International Comparison CCQM-K7

Final Report

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Field

Amount of Substance: Gas Standards

Subject

Comparison of primary gas standards containing benzene, toluene, ethylbenzene, *m*-xylene and *o*-xylene in a balance of nitrogen.

Participants

DE (UBA), FR (BNM), JP (NMIJ), KP (KRISS), NL (NMi), RF (VNIIM), UK (NPL), US (NIST)

Organizing body

CCQM Gas Standards Working Group

Background

This key comparison was intended to compare the capabilities for the preparation and value assignment of gas standards for benzene, toluene, ethylbenzene, *m*-xylene, and *o*-xylene in nitrogen (subsequently referred to as BTX), maintained at the participating national metrology institutes. The range of the nominal amount-of-substance fractions of the comparison standard is 50 nmol/mol to 100 nmol/mol, which is higher than regulations in most countries for allowable ambient quantities. Another BTX comparison (CCQM-K10) is planned to test the amount-of-substance fraction of 4 nmol/mol to 10 nmol/mol, which is closer to regulatory levels.

Conduct of the Comparison

The National Institute of Standards and Technology (NIST) prepared two 30-liter primary standard gas mixtures (PSM) of BTX in nitrogen using normal gravimetric procedures [1]. These two PSMs were then rigorously compared to other PSMs maintained at NIST to verify the gravimetrically determined amount-of-substance fraction. A total of eight 6-liter cylinders, treated with the proprietary deactivation process called Aculife-IV, were procured from Scott Specialty Gases in Plumsteadville PA.[1] These cylinders were filled through a gas manifold from one of the gravimetrically prepared PSMs. The cylinders were held at NIST for a two-month period and compared to the parent PSM to confirm that the BTX samples were stable.

Each participating laboratory was shipped one 6-liter cylinder. This cylinder was to be analyzed by the receiving laboratory and then returned to NIST. NIST then reanalyzed the cylinder contents to assure that the compounds remained stable throughout the comparison.

The comparison was officially declared closed at the gas working group meeting of November 29, 1999. All participating laboratories, except for KRISS and NMIJ, had submitted complete reports by this date. The data values reported by KRISS were received on November 27, 1999, in time for inclusion in a report to the working group on November 29, 1999. However, the KRISS report was incomplete since it did not contain an estimate of the expanded uncertainties. A subsequent report dated March 25, 2000 included adjusted data values and an estimate of the expanded uncertainties. KRISS had adjusted the data values after carefully considering purity, loss by absorption and incomplete evaporation. It was determined that since the comparison was officially closed before receipt of the latter report, only the expanded uncertainties would be accepted from that report, along with the originally submitted data values.

Due to a problem in shipping, Japan (NMIJ) did not receive the original gas mixture. It was determined that Japan would participate in a subsequent bilateral comparison with NIST. This comparison was completed in October 2000 and is included in this report. The comparison was conducted using the second gravimetric standard described above, not used in the original key comparison. The protocol used in this bilateral comparison was identical to that described in this report.

Gravimetric Preparation Calculations

The mass determination equation of the organic liquid using the method of filling and sealing glass capillary tubes is:

$$m_{Organic} = m_{Diff} + S_C + D_{Liquid} + D_{Vapor}$$

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[1] Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is and best available for the purpose.

where m_{Diff} is the mass difference of the full capillary and the empty capillary, S_C is a correction factor for loss of mass upon sealing, D_{Liquid} is the mass of air displaced by the liquid organic, and D_{Vapor} is the mass of air displaced by the organic vapor. The standard uncertainty of m_{Diff} is estimated from three repeat measurements of the mass of the capillary tube before and after filling. The value of S_C was estimated by sealing 10 empty capillaries and measuring the subsequent mass loss, and is equal to 0.8 μg with a standard uncertainty of 0.5 μg. The quantity D_{Liquid} is estimated using the mass of organic liquid (m_{Diff}), the organic liquid density, and the density of air. The standard uncertainty is estimated by combining the standard uncertainty of m_{Diff} and an estimated uncertainty of 1 % for the liquid density (rectangular distribution). The quantity D_{Vapor} is estimated using the vapor pressure of the organic and the gas equation (PV=nRT). Equilibrium conditions and ideal gas behavior are not assumed, thus only 50 % of the calculated equilibrium value is used, with an uncertainty equal to the estimated value.

The total moles of gas added to the cylinder is calculated by:

$$Z_{Balance} = \frac{m_{N_2}}{M_{N_2}} + \frac{m_{Air}}{M_{Air}} + \frac{m_{Organic}}{M_{Organic}}$$

The quantity m is the mass of nitrogen, air, or organic liquid added, and the quantity M is the associated molar mass. The amount of air is quite small, equal to approximately 0.15 % of the nitrogen mass. The amount of organic added is also very small, and was ignored in this calculation. The standard uncertainty of these mass determinations is 1 g, or approximately 0.02 % relative.

Finally the amount-of-substance fraction (concentration) is calculated using:

$$Concentration = \frac{\dfrac{(m_{Organic} \times P_{Organic})}{M_{Organic}} + N_{Organic}}{Z_{Balance}}$$

where $M_{Organic}$ is the molar mass of the organic liquid, $P_{Organic}$ is the purity of the organic liquid, $N_{Organic}$ is the moles of added BTX due to the balance gas, and $Z_{Balance}$ is the total moles of gas added. The molar masses are assumed to have relatively small uncertainties, which are ignored. The quantity $P_{Organic}$ was determined by gas chromatography with flame ionization detection, gas chromatography with mass selective detection, and by differential scanning calorimetry. The worst-case result was used as the purity estimate and the uncertainty was estimated to cover the interval over all the method results. The pure benzene, toluene and ethylbenzene were determined to be a minimum 99.90 % pure with a standard uncertainty of 0.06 %, and contained insignificant levels of BTX impurities (< 0.01 %). The o-xylene and m-xylene were found to be a minimum 99.60 % pure with a standard uncertainty of 0.05%.

The nitrogen dilution gas was labeled as 99.999 % pure with a maximum of 2 μmol/mol water and 5 μmol/mol oxygen. The nitrogen and room air were analyzed and found not to contain BTX to the detection limit of the method (0.05 nmol/mol). The standard uncertainty was estimated as the detection limit value.

The final combined uncertainty was expanded using a *k* factor of 2. The gravimetric amount-of-substance fraction and expanded uncertainty for the BTX are listed in Table 1. These uncertainties do not take into account the uncertainties of the cylinder treatment, potential problems due to transport and storage temperatures, and potential problems with the external connections made by the receiving laboratory. Therefore it is NIST's standard procedure to claim a 1 % relative expanded uncertainty for gravimetrically prepared organic standards.

Results

The distributed protocol instructed the participants to measure the concentration of the BTX in the cylinder with respect to their primary standards of BTX a minimum of three times.   The participating laboratories are listed in Table 2 along with the method used to analyze the BTX sample, and the date of the submitted report. In Tables 3 through 7, the participating laboratories reported concentrations and uncertainties are given along with the calculated relative difference from the gravimetric concentration. In the case of two cylinders, analyzed by NIST and KRISS, the BTX contents changed appreciably during the exercise. This degradation in concentration may be attributed to a failed cylinder treatment by the vendor from which the cylinders were procured, or the valve. This degradation is evident in the result submitted by NIST but is not evident in the KRISS results. It can only be concluded that the degradation occurred after KRISS analyzed the cylinder and before the reanalysis by NIST.

In Figures 1 through 5 the results are plotted in terms of the deviation in nmol/mol from the gravimetric value. The gravimetric value is represented by zero deviation. The uncertainty bars represent the expanded uncertainties at a level of confidence of 95 %, reported by the participant. Six of the seven participants had results that were within 5 % of the relevant reference values. The largest deviations were associated with the ethylbenzene analysis, which was probably due to the lack of experience with this compound. Ethylbenzene is not a regulated compound in most countries, and thus not normally analyzed. The relatively high concentration of this comparison may have also been a cause for higher deviations. Normal analytical methods in current use are optimized for the 1 nmol/mol to 10 nmol/mol concentration range, and therefore the higher concentrations were outside the optimum range for analysis.

Equivalence Statements

Key comparison reference value: there is no single reference value for this comparison, the value $x_{i\mathrm{grav}}$ (see Table 1, Amount fraction) is taken as the reference value for laboratory *i*.

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms;

D_i = $(x_i - x_{i\mathrm{grav}})$, the degree of equivalence, and $U_i = k\sqrt{u_i^2 + u_{igrav}^2}$, its

expanded uncertainty (where *k* = 2), both expressed in nmol/mol.

This calculation presents a problem with the UBA value, as they choose to use *k* = 3 to expand their standard uncertainty to a 95 % confidence interval. To provide consistency in the calculated degree of equivalence, we choose to calculate the standard uncertainty

(u_i) using the provided coverage factor, and then applied the above formula with $k = 3$ to calculate the expanded uncertainty of the degree of equivalence.

The degree of equivalence between two laboratories may be computed using $D_{ij} = D_i - D_j$, and its uncertainty;

$$U_{ij} = 2\sqrt{u^2(D_i) + u^2(D_j)} = 2\sqrt{\frac{U_i^2}{2^2} + \frac{U_j^2}{2^2}} = \sqrt{U_i^2 + U_j^2} \;,$$

where the factors 2 are coverage factors. In this particular case, the direct manipulation of the expanded uncertainties leads numerically to the same result as the path over the standard uncertainties. It is important to note that it is impossible to directly manipulate expanded uncertainties as if they were standard uncertainties. Calculations of the degree of equivalence between two laboratories involving UBA may not be computed using the above formula. This calculation is the subject of debate within the CCQM, and was not resolved at the time of this report.

References

1. G. C. Rhoderick and W. L. Zielinski, Jr., ”*Preparation of Accurate Multicomponent Gas Standards of Volatile Toxic Organic Compounds in the Low-Parts-per-Billion Range”*, Analytical Chemistry, 7(11), 1988.

Coordinator

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Project Reference:

CCQM-K7

Completion Date:

November 1999 (excluding Japan), and October 2000 (Japan)

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Table 1: Concentration of gravimetric primary standards

Compound	Amount fraction (nmol/mol)	Expanded Uncertainty (nmol/mol)	% Relative Uncertainty
CCQM-K7			
Benzene	56.94	0.19	0.33%
Toluene	79.76	0.17	0.21%
Ethylbenzene	83.82	0.17	0.20%
m-Xylene	92.77	0.16	0.18%
o-Xylene	60.90	0.14	0.23%
Bilateral - NIST/NMIJ (Japan)			
Benzene	44.95	0.20	0.45%
Toluene	76.64	0.16	0.21%
Ethylbenzene	68.81	0.13	0.19%
m-Xylene	92.89	0.16	0.18%
o-Xylene	66.40	0.14	0.22%

Table 2: Participating Laboratories analytical methods

Laboratory	Analytical Method	Analytical Standard	Sampled Volume (mL)	Trap Material	Date of Report
France (LNE)	GC-FID	Permeation Tube			Oct-99
Germany (UBA)	Cold Trap GC-FID	PSM	220	Carbotrap C	Nov-99
Japan (NMIJ)	Cold Trap GC-FID	PSM	240	Tenax	Oct-00
Korea (KRISS)	Cryotrap GC-FID	PSM	200	Glass Beads	Nov-99
Netherlands (NMi)	Cold Trap GC-FID	PSM	39	Tenax	Oct-99
Russia (VNIIM)	Cryotrap GC-FID	Permeation Tube	200	PDF	Nov-99
United Kingdom (NPL)	Cryotrap GC-FID	PSM	20	Tenax	Nov-99
USA (NIST)	Cryotrap GC-FID	PSM	100	1 mL SS Loop	Oct-99

Table 3: Results of CCQM K7: Comparison of Benzene

Laboratory	Submitted Analytical Result (nmol/mol)	k Factor	Submitted Expanded Uncertainty (nmol/mol)	Gravimetric Amount Fraction (nmol/mol)	Gravimetric Expanded Uncertainty (nmol/mol)	% Relative Difference
France (LNE)	58.2	2	3.00	56.94	0.19	2.2%
Germany (UBA)	58.6	3	2.10	56.94	0.19	2.9%
Japan (NMIJ)	44.9	2	1.49	44.95	0.20	-0.2%
Korea (KRISS)	59.0	2	2.40	56.94	0.19	3.6%
Netherlands (NMi)	56.0	2	1.10	56.94	0.19	-1.7%
Russia (VNIIM)	58.5	2	3.40	56.94	0.19	2.7%
United Kingdom (NPL)	57.3	2	1.90	56.94	0.19	0.6%
USA (NIST)	56.2	2	1.50	56.94	0.19	-1.3%

Figure 1. CCQM-K7
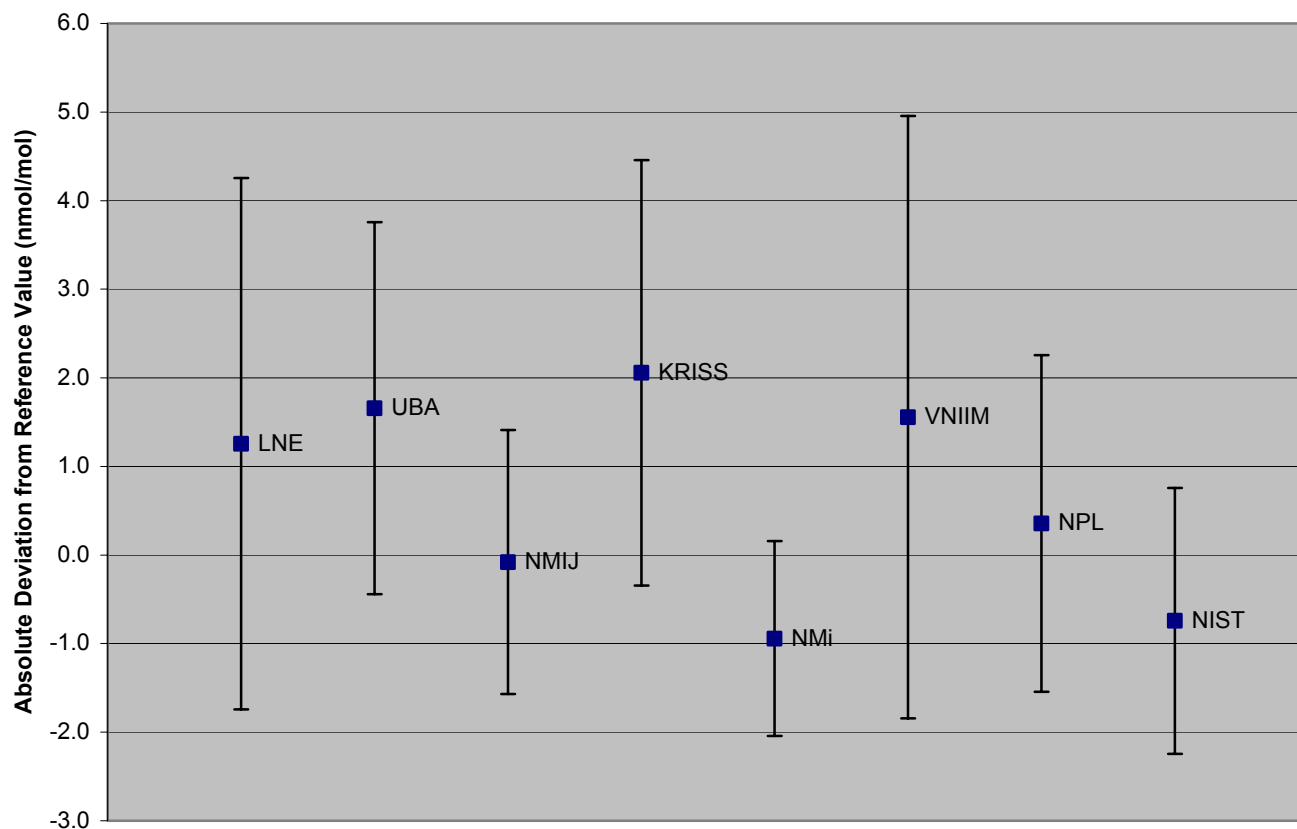**Comparison of benzene in nitrogen standards**

Table 4: Results of CCQM K7: Comparison of Toluene

Laboratory	Submitted Analytical Result (nmol/mol)	k Factor	Submitted Expanded Uncertainty (nmol/mol)	Gravimetric Amount Fraction (nmol/mol)	Gravimetric Expanded Uncertainty (nmol/mol)	% Relative Difference
France (LNE)	78.2	2	7.9	79.76	0.17	-2.0%
Germany (UBA)	78.5	3	2.9	79.76	0.17	-1.6%
Japan (NMIJ)	76.71	2	0.85	76.64	0.16	0.1%
Korea (KRISS)	81.5	2	2.8	79.76	0.17	2.2%
Netherlands (NMi)	80.0	2	1.0	79.76	0.17	0.3%
Russia (VNIIM)	75.0	2	4.4	79.76	0.17	-6.0%
United Kingdom (NPL)	80.1	2	2.6	79.76	0.17	0.4%
USA (NIST)	77.5	2	2.2	79.76	0.17	-2.8%

Figure 2. CCQM K7
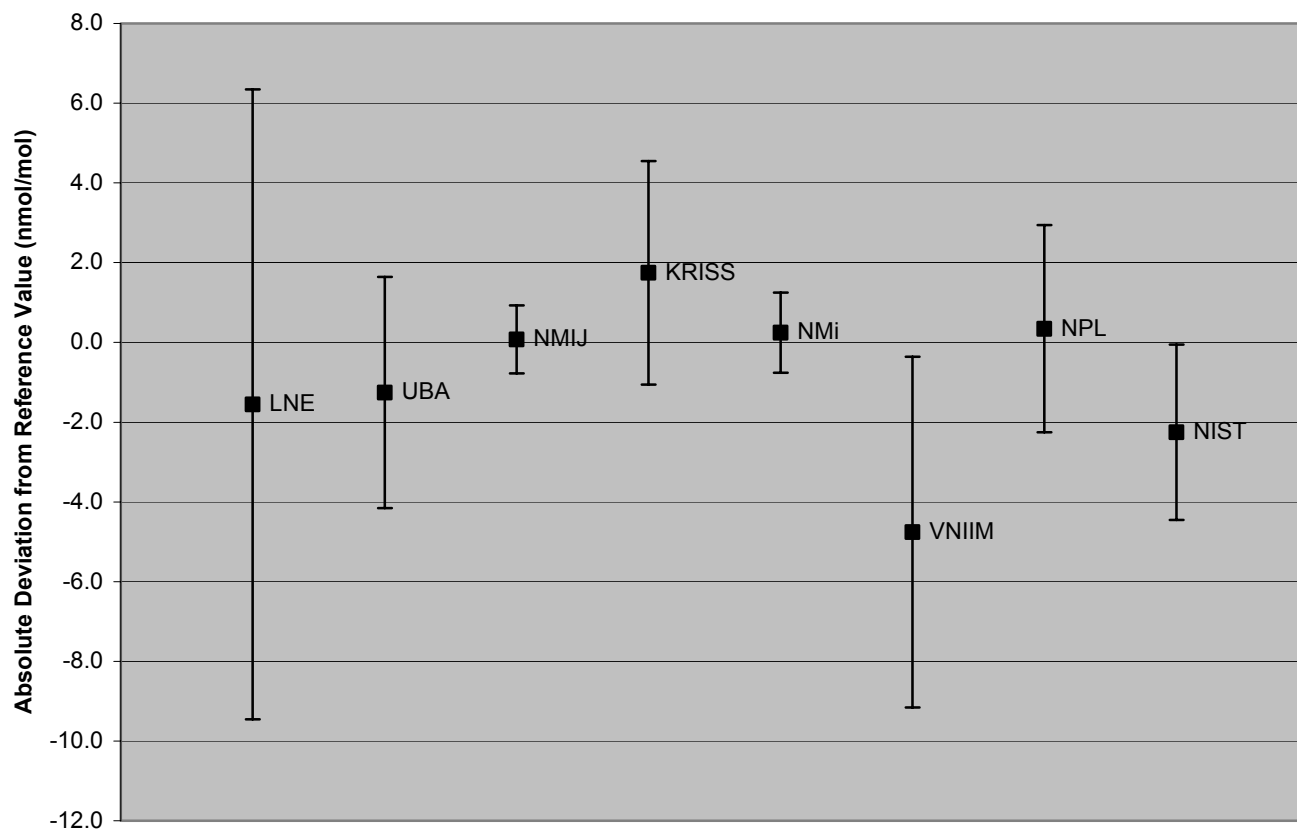**Comparison of toluene in nitrogen standards**

Table 5: Results of CCQM K7: Comparison of Ethylbenzene

Laboratory	Submitted Analytical Result (nmol/mol)	k Factor	Submitted Expanded Uncertainty (nmol/mol)	Gravimetric Amount Fraction (nmol/mol)	Gravimetric Expanded Uncertrainty (nmol/mol)	% Relative Difference
France (LNE)	70.6	2	5.9	83.82	0.17	-15.8%
Germany (UBA)	90.0	3	4.3	83.82	0.17	7.4%
Japan (NMIJ)	68.43	2	0.91	68.81	0.13	-0.5%
Korea (KRISS)	85.9	2	2.9	83.82	0.17	2.5%
Netherlands (NMi)	85.6	2	1.3	83.82	0.17	2.1%
Russia (VNIIM)	67.1	2	5.0	83.82	0.17	-19.9%
United Kingdom (NPL)	85.1	2	4.0	83.82	0.17	1.5%
USA (NIST)	78.7	2	2.9	83.82	0.17	-6.1%

Figure 3. CCQM K7
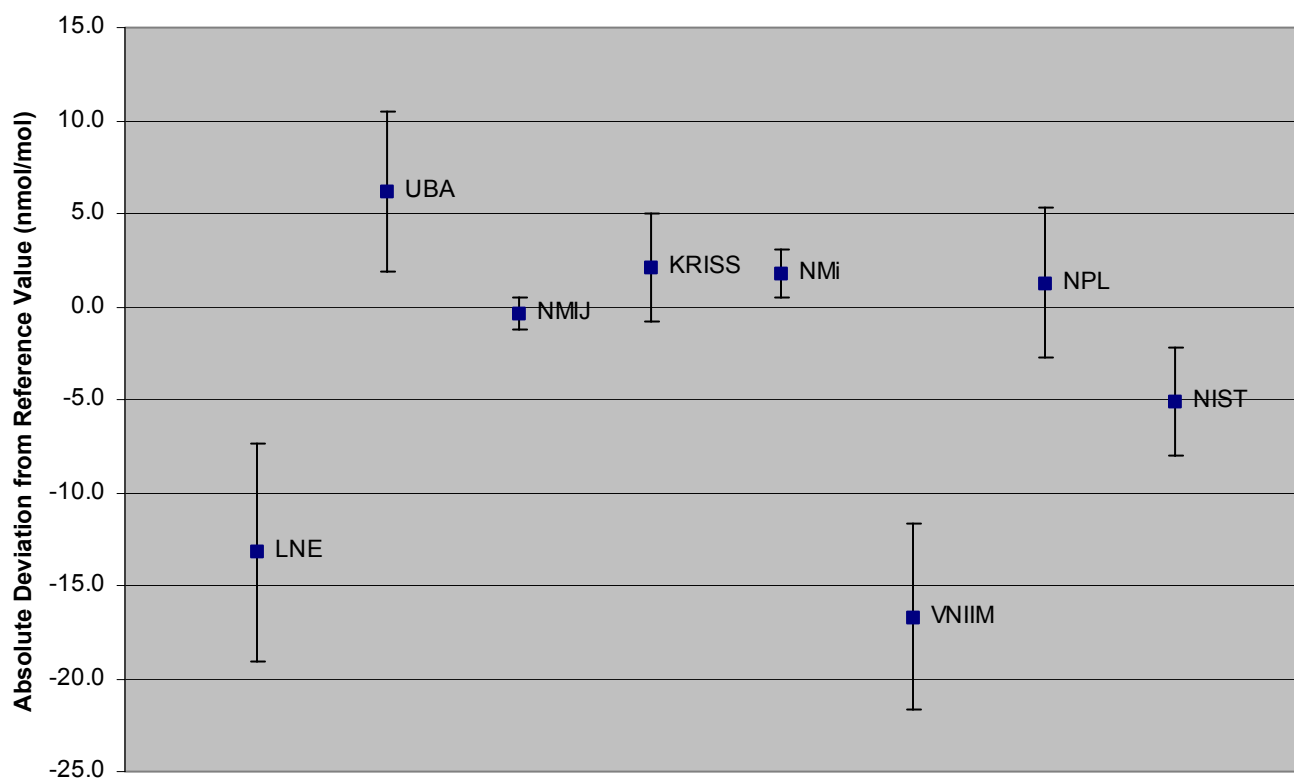Comparison of ethylbenzene in nitrogen standards

Table 6: Results of CCQM K7: Comparison of m-Xylene

Laboratory	Submitted Analytical Result (nmol/mol)	k Factor	Submitted Expanded Uncertainty (nmol/mol)	Gravimetric Amount Fraction (nmol/mol)	Gravimetric Expanded Uncertrainty (nmol/mol)	% Relative Difference
France (LNE)	91.9	2	7.8	92.77	0.16	-0.9%
Germany (UBA)	89.7	3	4.0	92.77	0.16	-3.3%
Japan (NMIJ)	91.70	2	0.97	92.89	0.16	-1.3%
Korea (KRISS)	95.1	2	3.2	92.77	0.16	2.5%
Netherlands (NMi)	95.2	2	1.3	92.77	0.16	2.6%
Russia (VNIIM)	75.6	2	5.4	92.77	0.16	-18.5%
United Kingdom (NPL)	94.2	2	4.5	92.77	0.16	1.5%
USA (NIST)	87.5	2	4.1	92.77	0.16	-5.7%

Figure 4. CCQM K7
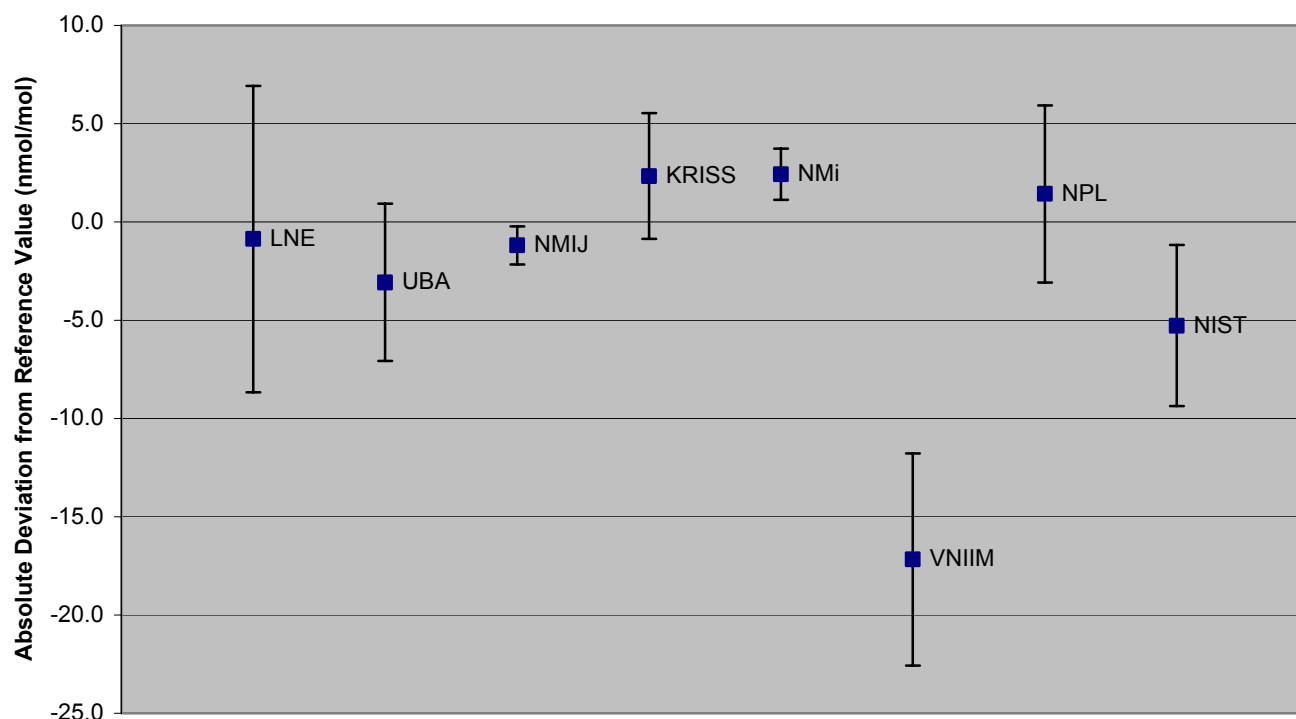**Comparison of m-xylene in nitrogen standards**

Table 7: Results of CCQM K7: Comparison of o-Xylene

Laboratory	Submitted Analytical Result (nmol/mol)	k Factor	Submitted Expanded Uncertainty (nmol/mol)	Gravimetric Amount Fraction (nmol/mol)	Gravimetric Expanded Uncertainty (nmol/mol)	% Relative Difference
France (LNE)	61.1	2	6.4	60.90	0.14	0.3%
Germany (UBA)	60.4	3	2.3	60.90	0.14	-0.8%
Japan (NMIJ)	65.05	2	0.90	66.40	0.14	-2.0%
Korea (KRISS)	61.8	2	2.1	60.90	0.14	1.5%
Netherlands (NMi)	62.4	2	1.1	60.90	0.14	2.5%
Russia (VNIIM)	48.6	2	4.8	60.90	0.14	-20.2%
United Kingdom (NPL)	61.2	2	2.9	60.90	0.14	0.5%
USA (NIST)	56.4	2	3.3	60.90	0.14	-7.4%

Figure 5. CCQM K7
Comparison of o-xylene in nitrogen standards
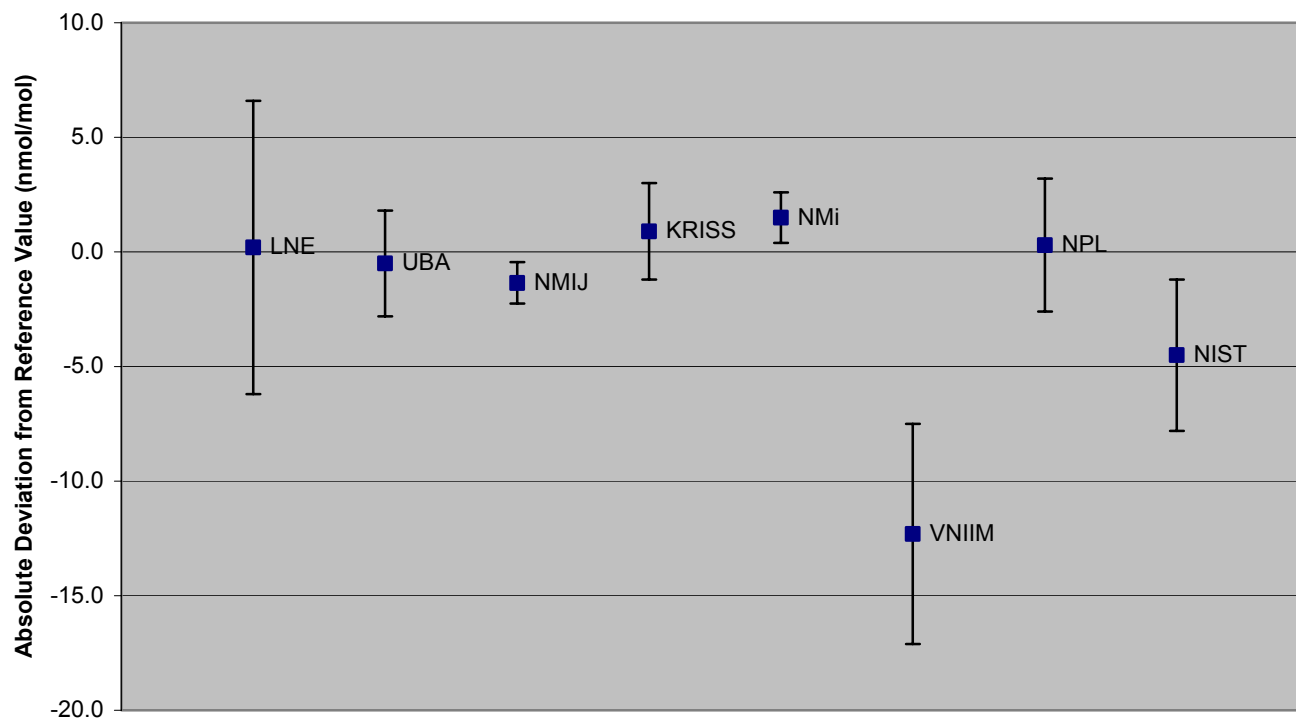
Annex 1 – Entry in Appendix B

Measurand: Benzene

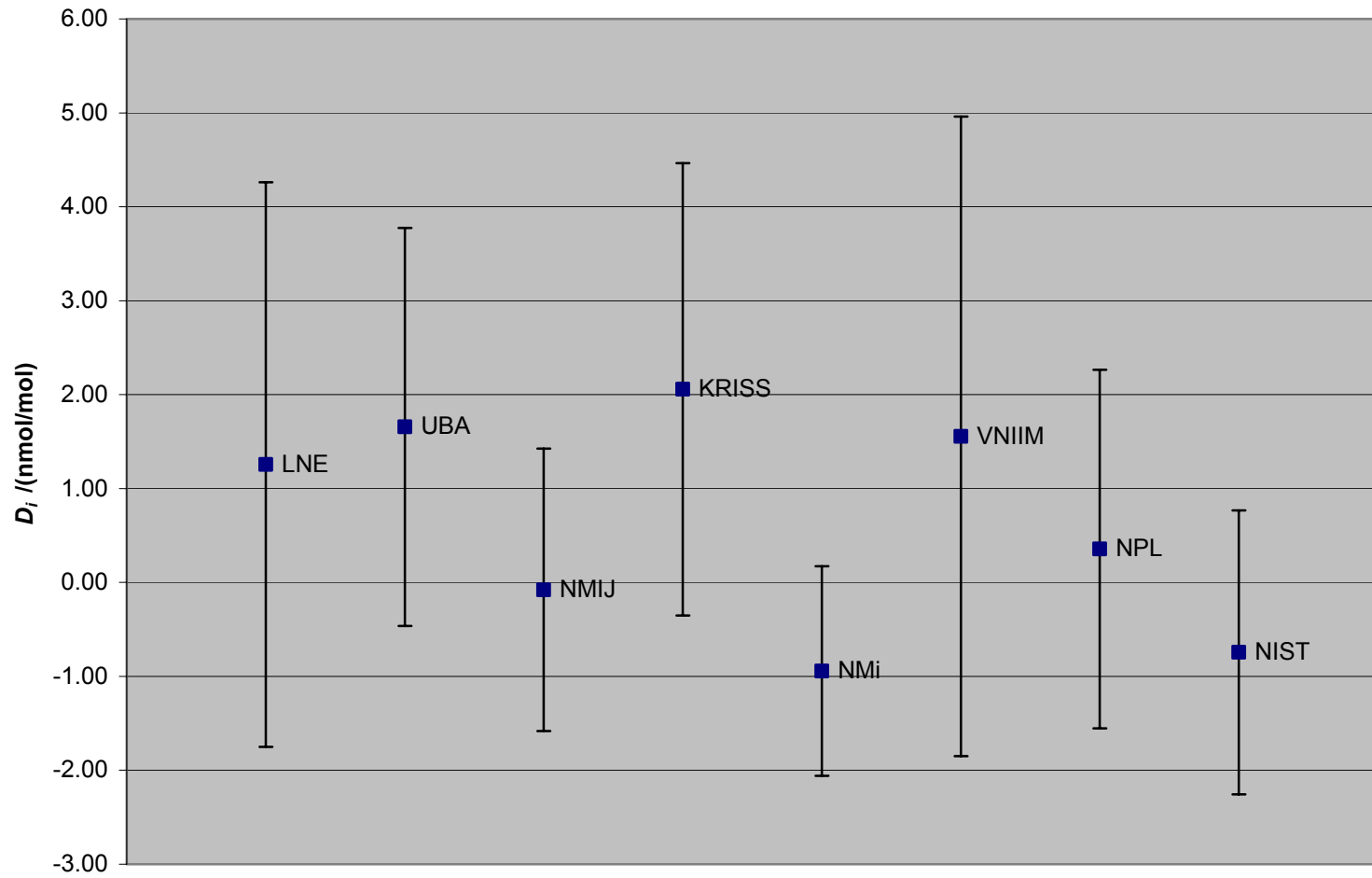x_i: result of measurement carried out by laboratory i

u_i combined standard uncertainty of x_i

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

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

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement
LNE	58.20	1.50	56.94	0.09	Oct-99
UBA	58.60	0.70	56.94	0.09	Nov-99
NMIJ	44.87	0.75	44.95	0.10	Oct-00
KRISS	59.00	1.20	56.94	0.09	Nov-99
NMi	56.00	0.55	56.94	0.09	Oct-99
VNIIM	58.50	1.70	56.94	0.09	Nov-99
NPL	57.30	0.95	56.94	0.09	Nov-99
NIST	56.20	0.75	56.94	0.09	Oct-99

CCQM-K7

Degrees of equivalence for benzene in nitrogen at nominal 50 nmol/mol

D_i /(nmol/mol)

6.00
5.00
4.00
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00

LNE

UBA

NMIJ

KRISS

NMi

VNIIM

NPL

NIST

Matrix of Equivalence

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

Nominal Value: 50 nmol/mol

Lab *i*	*D*$_i$	*U*$_i$
	nmol/mol	
LNE	1.26	3.01
UBA	1.66	2.12
NMIJ	-0.08	1.50
KRISS	2.06	2.41
NMi	-0.94	1.12
VNIIM	1.56	3.41
NPL	0.36	1.91
NIST	-0.74	1.51

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms; $D_i = (x_i - x_{igrav})$ and U_i, its expanded uncertainty.

The degree of equivalence between any two laboratories may be calculated by;
$D_{ij} = D_i - D_j$ and its expanded uncertainty;

$$U_{ij} = 2\sqrt{u^2(D_i) + u^2(D_j)} = 2\sqrt{\frac{U_i^2}{2^2} + \frac{U_j^2}{2^2}} = \sqrt{U_i^2 + U_j^2}$$

Note: Use of this equation is allowed for all laboratories except UBA, see report for explanation.

Measurand: Toluene

x_i: result of measurement carried out by laboratory i

u_i combined standard uncertainty of x_i

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

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

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement
LNE	78.20	3.95	79.76	0.08	Oct-99
UBA	78.50	0.97	79.76	0.08	Nov-99
NMIJ	76.71	0.43	76.64	0.08	Oct-00
KRISS	81.50	1.40	79.76	0.08	Nov-99
NMi	80.00	0.50	79.76	0.08	Oct-99
VNIIM	75.00	2.20	79.76	0.08	Nov-99
NPL	80.10	1.30	79.76	0.08	Nov-99
NIST	77.50	1.10	79.76	0.08	Oct-99

CCQM-K7
Degrees of equivalence for toluene in nitrogen at nominal 80 nmol/mol
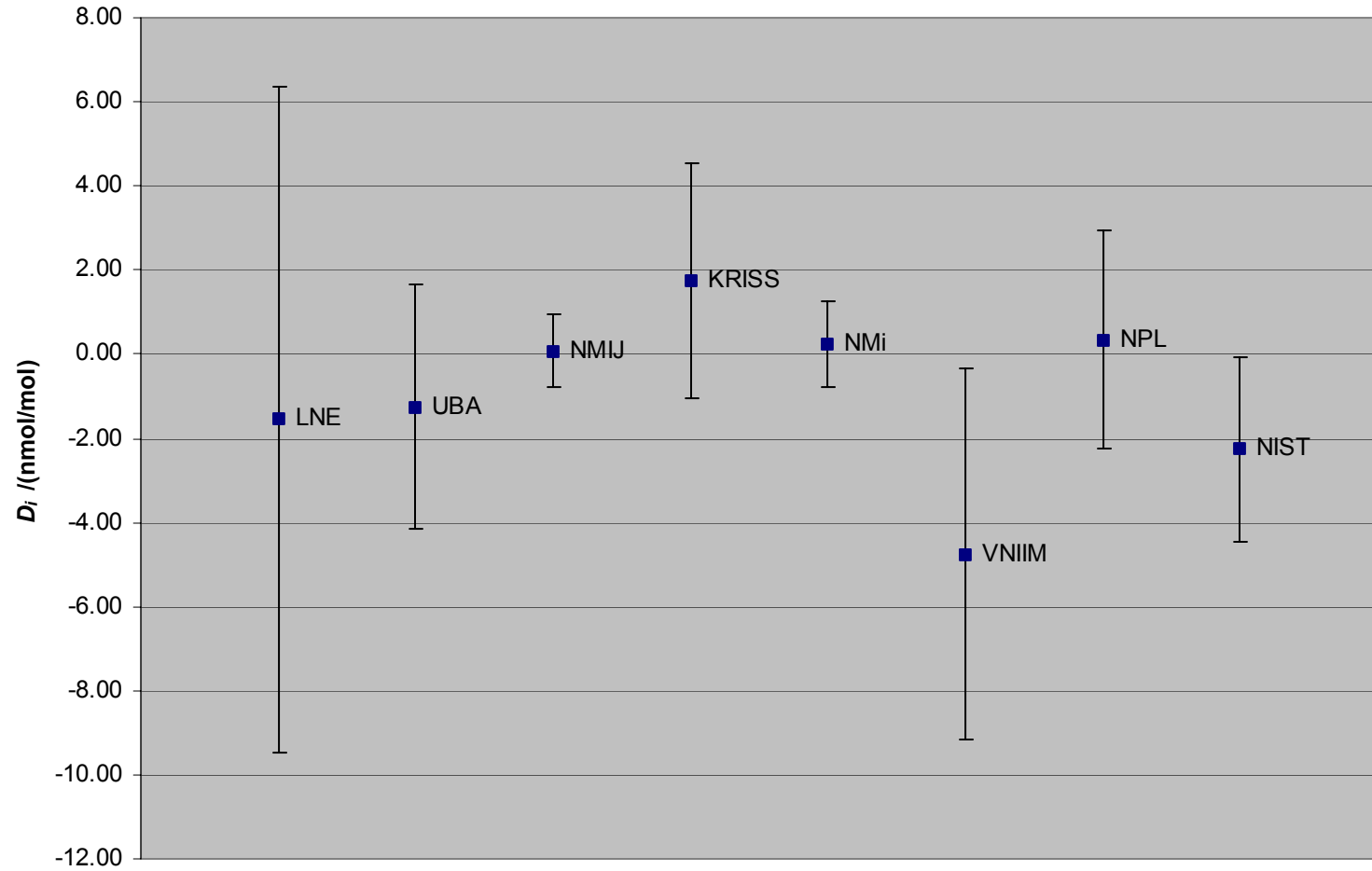
Matrix of Equivalence

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

Nominal Value: 80 nmol/mol

Lab i	D_i	U_i
	nmol/mol	
LNE	-1.56	7.90
UBA	-1.26	2.91
NMIJ	0.07	0.87
KRISS	1.74	2.80
NMi	0.24	1.01
VNIIM	-4.76	4.40
NPL	0.34	2.61
NIST	-2.26	2.21

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms; $D_i = (x_i - x_{igrav})$ and U_i, its expanded uncertainty.

The degree of equivalence between any two laboratories may be calculated by;
$D_{ij} = D_i - D_j$ and its expanded uncertainty;

$$U_{ij} = 2\sqrt{u^2(D_i) + u^2(D_j)} = 2\sqrt{\frac{U_i^2}{2^2} + \frac{U_j^2}{2^2}} = \sqrt{U_i^2 + U_j^2}$$

Note: Use of this equation is allowed for all laboratories except UBA, see report for explanation.

Measurand: Ethylbenzene

x_i: result of measurement carried out by laboratory i

u_i combined standard uncertainty of x_i

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

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

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement
LNE	70.60	2.95	83.82	0.08	Oct-99
UBA	90.00	1.43	83.82	0.08	Nov-99
NMIJ	68.43	0.46	68.81	0.07	Oct-00
KRISS	85.90	1.45	83.82	0.08	Nov-99
NMi	85.60	0.65	83.82	0.08	Oct-99
VNIIM	67.10	2.50	83.82	0.08	Nov-99
NPL	85.10	2.00	83.82	0.08	Nov-99
NIST	78.70	1.45	83.82	0.08	Oct-99

CCQM-K7
Degrees of equivalence for ethylbenzene in nitrogen at nominal 80 nmol/mol
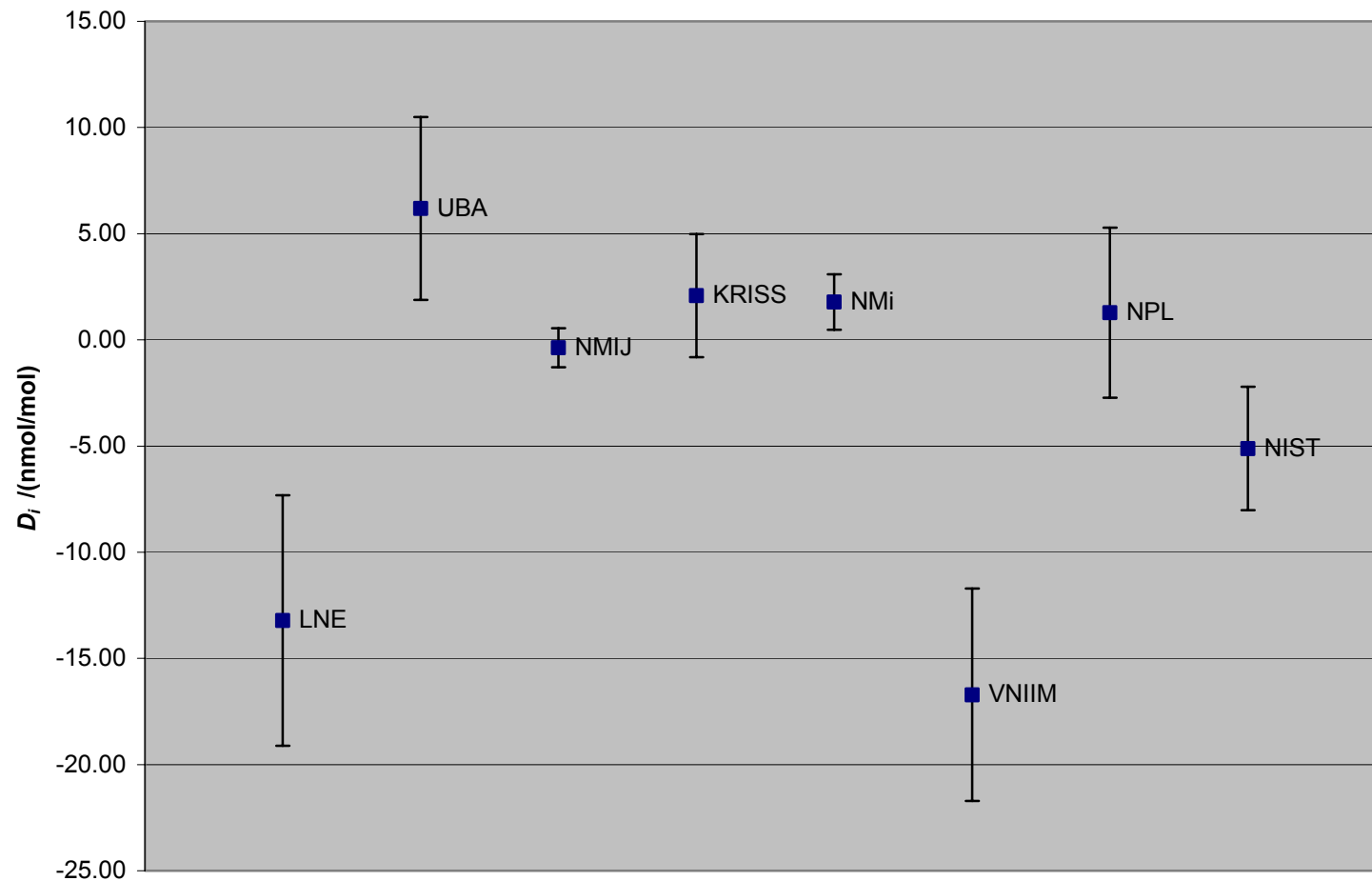
Matrix of Equivalence

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

Nominal Value: 70 nmol/mol

Lab i	D_i	U_i
	nmol/mol	
LNE	-13.22	5.90
UBA	6.18	4.31
NMIJ	-0.38	0.92
KRISS	2.08	2.90
NMi	1.78	1.31
VNIIM	-16.72	5.00
NPL	1.28	4.00
NIST	-5.12	2.90

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms; $D_i = (x_i - x_{igrav})$ and U_i, its expanded uncertainty.

The degree of equivalence between any two laboratories may be calculated by;
$D_{ij} = D_i - D_j$ and its expanded uncertainty;

$$U_{ij} = 2\sqrt{u^2(D_i) + u^2(D_j)} = 2\sqrt{\frac{U_i^2}{2^2} + \frac{U_j^2}{2^2}} = \sqrt{U_i^2 + U_j^2}$$

Note: Use of this equation is allowed for all laboratories except UBA, see report for explanation.

Measurand: m-Xylene

x_i: result of measurement carried out by laboratory i

u_i combined standard uncertainty of x_i

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

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

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement
LNE	91.90	3.90	92.77	0.08	Oct-99
UBA	89.70	1.33	92.77	0.08	Nov-99
NMIJ	91.70	0.49	92.89	0.08	Oct-00
KRISS	95.10	1.60	92.77	0.08	Nov-99
NMi	95.20	0.65	92.77	0.08	Oct-99
VNIIM	75.60	2.70	92.77	0.08	Nov-99
NPL	94.20	2.25	92.77	0.08	Nov-99
NIST	87.50	2.05	92.77	0.08	Oct-99

CCQM-K7
Degrees of equivalence for m-xylene in nitrogen at nominal 90 nmol/mol
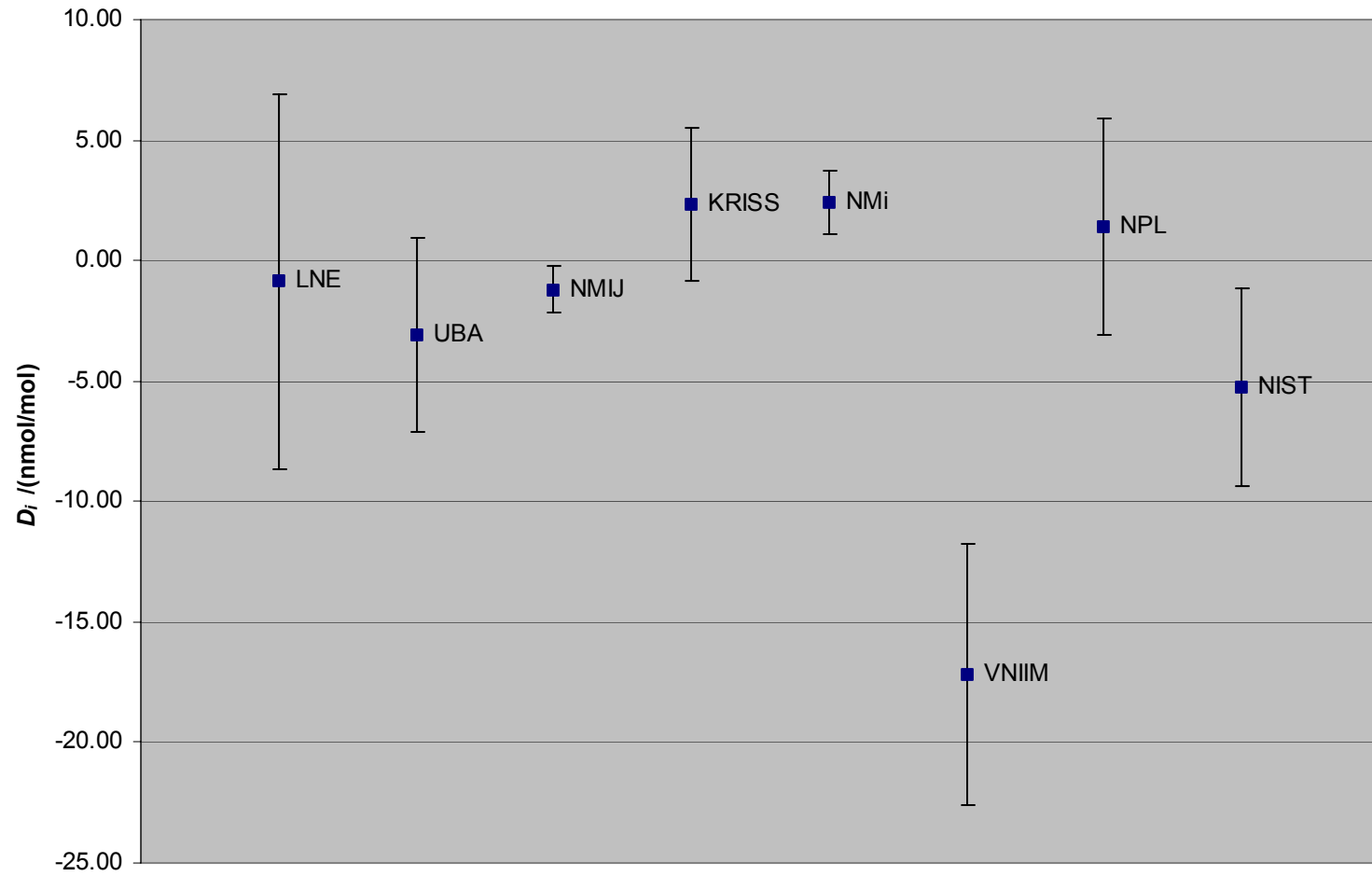
Matrix of Equivalence

Measurand: Amount-of-substance fraction of m-xylene in nitrogen

Nominal Value: 90 nmol/mol

Lab i	D_i	U_i
	nmol/mol	
LNE	-0.87	7.80
UBA	-3.07	4.01
NMIJ	-1.19	0.98
KRISS	2.33	3.20
NMi	2.43	1.31
VNIIM	-17.17	5.40
NPL	1.43	4.50
NIST	-5.27	4.10

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms; $D_i = (x_i - x_{igrav})$ and U_i, its expanded uncertainty.

The degree of equivalence between any two laboratories may be calculated by;

$D_{ij} = D_i - D_j$ and its expanded uncertainty;

$$U_{ij} = 2\sqrt{u^2(D_i) + u^2(D_j)} = 2\sqrt{\frac{U_i^2}{2^2} + \frac{U_j^2}{2^2}} = \sqrt{U_i^2 + U_j^2}$$

Note: Use of this equation is allowed for all laboratories except UBA, see report for explanation.

Measurand: o-Xylene

x_i:　　　result of measurement carried out by laboratory i

u_i　　　combined standard uncertainty of x_i

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

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

Lab i	x_i nmol/mol	u_i nmol/mol	x_{igrav} nmol/mol	u_{igrav} nmol/mol	Date of measurement
LNE	61.10	3.20	60.90	0.07	Oct-99
UBA	60.40	0.77	60.90	0.07	Nov-99
NMIJ	65.05	0.45	66.40	0.07	Oct-00
KRISS	61.80	1.05	60.90	0.07	Nov-99
NMi	62.40	0.55	60.90	0.07	Oct-99
VNIIM	48.60	2.40	60.90	0.07	Nov-99
NPL	61.20	1.45	60.90	0.07	Nov-99
NIST	56.40	1.65	60.90	0.07	Oct-99

CCQM-K7
Degrees of equivalence for o-xylene in nitrogen at nominal 60 nmol/mol
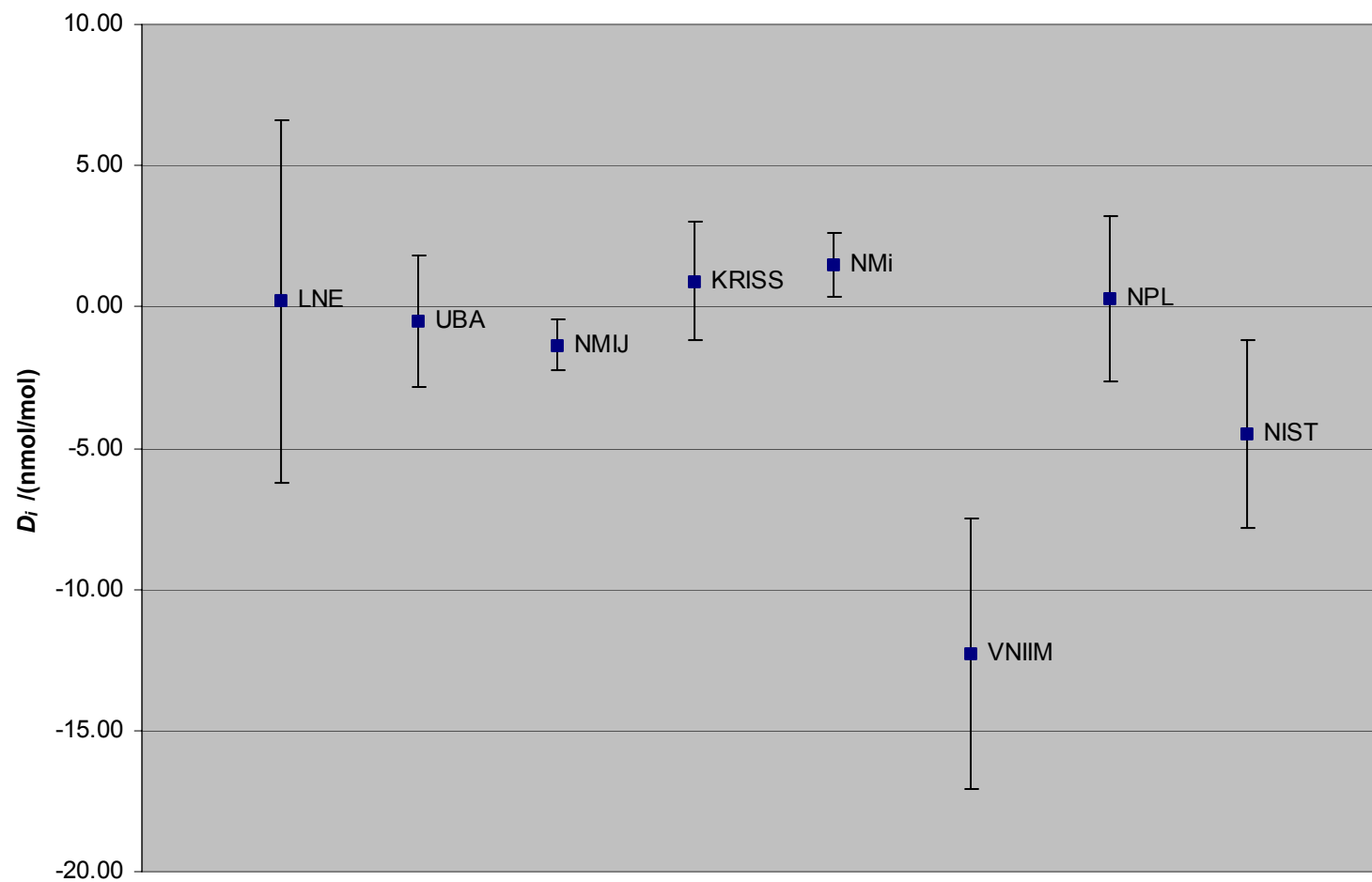
Matrix of Equivalence

Measurand: Amount-of-substance fraction of o-xylene in nitrogen

Nominal Value: 60 nmol/mol

Lab i	D_i	U_i
	nmol/mol	
LNE	**0.20**	6.40
UBA	**-0.50**	2.31
NMIJ	**-1.35**	0.91
KRISS	**0.90**	2.10
NMi	**1.50**	1.11
VNIIM	**-12.30**	4.80
NPL	**0.30**	2.90
NIST	**-4.50**	3.30

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms; $D_i = (x_i - x_{igrav})$ and U_i, its expanded uncertainty.

The degree of equivalence between any two laboratories may be calculated by;

$D_{ij} = D_i - D_j$ and its expanded uncertainty;

$$U_{ij} = 2\sqrt{u^2(D_i) + u^2(D_j)} = 2\sqrt{\frac{U_i^2}{2^2} + \frac{U_j^2}{2^2}} = \sqrt{U_i^2 + U_j^2}$$

Note: Use of this equation is allowed for all laboratories except UBA, see report for explanation.