ %					
n _{n1100}	0.414492 mol	377·10 ⁻⁶ mol					
n _{n2100}	25.308285 mol	399·10 ⁻⁶ mol					
x _{n06}	98.75435 %	1.51·10 ⁻³ %					
n ₃₅₀	1.233018·10 ⁻³ mol	957·10 ⁻⁹ mol					
n _{tot50}	24.90804768 mol	9.14·10 ⁻⁶ mol					
n ₄₅₀	1.262567·10 ⁻³ mol	681·10 ⁻⁹ mol					
n ₅₅₀	1.270847·10 ⁻³ mol	821·10 ⁻⁹ mol					
n ₆₅₀	1.25063·10 ⁻³ mol	1.04·10 ⁻⁶ mol					
n ₇₅₀	1.253010·10 ⁻³ mol	619·10 ⁻⁹ mol					
n ₈₅₀	1.288987·10 ⁻³ mol	490·10 ⁻⁹ mol					
n _{n50}	24.90048862 mol	8.30·10 ⁻⁶ mol					
m ₃₅₀	0.1047227 g	81.2·10 ⁻⁶ g					
m ₄₅₀	0.1507211 g	81.2·10 ⁻⁶ g					

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr.-coeff.	Index
m ₅₅₀	0.1257612 g	81.2·10 ⁻⁶ g					
m ₆₅₀	0.0981098 g	81.2·10 ⁻⁶ g					
m ₇₅₀	0.1646297 g	81.2·10 ⁻⁶ g					
m ₈₅₀	0.2137555 g	81.2·10 ⁻⁶ g					
m _{n50}	697.549340 g	196·10 ⁻⁶ g	9	0.0	0.0 ppb	0.0	0.0
n ₁₀₆	0.159167 mol	179·10 ⁻⁶ mol					
n _{tot06}	25.184621 mol	386·10 ⁻⁶ mol					
n ₂₀₆	0.154546 mol	207·10 ⁻⁶ mol					
n _{n06}	24.87090751 mol	9.94·10 ⁻⁶ mol					
m ₁₀₆	9.9476 g	0.0112 g					
m ₂₀₆	8.3595 g	0.0112 g					
m _{n06}	696.720670 g	249·10 ⁻⁶ g	9	-0.138	-34.4·10 ⁻⁶ ppb	0.00	0.000
W _{bal1}	21.82958 g	3.01·10 ⁻³ g	7	4.43	0.0133 ppb	0.02	0.000
m _{n100}	708.9731 g	0.0112 g					
A _{Ratio}	0.96550	2.25·10 ⁻³	4	102	0.230 ppb	0.35	0.124
f _{press}	1.00000	1.00·10 ⁻³	50	98.6	0.0986 ppb	0.15	0.023
f _{ads2}	1.00000	5.00·10 ⁻³	50	98.6	0.493 ppb	0.75	0.570
f _{ads1}	1.00000	1.00·10 ⁻³	50	98.6	0.0986 ppb	0.15	0.023
□W _g	0.0 mg	10.0 mg	50	0.0244	0.244 ppb	0.37	0.139
W _{bal15}	35.225083 g	245·10 ⁻⁶ g	7	2.66	651·10 ⁻⁶ ppb	0.00	0.000
W _{bal25}	69.728708 g	431·10 ⁻⁶ g	7	-0.139	-59.8·10 ⁻⁶ ppb	0.00	0.000
W _{baln5}	605.874170 g	267·10 ⁻⁶ g	7	-0.139	-37.0·10 ⁻⁶ ppb	0.00	0.000
W _{bal1100}	11.916470 g	295·10 ⁻⁶ g	9	8.14	2.40·10 ⁻³ ppb	0.00	0.000
W _{baln100}	708.973130 g	278·10 ⁻⁶ g	9	-0.137	-38.0·10 ⁻⁶ ppb	0.00	0.000
W _{baln}	1069.62470 g	2.98·10 ⁻³ g	7	-0.0904	-270·10 ⁻⁶ ppb	0.00	0.000
W _{bal350}	0.1047227 g	50.0·10 ⁻⁶ g	50	0.0	0.0 ppb	0.0	0.0
W _{bal450}	0.1507211 g	50.0·10 ⁻⁶ g	50	0.0	0.0 ppb	0.0	0.0
W _{bal550}	0.1257612 g	50.0·10 ⁻⁶ g	50	0.0	0.0 ppb	0.0	0.0
W _{bal650}	0.0981098 g	50.0·10 ⁻⁶ g	50	0.0	0.0 ppb	0.0	0.0
W _{bal750}	0.1646297 g	50.0·10 ⁻⁶ g	50	0.0	0.0 ppb	0.0	0.0
W _{bal850}	0.2137555 g	50.0·10 ⁻⁶ g	50	0.0	0.0 ppb	0.0	0.0
W _{bal106}	9.947600 g	302·10 ⁻⁶ g	9	9.78	2.95·10 ⁻³ ppb	0.00	0.000
W _{bal206}	8.359467 g	362·10 ⁻⁶ g	9	-0.138	-49.9·10 ⁻⁶ ppb	0.00	0.000
□W _{had1}	0.0 mg	0.0500 mg	50	0.0	0.0 ppb	0.0	0.0
□W _{had2}	0.0 mg	5.00 mg	50	0.0244	0.122 ppb	0.19	0.035
C _{sample1}	98.641 ppb	0.653 ppb	91				

Result:

Quantity: C_{sample1}

Value: 98.6 ppb

Expanded uncertainty: ±1.3 ppb

Coverage factor: 2.0
 Coverage probability: 95.45%

Raw data of GC-FID in analysis of K-22 sample

1	CCQM	03092607	03092608	03092609	03092610	03092611	average	rsd %	u %	reported conc. (nmol/mol)
	Vinyl chloride	92.2	91.8	91.9	91.9	91.7	91.9	0.2	0.1	98.717
	1,3-butadiene	184.0	183.1	183.5	183.5	183.0	183.4	0.2	0.1	100.270
	Dichloromethane	41.6	41.6	41.7	41.6	41.6	41.6	0.1	0.0	101.699
	Chloroform	37.3	37.4	37.3	37.6	37.2	37.4	0.4	0.2	97.788
	1,2-Dichloroethane	95.4	96.2	95.9	95.9	97.1	96.3	0.7	0.3	100.790
	Benzene	257.7	258.2	258.1	258.1	258.0	258.0	0.1	0.0	92.053
	Trichloroethylene	97.9	98.2	98.2	98.2	''	98.1	0.1	0.1	103.944
	Tetrachloroethylene	92.1	92.1	92.2	92.2	92.2	92.2	0.1	0.0	95.373

1	CPB 29492	03092612	03092613	03092614	03092615	03092616	average	rsd %	u %	conc. (nmol/mol)
	Vinyl chloride	94.5	94.8	94.7	94.4	94.6	94.6	0.2	0.1	102.165
	1,3-butadiene	180.4	180.8	180.7	180.1	180.4	180.5	0.2	0.1	99.199
	Dichloromethane	39.5	39.6	39.5	39.3	39.5	39.5	0.3	0.1	97.032
	Chloroform	37.5	37.8	37.7	37.6	37.7	37.7	0.3	0.1	99.358
	1,2-Dichloroethane	98.9	97.7	97.7	97.8	99.0	98.1	0.7	0.3	101.719
	Benzene	274.3	275.2	275.2	274.0	274.6	274.7	0.2	0.1	98.418
	Trichloroethylene	92.6	92.9	92.8	92.5	92.6	92.7	0.2	0.1	98.605
	Tetrachloroethylene	97.0	97.6	97.9	97.5	97.6	97.5	0.3	0.2	101.437

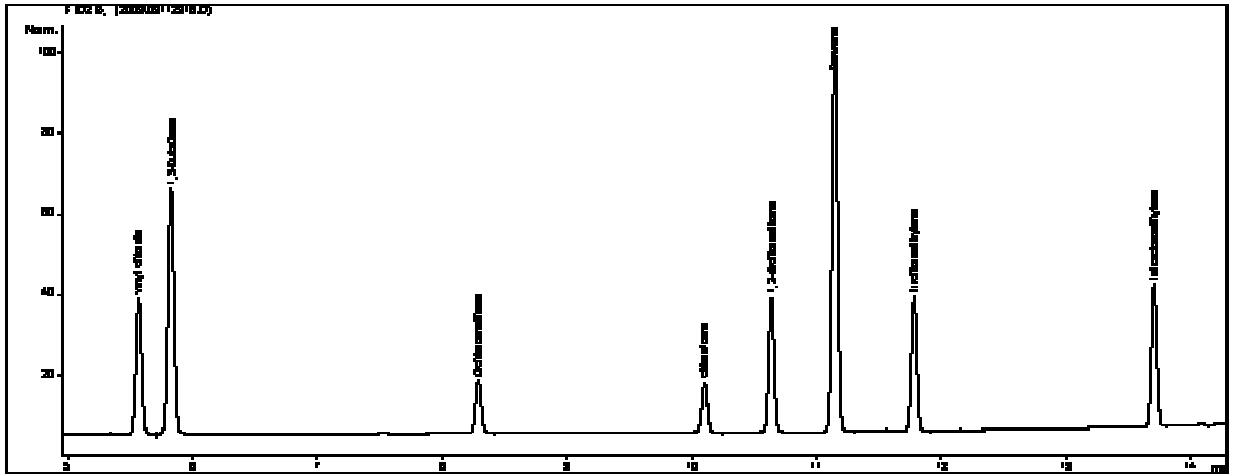
2	CCQM	03092906	03092907	03092908	03092909	03092910	average	rsd %	u %	reported conc. (nmol/mol)
	Vinyl chloride	91.8	90.7	91.8	90.9	91.8	91.4	0.6	0.3	98.035
	1,3-butadiene	183.1	181.1	183.2	181.6	183.4	182.5	0.6	0.3	99.597
	Dichloromethane	41.4	41.2	41.6	41.1	41.6	41.4	0.6	0.2	101.074
	Chloroform	37.4	36.8	37.2	36.7	37.3	37.1	0.8	0.4	97.112
	1,2-Dichloroethane	97.9	97.4	98.4	97.0	97.7	97.6	0.4	0.2	100.395
	Benzene	257.4	254.9	258.2	255.1	258.1	256.7	0.6	0.3	91.418
	Trichloroethylene	97.8	96.8	98.1	96.8	98.0	97.5	0.7	0.3	103.141
	Tetrachloroethylene	91.9	91.3	92.5	91.1	92.4	91.8	0.7	0.3	94.723

2	CPB 29492	03092911	03092912	03092913	03092914	03092915	average	rsd %	u %	conc. (nmol/mol)
	Vinyl chloride		95.9	94.6	95.9	94.5	95.2	0.8	0.4	102.165
	1,3-butadiene		182.9	180.5	182.9	180.2	181.6	0.8	0.4	99.199
	Dichloromethane		39.9	39.3	39.9	39.3	39.6	0.9	0.4	97.032
	Chloroform		38.1	37.6	38.2	37.6	37.9	0.8	0.4	99.358
	1,2-Dichloroethane		100.0	100.2	98.7	100.0	99.7	0.7	0.3	101.719
	Benzene		277.2	273.9	277.5	273.6	275.6	0.8	0.4	98.418
	Trichloroethylene		93.7	92.5	93.7	92.6	93.1	0.7	0.4	98.605
	Tetrachloroethylene		98.5	97.9	98.5	97.5	98.1	0.5	0.2	101.437

3	CCQM	03092916	03092917	03092918	03092919	03092920	average	rsd %	u %	reported conc. (nmol/mol)
	Vinyl chloride	91.3	91.1	92.3	91.1		91.5	0.6	0.3	98.355
	1,3-butadiene	182.1	181.8	184.2	181.8		182.5	0.6	0.3	99.885
	Dichloromethane	41.2	41.3	41.9	41.2		41.4	0.8	0.4	101.596
	Chloroform	37.0	37.0	37.5	36.9		37.1	0.7	0.4	97.654
	1,2-Dichloroethane	99.1	99.8	98.4	99.5		99.0	0.6	0.3	100.873
	Benzene	255.7	256.2	259.8	256.2		257.0	0.7	0.4	91.932
	Trichloroethylene	97.2	97.4	98.8	97.5		97.7	0.7	0.4	103.746
	Tetrachloroethylene	91.4	91.6	93.1	91.7		92.0	0.8	0.4	95.350

3	CPB 29492	03092921	03092922	03092923	03092924	03092925	average	rsd %	u %	conc. (nmol/mol)
	Vinyl chloride	95.0	95.4	94.2	95.3	93.9	94.8	0.7	0.3	102.165

1,3-butadiene	181.2	182.1	180.0	181.7	179.1	180.8	0.7	0.3	99.199	
Dichloromethane	39.6	39.7	39.2	39.7	39.2	39.5	0.7	0.3	97.032	
Chloroform	37.5	37.9	37.4	37.9	37.4	37.6	0.7	0.3	99.358	
1,2-Dichloroethane	100.3	100.1	98.8	100.1	100.1	99.9	0.6	0.3	101.719	
Benzene	275.0	276.3	272.7	276.6	272.7	274.7	0.7	0.3	98.418	
Trichloroethylene	92.8	93.1	92.0	93.3	92.0	92.6	0.7	0.3	98.605	
Tetrachloroethylene	97.3	98.2	96.9	98.2	97.1	97.5	0.6	0.3	101.437	
4	CCQM	03093006	03093007	03093008	03093009	03093010	average	rsd %	u %	reported conc. (nmol/mol)
	Vinyl chloride	93.2	92.9	91.8		92.9	92.7	0.7	0.3	99.414
	1,3-butadiene	186.0	185.5	183.6		185.8	185.2	0.6	0.3	101.032
	Dichloromethane	42.3	42.2	41.8		42.2	42.1	0.5	0.3	102.694
	Chloroform	38.0	37.8	37.3		37.7	37.7	0.8	0.4	98.561
	1,2-Dichloroethane	100.4	99.2	100.7		100.4	100.2	0.7	0.3	101.592
	Benzene	261.8	261.6	258.1		261.5	260.8	0.7	0.3	92.835
	Trichloroethylene	99.4	99.5	98.0		99.5	99.1	0.7	0.4	104.724
	Tetrachloroethylene	93.5	93.5	92.3		93.4	93.2	0.6	0.3	96.234
4	CPB 29492	03093011	03093012	03093013	03093014	03093015	average	rsd %	u %	conc. (nmol/mol)
	Vinyl chloride	94.6	96.0	94.7	95.9	94.7	95.2	0.7	0.3	102.165
	1,3-butadiene	180.9	183.2	180.7	182.9	180.7	181.7	0.7	0.3	99.199
	Dichloromethane	39.6	40.1	39.6	40.0	39.6	39.8	0.6	0.3	97.032
	Chloroform	37.5	38.2	37.7	38.2	37.7	37.9	0.8	0.4	99.358
	1,2-Dichloroethane	101.4	101.2	100.0	99.2	99.8	100.3	0.9	0.5	101.719
	Benzene	274.0	278.7	275.0	278.5	275.1	276.3	0.8	0.4	98.418
	Trichloroethylene	92.6	94.0	92.8	93.9	92.8	93.2	0.7	0.3	98.605
	Tetrachloroethylene	97.4	98.9	97.7	99.2	97.8	98.2	0.8	0.4	101.437
5	CCQM	03093016	03093017	03093018	03093019	03093020	average	rsd %	u %	reported conc. (nmol/mol)
	Vinyl chloride	92.3	92.4	91.2	91.0	92.1	91.8	0.7	0.3	98.672
	1,3-butadiene	184.1	184.7	182.2	181.7	184.0	183.3	0.7	0.3	100.243
	Dichloromethane	41.7	41.9	41.4	41.3	41.8	41.6	0.6	0.3	101.699
	Chloroform	37.5	37.5	37.0	37.0	37.5	37.3	0.7	0.3	97.992
	1,2-Dichloroethane	99.4	99.5	99.6	99.6	101.0	99.9	0.7	0.3	100.487
	Benzene	258.6	259.8	256.5	256.4	259.9	258.2	0.7	0.3	92.125
	Trichloroethylene	98.1	98.7	97.6	97.5	98.8	98.1	0.6	0.3	103.965
	Tetrachloroethylene	92.3	92.7	91.6	91.7	92.8	92.2	0.6	0.3	95.415
5	CPB 29492	03093021	03093022	03093023	03093024	03093025	average	rsd %	u %	conc. (nmol/mol)
	Vinyl chloride	95.6	94.7	95.6	94.4	94.3	94.9	0.7	0.3	102.165
	1,3-butadiene	182.5	180.8	182.5	180.2	179.9	181.2	0.7	0.3	99.199
	Dichloromethane	39.9	39.5	40.0	39.4	39.4	39.6	0.7	0.3	97.032
	Chloroform	37.9	37.6	38.2	37.6	37.6	37.8	0.7	0.3	99.358
	1,2-Dichloroethane	101.0	100.2	100.4	100.5	101.1	100.6	0.4	0.2	101.719
	Benzene	276.6	274.5	278.2	274.2	274.0	275.5	0.7	0.3	98.418
	Trichloroethylene	93.6	92.6	93.4	92.6	92.5	92.9	0.6	0.2	98.605
	Tetrachloroethylene	98.1	97.5	98.6	97.6	97.6	97.9	0.5	0.2	101.437



Cryogenic concentration GC-FID chromatograms of VOCs (8-HAP components),
Elution order: vinylchloride, 1,3-butadiene, dichloromethane, chloroform 1,2-
dichloroethane, benzene, trichloroethylene, tetrachloroethylene

Measurement report of NIST

Laboratory : NIST

Cylinder number : CPB27162

NOMINAL COMPOSITION : $90. \cdot 10^{-9} - 110. \cdot 10^{-9}$ mol/mol

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	11-18-03	96.4×10^{-9}	0.45	3
Chloroform	11-10-03	102.4×10^{-9}	0.93	3
Dichloromethane	11-10-03	103.7×10^{-9}	0.11	3
Trichloroethylene	11-10-03	111.2×10^{-9}	0.45	3
Tetrachloroethylene	11-18-03	101.3×10^{-9}	0.31	3
1,2-dichloroethane	11-10-03	101.8×10^{-9}	0.26	3
1,3-butadene	11-10-03	99.2×10^{-9}	0.16	3
Vinyl chloride	11-10-03	99.6×10^{-9}	0.18	3

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	11-19-03	96.2×10^{-9}	0.54	3
Chloroform	11-12-03	103.4×10^{-9}	1.20	3
Dichloromethane	11-12-03	102.9×10^{-9}	1.36	3
Trichloroethylene	11-12-03	109.5×10^{-9}	0.94	3
Tetrachloroethylene	11-20-03	100.8×10^{-9}	0.13	3
1,2-dichloroethane	11-12-03	100.5×10^{-9}	0.99	3
1,3-butadene	11-12-03	96.1×10^{-9}	0.65	3
Vinyl chloride	11-12-03	99.0×10^{-9}	0.43	3

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	11-20-03	96.6×10^{-9}	0.10	3
Chloroform	11-14-03	105.3×10^{-9}	0.11	3
Dichloromethane	11-14-03	104.3×10^{-9}	2.77	3
Trichloroethylene	11-14-03	114.3×10^{-9}	0.31	3
Tetrachloroethylene	12-03-03	99.2×10^{-9}	0.11	3
1,2-dichloroethane	11-14-03	103.9×10^{-9}	0.44	3
1,3-butadene	11-14-03	98.5×10^{-9}	0.02	3
Vinyl chloride	11-14-03	99.2×10^{-9}	0.18	3

Measurement No. 4	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	- -			

Chloroform	11-18-03	105.6 x 10 ⁻⁹	0.52	3
Dichloromethane				
Trichloroethylene	11-18-03	113.0 x 10 ⁻⁹	0.36	3
Tetrachloroethylene				
1,2-dichloroethane	11-18-03	102.9 x 10 ⁻⁹	0.48	3
1,3-butadene	11-20-03	98.5 x 10 ⁻⁹	0.11	3
Vinyl chloride	11-19-03	99.1 x 10 ⁻⁹	0.07	3

Measurement No. 5	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene				
Chloroform	11-19-03	102.7 x 10 ⁻⁹	0.82	3
Dichloromethane				
Trichloroethylene	11-19-03	110.1 x 10 ⁻⁹	0.73	3
Tetrachloroethylene				
1,2-dichloroethane	11-20-03	101.9 x 10 ⁻⁹	0.11	3
1,3-butadene				
Vinyl chloride				

Measurement No. 6	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene				
Chloroform	11-20-03	103.3 x 10 ⁻⁹	0.18	3
Dichloromethane				
Trichloroethylene	11-20-03	112.2 x 10 ⁻⁹	0.08	3
Tetrachloroethylene				
1,2-dichloroethane				
1,3-butadene				
Vinyl chloride				

Note: Please copy this table as many times as needed for reporting additional measurements

Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Benzene	96.4 x 10 ⁻⁹	2	1.7 x 10 ⁻⁹
Chloroform	103.8 x 10 ⁻⁹	2	2.9 x 10 ⁻⁹
Dichloromethane	103.6 x 10 ⁻⁹	2	1.7 x 10 ⁻⁹
Trichloroethylene	111.7 x 10 ⁻⁹	2	2.5 x 10 ⁻⁹
Tetrachloroethylene	100.4 x 10 ⁻⁹	2	1.7 x 10 ⁻⁹
1,2-dichloroethane	102.2 x 10 ⁻⁹	2	2.2 x 10 ⁻⁹
1,3-butadene	98.1 x 10 ⁻⁹	2	3.6 x 10 ⁻⁹

Vinyl chloride	99.2×10^{-9}	2	2.2×10^{-9}
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Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

An Agilent 6890 Gas Chromatograph equipped with a flame ionization detector (FID) and a 30m x 0.32mm capillary column coated with GS-GASPRO was used to determine the vinyl chloride, 1,3-butadiene, dichloromethane, chloroform, 1,2-dichloroethane, and trichloroethylene. An Entech 7100 cryogenic preconcentrator was used to collect 500 mL samples and inject them onto the capillary column.

An Agilent 6890 Gas Chromatograph equipped with a flame ionization detector (FID) and a 30m x 0.32mm capillary column coated with HP-5 was used to determine the chloroform, 1,2-dichloroethane, benzene, trichloroethylene and tetrachloroethylene. An Entech 7100 cryogenic preconcentrator was used to collect 500 mL samples and inject them onto the capillary column.

A HP 5890 Gas Chromatograph equipped with a flame ionization detector and a 2.44m x 0.32mm stainless steel column packed with 1% SP-1000 on 60/80 Carbopack B was used to determine vinyl chloride, 1,3-butadiene, dichloromethane and chloroform. A Nutech cryogenic preconcentrator was used to collect a 50 mL sample and inject onto the column. Peak area responses were determined using HP Chemstation software and sent to excel spreadsheets.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

Primary standards by gravimetry. Organics weighed into 2.5cm capillary tubes and weighed on a Mettler single pan balance with a 10^{-7} g resolution. 30-Liter volume aluminum cylinders weighed on a Mettler top-loading floor balance with a 1 g resolution. Purity analysis by GC and FTIR. Purity analysis done by GC/FID, GC/MS. Gravimetric standards uncertainty ≤ 0.60 %.

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.):

1st order linear regression calibration curve using 3-4 primary gravimetric standards (PSM) used: concentrations:

vinyl chloride: 34.41, 45.51, and 119.4×10^{-9} mol/mol (nmol/mol)
 1,3-butadiene: 94.81, 112.7, and 113.3×10^{-9} mol/mol (nmol/mol)
 dichloromethane: 90.57, 91.34, and 106.2×10^{-9} mol/mol (nmol/mol)
 chloroform: 62.10, 89.86, and 101.15×10^{-9} mol/mol (nmol/mol)
 1,2-dichloroethane: 90.56, 97.76, 99.26, and 101.5×10^{-9} mol/mol (nmol/mol)
 trichloroethylene: 89.89, 90.98, and 101.36×10^{-9} mol/mol (nmol/mol)
 benzene: 78.73, 95.80, 100.2, and 101.72×10^{-9} mol/mol (nmol/mol)
 tetrachloroethylene: 91.11, 101.9, and 102.2×10^{-9} mol/mol (nmol/mol)

measurement sequence: PSM₁, K22_{sample}, PSM₁, PSM₂, PSM₁, PSM₃, PSM₁, PSM_x, PSM₁
 PSM₁ used as a control to correct for instrument drift due to temperature and pressure fluctuations. Each sample or standard sampled a minimum of 3 consecutive times.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument. (automatic, high pressure, mass-flow controller, dilution etc.):

Cylinders transferred to laboratory in which measurements were taken to equilibrate temperature.

Low dead volume stainless steel regulators attached to cylinders. Heated sample lines from regulators to the cryogenic preconcentrator.

Uncertainty:

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

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

In support of this action, a list of potential uncertainty sources is given. This list may not be complete and is compiled from ISO-Standards, ISO-6142 and ISO-6143.

- a. Uncertainty related to the balance and mass pieces
 - Readability of balance.
 - Accuracy of balance including linearity.
 - Incorrect zero point.
 - Drift (thermal and time effects).
 - Instability due to draught.
 - Location of cylinder on the balance pan.
 - Errors in the mass pieces used.
 - Buoyancy effects on the weights used.
- b. Uncertainties related to the gas cylinder
 - Mechanical handling of cylinder due to:
 - loss of metal, paints or labels from surface of cylinder;
 - loss of metal from threads of valve/fitting;
 - dirt on cylinder, valves or associated fitting.
 - Adsorption/desorption effects on the external cylinder surface.
 - Buoyancy effects resulted from:
 - the cylinder itself;
 - differences in temperature of the cylinder from surrounding air due to e.g. filling with gas;
 - change of cylinder volume during filling;
 - change of density of air due to changes in temperature, air pressure, humidity, and carbon dioxide content.
 - Uncertainty in determination of external cylinder volume.
- c. Uncertainties related to the component gases
 - Residual gas in cylinder.
 - Leakage resulting from;
 - leakage of air into the cylinder after evacuation;
 - leakage of gas from the cylinder valve during filling;
 - escape of gas from cylinder into transport lines.
 - Gas remaining in transfer system when weight loss method is used.
 - Absorption/reaction of components on internal cylinder surface.
 - Reaction between components.
 - Impurities in the gases used.
 - Impurities in the parent gases.
 - Insufficient homogenization.
 - Uncertainty of molecular mass.
- d. Uncertainties related to the analysis
 - Repeatability and selectivity of the analyzer.
 - Appropriateness of the calibration curve:
 - response model and its residuals;
 - mismatch of the sample gas and the calibration gas.
 - Uncertainty related the corrections for the sampling:
 - change in atmospheric pressure, temperature, sample flow rate, and sampling time.

Uncertainty table: Benzene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight benzene	2.2×10^{-6} g	Gaussian	0.20 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
Benzene purity	<0.02	rectangular	0.012 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
Benzene in nitrogen	$<0.05 \times 10^{-9}$	rectangular	0.05 %	1	
Balance resolution	1×10^{-7}	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.54 %	1	
Calibration curve		Gaussian	0.71 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 1.8 % or 1.7×10^{-9} mol/mol

Uncertainty table: Chloroform

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight chloroform	2.5×10^{-6} g	Gaussian	0.15 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
chloroform purity	<0.18 %	rectangular	0.05 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
chloroform in N2	$<0.05 \times 10^{-9}$	rectangular	0.05 %	1	
Balance resolution	1×10^{-7}	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.93 %	1	
Calibration curve		Gaussian	1.01 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 2.8 % or 2.9×10^{-9} mol/mol

Uncertainty table: Dichloromethane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight CH ₂ Cl ₂	3.5 x 10 ⁻⁶ g	Gaussian	0.30 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
CH ₂ Cl ₂ purity	<0.009	rectangular	0.009 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
CH ₂ Cl ₂ in nitrogen	<0.05 x 10 ⁻⁹	rectangular	0.05 %	1	
Balance resolution	1 x 10 ⁻⁷	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.57 %	1	
Calibration curve		Gaussian	0.51 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 1.6 % or 1.7 x 10⁻⁹ mol/mol

Uncertainty table: Trichloroethylene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight C ₂ HCl ₃	1.7 x 10 ⁻⁶ g	Gaussian	0.10 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
C ₂ HCl ₃ purity	<0.20	rectangular	0.10 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
C ₂ HCl ₃ in nitrogen	<0.05 x 10 ⁻⁹	rectangular	0.05 %	1	
Balance resolution	1 x 10 ⁻⁷	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.73 %	1	
Calibration curve		Gaussian	0.80 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 2.2 % or 2.5 x 10⁻⁹ mol/mol

Uncertainty table: Tetrachloroethylene

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Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight C ₂ Cl ₄	3.6 x 10 ⁻⁶ g	Gaussian	0.16 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
C ₂ Cl ₄ purity	<0.032	rectangular	0.001 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
C ₂ Cl ₄ in nitrogen	<0.05 x 10 ⁻⁹	rectangular	0.05 %	1	
Balance resolution	1 x 10 ⁻⁷	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.31 %	1	
Calibration curve		Gaussian	0.6 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 1.7 % or 1.7 x 10⁻⁹ mol/mol

Uncertainty table: 1,2-dichloroethane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight C ₂ H ₂ Cl ₄	2.5 x 10 ⁻⁶ g	Gaussian	0.18 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
C ₂ H ₂ Cl ₄ purity	<0.001	rectangular	0.001 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
C ₂ H ₂ Cl ₄ in nitrogen	<0.05 x 10 ⁻⁹	rectangular	0.05 %	1	
Balance resolution	1 x 10 ⁻⁷	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.48 %	1	
Calibration curve		Gaussian	0.96 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 2.2 % or 2.3 x 10⁻⁹ mol/mol

Uncertainty table: 1,3-butadiene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight 1,3-butadiene	1.6×10^{-6} g	Gaussian	0.17 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
1,3-butadiene purity	<0.1	rectangular	0.05 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
1,3-butadiene in N2	$<0.05 \times 10^{-9}$	rectangular	0.05 %	1	
Balance resolution	1×10^{-7}	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.65 %	1	
Calibration curve		Gaussian	1.5 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 3.7 % or 3.6×10^9 mol/mol

Uncertainty table: Vinyl chloride

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Weight vinyl chloride	1.2×10^{-6} g	Gaussian	0.12 %	1	
Weight nitrogen	1 g	Gaussian	0.02 %	1	
Vinyl chloride purity	<0.1	rectangular	0.05 %	1	
Nitrogen purity	<0.0005	rectangular	0.05 %	1	
Vinyl chloride in N2	$<0.05 \times 10^{-9}$	rectangular	0.05 %	1	
Balance resolution	1×10^{-7}	rectangular	0.01 %	1	
Weights		Gaussian	0.002 %	1	
Balance accuracy		Gaussian	0.001%	1	
Metal loss		rectangular	0.02 %	1	
Repeat analysis		Gaussian	0.43 %	1	
Calibration curve		Gaussian	1.0 %	1	

Coverage factor or degree of freedom: 2

Expanded uncertainty: 2.2 % or 2.2×10^9 mol/mol

Measurement report of NMI

Laboratory : NMi

Cylinder number : CPB-26346

NOMINAL COMPOSITION : $90 \cdot 10^{-9} - 110 \cdot 10^{-9}$ mol/mol

Measurement No. 1	Date	Result (mol/mol)	U, (k=2) (mol/mol)	number of sub-measurements
Benzene	21-10-2003	92.2E-9	4.5	5
Chloroform	21-10-2003	97.9E-9	4.4	5
Dichloromethane	21-10-2003	101.9E-9	4.0	5
Trichloroethylene	21-10-2003	103.1E-9	4.2	5
Tetrachloroethylene	21-10-2003	95.9E-9	4.9	5
1,2-dichloroethane	21-10-2003	93.6E-9	5.7	5
1,3-butadiene	14-10-2003	98.9E-9	2.9	5
Vinyl chloride	14-10-2003	100.2E-9	4.6	5

Measurement No. 2	Date	Result (mol/mol)	U, (k=2) (mol/mol)	number of sub-measurements
Benzene	22-10-2003	93.6E-9	3.9	5
Chloroform	22-10-2003	99.1E-9	3.1	5
Dichloromethane	22-10-2003	102.1E-9	3.1	5
Trichloroethylene	22-10-2003	106.2E-9	3.7	5
Tetrachloroethylene	22-10-2003	97.9E-9	4.3	5
1,2-dichloroethane	22-10-2003	93.0E-9	8.2	5
1,3-butadiene	15-10-2003	99.0E-9	2.5	5
Vinyl chloride	15-10-2003	102.3E-9	5.5	5

Measurement No. 3	Date	Result (mol/mol)	U, (k=2) (mol/mol)	number of sub-measurements
Benzene	23-10-2003	92.2E-9	3.1	5
Chloroform	23-10-2003	97.8E-9	3.0	5
Dichloromethane	23-10-2003	102.0E-9	3.8	5
Trichloroethylene	23-10-2003	104.7E-9	3.3	5
Tetrachloroethylene	23-10-2003	96.7E-9	3.3	5
1,2-dichloroethane	23-10-2003	96.6E-9	4.1	5
1,3-butadiene	16-10-2003	99.5E-9	2.5	5
Vinyl chloride	16-10-2003	101.0E-9	3.6	5

Results:

Gas mixture	result	Coverage factor	Assigned
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	(assigned value)		expanded uncertainty (%)
Benzene	92.7E-9	2	4.3
Chloroform	98.3E-9	2	3.7
Dichloromethane	102.0E-9	2	3.6
Trichloroethylene	104.7E-9	2	4.0
Tetrachloroethylene	96.8E-9	2	4.5
1,2-dichloroethane	94.4E-9	2	7.0
1,3-butadiene	99.1E-9	2	2.7
Vinyl chloride	101.2E-9	2	4.7

Reference Method:

The sampling and analysis of the sample (K22) gas mixture and of the calibration standards is done by sorbent tube/ thermal desorption/ capillary gas chromatography according to ISO 16017-1.

Gases are sampled using Perkin Elmer-type samplers. For the measurement of Benzene, Chloroform, Dichloromethane, Trichloroethylene, Tetrachloroethylene, 1,2-dichloroethane, the tube packing material is Chromosorb 106 (300mg). For 1,3-Butadiene and Vinyl Chloride the packing materials are Carbopack X (300 mg) and Unicarb (300 mg), respectively.

VOC gas mixtures are trapped onto the tubes by pumped sampling. A glass rig for parallel multi-point sampling is connected to sample gas mixture or to the calibration standards mixtures. Time, sampling flow, temperature and pressure are measured so that the exact volume of gas collected is known. A typical volume sampled is between 0.5 – 2 L, to avoid any breakthrough.

The trapped gases are then analyzed according to the analytical conditions indicated in table 1.

Table 1. Analytical conditions

Thermal desorption (PE ATD-400 with autosampler, cold trap sorbent: Tenax GR)	<p><i>Unicarb and Carbopack X:</i> 1st desorption 300°C/-30°C, 5 min; 2nd desorption 225°C, 1 min; No inlet split, outlet split 10 ml/min, desorption flow 30 ml/min.</p> <p><i>Chromosorb 106:</i> 1st desorption 190°C/-30°C, 5 min; 2nd desorption 225°C, 1 min; No inlet split, outlet split 10 ml/min, desorption flow 30 ml/min.</p>
Gas chromatograph	PE Autosystem XL
Column	CP-Sil 5-CB, 60 m x 0.32 mm ID
Desorption technique	Thermal desorption of the cold trap (200 °C)
Elution flow	Helium, 18 psi head pressure
Run time	20 min
Temperature program	35°C, hold 2min, temp. rate 10°C/min to 100°C and 15°C/min to 250°C, hold 2min.
Detector	FID, 350 °C

Calibration Standards:

Calibration standards are prepared by dynamic volumetric method (ISO6145-part 5 capillary calibration devices for Benzene, Chloroform,

Dichloromethane, Trichloroethylene, Tetrachloroethylene and 1,2-dichloroethane and ISO 6145-part 7 thermal mass flow controllers for 1,3-Butadiene and Vinyl Chloride).

In detail, the generation of standard atmospheres is performed by dynamic dilution in zero air of vapours of pure compounds having constant flow. The constant flow is obtained either by means of a capillary tube under conditions of constant pressure drop or by a calibrated mass flow controller.

A known volume of standard atmosphere is then trapped into the sorbent tubes by pumped sampling (as described above) and serves as calibration standard. All procedures are fully traceable to SI units.

For the preparation of Benzene, Chloroform, Dichloromethane, Trichloroethylene, Tetrachloroethylene and 1,2-dichloroethane calibration standards, two independent standard gas atmospheres were generated from the dynamic dilution of two gravimetrically prepared liquid mixtures into zero air. In total 5 calibration levels were obtained by trapping different measured volumes of gas into sorbent tubes (2 standards per level) so that the amount loaded from the sample gas mixture (K22) is within the range. Five levels of calibrations standards for Vinyl Chloride and 1,3-Butadiene (2 standards per level) were prepared by pumped sampling of different volumes of a standard atmosphere obtained by dilution of a gravimetric gas mixture (ISO 6142) in zero air. The gravimetric gas mixture was prepared in house using a Scott Specialty Gases ACULife 5 L cylinder.

The purities of the liquids, of the pure gases and of the nitrogen balance gas used for the preparation of the calibrations standards were checked in the laboratory and agreed with the manufacturer's specifications. The zero air was checked by an online GC and showed no traces of the VOCs (above 0,1 ppb (v/v)).

The sorbent tubes were cleaned before use and a blank check was done in order to confirm the absence of VOC traces (below 1 ng).

Instrument Calibration:

Measurement procedure:

First the components 1,3-Butadiene and Vinyl Chloride were analyzed. Secondly, the components Benzene, Chloroform, Dichloromethane, Trichloroethylene, Tetrachloroethylene and 1,2-dichloroethane were measured together. All raw data obtained for each component were individually processed.

Three series of measurements (calibration + sample measurement) were performed. The analysis of each series took one day and it consisted of the measurement of the calibration standards (2x per calibration level, five levels) and the K22 samples (5 sorbent tubes were loaded from the sample cylinder for each series of measurements and analyzed).

The mathematical model adopted for each component and for each series of measurements was a weighted linear regression of y on x , where y represents the mean response (peak area) of the GC measurements of the calibration standards and x its amount (mass). The weights given to the y -values of the curve are inversely proportional to their variances.

The results, reported in the tables above, are the average values of each series of measurements while the table with the final results is the mean of the mean results of each series.

Sample Handling:

The cylinder arrived August 2003 and it was kept in the laboratory where the analysis was done at a temperature of $20.0 \pm 0.5^\circ\text{C}$.

Uncertainty:

For each series of measurements, the sample concentration and its expanded uncertainty ($k=2$) are calculated (see tables). The contributions to the uncertainty (standard preparation and analytical measurement) have approximately the same weight for most of the

components with exception of 1,2-Dichloroethylene, where the uncertainty of the analysis has a major influence in all three series of measurements.

The estimated standard uncertainty of the calibration standards is calculated from the uncertainty in the preparation of the standard atmospheres, the uncertainty on the sampling into sorbent tubes and the purity of the pure compounds.

The uncertainty of the analysis takes into account the calibration (lack-of-fit uncertainty) and the repeatability variance of the K22 sample response.

The uncertainty of the final result is the pooled estimate of uncertainty of the three series added of the mean standard deviation of the measurement results of the three series. The reported expanded uncertainty is expressed in percentage and has a coverage factor $k=2$.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

In support of this action, a list of potential uncertainty sources is given. This list may not be complete and is compiled from draft ISO-Standards currently under development in ISO/TC158

a. Uncertainty related to the balance and the weights:

- Resolution of balance
- Accuracy of balance including linearity
- Incorrect zero point
- Drift (thermal and time effects)
- Instability due to draught
- Location of cylinder on the balance pan
- Uncertainties in the weights used
- Buoyancy effects on the weights used

b. Uncertainties related to the gas cylinder:

- Mechanical handling of cylinder
 - Loss of metal, paints or labels from surface of cylinder
 - Loss of metal from threads of valve/fitting
 - Dirt on cylinder, valves or associated fitting
- Adsorption/desorption effects on the external cylinder surface
- Buoyancy effects on the cylinder itself
 - Cylinder temperature differs from surrounding air due to e.g. filling with gas
 - Change of cylinder volume during filling
 - Change of density of surrounding air due to changes in temperature, air pressure,
 - Humidity and carbon dioxide content
- Uncertainty in determination of external cylinder volume

c. Uncertainties related to the component gases

- Residual gas in cylinder
- Leakage; Leakage of air into the cylinder after evacuation
 - Leakage of gas from the cylinder valve during filling
 - Escape of gas from cylinder into transport lines
- Gas remaining in transfer system when weight loss method is used
- Absorption/reaction of components on internal cylinder surface
- Reaction between components
- Impurities in the gases used
- Impurities in the component gases
- Impurities present in the balance gas (or in other components)
- One or more of the mixture components present in other component gases
- Insufficient homogenization
- Uncertainty of molecular mass

d. Uncertainties related to the analysis

- Repeatability and selectivity of the analyzer

Appropriateness of the calibration curve (model and its residuals)

Measurement report of CERI

Laboratory : National Metrology Institute of Japan (NMIJ) /
Chemicals Evaluation and Research Institute, Japan (CERI)

Cylinder number : CPB-28005

NOMINAL COMPOSITION : 90.10^{-9} – 110.10^{-9} mol/mol

Measurement No. 1	Date	Result ($\times 10^{-9}$ mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	25-08-03	93.86	0.04	3
Chloroform		99.76	0.05	
Dichloromethane		102.78	0.17	
Trichloroethylene		105.27	0.12	
Tetrachloroethylene		96.39	0.16	
1,2-dichloroethane		97.27	0.12	
1,3-butadiene		99.54	0.10	
Vinyl chloride		99.23	0.13	

Measurement No. 2	Date	Result ($\times 10^{-9}$ mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	26-08-03	94.31	0.15	3
Chloroform		99.74	0.10	
Dichloromethane		102.78	0.07	
Trichloroethylene		105.18	0.29	
Tetrachloroethylene		96.38	0.41	
1,2-dichloroethane		97.54	0.25	
1,3-butadiene		99.55	0.08	
Vinyl chloride		99.18	0.08	

Measurement No. 3	Date	Result ($\times 10^{-9}$ mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	27-08-03	94.17	0.20	3
Chloroform		99.86	0.14	
Dichloromethane		102.74	0.14	
Trichloroethylene		105.24	0.29	
Tetrachloroethylene		96.30	0.24	
1,2-dichloroethane		97.60	0.48	
1,3-butadiene		99.55	0.15	
Vinyl chloride		99.19	0.13	

Measurement No. 4	Date	Result (x10 ⁻⁹ mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	28-08-03	94.00	0.23	3
Chloroform		99.86	0.13	
Dichloromethane		102.64	0.07	
Trichloroethylene		105.18	0.22	
Tetrachloroethylene		96.26	0.19	
1,2-dichloroethane		97.42	0.27	
1,3-butadene		99.55	0.08	
Vinyl chloride		99.20	0.12	

Measurement No. 5	Date	Result (x10 ⁻⁹ mol/mol)	stand. deviation (% relative)	number of sub-measurements
Benzene	29-08-03	94.05	0.09	3
Chloroform		99.73	0.13	
Dichloromethane		102.77	0.13	
Trichloroethylene		105.22	0.19	
Tetrachloroethylene		96.31	0.13	
1,2-dichloroethane		97.25	0.24	
1,3-butadene		99.47	0.00	
Vinyl chloride		99.16	0.04	

Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Benzene	94.1	2	0.8
Chloroform	99.8		0.6
Dichloromethane	102.7		0.7
Trichloroethylene	105.2		0.9
Tetrachloroethylene	96.3		0.6
1,2-dichloroethane	97.4		1.5
1,3-butadene	99.5		0.5
Vinyl chloride	99.2		0.5

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

Instruments for VOCs gases measurement

Instrument 1: for Vinyl chloride, Dichloromethane and 1,3-butadiene

Principles : GC-FID (Type:GC-9A, Make : Shimadzu corporation)

Column : G-205 40mx1.2mm (Make CERI)

55 degree constant

He : 20ml/min

The gas concentrator (cold trap : tenax, sample 300ml

Type : GAS-10, Make : DKK corporation)

Data collection : output of integrator of data C-R6A (Shimadzu corporation)

Instrument 2: for Benzene, Chloroform, 1,2-dichloroethane, Trichloroethylene and Tetrachloroethylene

Principles : GC-FID (Type:GC-14B, Make : Shimadzu corporation)

Column : G-950 40mx1.2mm (Make CERI)

90 degree (30min) - (20 degree/min) - 190degree (5min)

He : 30ml/min

The gas concentrator (cold trap : tenax, sample 300ml

Type : GAS-10, Make : DKK corporation)

Data collection : output of integrator of data C-R7A (Shimadzu corporation)

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

preparation method: gravimetry

purity analyses: The impurities in a pure parent gas are determined by analyses and the amount of the major component is conventionally determined by,

$$X_{pure} = 1 - \sum_{i=1}^N x_i$$

where:

x_i = mole fraction of impurity i , determined by analysis

N = number of impurities likely in the final mixture

X_{pure} = mole fraction 'purity' of the 'pure' parent gas

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.):

Table 1 concentration of PSMs

Component	Concentration (mol/mol)
	R
Benzene	97.48 x 10 ⁻⁹
Chloroform	100.31 x 10 ⁻⁹
Dichloromethane	100.35 x 10 ⁻⁹
Trichloroethylene	100.69 x 10 ⁻⁹
Tetrachloroethylene	101.76 x 10 ⁻⁹
1,2-dichloroethane	98.34 x 10 ⁻⁹
1,3-butadiene	102.24 x 10 ⁻⁹
Vinyl chloride	104.53 x 10 ⁻⁹

Measurement sequence:

This procedure is for the determination of VOCs in a sample using a gas chromatograph and a gas concentrator.

- 1) Inject the calibration standard (R) into the column using a gas concentrator. Record the retention times and peak areas.
- 2) Inject the sample to be tested in same manner as the calibration standard. Record the retention times and peak areas.
- 3) Inject the calibration standard (R'). Record the retention times and peak areas.
- 4) Calculate the concentration of VOCs using the formula below.

$$Y = E \frac{2 A}{(B + C)}$$

where Y: Concentration of sample
 A: Concentration of standard (R and R')
 B: Standard (R) peak area
 C: Standard (R') peak area
 E: Sample peak area

Following above procedure, 3 measurements are repeated subsequently in a day and iterated for 5 days.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument. (automatic, high pressure, mass-flow controller, dilution etc).:

Stabilization : none
 Pressure : 100 kPa
 Sample flow : 100ml/min (mass-flow controller)
 Sample line temperature : 90 °C
 Dilution : none

Uncertainty:

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

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

In support of this action, a list of potential uncertainty sources is given. This list may not be complete and is compiled from ISO-Standards, ISO-6142 and ISO-6143.

- a. Uncertainty related to the balance and mass pieces
 - Readability of balance.
 - Accuracy of balance including linearity.
 - Incorrect zero point.
 - Drift (thermal and time effects).
 - Instability due to draught.
 - Location of cylinder on the balance pan.
 - Errors in the mass pieces used.
 - Buoyancy effects on the weights used.

Table 2 Uncertainty related to the balance and the weights

Item	weight of BTX	weights of N ₂
------	---------------	---------------------------

Readability of balance	0.01 mg	1 mg
Accuracy of balance including linearity	Less than 0.01 mg	Less than 1 mg
Incorrect zero point	none	none
Drift (thermal and time effects)	negligible	negligible
Instability due to draught	negligible	negligible
Location of cylinder on the balance pan	none	none
Errors in mass pieces used	4×10^{-5}	5×10^{-7}
Buoyancy effects on the weights used	negligible	negligible

b. Uncertainties related to the gas cylinder

Mechanical handling of cylinder due to:

Loss of metal, paints or labels from surface of cylinder: (1)

Loss of metal from threads of valve/fitting: negligible

Dirt on cylinder, valves or associated fitting: (2)

Adsorption/desorption effects on the external cylinder surface : (3)

Buoyancy effects resulted from:

the cylinder itself; : (4)

differences in temperature of the cylinder from surrounding air due to e.g. filling with gas;

change of cylinder volume during filling; (5)

change of density of air due to changes in temperature, air pressure, humidity, and carbon dioxide content.

Uncertainty in determination of external cylinder volume.

For the combined standard uncertainties related to the weighing, including terms in a. and (1)-(5) of b., pooled standard uncertainty of 3 mg are used for the calculation.

c. Uncertainties related to the component gases

Residual gas in cylinder. : negligible

Leakage resulting from;

leakage of air into the cylinder after evacuation; : negligible

leakage of gas from the cylinder valve during filling; : negligible.

escape of gas from cylinder into transport lines : negligible.

Gas remaining in transfer system when weight loss method is used.

Absorption/reaction of components on internal cylinder surface: negligible.

Reaction between components: negligible.

Impurities in the gases used.

Impurities in the parent gases.

Component gases: Every component gases were produced by NMIJ. The purity of every component gases was over 99.9 %. The uncertainty of each component gases was 0.1%.

Dilution gas: The impurity of N₂ was analyzed by CERI. The uncertainty of N₂ was 99.9999%.

Insufficient homogenization: negligible.

Uncertainty of molecular mass: negligible.

d. Uncertainties related to the analysis

Repeatability and selectivity of the analyzer.

Appropriateness of the calibration curve:

Uncertainty of chemical analysis is calculated as a combined standard deviation of between-days and within-day components using the results of ANOVA.

e. Reproducibility of PSMs

The uncertainty of reproduced each components was included in combined uncertainty.

Uncertainty table: Benzene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	94.08	normal	0.20	1	0.20
Preparation of reference gas	97.48	normal	0.15	1	0.15
Reproducibility of reference gas	97.48	normal	0.30	1	0.30
					0.39

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0.8×10^{-9} mol/mol

Uncertainty table: Chloroform

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	99.79	normal	0.11	1	0.11
Preparation of reference gas	100.31	normal	0.15	1	0.15
Reproducibility of reference gas	100.31	normal	0.23	1	0.23
					0.30

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0.6×10^{-9} mol/mol

Uncertainty table: Dichloromethane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	102.74	normal	0.12	1	0.12
Preparation of reference gas	100.35	normal	0.15	1	0.15
Reproducibility of reference gas	100.35	normal	0.25	1	0.25
					0.32

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0.7×10^{-9} mol/mol

Uncertainty table: Trichloroethylene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	105.22	normal	0.20	1	0.20
Preparation of reference gas	100.69	normal	0.15	1	0.15
Reproducibility of reference gas	100.69	normal	0.35	1	0.35
					0.43

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0.9×10^{-9} mol/mol

Uncertainty table: Tetrachloroethylene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	96.33	normal	0.21	1	0.21
Preparation of reference gas	101.76	normal	0.15	1	0.15
Reproducibility of reference gas	101.76	normal	0.15	1	0.15
					0.30

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0.6×10^{-9} mol/mol

Uncertainty table: 1,2-dichloroethane

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	97.42	normal	0.29	1	0.29
Preparation of reference gas	98.34	normal	0.15	1	0.15
Reproducibility of reference gas	98.34	normal	0.66	1	0.66
					0.74

Coverage factor or degree of freedom: 2
Expanded uncertainty: 1.5×10^{-9} mol/mol

Uncertainty table: 1,3-butadiene

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	99.53	normal	0.09	1	0.09
Preparation of reference gas	102.24	normal	0.15	1	0.15
Reproducibility of reference gas	102.24	normal	0.16	1	0.16
					0.24

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0.5×10^{-9} mol/mol

Uncertainty table: Vinyl chloride

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability of analysis	99.19	normal	0.09	1	0.09
Preparation of reference gas	104.53	normal	0.15	1	0.15
Reproducibility of reference gas	104.53	normal	0.16	1	0.16
					0.24

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0.5×10^{-9} mol/mol

Measurement report of NPL

CCQM-K22 COMPARISON OF VOCs IN NITROGEN REPORT OF ANALYSIS FROM NPL

National Physical Laboratory,
Teddington, UK

D Alphonso, C Brookes, G Vargha and M J T Milton

March 04

Introduction

The standard submitted by CERI (CPB 28006) contained a mixture of 8 Hazardous Air Pollutants (HAPs) at 90 to 110 nmol/mol:

benzene, chloroform, dichloromethane, trichloroethylene, tetrachloroethylene,
1,2-dichloroethane, 1,3-butadiene, and vinyl chloride

(Acrylo-nitrile was also included in the pilot study, but was not included in the main part of CCQM K22). This report describes the analysis of this unknown at NPL by Gas Chromatography utilizing cryo-focussing against two pairs of independently-prepared gravimetric gas standards.

Preparation of Reference Standards

Four primary standards were prepared gravimetrically at NPL for this analysis. The standards in Sets A and B were prepared by different scientists with different equipment using independent procedures.

Amount Fraction [nmol/mol] of Primary Standards Prepared at NPL

GC REF:	CL209(a)	CL211(a)	CL210(b)	CL208(b)
Cyl no:	D23 4918	D23 4909	APE 201927	APE 201928
vinyl chloride	110.924	90.341	109.37	90.24
1,3-butadiene	110.589	90.068	109.04	89.97
dichloromethane	108.165	88.094	109.52	90.36
chloroform	110.426	89.935	108.73	89.71
1,2-dichloroethane	110.99	90.395	111.04	91.61
benzene	108.579	88.431	107.28	88.51
trichloroethylene	111.451	90.77	110.74	91.36
tetrachloroethylene	110.867	90.294	109.05	89.97

Purity Analysis

All of the pure liquids were analysed by GC on two different high-resolution capillary columns with an FID. They were all found to have a purity of at least 99.95%.

Air products “Quantum” cylinders were used for Set A and Scott Gases Aculife cylinders for Set B. The stability of ppb mixtures in these cylinders had been verified by NPL.

Procedure for the Preparation of Gravimetric Standards – Set A (CB)

1. 1% binaries of Vinyl Chloride and 1,3-Butadiene in nitrogen were made.
The masses were 28.5 and 23.9 g respectively, weighed with a resolution of 1 mg.
2. The Vinyl Chloride and 1,3-Butadiene at 1% were then combined and diluted to make a tertiary of 200 $\mu\text{mol/mol}$.
The mass of the binary mixture was 25g. It was weighed with a resolution of 1 mg.
3. The 6 liquids – Tetrachloroethylene, Trichloroethylene, Benzene, 1,2-Dichloroethane, Chloroform, and Dichloromethane – were combined gravimetrically in a vial.
The mass of each liquid was approximately 1 g, weighed with a resolution of 0.01 mg.
4. A small sample of the 6 liquids mixture was injected into a U-tube, and this was subsequently equilibrated and blown into an evacuated cylinder with cryogenically-dried nitrogen, to approximately 40 bar.
The mass of liquid mixture was approximately 150 mg, weighed with a resolution of 0.01 mg.
5. A small amount of the 200 $\mu\text{mol/mol}$ tertiary gas mix was added to this cylinder.
The mass of the tertiary mixture was approximately 30g. It was weighed with a resolution of 1 mg.
6. More nitrogen was added, to make an 8 component mixture at 5 $\mu\text{mol/mol}$.
The mass of nitrogen added was approximately 1250g. It was weighed with a resolution of 1 mg.
7. The 5 $\mu\text{mol/mol}$ mixture was then diluted to 90, 100, and 110 nmol/mol .
The mass of the 5 $\mu\text{mol/mol}$ mixture in each case was approximately 30g. It was weighed with a resolution of 1 mg.

Procedure for the Preparation of Gravimetric Standards – Set B (GV)

Step 1: Liquid components were added directly to an evacuated cylinder using a 1/8 inch diameter loop with a valve at each end. The mass of each component was approximately 250 mg and was weighed independently on a balance with a resolution of 0.01 mg. The loops were measured twice, before and after the addition. The composition of the first mixture can be seen below.

Component	%mol/mol
Nitrogen	99.9124
Dichloroethane	0.0148
Chloroform	0.0145
Dichloromethane	0.0146
Tetrachloroethane	0.0146
Benzene	0.0143
Trichloroethane	0.0148

Component	%mol/mol
nitrogen	99.9964
Dichloroethane	0.000462
Chloroform	0.000452
Dichloromethane	0.000456
Tetrchloroethane	0.000454
Benzene	0.000446
Trichloroethane	0.000461
Butadiene	0.000454
VynilChloride	0.000455

A mixture of 200 ppm butadiene and Vinyl Chloride in nitrogen was prepared using NPL's standard procedure for preparation of gas standards on a two-pan balance. The mass of each gas was approximately 60 g and the balance resolution was 1 mg.

Step 2: Using the two mixtures prepared in Step 1, the following mixture was prepared:

Step 3 & 4: Diluting the mixture prepared in Step 2 with Air Products BIP nitrogen purified on a freshly activated molecular sieve 5A scrubber the mixtures CL208(b) and CL210(b) were prepared (as listed above).

Analytical Equipment

Gas Chromatograph:	Varian 3600 fitted with Flame Ionisation Detector (FID)
GC Column:	50m x 0.53mm CP-Sil 5 CB (100% dimethyl polysiloxane)
Detector temperature:	FID 220 °C
Injector temperature:	Set at 220°C

Pre-concentration trap:	Tenax TA adsorbent Temperature variable from 0°C to a maximum of 220°C.
Column temperature:	30°C for 10 minutes, programme to 80°C at 5°C/min.
Carrier gas:	High purity helium 15ml/min
Detector gases:	Hydrogen 30ml/min and Air 300ml/min.
Sample volume:	60 cc
Sampling procedure:	Scott Low Volume Regulator & 1 needle valve
Data collection:	Varian Star Software

Analytical Procedure

- The GC inlet pipe-work, needle valves and low volume regulators were purged with ‘high purity’ nitrogen and an analysis of the nitrogen was performed as a blank run. The resulting chromatogram was examined for baseline stability and for any contaminants in the GC system.
- Sequence of CERI analysis:
 - 1st day: 4 analysis runs of CERI mixture and
4 runs of low concentration NPL standard (set A) and
4 runs of high concentration NPL standard (set A).
 - 2nd day: 4 analysis runs of CERI mixture and
4 runs of low concentration NPL standard (set B) and
4 runs of high concentration NPL standard (set B).
- The GC inlet system was purged with nitrogen and a blank run performed after each set of 4 CERI mixture and NPL calibration standard runs.
- The above sequence was repeated one week after the initial analytical runs.

Results

- Day 1 – analysis of CPB 28006 against set A

Species	k=1	
	Mole fraction [CB] μmol/mol	Combined uncertainty [CB] nmol/mol
1,3-butadiene	103.08	0.97
Dichloromethane	106.16	1.57
vinyl chloride	101.76	1.06
Chloroform	102.35	1.22
1,2-dichloroethane	102.68	1.07
Benzene	97.05	0.97
Trichloroethylene	109.09	1.33
Tetrachloroethylene	99.18	0.87

- Day 2 – analysis of CPB 28006 against set B

k=1	
Mole fraction [GV] nmol/mol	Combined uncertainty [GV] nmol/mol
102.77	0.90
107.77	1.06
101.55	0.87
101.28	1.00
101.04	1.33
97.11	0.81
108.91	1.28
98.79	1.03

Mean of Results on Days 1 and 2

Species	Mole fraction nmol/mol	Exp uncertainty nmol/mol
		k=2
1,3-butadiene	102.9	1.9
Dichloromethane	106.2	3.1
vinyl chloride	101.7	1.9
Chloroform	101.8	2.2
1,2-dichloroethane	101.9	2.4
Benzene	97.1	1.8
Trichloroethylene	109.0	2.6
Tetrachloroethylene	99.0	1.9

The comparison of dichloromethane in the set B standards was influenced by co-elution of an un-identified peak. Consequently, the final results for dichloromethane are the results of analysis against set A only.

Calculation and Uncertainty

Sources of uncertainty in the values of the reference standards prepared at NPL were:

- Cylinder stability.
- Purity of source materials.
- Bias in the gravimetric steps due to loss of material during transfer.

All of these uncertainties were of Type B and were estimated to have a total uncertainty of 1% . (The uncertainty in the weighing steps is at least an order of magnitude smaller than this). The uncertainty in the analysis was calculated from the standard deviation of the repeated measurements combined with the uncertainty in the reference values.

Additionally the two following sources of uncertainty were observed in the analysis step:

- The presence of approximately 4 ppb of unidentified impurities in the chromatogram of the unknown.
- Baseline valley separation in the unknown cylinder between vinyl chloride and 1,3-butadiene.

Measurement report of VNIIM

D.I.Mendeleev Institute for Metrology

RESEARCH DEPARTMENT FOR THE STATE MEASUREMENT STANDARDS IN THE FIELD OF PHYSICO-CHEMICAL MEASUREMENTS

REPORT

Key Comparisons CCQM-K22 (VOCs in nitrogen)

Authors: L.A.Konopelko
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I.M. Vishnyakov
V.V.Pankratov
O.V. Efremova

Reference method

Gas chromatography with flame ionization detection.

Instrument: Gas chromatograph "Crystal-5000.1", Chromatec;

High resolution capillary column: DB-1, 60 m × 0,53 mm, 1,5 μ, ser. N US2416414H, J α
W Scientific.

Data collection: Software support "Chromatec Analytic 2.0"

Calibration standards

Characteristics of pure substances used for preparation of the calibration standards are shown in table 1.

Table 1 – Description of pure components

Component	Molar fraction, ppm	Standard uncertainty, ppm	Relative standard uncertainty, %	Presence of cross-admixtures
Benzene	999200	50	0,005	were not detected
Chloroform	998500	250	0,025	Trichloroethylene - 0,01 % 1,3-butadiene 0,02 %
Dichloromethane	992700	100	0,01	Chloroform – 0,02 %
Trichloroethylene	998400	51	0,005	Chloroform – 0,02 % Dichloromethane - 0,0005 % Tetrachloroethylene - 0,1 %
Tetrachloroethylene	999900	50	0,005	Trichloroethylene – 0,003 %
1,2-dichloroethane	999800	250	0,025	Tetrachloroethylene - 0,03 % Vinyl chloride – 0,0006 %
1,3-butadiene*	—	—	—	—
Vinyl chloride	999900	102	0,01	were not detected
N ₂	999988,5	0,812	0,0000812	—

* 1,3-butadiene was not prepared in calibration standard, because of unsatisfactory quality of the original substance.

Aluminium cylinder, used for standard gas mixture preparation was trained beforehand with the appropriate mixture.

Preparation of calibration standard (7 components+N₂) at the required level of molar fractions was carried out in 3 stages:

1 stage: preparation of a) binary gas pre-mixture (Vinyl chloride) /N₂ with molar fraction 0,211 %;
 b) 6-liquid component mixture of Benzene (with molar fraction 16,66 %),
 Chloroform (with molar fraction 16,97 %),
 Dichloromethane (with molar fraction 16,28 %),
 Trichloroethylene (with molar fraction 16,26 %),
 Tetrachloroethylene (with molar fraction 16,64 %),
 1,2-dichloroethane (with molar fraction 17,17 %);

2 stage: preparation of 7 component (+N₂) pre-mixture at the components' mole fraction level of 10 ppm;

3 stage: preparation of final 7 component (+N₂) standard gas mixture at the components' mole fraction level of 100 ppb.

The characteristics of calibration standard are shown in table 2.

Table 2 – Characteristics of calibration standard

Cylinder N	Measured component	Molar fraction, (mol/mol)	Relative standard uncertainty, %
0474	Benzene	$100,8 \cdot 10^{-9}$	0,215
	Chloroform	$102,6 \cdot 10^{-9}$	0,211
	Dichloromethane	$98,4 \cdot 10^{-9}$	0,212
	Trichloroethylene	$98,3 \cdot 10^{-9}$	0,196
	Tetrachloroethylene	$100,7 \cdot 10^{-9}$	0,191
	1,2-dichloroethane	$103,9 \cdot 10^{-9}$	0,217
	1,3-butadiene	—	—
	Vinyl chloride	$104,0 \cdot 10^{-9}$	0,244
	N ₂	balance	

Instrument calibration:

The method of external standard (comparison method) was used.

There were made 4 independent measurements under repeatability conditions with 4 independent calibrations (in 4 days). One single measurement is derived from 3 to 5 sub-measurements. The measurement sequence was calibration→measurement

Temperature correction was not made - the valves were heated (80⁰ C).

Pressure changes were negligible (especially in comparison method) and were not taken into account.

Sample handling

Prior to measurements cylinders were stabilized to room temperature.

The samples were transferred to Gas-chromatograph through the heated valve with sample loop (V=1 cm³), i.e. direct dosing to the instrument.

Evaluation of uncertainty of measurement

Table 3 – Evaluation of uncertainty of Benzene molar fraction in the 7 component (+N₂) standard gas mixture (100,8 ppb – cylinder № 0474)

Value X_i	Estimation, x_i	Standard uncertainty $u(x_i)$, %
Pure components		
Molar fraction of Benzene ppm	999200	0,005
Molar fraction of N ₂ , ppm	999988,5	0,0000812
Preparation of the 6-liquid component mixture (1 stage)		
Mass of Benzene, g	0,46546	0,037
Preparation of the gas pre-mixture at the mole fraction level of 10 ppm (2 stage)		
Mass of the liquid mixture with Benzene, g	0,33512	0,051
Preparation of the final gas mixture at the mole fraction level of 100 ppb (3 stage)		
Mass of the gas pre-mixture with Benzene, g	5,001	0,034
Total standard uncertainty		0,0718
Expanded standard uncertainty ($k=3$)		0,215

Table 4– Evaluation of uncertainty of Chloroform molar fraction in the 7 component (+N₂) standard gas mixture (102,6 ppb – cylinder № 0474)

Value X_i	Estimation, x_i	Standard uncertainty $u(x_i)$, %
Pure components		
Molar fraction of Chloroform, ppm	998500	0,025
Molar fraction of N ₂ , ppm	999988,5	0,0000812
Preparation of the 6-liquid component mixture (1 stage)		
Mass of Chloroform, g	0,70970	0,024
Preparation of the gas pre-mixture at the mole fraction level of 10 ppm (2 stage)		
Mass of the liquid mixture with Chloroform, g	0,33512	0,051
Preparation of the final gas mixture at the mole fraction level of 100 ppb (3 stage)		
Mass of the gas pre-mixture with Chloroform, g	5,001	0,034
Total standard uncertainty		0,0704
Expanded standard uncertainty ($k=3$)		0,211

Table 5– Evaluation of uncertainty of Dichloromethane molar fraction in the 7 component (+N₂) standard gas mixture (98,4 ppb – cylinder № 0474)

Value X_i	Estimation, x_i	Standard uncertainty $u(x_i)$, %
Pure components		
Molar fraction of Dichloromethane, ppm	992700	0,010
Molar fraction of N ₂ , ppm	999988,5	0,0000812
Preparation of the 6-liquid component mixture (1 stage)		
Mass of Dichloromethane, g	0,50480	0,034
Preparation of the gas pre-mixture at the mole fraction level of 10 ppm (2 stage)		
Mass of the liquid mixture with Dichloromethane, g	0,33512	0,051
Preparation of the final gas mixture at the mole fraction level of 100 ppb (3 stage)		
Mass of the gas pre-mixture with Dichloromethane, g	5,001	0,034
Total standard uncertainty		0,0708
Expanded standard uncertainty ($k=3$)		0,212

Table 6– Evaluation of uncertainty of Trichloroethylene molar fraction in the 7 component (+N₂) standard gas mixture (98,3 ppb – cylinder № 0474)

Value X_i	Estimation, x_i	Standard uncertainty $u(x_i)$, %
Pure components		
Molar fraction of Trichloroethylene, ppm	998400	0,005
Molar fraction of N ₂ , ppm	999988,5	0,0000812
Preparation of the 6-liquid component mixture (1 stage)		
Mass of Trichloroethylene, g	0,78090	0,022
Preparation of the gas pre-mixture at the mole fraction level of 10 ppm (2 stage)		
Mass of the liquid mixture with Trichloroethylene, g	0,33512	0,051
Preparation of the final gas mixture at the mole fraction level of 100 ppb (3 stage)		
Mass of the gas pre-mixture with Trichloroethylene, g	5,001	0,034
Total standard uncertainty		0,0653
Expanded standard uncertainty ($k=3$)		0,196

Table 7– Evaluation of uncertainty of Tetrachloroethylene molar fraction in the 7 component (+N₂) standard gas mixture (100,7 ppb – cylinder № 0474)

Value X_i	Estimation, x_i	Standard uncertainty $u(x_i)$, %
Pure components		
Molar fraction of Tetrachloroethylene, ppm	999900	0,005
Molar fraction of N ₂ , ppm	999988,5	0,0000812
Preparation of the 6-liquid component mixture (1 stage)		
Mass of Tetrachloroethylene, g	0,98590	0,017
Preparation of the gas pre-mixture at the mole fraction level of 10 ppm (2 stage)		
Mass of the liquid mixture with Tetrachloroethylene, g	0,33512	0,051
Preparation of the final gas mixture at the mole fraction level of 100 ppb (3 stage)		
Mass of the gas pre-mixture with Tetrachloroethylene, g	5,001	0,034
Total standard uncertainty		0,0638
Expanded standard uncertainty ($k=3$)		0,191

Table 8– Evaluation of uncertainty of 1,2-dichloroethane molar fraction in the 7 component (+N₂) standard gas mixture (103,9 ppb – cylinder № 0474)

Value X_i	Estimation, x_i	Standard uncertainty $u(x_i)$, %
Pure components		
Molar fraction of 1,2-dichloroethane, ppm	999800	0,025
Molar fraction of N ₂ , ppm	999988,5	0,0000812
Preparation of the 6-liquid component mixture (1 stage)		
Mass of 1,2-dichloroethane, g	0,58850	0,029
Preparation of the gas pre-mixture at the mole fraction level of 10 ppm (2 stage)		
Mass of the liquid mixture with 1,2-dichloroethane, g	0,33512	0,051
Preparation of the final gas mixture at the mole fraction level of 100 ppb (3 stage)		
Mass of the gas pre-mixture with 1,2-dichloroethane, g	5,001	0,034
Total standard uncertainty		0,0723
Expanded standard uncertainty ($k=3$)		0,217

Table 9– Evaluation of uncertainty of Vinyl chloride molar fraction in the 7 component (+N₂) standard gas mixture (104,0 ppb – cylinder № 0474)

Value X_i	Estimation, x_i	Standard uncertainty $u(x_i)$, %
Pure components		
Molar fraction of Vinyl chloride, ppm	999900	0,010
Molar fraction of N ₂ , ppm	999988,5	0,0000812
Preparation of the gas pre-mixture Vinyl chloride/ N ₂ – 0,4727 % (1 stage)		
Mass of Vinyl chloride, g	2,461	0,069
Preparation of the gas pre-mixture at the mole fraction level of 10 ppm (2 stage)		
Mass of the gas pre-mixture with Vinyl chloride, g	6,762	0,025
Preparation of the final gas mixture at the mole fraction level of 100 ppb (3 stage)		
Mass of the gas pre-mixture with Vinyl chloride, g	5,001	0,034
Total standard uncertainty		0,0815
Expanded standard uncertainty ($k=3$)		0,244

Table 10 - Results of measurements of VOCs molar fraction in cylinder № CPB-28010

Measurement No. 1	Date (dd/mm/yy)	Result (mol/mol)	Stand. deviation (% relative)	Number of submeasurements
Benzene	17/12/03	$90,2 \cdot 10^{-9}$	1,2	4
Chloroform		$99,1 \cdot 10^{-9}$	1,6	4
Dichloromethane		$103,6 \cdot 10^{-9}$	2,2	4
Trichloroethylene		$104,1 \cdot 10^{-9}$	0,7	4
Tetrachloroethylene		$95,2 \cdot 10^{-9}$	0,9	4
1,2-dichloroethane		$96,8 \cdot 10^{-9}$	1,4	4
1,3-butadiene		—	—	—
Vinyl chloride		$100,6 \cdot 10^{-9}$	0,9	4

Measurement No. 2	Date (dd/mm/yy)	Result (mol/mol)	Stand. deviation (% relative)	Number of submeasurements
Benzene	19/12/03	$89,8 \cdot 10^{-9}$	1,2	4
Chloroform		$99,8 \cdot 10^{-9}$	1,7	4
Dichloromethane		$101,9 \cdot 10^{-9}$	2,4	4
Trichloroethylene		$103,9 \cdot 10^{-9}$	1,1	4
Tetrachloroethylene		$93,9 \cdot 10^{-9}$	1,6	4
1,2-dichloroethane		$95,9 \cdot 10^{-9}$	0,9	4
1,3-butadiene		—	—	—
Vinyl chloride		$100,0 \cdot 10^{-9}$	1,6	4

Measurement No. 3	Date (dd/mm/yy)	Result (mol/mol)	Stand. deviation (% relative)	Number of submeasurements
Benzene	22/12/03	$90,5 \cdot 10^{-9}$	0,5	5
Chloroform		$100,3 \cdot 10^{-9}$	4,3	5
Dichloromethane		$105,4 \cdot 10^{-9}$	3,2	5
Trichloroethylene		$102,9 \cdot 10^{-9}$	1,2	5
Tetrachloroethylene		$92,2 \cdot 10^{-9}$	1,3	5
1,2-dichloroethane		$95,9 \cdot 10^{-9}$	1,1	5
1,3-butadiene		—	—	—
Vinyl chloride		$100,3 \cdot 10^{-9}$	1,1	5

Measurement No. 4	Date (dd/mm/yy)	Result (mol/mol)	Stand. deviation (% relative)	Number of submeasurements
Benzene	24/12/03	$90,9 \cdot 10^{-9}$	0,6	3
Chloroform		$96,9 \cdot 10^{-9}$	1,5	3
Dichloromethane		$102,9 \cdot 10^{-9}$	0,5	3
Trichloroethylene		$103,8 \cdot 10^{-9}$	1,3	3
Tetrachloroethylene		$94,6 \cdot 10^{-9}$	1,1	3
1,2-dichloroethane		$96,9 \cdot 10^{-9}$	1,7	3
1,3-butadiene		—	—	—
Vinyl chloride		$99,6 \cdot 10^{-9}$	0,9	3

Table 11 – Estimation of uncertainty of Benzene molar fraction in gas mixture in cylinder

№ CPB-28010, presented for comparison

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y)$, %
Preparation of Benzene in final mixture	B	0,072	1	0,072
Calibration	A	0,309	1	0,309
Sorption of the components by cylinder's walls	A	0,219	1	0,219
Standard deviation of the result of measurement of Benzene molar fraction	A	0,258	1	0,258
Total standard uncertainty				0,464
Expanded uncertainty ($k=2$, $P=95$ %)				0,93

Table 12 – Estimation of uncertainty of Chloroform molar fraction in gas mixture in cylinder № CPB-28010, presented for comparison

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y)$, %
Preparation of Chloroform in final mixture	B	0,0704	1	0,0704
Calibration	A	0,565	1	0,565
Sorption of the components by cylinder's walls	A	0,40	1	0,40
Standard deviation of the result of measurement of Chloroform molar fraction	A	0,757	1	0,757
Total standard uncertainty				1,03
Expanded uncertainty ($k=2$, $P=95$ %)				2,06

Table 13 – Estimation of uncertainty of Dichloromethane molar fraction in gas mixture in cylinder № CPB-28010, presented for comparison

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y)$, %
Preparation of Dichloromethane in final mixture	B	0,0708	1	0,0708
Calibration	A	0,601	1	0,601
Sorption of the components by cylinder's walls	A	0,425	1	0,425
Standard deviation of the result of measurement of Dichloromethane molar fraction	A	0,713	1	0,713
Total standard uncertainty				1,03
Expanded uncertainty ($k=2$, $P=95$ %)				2,06

Table 14 – Estimation of uncertainty of Trichloroethylene molar fraction in gas mixture in cylinder № CPB-28010, presented for comparison

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y)$, %
Preparation of Trichloroethylene in final mixture	B	0,0653	1	0,0653
Calibration	A	0,38	1	0,38
Sorption of the components by cylinder's walls	A	0,27	1	0,27
Standard deviation of the result of measurement of Trichloroethylene molar fraction	A	0,256	1	0,256
Total standard uncertainty				0,536
Expanded uncertainty ($k=2$, $P=95$ %)				1,07

Table 15 – Estimation of uncertainty of Tetrachloroethylene molar fraction in gas mixture in cylinder № CPB-28010, presented for comparison

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y)$, %
Preparation of Tetrachloroethylene in final mixture	B	0,0638	1	0,0638
Calibration	A	0,433	1	0,433
Sorption of the components by cylinder's walls	A	0,306	1	0,306
Standard deviation of the result of measurement of Tetrachloroethylene molar fraction	A	0,690	1	0,690
Total standard uncertainty				0,873
Expanded uncertainty ($k=2$, $P=95$ %)				1,75

Table 16 – Estimation of uncertainty of 1,2-dichloroethane molar fraction in gas mixture in cylinder № CPB-28010, presented for comparison

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y)$, %
Preparation of 1,2 dichloroethane in final mixture	B	0,0723	1	0,0723
Calibration	A	0,451	1	0,451
Sorption of the components by cylinder's walls	A	0,319	1	0,319
Standard deviation of the result of measurement of 1,2-dichloroethane molar fraction	A	0,285	1	0,285
Total standard uncertainty				0,626
Expanded uncertainty ($k=2$, $P=95$ %)				1,25

Table 17 – Estimation of uncertainty of Vinyl chloride molar fraction in gas mixture in cylinder № CPB-28010, presented for comparison

Source of uncertainty	Type of	Standard uncertainty,	Coefficient of	Contribution
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	evaluation	$u(x_i)$, %	sensitivity	$U_i(y)$, %
Preparation of Vinyl chloride in final mixture	B	0,0815	1	0,0815
Calibration	A	0,398	1	0,398
Sorption of the components by cylinder's walls	A	0,281	1	0,281
Standard deviation of the result of measurement of Vinyl chloride molar fraction	A	0,213	1	0,213
Total standard uncertainty				0,538
Expanded uncertainty ($k=2$, $P=95$ %)				1,08

Table 18 – Final results of measurements

Obtained values of molar fraction of VOCs in gas mixture in cylinder № CPB-28010 and expanded uncertainties.

Component	Result (mol/mol)	Expanded Uncertainty, %	Coverage factor
Benzene	$90,4 \cdot 10^{-9}$	0,9	2,0
Chloroform	$99,0 \cdot 10^{-9}$	2,1	2,0
Dichloromethane	$103,5 \cdot 10^{-9}$	2,1	2,0
Trichloroethylene	$103,7 \cdot 10^{-9}$	1,1	2,0
Tetrachloroethylene	$94,0 \cdot 10^{-9}$	1,7	2,0
1,2-dichloroethane	$96,4 \cdot 10^{-9}$	1,3	2,0
1,3-butadiene	—	—	—
Vinyl chloride	$100,1 \cdot 10^{-9}$	1,1	2,0
N ₂	balance	—	—