

**Draft B report 10/31/2008**

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**Field** – Gas standards

**Subject** - Comparison of primary standards of nitrogen monoxide (NO) in nitrogen

**Participants**

KRISS (Korea), NRCCRM (China)

**Introduction**

Measurements of the concentration of nitrogen dioxide (NO<sub>2</sub>) in ambient air have become important item in the regulation of ambient air quality. In general, NO<sub>2</sub> analyzers based on the chemiluminescence detection is calibrated using an NO mixture in a balance of nitrogen. The key comparison for high concentration NO in nitrogen, CCQM-K1.c, was conducted from 1995 to 1996. Recently, the key comparison for low concentration NO in nitrogen, CCQM-K26.a, was conducted from 2004 to 2006.

This APMP\_QM-K1.c was intended to be a re-run of the CCQM-K1.c in APMP(Asia Pacific Metrology Program) region, and the nominal amount fraction of the gas mixture was 90 ~ 100 μmol/mol.

**Preparation of Gravimetric Standards**

Pure NO and N<sub>2</sub> were purchased from Air Liquid Corp and Deokyang Energen (Korea), respectively. The purity of each pure gas was measured using Gas MS, FTIR, Dew point meter and GCs. The results of the analysis are shown in Table1.

Table 1. Purity of NO and N<sub>2</sub> gases.

Gas name	Source	Purity (μmol/mol)	Uncertainty(k=2) (μmol/mol)
Nitrogen	Deokyang Energen	999966.6	1.74
Nitrogen monoxide	Air Liquid Corp	997394	96

The hierarchy of gravimetric standards prepared by KRIS for this comparison is shown in Figure 1. 10 L Aluminium cylinders from Luxfur were used for all standards. MD0834 cylinder was used as the transfer standard in this comparison.

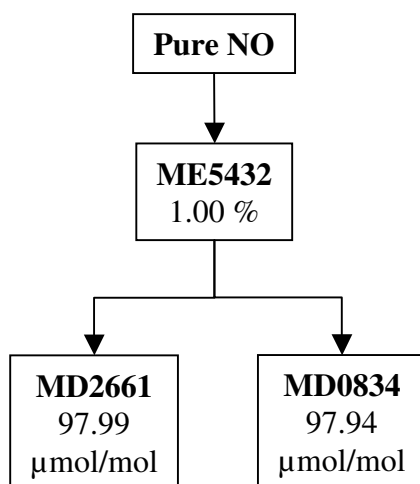


Figure 1. The hierarchy of the gravimetric standards of NO/N<sub>2</sub> prepared by KRIS.

### Consistency and Stability of the Standards Prepared by KRIS

The consistency and stability of the standards in the hierarchy shown in Figure 1 were validated by comparison of the old standards which concentration was 99.80 μmol/mol (ME6797) and was prepared about 8 months ago (2005/04/29) than two cylinders being compared. Figure 2 shows the difference between the analytical amount fraction of the two cylinders being compared and the gravimetric amount fraction of old standard. As can be seen, two cylinders were consistent to within 0.1 % (relative) and stable within 0.1 % (relative) for 8 months.

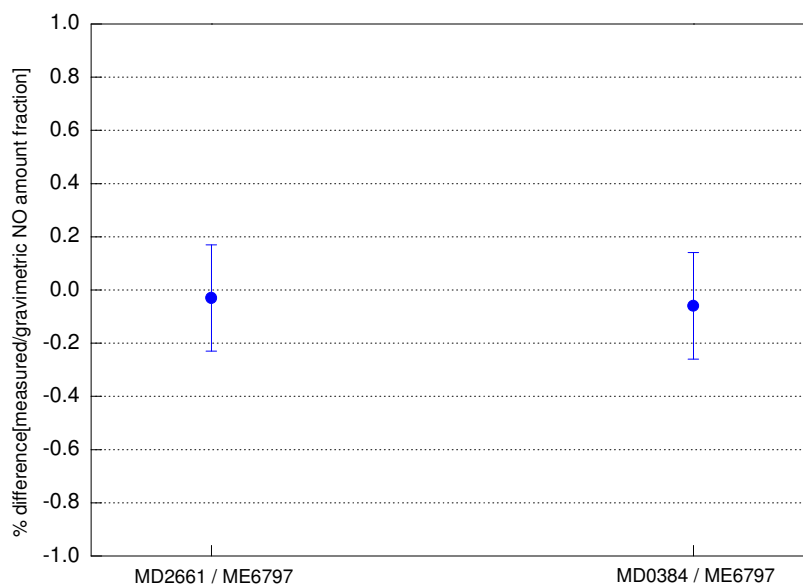


Figure 2. The difference between the analytical amount fraction of the two cylinders being compared and the gravimetric amount fraction of old standard.

## Results Submitted by the Participants

The test condition submitted by the participants are listed in Table 2.

Table 2. Test conditions of APMP\_QM-K1.c.

Lab.	Cylinder Number	Analytical Method	Standard	Calibration Model	No. of measurements	Total No. of Sub-measurements	Date
NRCCRM	MD0384	Chemiluminescence	gravimetric	5 point calibration	6	36	2006.6.16
KRISS	MD0384	Chemiluminescence	gravimetric	1 point calibration	5	25	2006.8.13

The participants measured the concentration of nitrogen monoxide in the cylinder using their own standards. After the completion, transfer standard was re-analyzed and concentration of nitrogen monoxide was not changed within measurement uncertainty.

The result of KRISS in CCQM-K1.c was deviated about 0.77  $\mu\text{mol/mol}$  from KCRV. To link APMP\_QM-K1.c to CCQM-K1.c, the difference was added to the uncertainty for the gravimetric value of KRISS (0.1  $\mu\text{mol/mol}$ ) in order to calculate the uncertainty in the KCRV. The corrected results are listed in Table 3.

Table 3. Results of APMP\_QM-K1.c.

Lab.	$x_i$ / ( $\mu\text{mol/mol}$ )	$u_i$ / ( $\mu\text{mol/mol}$ )	$x_{i\text{KCRV}}$ / ( $\mu\text{mol/mol}$ )	$u_{i\text{KCRV}}$ / ( $\mu\text{mol/mol}$ )	Date of measure
NRCCRM	99.07	0.50	97.94	0.40	Jun 06
KRISS	97.88	0.11	97.94	0.40	Aug 06

## Degree of Equivalence

$D_i$  and  $U_i$  are summarized in Table 4 and Figure 2 shows the Degree of Equivalence for APMP\_QM-K1.c.

Table 4. The degree of equivalence of each laboratory

Lab.	$D_i$ / ( $\mu\text{mol/mol}$ )	$U_i (k=2)$ / ( $\mu\text{mol/mol}$ )
NRCCRM	1.13	1.28
KRISS	-0.06	0.83

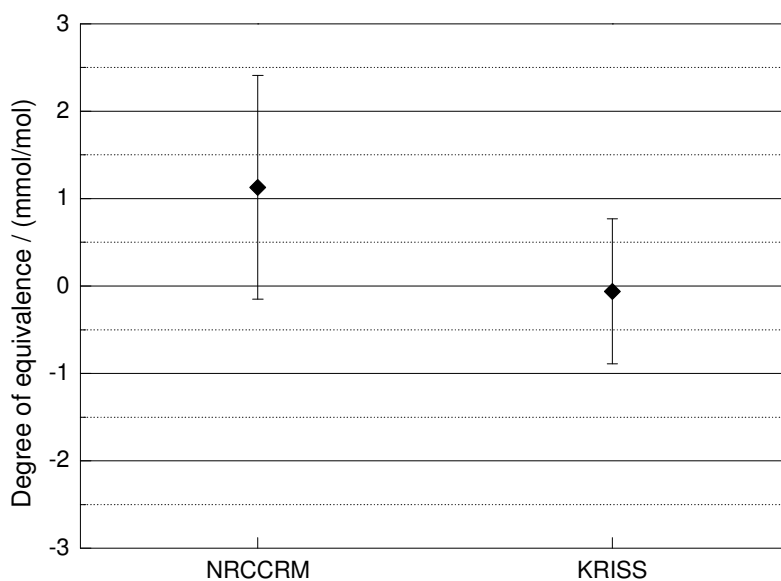


Figure 3. Degrees of equivalence.

## Results

In this comparison, the estimated uncertainty was larger than the deviation from the reference value. Consequently, the results from NRCCRM and KRISS were agreed.

## References

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

## Coordinators

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Report form NRCCRM

## Bilateral Comparison Nitric monoxide in nitrogen

Laboratory: NRCCRM

Cylinder number: MD0384

NOMINAL COMPOSITION

- nitrogen monoxide :  $90$  to  $100 \times 10^{-6}$  mol/mol

- nitrogen : balance

Measurement No . 1	Date	Result ( $\times 10^{-6}$ mol/mol)	Stand. deviation (%relative)	Number of submeasurements
NO/N <sub>2</sub>	2006-5-15	99.09	0.2	6

Measurement No . 2	Date	Result ( $\times 10^{-6}$ mol/mol)	Stand. deviation	Number of submeasurements
NO/N <sub>2</sub>	2006-5-25	98.93	0.3	6

Measurement No . 3	Date	Result ( $\times 10^{-6}$ mol/mol)	Stand. deviation	Number of submeasurements
NO/N <sub>2</sub>	2006-5-30	99.02	0.3	6

Measurement No . 4	Date	Result ( $\times 10^{-6}$ mol/mol)	Stand. deviation	Number of submeasurements
NO/N <sub>2</sub>	2006-6-14	99.20	0.3	6

Measurement No . 5	Date	Result ( $\times 10^{-6}$ mol/mol)	Stand. deviation	Number of submeasurements
NO/N <sub>2</sub>	2006-6-15	98.95	0.3	6

Measurement No . 6	Date	Result ( $\times 10^{-6}$ mol/mol)	Stand. deviation	Number of submeasurements
NO/N <sub>2</sub>	2006-6-16	99.22	0.4	6

**Results:**

Analyte	Result(assigned value) ( $\times 10^{-6}$ mol/mol )	Coverage factor	Assigned expanded uncertainty
NO/N <sub>2</sub>	99.07	2	$1.0 \times 10^{-6}$ mol/mol

**Reference Method:**

Chemiluminescence (Model 42C NO-NO<sub>2</sub>-NO<sub>x</sub> Analyzer; Thermo)

EURACHEM / CITAC Guide: “Quantifying Uncertainty in Analytical measurement”

**Calibration Standards:**

Five gas mixtures were used as calibration standards to analyse the sample. The calibration standards were prepared by gravimetric method, according to ISO 6142, which detail information was listed in table 1.

The impurities of complementary gas and impurities of components interested were determined with a standard normalized method by spectroscopic analysis.

Experiments showed that the impurities of the material gases have no effects to the results within the measurement uncertainties. So the purity of pure gases used for preparation was taken from the certificates of producer. Their uncertainties were calculated by type B evaluation.

**Table 1 Calibration Standards**

Components	Assigned value ( $\times 10^{-6}$ mol/mol)					Relative standard uncertainty ( $u(x)$ ), %
	Cylinder No.	241004	241183	240951	104557	
Nitric monoxide in Nitrogen	48.81	55.0	67.47	92.19	101.0	0.4

### **Instrument Calibration:**

The concentration of NO in nitrogen is calculated using a manually prepared calibration curve. For this purpose five gas calibration standards were prepared by gravimetric method. Six subsequent measurement results were obtained under repeatable conditions by the linear least squares calibration. (calibration curve > measurement; calibration curve > measurement; .....).

### **Sample Handling:**

Sample cylinder after arrival was stored in the room temperature. Sample and standard gas were all directly led to monitor by a regulator, a flow meter and a teflon pipe. Each sample flows in the monitor for at least 5 minutes. After injection, the monitor and pipe system was purged 5 minutes.

### **Uncertainty**

We established two types of uncertainty:

- gravimetric uncertainty
- Analytical uncertainty

The Gravimetric uncertainty contributions included:

- Balance uncertainty
- Buoyancy of cylinders
- Impurity of gases
- Leakage
- Absorption

The analytical uncertainty was evaluated by repeating the measurement.

The relative standard uncertainty of NO in sample mixture was evaluated by equation (1)

$$u^2(C_{sample} \%) = u^2_{gravi} + u^2_{repeatability} \quad (1)$$

The relative standard uncertainty of standard mixture was the gravimetric uncertainty.

The relative standard uncertainty of repeatability was the RSD% .

The amount of each contribution to the measurement uncertainty was listed in table 2.

Expanded uncertainty can be calculated with a confidence interval 95% and a coverage factor  $k= 2$ . The expanded uncertainty was:

$$U_i = k \cdot u(C_{sample,i}) \quad (2)$$

**Table 2 Uncertainty Evaluation**

Uncertainty	Estimate	Assumed	Standard	Sensitivity	Contributio
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source	(relative,%)	distribution	uncertainty	coefficient	n to standard uncertainty $u_i(y)$ (relative,%)
<b>Gravimetric method</b>	<b>0.7</b>	<b>Rectangle</b>	<b>0.4</b>	<b>1</b>	<b>0.4</b>
<b>Analytical</b>	<b>0.2</b>	<b>Normal</b>	<b>0.2</b>	<b>1</b>	<b>0.2</b>

Coverage factor:2

Expanded uncertainty:1%

Report from KRISS

– Results for NO in nitrogen –

Laboratory : KRISS  
Cylinder number : MD0384

NOMINAL COMPOSITION

- Sulfur dioxide : 90 to 100 · 10<sup>-6</sup> mol/mol  
- Nitrogen : balance

Measurement No.	Date	Result (10 <sup>-6</sup> mol/mol)	Standard deviation (% relative)	number of sub-measurements
1	2006/08/09	98.00	0.17	5
2	2006/08/10	97.96	0.03	5

3	2006/08/11	97.87	0.19	5
4	2006/08/12	97.80	0.06	5
5	2006/08/13	97.79	0.13	5

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	97.88	2	0.22

Reference Method:

NO analyzer (Model 42C NO<sub>x</sub> Analyzer, TEI) was used for this measurement. We made a new auto sampling system using one regulator to remove adsorption problems on the regulator. Sample and zero gases were introduced into analyzer for 4 minutes with 400 ml/min and sample was analyzed 5 times.

Calibration Standard:

We used Al cylinders from Luxfer with stainless steel valve. ME6797 cylinder (99.8010 μmol/mol) was used as calibration standard.

Purity of NO source gas was determined by impurity analysis. Expanded uncertainty of the calibration standard including purity of the source gas, weighing uncertainty, and manufacturing uncertainty was about 0.1 % (relative).

Instrument Calibration:

NO analyzer was calibrated with zero gas and calibration standard gas prepared by gravimetric method and ABA method was used.

Sample Handling:

After receiving sample cylinder, cylinder was stood at room temperature with reference cylinders before measurements.

Uncertainty:

$$C_{sample} = \frac{S_{sample}}{S_{std}} \times C_{std}$$

where,  $C_{sample}$  : concentration of sample

$S_{sample}$  : output signal of sample

$C_{std}$  : concentration of standard

$S_{std}$  : output of standard

The uncertainties of  $S_{sample}$  and  $S_{std}$  have been estimated using the pooled standard deviation of 5 x 5 analysis.

Uncertainty Budgets:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution ( $\mu\text{mol/mol}$ )	Corr.-Coeff.	Index (%)
$S_{sample}$	91.0380 AU	0.0251 AU	normal	1.1	0.027	0.25	6.2
$S_{std}$	92.8150 AU	0.0356 AU	normal	-1.1	-0.038	-0.35	12.0
$C_{std}$	99.801 $\mu\text{mol/mol}$	0.100 $\mu\text{mol/mol}$	normal	0.98	0.098	0.90	81.8

Results :

Quantity: 97.88  $\mu\text{mol/mol}$

Coverage factor: 2.0

Expanded uncertainty: 0.22  $\mu\text{mol/mol}$