International Key Comparison CCQM-K26b and Pilot Study CCQM P50b (SO₂)

Field - Gas standards

Subject - Comparison of primary standards of sulphur dioxide (SO₂) in synthetic air.

Participants (in CCQM K26b)

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Introduction

Applicability of this Key Comparison to CMC Claims

The following statement for "how far the light shines" from this comparison was agreed by the CCQM GAWG in April 2004:

"The comparison is aimed at typical calibration requirements for ambient SO2 analysers, which monitor concentrations using ultraviolet fluorescence. The techniques used for the comparison should be applicable to concentrations of SO2 between around 100 nmol/mol and 1 μ mol/mol."

Overview of the Comparison

The Key comparison CCQM-K26b and the Pilot Study CCQM P50b were conducted in parallel according to the protocol given in Annex A. The key features of this key comparison were:

- Travelling standards were prepared commercially (one for each participant).
- Each travelling standard was measured against a permeation standard at the coordinating laboratory before despatch to each participating laboratory.
- Travelling standards were measured by participating laboratories.
- Each travelling standard was re-measured by the coordinating laboratory on return.
- Drift of each standard was estimated from measurements carried out by the coordinating laboratory.
- The Key Comparison Reference Value (KCRV) and its uncertainty was calculated for each travelling standard.
- The Degree of Equivalence (and its uncertainty) was calculated for each laboratory as the difference between the KCRV and the submitted result.

Work Carried out by the Coordinating Laboratory

Stability of Standards of Sulphur Dioxide in Air

The SO₂ travelling standards used for this comparison were acquired from BOC Gases who have a record of preparing stable SO₂ mixtures at the relevant concentration. The standards were prepared in 10 litre aluminium cylinders treated using their proprietary Spectra-Seal process. The cylinders were fitted with stainless steel diaphragm valves with BS341 No. 14 outlet connections. They were filled to 150 bar.

Three samples from the batch of standards used for this comparison were analysed by FTIR for trace contaminants. The levels of nitrous oxide and carbon dioxide found in the range 30 to 40 nmol/mol and 20 to 30 nmol/mol respectively.

Gravimetric Permeation Standard Developed by the Coordinating Laboratory

The system used for the primary permeation standard is described in Annex B.

High Accuracy Comparison Method Developed by the Coordinating Laboratory

This key comparison imposed a requirement on the coordinating laboratory to carry out a large number of comparisons. The procedure used for these comparisons is described in Annex B.

Stability of the Travelling Standards

In order to eliminate any effects of drift due to instability in the amount fraction in the travelling standards, the drift of each travelling standard was determined individually, and the amount fraction in the cylinder was calculated at the time when it was analysed by each participant. An example of the results of a series of measurements on a travelling standard is shown in Figure 1.



Figure 1 - Example of the estimation of the drift of a travelling standard. The measurements shown were carried out by the coordinating laboratory. The error bars indicate the standard deviation of the repeat measurements. The regression line has been fitted by ordinary least squares.

Standard Identifier	Z ₁₀	Estimated drift	Standard error of		
		m	m		
	[nmol/mol]	[nmol/mol/day]	[nmol/mol/day]	[nmol/mol]	[nmol/mol]
172473	285.29	0.05826	0.00696	279.3	0.37
172468	288.86	0.04841	0.00938	284.8	0.20
172508	282.19	0.04244	0.00516	276.0	0.27
172704	278.57	0.04101	0.00991		
172469	273.84	0.03900	0.00263	269.2	0.25
172500	268.98	0.03586	0.00326		
172472	281.38	0.03473	0.00621	275.8	0.23
172505	281.62	0.02752	0.00356	277.7	0.17
172698	288.47	0.02675	0.00767	286.4	0.40
172703	279.76	0.02668	0.00266	275.5	0.24
172509	290.15	0.02409	0.00615	288.3	0.29
172506	282.24	0.02109	0.00269	279.2	0.37
172467	271.89	0.01878	0.00269	268.5	0.23

Table 1 – Estimated drifts for each travelling standard. z_{i0} is the estimated amount fraction on the 4th March 2004. The standard errors in the values are calculated according to the equation given in the text. These values are plotted in Figure 2. Values for z_T have not been calculated for two of the standards because results were not submitted by the relevant participants in respect of them.

Decay rates for CCQM-K26 SO2 standards



Figure 2 – Measured decay rates for the travelling standards listed in Table 1 displayed in ascending order. The standard errors in the values are calculated according to the equation given in the text.

An example of one of these plots is given in Figure 3. In all cases it was found that the following straight line was a good fit to the data.

$$z = z_{i0} + m_i(t - t_0)$$

where z_{i0} is the value of the standard on 4th March 2004 and m_i is the estimated drift rate (the date 04/03/04 was chosen for convenience and has no influence on the calculation of the degrees of equivalence). The use of a linear fit is further justified because it is consistent with typical chemical decay or absorption processes over a small range of concentrations.

The gradient of the straight line fitted through the coordinating laboratories' analytical data is taken as the "drift" of each travelling standard. The values of the drift for each travelling standard are tabulated in Table 1. The standard error of the drift (se(m)) was estimated using the usual method for calculating the standard error in the gradient of a line calculated by ordinary least squares:

$$se(m) = \sqrt{\frac{\sum (Y_j - \overline{Y})^2}{\sum (Z_j - \overline{Z})^2}}$$

Figure 2 shows the estimated drift of each travelling standard, and its standard error. Inspection of the graph shows that the estimated drifts are distributed around a median value of 0.035 nmol/mol/day. The population has no significant outliers. The median drift corresponds to a decay of 2.2% over 6 months in the nominal amount fraction of 280 nmol/mol.

Determination of the Amount Fraction of the Travelling Standards at the Time of Analysis

After estimating the drift of each travelling standard, it is possible to estimate the amount fraction in each standard at the time (T) when it was analysed by the relevant participating laboratory (z_T).

The uncertainty in the estimated value of z_T is straightforward to estimate. If we consider the hypothetical case where the participant carries out the analysis at a time \overline{T} which is the mean of the times (t_j) at which the coordinating laboratory carried out its analyses:

$$\overline{T} = \left(\sum_{j=1}^{N} t_j\right) / N$$

then the estimated value of the amount fraction in the cylinder $z_{\overline{T}}$ is given by the mean of the results of the coordinating laboratory

$$z_{\overline{T}} = \left(\sum_{j=1}^{N} z_j\right) / N$$

The random component in the uncertainty of $z_{\overline{\tau}}$ is given by

$$u(z_{\overline{T}})_{random} = \left(\sum_{j=1}^{N} \sigma_{j}\right) / N^{3/2}$$

where σ_{j} is the standard deviation of the measurements j.

In addition, a contribution due to the uncertainty in the amount fraction generated by the primary permeation facility (u_{primary}) is added in quadrature.

$$u(z_{\overline{T}}) = \sqrt{u(z_{\overline{T}})^2_{random} + u^2_{primary}}$$

Inspection of Annex C shows that 1.4 nmol/mol (or 0.5% relative to value) is a reasonable estimate of this "primary" uncertainty. The uncertainty in the estimated values of $z_{\overline{\tau}}$ are listed in Table 3.

Calculation of the Key Comparison Reference Value

The objective of this key comparison is to determine the degree of equivalence (D_i) of each laboratory with respect to the Key Comparison Reference Value (KCRV).

$$D_i = x_i - x_{i, KCRV}$$

During the planning of this key comparison, it was expected that there would be some small drift observed in the travelling standards. Consequently, it was not expected to be possible to use the values of the amount fraction in the standards derived from their gravimetric preparation as the reference values. The planning of the key comparison also took account of the fact that the KCRV for each travelling standard would be different. Consequently, the analytical values from the coordinating laboratory were used to calculate a reference value for each travelling standard (z_i^{ref}) on the day that it was analysed by the participant. This reference value is used as the KCRV for that standard. Hence

and

$$D_i = x_i - z_i^{ref} \, .$$

 $x_{i \ KCRV} = z_i^{ref}$,

The values of the degrees of equivalence were studied for any indication that their mean was significantly different to zero. This was found not to be the case, hence the results it can be concluded that the results are unbiased.

Results Submitted by Participating Laboratories

A full list of the participants, including contact details is given in Annex E.

The results submitted by the participants are listed in Table 2. The travelling standard despatched to CERI/NMIJ was not permitted to enter Japan by customs authorities. Consequently, a further standard was used, as described in the following section. NIST did not submit any results. The methods used by the participants are discussed below.

Laboratory	Cylinder	Submitted	Uncertainty	Date	Date of	Date	
	number	result		despatched	participant	received at	
				from NPL	measurement	NPL	
		Key	comparison p	participants			
CERI/NMIJ	172704	No result	No result	04/06/2004	No result	05/08/2004	
CHMI	172468	285.20	4.60	04/06/2004	09/07/2004	06/08/2004	
FMI	172505	273.80	4.38	04/06/2004	03/09/2004	27/10/2004	
IPQ	172472	261.90	5.10	04/06/2004	22/09/2004	28/11/2004	
JRC	172698	284.50	2.90	04/06/2004	02/07/2004	03/08/2004	
KRISS	172469	275.10	3.00	04/06/2004	12/08/2004	10/09/2004	
LNE	172509	282.70	2.90	04/06/2004	30/06/2004	03/08/2004	
NIST	172500	No result	No result	03/06/2004	No result	24/08/2004	
NMi	172508	275.16	3.00	04/06/2004	08/09/2004	06/11/2004	
NPL	172506	280.01	0.64	04/06/2004	07/09/2004	08/09/2004	
UBA(D)	172473	282.00	5.60	04/06/2004	26/07/2004	18/08/2004	
VNIIM	172467	260.40	2.23	04/06/2004	13/10/2004	17/01/2005	
	Pilot study participants						
UBA(A)	172703	279.00	4.00	04/06/2004	23/09/2004	05/11/2004	

Table 2 – Results submitted by the participating laboratories for CCQM K26b and P50b. The results from CERI/NMIJ are discussed in the report.

Results Submitted by CERI/NMIJ

As noted above, no results were available from CERI/NMIJ because the cylinders used for the comparison were not considered suitable for import by the customs authorities in Japan. The CCQM GAWG decided that it would be acceptable for CERI/NMIJ to take part in the comparison be preparing a standard and sending it to the coordinating laboratory to be certified. Any drift in the standard was corrected by reference to analytical results from CERI/NMIJ who analysed the standard before and after it travelled to the coordinating laboratory.

The results of the analysis carried out by CERI/NMIJ are given in Table 3.

Date	Result	Expanded uncertainty (<i>k</i> =2)
26/04/2005	279.40	6.2
20/09/2005	275.60	6.2

Table 3 – Results submitted by CERI/NMIJ from the analysis of CPB-19107 prepared at CERI/NMIJ and sent to the coordinating laboratory.

The standard CPB-19107 was analysed by the coordinating laboratory on 27/06/2004 and found to have a value of 270.70 + 2.7 (k=2) nmol/mol. A linear interpolation between the two results in Table 3, gives a value of 277.80 for the value of CPB-19107 on 27/06/2005. In order to estimate the uncertainty in the value, it would be usual practice to combine the uncertainties of the results of the two analyses. This would reduce the uncertainty below that of either of them. In this case, since there is some additional uncertainty caused by the assumption that the drift in the standard is linear, we do not take advantage of this factor and estimate the expanded uncertainty to be +6.2 nmol/mol (k=2). The Degree of Equivalence for CERI/NMIJ is shown in Table 4 and has been calculated using the same formula for D_i as for all other participants.

Summary of methods

The methods used by the participating laboratories can de divided according to how the standard gas is handled at amount fractions close to the target composition. The dynamic methods generate a flowing stream of gas at these levels, and the static methods use a volume of gas contained within a vessel. Several methods combine static and dynamic stages, but we classify according them all according to whether they are static or dynamic at amount fractions close to the target composition.

Dynamic Methods

Five laboratories (NPL, NMi, VNIIM, JRC-IES and IPQ) used dynamic gravimetric methods. These make use of a permeation device containing pure sulphur dioxide. The permeation device is maintained in a constant flow of diluent gas, and the rate of loss of mass from the device is monitored. Three laboratories carried out the measurement of the mass loss rate on a continuous basis (NPL, NMi and VNIIM) and two measured it on a periodic basis (JRC-IES and IPQ). Unlike any of the other methods described here, the dynamic gravimetric method also requires an accurate measurement of the volume flow rate. They also depend on the assumption, which is generally verified experimentally, that all of the mass loss from the permeation device is due to the target analyte (sulphur dioxide in this case).

Participant	Method	Standard	Calibration Protocol	Static Vessel (if any)	Analyser
CERI/NMIJ	Static gravimetric	PRMs (prepared by CERI/NMIJ) at 250 ppb	2 point	10 litre e'polished Al cylinder (at 250 ppb)	UV fluorescence (Thermo)
CHMI	Static volumetric	Dilution of a PRM (prepared by NMi at 10 ppm)	Single point (ratio)	111 litre glass chamber(at 250 ppb)	UV fluorescence (Thermo)
FMI	Dynamic volumetric	Dilution of a PRM (prepared by NPL at 100 ppm) using a critical orifice dilution system (LNI)	5 point	10 litre cylinder (at 100 ppm)	UV fluorescence (Thermo)
IPQ	Dynamic gravimetric	Periodic weighing of a permeation device.	5 point	None	UV fluorescence (Thermo)
JRC-IES	Dynamic gravimetric	Periodic weighing of three permeation devices.	3 point	None	UV fluorescence (Env SA)
KRISS	Static gravimetric	PRMs (prepared by KRISS) at 250 ppb	4 point	10 litre e'polished Al cylinder (at 250 ppb)	UV fluorescence (Thermo)
LNE	Dynamic volumetric	Dilution of a PRM (prepared by LNE at 10 ppm) using high accuracy flow controllers (MolBloc)	Single point (ratio)	10 litre cylinder (at 10 ppm)	UV fluorescence (Env SA)
NMi	Dynamic gravimetric	Continuous weighing of a permeation device.	5 point	None	UV fluorescence (Thermo)
NPL	Dynamic gravimetric	Continuous weighing of a permeation device.	Single point (ratio)	None	UV fluorescence (Thermo)
UBA(A)	Dynamic volumetric	Dilution of a PRM (prepared by NMi) using a thermal mass flow controller system (Horiba)	2 point	5 litre cylinder (at 90 ppm)	UV fluorescence (Thermo)
UBA(D)	Static volumetric	Volumetric dilution from pure materials	2 point	14.7 litre (at 250 ppb)	UV fluorescence (Horiba)
VNIIM	Dynamic gravimetric	Continuous weighing of a permeation device.	Single point (ratio)	None	UV fluorescence (Env SA)

Table 4 – Summary of methods used by participants.

Three laboratories used a dynamic volumetric method. These involve the use of a gravimetrically prepared standard of sulphur dioxide in air at a higher concentration that is subsequently diluted dynamically. The three implementations of this method are each slightly different:

- FMI used a critical orifice dilution system (LNI) to dilute a PRM at 100 mmol/mol.
- UBA(A) used a thermal mass-low controller system (Horiba) to dilute a PRM at 90 mmol/mol.
- LNE used a laminar flow dilution system (MolBloc) to dilute a PRM at 10 mmol/mol.

The dynamic volumetric methods require some form of calibration for the dilution systems as well as an accurate static gravimetric method for the preparation of the higher- amount fraction PRMs.

Static Methods

The static methods all require the standard gas to be maintained without significant losses in a vessel at the target amount fraction. This generally requires the use of specially-passivated materials.

- Two laboratories (CERI/NMIJ and KRISS) performed a series of static gravimetric dilutions down to the target amount fraction. Both laboratories used electropolished 10 litre aluminium cylinders.
- One laboratory (UBA(D)) performed a single static volumetric dilution of pure material in a 14.7 litre glass vessel to the target amount fraction.
- One laboratory (CHMI) used a static method that combined a static gravimetric method to produce a PRM at 10 ppm, followed by a static volumetric dilution in a 111 litre glass vessel for the final step to the target amount fraction.

None of the static methods have any requirements for the calibration of flow measurement instruments or dilution systems, but they do require the calibration of mass pieces, pressure sensors and volumetric systems.

Conclusions

The degrees of equivalence for the comparison are given in Table 5 and Figure 3. The discussion above and the spread of the results and their uncertainties, suggest that there is no strong reason to dispute the validity of the KCRV established by the gravimetric method used by the coordinating laboratory.





Figure 3 – Degrees of equivalence for CCQM K26b.

Laboratory	Cylinder number	Xi	u i	Z _T	$\overline{\sigma}$	u(primary)	u(z)	D _i	U(D ;)
		nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol
CERI/NMIJ	CPB-19107	277.8	3.1	270.7	0.5	1.4	1.41	7.1	6.8
СНМІ	172468	285.2	2.30	284.8	0.50	1.4	1.41	0.4	5.4
FMI	172505	273.8	2.19	277.7	0.41	1.4	1.41	-3.9	5.2
IPQ	172472	261.9	2.55	275.8	0.57	1.4	1.42	-13.9	5.8
DG-JRC IES	172698	284.5	1.45	286.4	0.97	1.4	1.46	-1.9	4.1
KRISS	172469	275.1	1.50	269.2	0.60	1.4	1.42	5.9	4.1
LNE	172509	282.7	1.45	288.3	0.70	1.4	1.43	-5.6	4.1
NIST	172500								
NMi	172508	275.16	1.50	276.0	0.67	1.4	1.43	-0.8	4.1
NPL	172506	280.01	1.44	279.2	0.70	1.4	1.43	0.8	4.1
UBA(D)	172473	282	2.80	279.3	0.92	1.4	1.45	2.7	6.3
VNIIM	172467	260.4	2.23	268.5	0.55	1.4	1.42	-8.1	5.3
Pilot study									
UBA(A)	172703	279	2.00	275.5	0.60	1.4	1.42		

 Table 5 – Degrees of equivalence for CCQM K26b

Annexes

Annex A – Protocol

Key comparison of NO and SO₂ at ambient levels

CCQM K26 a and b - Protocol

Pilot Laboratory:- NPL, UK

Background

Accurate measurements of NO_2 and SO_2 at ambient air concentrations have become essential to support monitoring and legislation concerned with air quality.

In general, the primary element of quality assurance for field instruments is regular calibration using certified gas mixtures. In the case of NO_2 there is near universal use of analysers based on the chemiluminescent detection of NO, with NO_2 being measured as the difference between ambient NO and ambient NOx, this being the sum of NO and NO_2 measured by converting the NO_2 to NO with a catalyst. Analyser response is therefore calibrated using an NO mixture.

NO mixtures have a balance gas of nitrogen, to minimize oxidation to NO_2 , while SO_2 mixtures have a balance gas of synthetic air.

The concentrations involved in these comparisons have been chosen as those likely to be used for field calibrations within the appropriate European standards.

The protocol for this Key Comparison was initiated by NPL at the EUROMET Gas Analysis Working Group. Subsequently, laboratories from outside the EUROMET group expressed an interest in participation and the proposal was submitted to the CCQM Gas Working Group as a Key Comparison. This proposal was ratified by the CCQM in April 2002.

Comparison protocol

The mixtures used for the comparison will be acquired from commercial suppliers with a proven track record of preparing stable mixtures of the relevant gases. The analyte amount fractions will lie within the ranges:

Nitrogen monoxide	600. $10^{-9} - 850. 10^{-9}$ mol/mol
Sulphur dioxide	240. 10 ⁻⁹ – 320. 10 ⁻⁹ mol/mol

NPL will carry out stability checks on the mixtures and will make a determination of their amount fraction using primary facilities at NPL before dispatch to participating laboratories. The stability of the cylinders will be confirmed by a second measurement after they have been returned to the pilot laboratory.

Transport of cylinders to participating laboratories will be organized and paid for by NPL. Participants must arrange and pay for transport of the cylinders back to the pilot laboratory.

Participating laboratories should specify the method and calibration procedure used for the comparison in detail. *They should also state the route through which the calibration procedure provides traceability to the SI.*

Participating laboratories should make at least three measurements of the amount fraction of the analyte in each cylinder. The results of these measurements should be combined to provide the final result and the expanded uncertainty should be calculated. Detailed information should be provided about how the uncertainty budget was calculated, including an explanation of the sources of uncertainty accounted for and the total number of degrees of freedom in the final result.

NPL will be responsible for collecting and reporting measurement results.

After analysis by participating laboratories, the cylinders must be returned to the pilot laboratory with sufficient pressure for re-analysis. If a participant is not able tp return the cylinder to the pilot laboratory with sufficient gas to carry out a further analysis, it may not be possible to allocate an appropriate KCRV to that laboratory.

Blank measurement reports for measurement data and other relevant information are appended.

The final timings of the comparison will be agreed with the CCQM and EUROMET Gas Working Groups and sent out at the time that the cylinders are distributed.

Annex B – Analytical Procedure Used by the Coordinating Laboratory

The output of the primary SO_2 facility was compared directly with the travelling standards.

- 1. Pipe-work was conditioned using the mixtures under investigation for an appropriate time. The oxygen content of the diluent gas and unknown were measured to confirm that this would not result in cross-interference.
- 2. A dilution was set up such that the analyser measured within 3% of the reading from the travelling standard. The necessary flows were measured and the permeation rate was recorded.
- 3. Analyser input pressures from the diluted permeation and travelling standard flows were matched.
- 4. A sequence of pneumatic switching was carried out, such that the gas analyser receives flows alternately from the diluted permeation flow and the travelling standard for a number of four-minute cycles.
- 5. Following analysis, the flow measurements were repeated. The permeation rate was calculated from analysis of the permeation mass measurements.

This process was repeated three times for each certification cylinder.

Annex C – Gravimetric Permeation Standard Developed by the Coordinating Laboratory

Measurements of the CCQM K26 sulphur dioxide (SO₂) cylinders were made by comparison with NPL's Primary SO₂ facility. This facility is based on the dynamic dilution of the output of a permeation device, consisting of a permeable tube containing liquid sulphur dioxide, suspended at a constant temperature on a high-accuracy microbalance (Figure C1).

Under the measurement conditions, gaseous SO_2 continuously permeated through the membrane that made up the tube wall at a constant rate, determined by continuous weighing of the tube. The tube output was diluted with a known flow of high-purity air. In this way it was possible to vary the output amount fraction of SO_2 within a gas stream, and by measurement of the necessary parameters it was possible to determine the SO_2 amount fraction. A diagram of the facility is shown in Figure 2C.

A microbalance (Sartorius model, M25D) was used to measure the mass of the permeation tube continuously. It was mounted on a marble bench and enclosed within a protective screen to eliminate the effect of changes in ambient temperature. The permeation tube and surrounding balance were maintained at a nominal temperature of 30°C by means of a thermally-controlled fluid jacket and bath. The actual temperature achieved does not influence the results, but any variations in the temperature must be minimised in order to limit drift in wither the balance or the permeation rate. Measurements with a platinum resistance probe showed that the temperature was typically controlled to within 0.05°C of the median value. The balance was calibrated prior to use in CCQM K26b with calibrated mass pieces, and its long-term drift was assessed.



Figure C1 - Dual-pan balance used for on-line determination of the permeation rate



Figure C2 - Schematic diagram of primary SO_2 generation/measurement facility

Resolution	1 μg
Balance Temperature Drift	<6 µg/K
Linearity Error	<1 µg within 30 mg

Table C1 - Specified performance of Sartorius microbalance (from manufacturer's manual)

An example of the results of continuous mass measurements from this microbalance is given in Figure C3. The mass is measured typically every 8s and the typical mass loss over a seven hour period is approximately 1300 μ g. Figure C3 shows that the measured drift of the permeation rate is generally within the 1 μ g resulstion of the balance.

The permeation device (Kin-Tek) consisted of a sealed FEP tube containing liquid sulphur dioxide at a nominal purity of 99.98%.

"Metrology Grade" (BOC) air was used as the matrix, after verification that it contained much less than 1 nmol/mol of SO₂. Additionally, owing to the oxygen cross-interference with the fluorescence reaction within the analyser it was necessary to ensure that the oxygen content of the matrix was within 0.1% of that of the commercially prepared mixtures. This test was performed using a paramagnetic oxygen analyser, calibrated using gravimetrically prepared oxygen standards.

Dilution flows were regulated by means of a thermal mass-flow controller. They were calibrated against a Brookes Vol-U-Meter with a manufacturer's claimed uncertainty of 0.2%. This device is regularly checked by NPL by measuring a known mass flow of gas from an accurately weighed gas cylinder.



Figure C3. (a) Continuous mass measurements of permeation device. (b) Deviation of each measured point from a straight line fitted to the measured data.

Annex D – Results and reports as submitted by participating laboratories

Key comparison participants:

<u>Final Report - Chemicals Evaluation and Research Institute, Japan</u> (CERI/NMIJ)

Laboratory : National Metrology Institute of Japan (NMIJ) (Performed by Chemicals Evaluation and Research Institute, Japan)

Cylinder number : CPB-19107

nominal composition

- sulphur dioxide : 240 to 320 .10⁻⁹ mol/mol - synthetic air : balance

Results: gravimetric value

Analyte	Result (assigned value) (nmol/mol)	Coverage factor	Assigned expanded uncertainty
SO_2	278.4	2	6.2

Reference Method:

Instruments for SO₂ measurement Principles: UV fluorescence SO₂ Analyzer Make: Thermo Environmental Instruments Inc. Type: Model 43C Trace Level Data collection: output of integrator recording

Sample:

Preparation : Gravimetric method

Purity analysis ;

SO₂ : certified by NMIJ(National Metrology Institute of Japan)

 O_2 , N_2 : The impurities in O_2 and N_2 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 verification: Table 1 concentration of PSMs

Table 1 concentration of PSIMs				
Component	Concentration (nmol/mol)			
Component	R ₁	R ₂		
SO ₂	296.7	251.8		

This procedure is for the verification of SO_2 in a sample using UV fluorescence analyzer.

- 1) Inject the calibration standard (R_1) into UV fluorescence analyzer. Record the output.
- 2) Inject the sample to be tested in same manner as the calibration standard. Record the output.
- 3) Inject the calibration standard (R₂). Record the output.
- 4) Calculate the concentration of SO₂ using the formula below.

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

where *Y*: Concentration of sample

- A: Concentration of standard (R_1)
- *B*: Concentration of standard (R₂)
- *C*: Standard (R₁) output
- D: Standard (R₂) output
- *E*: Sample output

Above procedure is repeated subsequently 4 times in a day.

(Date: 26/04/2005)

Measurement	Concentration of SO ₂
1	278.8 nmol/mol
2	280.7 nmol/mol
3	279.1 nmol/mol
4	279.1 nmol/mol

Average value: 279.4 nmol/mol Standards deviation: 0.86 nmol/mol

Stability:

After the sample was compared by NPL and returned to CERI, CERI was re-analyzed using new PSMs by above procedure.

Table 2 concentration of new PSMs

Component	Concentration (nmol/mol)		
component	R_1	R ₂	
SO ₂	289.6	239.0	

(Date: 20/09/2005)

Measurement	Concentration of SO ₂
1	277.3 nmol/mol
2	274.0 nmol/mol
3	275.2 nmol/mol
4	275.8 nmol/mol

Average value: 275.6 nmol/mol Standards deviation: 1.37 nmol/mol

The changed value is 3.8 nmol/mol (279.4 – 275.6) during the period of the comparison (5 months). The uncertainty of stability is $2.2 = (3.8 / 3^{1/2})$. We evaluate it as stability in this comparison.

Sample Handling:

Stabilization : none Gauge pressure: 100 kPa Sample flow: 1.0 L/min Sample line temperature: room temperature (25 degrees Celsius) Dilution: none

Uncertainty:

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c _I	Contribution to standard uncertainty $u_1(y)$
Preparation (gravimetric)	278.4	normal	1.96	1	1.96
Verification	279.4	normal	0.86	1	0.86
Stability	278.4	rectangular	2.2	1	2.2
Total					3.07

Coverage factor: 2 Expanded uncertainty: 6.2 nmol/mol

Final Report - Czech Hydrometeorological Institute (CHMI)

Laboratory: Czech Hydrometeorological Institute, Na Sabatce 17, 143 06 Prague 4

Calibration Laboratory of Immission, Gen. Sisky 942, Prague 4

Cylinder number: BOC 172468 SG

NOMINAL COMPOSITION			
- Sulphur dioxide	:	240 to 320 .10 ⁻⁹	mol/mol
- synthetic air	:	balance	

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub- measurements
SO ₂	2.7.2004	284,5 . 10 ⁻⁹	0,67	2

Measurement	Date	Result	stand. deviation	number of sub-
No. 2		(mol/mol)	(% relative)	measurements
SO ₂	8.7.2004	283,3 . 10 ⁻⁹	0,74	2

Measurement	Date	Result	stand. deviation	number of sub-
No. 3		(mol/mol)	(% relative)	measurements
SO ₂	9.7.2004	286,4.10-9	0,80	2

Measurement	Date	Result	stand. deviation	number of sub-
INO.		(mol/mol)	(% relative)	measurements
SO ₂	9.7.2004	286,8 . 10 ⁻⁹	0,80	2

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO_2	285,2 . 10 ⁻⁹	2	4,6 . 10 ⁻⁹ mol/mol
	mol/mol		

Reference Method: Diluted PRM by manometric static injection

Calibration Standards: NMi gaseous primary reference material (PRM), cyl. No. 153670

concentration sulfur dioxide $(9,99 \pm 0,10) \ge 10^{-6}$ mol/mol in certificate 318319-02 issue 18.6.2004

Instrument Calibration: Work etalons: Thermo Environmental Instruments 43C and 43A

Sample Handling: Direct from manometric static injection system to analyzers Cylinder without reduction valve to analyzers

Uncertainty:

Uncertainty source	Estimate <i>x_I</i>	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c _I	Contribution to standard uncertainty <i>u₁(y)[%]</i>
PRM SO2 in N2	9990µmol/mo 1	normal	50 µmol/mol	100	0,501
Pressure <i>p1</i>	~ 1000 hPa	normal	0,135 hPa	-	-
Pressure <i>p2</i>	~ 1040 hPa	normal	0,135 hPa	-	-
Pressure <i>p3</i>	~ 1450 hPa	normal	0,275 hPa	-	-
Dilution <i>f1</i>	~ 0,0285	normal	0,000132	100	0,464
ΔT	300 K	rectangular	0,173	100	0,058
Work etalon D_{PRM}	284 ppb	rectangular	0,577ppb abs + 0,173% rel	100	0,267
Work etalon D_{CYL}	285 ppb	rectangular	0,577ppb abs + 0,231% rel	100	0,307
SO2 in Air cyl.	285,2 μmol/mol				0,800

Coverage factor: k = 2Expanded uncertainty: 4,6 . 10^{-9} mol/mol

Final Report - Finnish Meteorological Institute (FMI)

Laboratory : Finnish Meteorological Institute Cylinder number : 172505

NOMINAL COMPOSITION

- Sulphur dioxide : 240 to 320 .10⁻⁹ mol/mol - synthetic air : balance

Measurement	Date	Result	stand. Deviation	number of sub-
No. 1		(mol/mol)	(% relative)	measurements
SO ₂	31.8.04	273.6 10 ⁻⁹	0.3	20

Measurement	Date	Result (mol/mol)	stand. Deviation	number of sub- measurements
SO ₂	1.9.04	274.3 10 ⁻⁹	0.4	20

Measurement	Date	Result	stand. Deviation	number of sub-
No. 3		(mol/mol)	(% relative)	measurements
SO ₂	3.9.04	273.5 10 ⁻⁹	0.1	20

Measurement	Date	Result	stand. Deviation	number of sub-
110.			(70101011100)	measurements
SO ₂	3.9.04	273.6 10 ⁻⁹	0.1	20

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO ₂	273.8 10 ⁻⁹ mol/mol	K = 2	1,6 %

Reference Method:

Reference method for the analysis of the CCQM-K26 key comparison Sulphur dioxide gas cylinder was based on the UV-fluorescence method (ISO/FDIS 10498). The analyser, TEI 43 CTL s/n – 315, was calibrated by the dynamic dilution method (ISO 6145-6) in the range of 150 to 350 nmol/mol. The laboratory is accredited by the Centre for Metrology and Accreditation (MIKES/FINAS) as a calibration laboratory

according to the standard ISO/IEC 17025. The scope of accreditation is from 5 to 1000 nmol/mol for the calibration and measurement of sulphur dioxide.

Calibration Standards:

The gas standard used for the calibration of the Sulphur dioxide analyser was a secondary gas standard of the National Physical Laboratory (NPL) in UK. The details of the calibration certificate of the standard are: The certificate number is E04040336/A, dated 28, June 2004, and the content of the standard is sulphur dioxide in nitrogen C = 100.0 ±1.0 μ mol/mol where the uncertainty of the results is based on a standard uncertainty multiplied by a coverage factor k = 2, providing a level of confidence of approximately 95 %.

The other reference standards used in the measurements are:

Gas dilutor, Sonimix 6000A1 s/n 1585, calibrated at Laboratoire National de Metrologie, BNM-LNE; certificate C020080/1; March 2002

Pressure meter, Diptron 3 plus with the pressure probe UXD-95942, calibrated at MIKES (certificate no M-04P072) and used to control the dilution pressure of the gas dilutor.

Instrument Calibration:

The analyser TEI 43 CTL used for the analysis of the CCQM-K26 Sulphur dioxide cylinder was calibrated according to the standard operation procedure of the laboratory (SOP). The calibration range was 150 to 350 nmol/mol by fixed calibration concentration approximately at 50 nmol/mol intervals i.e. a five-point calibration. Synthetic air was used as the dilution gas. The calibration of the analyser took place before and after the analysis of the sample. The CCQM-K26 cylinders were analysed during three days with the same TEI 43 CTL analyser. The calibration results were treated according to the SOP of the laboratory: 10 individual values from the stable reading of the analyser were included in the data analysis. The mean value and the standard deviation of the stable reading were calculated and the MS-Excel sum of least squares analysis was used to obtain a linear curve fitting to the data. The response functions of each calibration were compared to each other throughout the measurements. No clear drift was observed.

The dynamic dilution device was used for obtaining the calibration concentration. The dilutor, Sonimix 6000A1 s/n 1585 by LN-Industries Switzerland, is based on the so-called critical orifices which produces multipoint calibration concentration by fixed dilution steps. The linearity of the dilution steps of the dilutor was checked with carbon monoxide using the reference gas standard of the laboratory (carbon monoxide in nitrogen from NPL, UK, $C = 0.991 \pm 0.008$ % certificate no QE11/N02/018/A, 9 July 2002) and the carbon monoxide analyser, APMA-360 s/n 910 007. To complete the correct dilution level of the dilutor the other reference gas standard was injected directly into the carbon monoxide analyser used in the measurements. The other reference gas standard was from the Nederlands Meetinstituut, The Netherlands, certificate no 318230 (carbon monoxide in nitrogen $C = 40.01 \pm 0.10 \mu mol/mol, 8$ March 2004). During the operation of the dilutor the pressure of the dilution line was controlled by the reference pressure meter of the laboratory. The pressure in the

calibration gas line was kept constant by a pressure regulator but not controlled by a pressure meter because of the danger of corrosion of the gauge. The traceability of the pressure meter goes to the national metrological institute (MIKES).

Sample Handling:

The sample was injected into the analyser through the sample port without particulate filter with the excess of gas of 1 l/min. The pressure of the reaction cell of the analyser was recorded during the measurements and normalised to the same condition as during the calibration of the analyser. The pressure of the reaction cell was between 5 to 15 mmHg higher than during the calibration of the analyser. The measurement results were corrected according to the equation:

$$C_p = C_{m,c} - B(p_m - p_c)$$

Eq(1)

Where

 C_p is corrected results due to pressure, $C_{m,c}$ is the corrected sample results due to calibration, B is the slope of the analyser respond due to the chamber pressure, p_m is the pressure of the reaction cell during the measurements of the sample p_c is the pressure of the reacton cell during calibration.

The tubing, the regulator and the connectors were conditioned during 30 min prior to the measurements.

The measurements of the samples took place according to a sequence of instrument calibration, sample analysis, injection of zero gas into the analyser, and calibration of the analyser. The sample analysis and the injection of zero gas were repeated two to three times in a day. The duration of the sample analysis and the injection of zero gas was at least 20 min in order to reach the stable reading of the analyser.

Uncertainty:

The standard uncertainty of the Sonimix 6000A gas dilutor for one dilution step can be expressed by:

$$u(C(1))^{2} = \left(\frac{C_{ST}}{f(bs1) + f(bs2)}\right)^{2} u(bs4)^{2} + \left(\frac{f(bs4) \cdot C_{ST}}{(f(bs1) + f(bs2))^{2}}\right)^{2} (u(bs1)^{2} + u(bs2)^{2}) + \left(\frac{f(bs4)}{f(bs1) + f(bs2)}\right)^{2} u(C_{ST})^{2} + u(C_{dil})^{2}$$

Eq(2)

Where

 $u(C(I))^2$ is the standard uncertainty of the first dilution step for the calibration concentration

C_{ST} is the concentration of the gas standard (Secondary reference material)

 $f(bs1) \dots f(bs4)$ are the flows of the critical orifices $bs1 \dots bs4$ $u(bs1) \dots u(bs4)$ standard uncertainty of the flows of the critical orifices $u(C_{ST})$ standard uncertainty of the gas standard (SRM) $u(C_{dil})$ standard uncertainty of the dilution gas (impurities)

Equation 1 is derived from

$$u_{c}(y)^{2} = \sum_{i} \left(\frac{\partial f(x_{i})}{\partial x_{i}} \right)^{2} u(x_{i})^{2}$$

Eq(3)

Here the equation for the produced calibration gas concentration can be expressed as a function of the contributing variables:

$$f = f(C, F, I)$$

Eq(4)

where C is the concentration of the reference gas standard, F is the flow rate of a single critical orifice in each of the dilution steps, and I is the impurities of the zero gas. The pressure on the span and zero line of the dilutor, also affects the results but we have recorded the pressure continuously at the dilution line and checked at frequent intervals that the pressure in the span line is constant. Also the temperature has an effect on the concentration but that is kept constant during the calibration.

We differentiate Eq(3) with respect to all the variables but in doing so we have omitted the cross terms i.e. the covariance terms in the calculations as second order terms. Since the Sonimix operates with fixed dilution steps (10 altogether) we have performed the uncertainty calculation for each of the dilution steps which are similar to Eq(2). The uncertainty components from the Eq(2) are listed in Table 1. Table 1. The uncertainty components of the sulphur dioxide concentration produced with the gas dilutor.

Parameter	Description of the effect	Standard uncertainty
u _{bs1} u _{bs7}	The uncertainty of the flow through an individual sonic orifice.	0.3 0.5 % of the flow of the sonic orifice
u(C) _{ST}	Standard uncertainty of the used gas standard.	0.5 % of the certified concentration.
u(C) _{dil}	The impurity of the zero gas as a mean value of the change of zero level by frequent calibration.	0 0.5 ppb

The uncertainty of the calibration concentration is an important factor in the uncertainty analysis since it also describes the uncertainty of the traceability chain to the SI-unit as a whole. In our case the gas standards go to gravimetric method conducted by NPL, UK, and to Nmi, The Netherlands. In addition to that the flow measurements were traced to the Laboratoire National de Metrologie, BNM-LNE, France. The pressure and temperature measurements are traced to the Centre for Metrology and Accreditation, MIKES, Finland.

The second part in the uncertainty budget is contributed by the analyser. Since the measurements took place in the laboratory at controlled conditions and the analyser was calibrated prior and after the measurements of the CCQM-K26 samples we have included into the uncertainty budget only those performance characteristics of the analyser that are important in this case. We have therefore included the following performance characteristics that we have tested in the laboratory:

- Linearity of the analyser in the range of 150 to 350 nmol/mol
- Repeatability

Short-term drift is not included, and interferences by other pollutants are also not taken into account here. The impurity of the zero gas is taken into account in the calibration concentration (see Table 1)

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c _I	Contribution to standard uncertainty $u_1(y)$
Uncertainty of calibration concentration including dilution and traceability chain to SI	See Eq (2)	rectancular	2.1 ppb	1	0.8 %
Uncertainty due to the analyser - Linearity - Repeatability	0.7 nmol/mol 0.3 % at 275 nmol/mol	Rectangular normal	0.4 nmol/mol 0.8 nmol/mol	1 1	0.15 % 0.3 %
					0.8 %

Coverage factor: k=2 Expanded uncertainty: 1.6 %

Final Report - Instituto Português da Qualidade IPQ

Laboratory: Portuguese Institute for Quality (IPQ) Cylinder number: 172472 SG

NOMINAL COMPOSITION

- Sulphur dioxide: 240 to 320 .10⁻⁹ mol/mol

- synthetic air: balance

Measurement	Date	Result	stand. deviation	number of sub-
110.1			(70101011100)	measurements
SO_2	17-09-2004	260,9 x 10 ⁻⁹	0,5	10

Measurement	Date	Result (mol/mol)	stand. deviation	number of sub- measurements
SO ₂	20-09-2004	261,3 x 10 ⁻⁹	0,3	10

Measurement	Date	Result	stand. deviation	number of sub-
No. 3		(mol/mol)	(% relative)	measurements
SO ₂	21-09-2004	263,2 x 10 ⁻⁹	0,4	10

Measurement	Date	Result	stand. deviation	number of sub-
INO.		(mol/mol)	(% relative)	measurements
SO ₂	22-09-2004	262,4 x 10 ⁻⁹	0,4	10

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO ₂	261,9 x 10 ⁻⁹	2	5,1 x 10 ⁻⁹

Reference Method:

Dynamic Generation by Permeation Technique (ISO 6145-10:2002).

Calibration Standards:

A series of 5 standard mixtures were prepared: 174.8×10^{-9} mol/mol; 224.6 x 10^{-9} mol/mol; 275.0 x 10^{-9} mol/mol; 323.3 x 10^{-9} mol/mol; 373.7 x 10^{-9} mol/mol;

Instrument Calibration:

Thermo 43C Analyzer (SO₂)

Sample Handling: The sample is introduced directly from cylinder to the analyzer, passing thru a flowmass controller.

Uncertainty:

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c _I	Contribution to standard uncertainty $u_l(y)$
Reproducibility	261,9 x 10 ⁻⁹	normal			0,5 x 10 ⁻⁹
Repeatability	-	normal			0,3 x 10 ⁻⁹
Interpolation	-	normal			0,9 x 10 ⁻⁹
Air Flow	-	normal			2,2 x 10 ⁻⁹
Mass-Flow Controllers Calibration	-	normal			0,3 x 10 ⁻⁹
Weighing	-	normal			0,0 x 10 ⁻⁹
Time					
Measurement	-	normal			0,1 x 10 ⁻⁹
Leaks	-	rectangular			0,1 x 10 ⁻⁹
Impurities	-	normal			0,8 x 10 ⁻⁹
Permeation Rate	-	normal			0,4 x 10 ⁻⁹

Coverage factor: 2 Expanded uncertainty: 5,1 x 10⁻⁹ mol/mol

Final Report - European Commission Joint Research Centre (JRC)

Laboratory : Cylinder number :

NOMINAL COMPOSITION

- Sulphur dioxide : $240 \text{ to } 320.10^{-9} \text{ mol/mol}$

:

- synthetic air

balance

Measurement	Date	Result	stand. deviation	number of sub-
No. 1		(mol/mol)	(% relative)	measurements
SO ₂	01.07.04	283.0	0.18	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 2		(mol/mol)	(% relative)	measurements
SO ₂	02.07.04	285.4	0.12	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 3		(mol/mol)	(% relative)	measurements
SO_2	02.07.04	285.2	0.09	5

Measurement	Date	Result	stand. deviation	number of sub-
No.		(mol/mol)	(% relative)	measurements
SO ₂	-			

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO ₂	284.5	2	2.9

Reference Method:

UV Fluorescence measurement, calibration with Permeation method

Calibration Standards:

Two calibration concentrations are generated dynamically by means of two permeation ovens containing two SO2 permeation tubes. The tubes are weighed every \sim 4 weeks. The flow measurement is carried out with a Brooks Vol-U-Meter

Instrument Calibration:

An Environnement AF 21M is calibrated with zero gas, span gas 1 (around 240 ppb) and span gas 2 (around 340 ppb). After the calibration the sample is measured.

Sample Handling:

The pressure reducer has been carefully purged several times (under vacuum). When the concentration stability was given the measurement results were recorded.

Uncertainty:

The standard uncertainty of the calibration gases is evaluated by estimating the error sources of the mass, flow and time measurement of the permeation systems. The analysis function between analyzer response (and its uncertainty) and analyte content (and its uncertainty) is calculated using ISO 6143 (Determination of composition and checking of calibration gas mixtures – comparison method); out of the comparison method the analyte content and uncertainty of the NPL gas cylinder are evaluated. Analyzer drift has not been taken into account as the measurement is done immediately after calibration.

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c _I	Contribution to standard uncertainty $u_1(y)$
u(x0)			0.29		
u(x1)			1.89		
u(x2)			1.93		

Coverage factor: 2 Expanded uncertainty: 2.9 mol/mol

Final Report - Korea Research Institute of Standards and Science (KRISS)

Laboratory : Cylinder number : 172469SG

NOMINAL COMPOSITION

240 to 320×10^{-9} mol/mol - Sulphur dioxide : balance

- synthetic air :

Measurement	Date	Result (10 ⁻⁹ mol/mol)	Stand. uncertainty (10 ⁻⁹ mol/mol)	Number of sub- measurements
No. 1	04/8/4	273.9	1.4	5
No. 2	04/8/6	276.4	1.5	5
No. 3	04/8/9	276.0	1.5	5
No. 4	04/8/10	275.4	1.5	5
No. 5	04/8/12	273.6	1.5	5

Results:

Analyte	Result (10 ⁻⁹ mol/mol)	Coverage factor	Expanded uncertainty (10 ⁻⁹ mol/mol)
SO ₂ / Air	275.1	<i>k</i> =2	3.0

Reference Method:

We used SO₂ analyzer (Model 43C, TEI) for this measurement. Configuration of analysis is as follows:



We designed a new gas inlet system using one regulator for this measurement to eliminate adsorption problems on the regulator. Sample and zero gases (pure nitrogen) were introduced into analyzer for 4 min alternatively. We used A-B-A method to correct instrumental drift. Sample and reference gases were determined 5 times, respectively. And gas flow rate was controlled to 700 ml/min by MFC.

Gas inlet sequences for SO₂ measurement:

Nitrogen - STD - Nitrogen - Sample (1st) - Nitrogen - STD -

Nitrogen - STD - Nitrogen - Sample (2nd) - Nitrogen - STD -

Nitrogen - STD - Nitrogen - Sample (3rd) - Nitrogen - STD -

Nitrogen - STD - Nitrogen - Sample (4th) - Nitrogen - STD -

Nitrogen - STD - Nitrogen - Sample (5th) - Nitrogen - STD - Nitrogen

Calibration Standards:

We used Al cylinders (Luxfer, Au) with stainless steel valve pretreated at CERI, Japan.

The calibration standards were prepared by gravimetry method in our institute as follow.

2 %mol/mol (4 cylinders) \rightarrow 1,000 µmol/mol (4 cylinders)

 \rightarrow 20 µmol/mol (6 cylinders) \rightarrow 280 nmol/mol (11 cylinders).

Pretreatment of cylinder:

- Evacuation with heating at 60 °C
- Leaving for one week in SO2 10 µmol/mol in nitrogen at 20 bar
- Leaving for one week in $SO_2 10 \mu mol/mol$ in nitrogen at 1 bar
- Evacuation with heating at 60 °C

Purity of SO_2 source gas was determined by impurity analysis. Overall uncertainty of the 280 nmol/mol standards including purity of the source gas, weighing uncertainty, and manufacturing uncertainty was about 0.2 %.

Instrument Calibration:

The four standard gases with similar concentration (about 280×10^{-9} mol/mol) were prepared by gravimetry method. Four standard gases were selected and checked by SO₂ analyzer to make sure their accuracy. We used A-B-A method and these standards were used as reference gases.

Sample Handling:

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

Uncertainty:

Quantity	Value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution (nmol/mol)	Corr coeff.	Index
No. 1	273.91 nmol/mol	1.43 nmol/mol	0.200	0.286	0.19	0.037
No. 2	276.44 nmol/mol	1.46 nmol/mol	0.200	0.292	0.20	0.039
No. 3	275.96 nmol/mol	1.45 nmol/mol	0.200	0.290	0.20	0.038
No. 4	275.43 nmol/mol	1.50 nmol/mol	0.200	0.300	0.20	0.041
No. 5	273.55 nmol/mol	1.47 nmol/mol	0.200	0.294	0.20	0.040
Factor related to the manufacturing uncertainty of PRM	1.00000	1.00.10-3	275	0.275	0.19	0.035
Factor related to the linearity of PRM	1.0	0.0	0.0	0.0	0.0	0.0
Factor related to the matrix effect	1.0	0.0	0.0	0.0	0.0	0.0
Factor related to the stability of PRM	1.00000	$2.50 \cdot 10^{-3}$	275	0.688	0.47	0.216
Factor related to the uncertainty of measurement reproduceability	1.00000	4.00.10-3	275	1.10	0.74	0.554

Coverage factor: 2.0 Expanded uncertainty: 3.0 nmol/mol

Final Report - Laboratoire national de métrologie et d'essais (LNE)

Laboratory : Laboratoire National d'Essais (LNE) Cylinder number : 172509

NOMINAL COMPOSITION

- Sulphur dioxide	:	240 to 320 $.10^{-9}$	mol/mol

- synthetic air : balance

SO2 25/06/2004 282.0 0.35 3	Measurement No. 1	Date	Result (10 ⁻⁹ mol/mol)	stand. deviation (% relative)	number of sub- measurements
282.0	SO2	25/06/2004	282.0 284.0 282.0	0.35	3

Measurement	Date	Result	stand. deviation	number of sub-
No. 1		(10 ⁻⁹ mol/mol)	(% relative)	measurements
SO2	29/06/2004	282.0 282.0 283.0	0.20	3

Measurement	Date	Result	stand. deviation	number of sub-
No. 1		(10 ⁻⁹ mol/mol)	(% relative)	measurements
SO2	30/06/2004	282.0 283.0 283.0	0.20	3

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO_2	282.7.10 ⁻⁹ mol/mol	2	2.9.10 ⁻⁹ mol/mol

Reference Method:

A AF21M (Environnement SA) analyser based on the principle of UV fluorescence is used to measure the SO₂.

Calibration Standards:

A high concentration gas mixture of SO_2 in nitrogen (at about 10.10^{-6} mol/mol) is prepared by a multistage gravimetric method.

Then, a gas mixture of SO₂ in synthetic air at about 300.10^{-9} mol/mol is generated by diluting the gravimetric gas mixture of SO₂ in nitrogen at about 10.10^{-6} mol/mol with synthetic air and by using flowmeters (Molbloc/Molbox).

Instrument Calibration:

Stage 1: Adjustment of the analyser

The analyser is adjusted at 2 points : zero and a full scale point (the concentration of the span gas must be slightly upper to the concentration of the unknown gas to be analysed afterwards).

Stage 2: Determination of the SO₂ concentration of the unknown gas mixture

The unknown gas mixture is injected 3 times into the SO₂ analyser. The SO₂ concentration of the unknown gas mixture is equal to the SO₂ concentration displayed by the analyser (C_{read}).

This procedure (stage 1 + stage 2) is carried out 3 times.

Sample Handling:

Cylinders were maintained inside a laboratory at a nominal temperature of (21 ± 2) °C for all the period.

Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

Uncertainty:

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c _I	Contribution to standard uncertainty $u_1(y)$
Zero gas concentration	0	rectangular	5.774.10 ⁻¹⁰	2.4.10 ⁻²	1.39.10 ⁻¹¹
Span gas concentration	291	-	1.12.10 ⁻⁹	9.8.10 ⁻¹	1.10.10 ⁻⁹
Reading for zero gas concentration	0	rectangular	5.774.10 ⁻¹⁰	2.4.10 ⁻²	1.39.10 ⁻¹¹
Reading for span gas concentration	291	rectangular	5.774.10 ⁻¹⁰	9.8.10 ⁻¹	5.66.10 ⁻¹⁰
Standard deviation of the mean of the 9 measurements	282.7	-	0.71.10 ⁻⁹	1	0.71.10 ⁻⁹

Coverage factor: 2 Expanded uncertainty: $U = 2.9.10^{-9}$ mol/mol

Final Report - Netherlands Meetinstituut (NMi)

Laboratory : NMi-VSL Cylinder number : 172508 SG

NOMINAL COMPOSITION

- Sulphur dioxide : 240 to 320 .10⁻⁹ mol/mol - synthetic air : balance

Measurement	Date	Result	stand. deviation	number of sub-
SO ₂	21-07-2004	275,80 10 ⁻⁰⁹	0,55	1

Measurement	Date	Result	stand. deviation	number of sub-
No. 2		(mol/mol)	(% relative)	measurements
SO ₂	22-07- 2004	275,15 10 ⁻⁰⁹	0,55	1

Measurement	Date	Result	stand. deviation	number of sub-
No. 3		(mol/mol)	(% relative)	measurements
SO ₂	23-07- 2004	274,66 10 ⁻⁰⁹	0,55	1

Measurement	Date	Result	stand. deviation	number of sub-
No. 4		(mol/mol)	(% relative)	measurements
SO ₂	06-09- 2004	273,92 10 ⁻⁰⁹	0,55	1

Measurement	Date	Result	stand. deviation	number of sub-
No. 5		(mol/mol)	(% relative)	measurements
SO ₂	08-09- 2004	274,64 10 ⁻⁰⁹	0,55	1

Measurement	Date	Result	stand. deviation	number of sub-
No. 6		(mol/mol)	(% relative)	measurements
SO ₂	08-09- 2004	276,77 10 ⁻⁰⁹	0,55	1

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO ₂	275,16 10 ⁻⁰⁹	2	$3,0\ 10^{-09}\ (1,1\%\ rel.)$

Reference Method:

The measurements have been performed with a model 43A Pulsed Fluorescence SO₂ Analyser from Thermo Electron with a measurement range of 2 ppm.

Calibration Standards:

Calibration has been performed by use of a permeation tube and dynamic dilution according to ISO 6145-10:2002 Gas analysis - Preparation of calibration gas mixtures – Part 10: Permeation method. The permeation rate is determined by continuous weighing using a Magnetic Suspension balance from Rubotherm. The dilution rate is determined by using a Brooks Vol-U-Meter Calibrator.

Instrument Calibration:

Between 260 and 290 ppb 5 dilutions covering this range have been measured for each calibration curve.

Sample Handling:

A pressure regulator from a dedicated sat for low ppm mixtures of SO_2 is connected on the cylinder. The reducer was cleaned at least 8 times by sequential purging over a two days period. Directly before the measurement the reducer was cleaned another 3 times. After a flushing time of 20 minutes for both static and dynamic mixtures 90 samples of the response (mV) are collected. The average and standard deviation of thes 90 samples are used for calculations.

Uncertainty:

Measurements are performed according to ISO 6143:2001(E) Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures. A straight line was used as calibration model throughout the measurements.

The main uncertainty source in the determination of the actual amount fraction of the dilution is the uncertainty in the determination of the permeation rate that is 1% rel (k=1). The uncertainty in the reading of the Brooks Vol-U-Meter is 0,1% rel. (k=1). The uncertainty in the response of the analyser is on average ≤ 20 mV, or 0,1% rel. (k=1).

On the basis of these considerations a TLS–regression with a standard uncertainty of 1% relative on the amount-of-substance fractions of the calibrants results in a standard uncertainty associated with the amount-of-substance fraction of SO₂ in the comparison cylinder of 0.55% relative. This estimate is the result of propagating the uncertainties associated with the composition of the calibrants and the responses.

Coverage factor: 2 Expanded uncertainty: 3,0 ppb

Final Report - National Physical Laboratory (NPL)

Report of Analysis for CCQM-K26b by NPL

NPL's measurements of the CCQM K26 sulphur dioxide (SO₂) cylinders were made by comparison with NPL's Primary SO₂ facility. This facility is based on the dynamic dilution of the output of a permeation device containing pure liquid sulphur dioxide, suspended in a constant temperature enclosure on a high-accuracy Sartorius microbalance.

Comparison Procedure

The output from the primary SO_2 facility was compared with the unknown mixture as follows:

- 6. Pipe-work was conditioned using the mixtures under investigation, for an appropriate time. The oxygen content of the diluent gas and unknown were measured to confirm that there will be no interference effects.
- 7. A dilution was set up such that the analyser measured within 3% of the reading from the unknown cylinder. The flows were measured and the mass loss from the permeation device was recorded.
- 8. Analyser input pressures from the dilution and certification cylinder were matched.
- 9. A series of pneumatic switching cycles was carried out, such that the gas analyser alternately sampled flow from the dilution and the certification cylinder for a number of four-minute sampling cycles.
- 10. The flow measurements were repeated after the analysis. The permeation rate was then calculated from analysis of the permeation mass measurements and combined with the other analytical results.

The comparison was carried out with an API Model 100A pulsed fluorescence analyser.

Results of Measurement of Cylinder 172506

Date of measurements = 07/09/2004.

Time (seconds)	Analyser output (V)	
18227	0.3792472	р
18523	0.3792534	u
18779	0.3792209	р
19019	0.3803000	u
19259	0.3764909	р
19498	0.3784003	u
19738	0.3769796	р
19970	0.3772790	u
20218	0.3770737	р
20458	0.3782294	u
20698	0.3767637	р
20946	0.3784390	u
21186	0.3760009	р
21426	0.3770984	u
21666	0.3772434	р
21906	0,3806457 41	u

The mean value of the ratio between the unknown (u) and the permeation flow (p) is 0.99658 with a standard deviation of 0.21% (relative).

Uncertainty Sources

The amount fraction of sulphur dioxide (X_P) in the flow from the standard permeation source is given in terms of the measured permeation rate ($\delta m / \delta t$) by

$$X_P = k \frac{\partial m}{\partial t} \frac{1}{F} \left(\frac{V}{M} \right)$$

 $F = \text{total gas flow } [\text{dm}^3 \text{s}^{-1}]$

k = correction for purity

M = relative molecular mass of SO₂ = 64.064 [gmol⁻¹]

V = volume of 1 mole of air at standard temperature and pressure= 22.401 dm³mol⁻¹

The drift in the balance dominates the uncertainty in the permeation rate over the measurement period. This is estimated to be approximately 3microg over a period of 300 minutes, corresponding to 0.36% of the permeation flow. The uncertainty in the flow (F) measured with the Brookes Vol-u-meter is estimated to be 0.3% (of value).

	Variable	Value	Uncertainty (<i>k</i> =1)	
_	$\frac{\delta m}{\delta t}$ F k	2.76381 3.4632 1.000	$0.36\% \\ 0.3\% \\ 0.01\%$	microg/min dm ³ /min
	Xp	279.05	0.47%	nmol/mol

The purity correction is estimated to be unity, with an uncertainty of 0.01%.

The value of the unknown (X_U) is calculated from the results of the comparison using

$$X_U = \frac{y_u}{y_v} X_P$$

 y_p = analyser response to dilution [mV] y_u = analyser response to unknown [mV]

Variable	Value	Uncertainty (<i>k</i> =1)	
$\frac{X_{\rm P}}{y_{\rm x}/y_{\rm p}}$	279.05 0.996589	0.47% 0.21%	nmol/mol
X_{U}	280.01	0.51%	nmol/mol

Hence, the measured value for cylinder 172506 on 07/09/2004 by NPL was 280.01 nmol/mol +/- 1.44 nmol/mol (*k*=1).

Final Report – Federal Environmental Agency [UBA (D)]

Laboratory : Federal Environmental Agency of Germany (UBA) Cylinder number : 172473

NOMINAL COMPOSITION

- Sulphur dioxide	:	240 to 320 .10 ⁻⁹ mol/mol
- synthetic air	:	balance

Measurement	Date	Result	stand. deviation	number of sub-
No. 1		(mol/mol)	(% relative)	measurements
SO ₂	07-08-04	281,85 E-09	0,07	4

Measurement	Date	Result	stand. deviation	number of sub-
110.2			(70 10101100)	measurements
SO_2	07-09-04	281,23 E-09	0,04	4

Measurement	Date	Result	stand. deviation	number of sub-
No. 3		(mol/mol)	(% relative)	measurements
SO ₂	07-14-04	281,55 E-09	0,16	4

Measurement	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub- measurements
SO ₂	07-26-04	283,25 E-09	0,18	4

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO_2	282,0 E-09	2	± 5,6 E-09

Reference Method:

For analyzing sulphur dioxide at the UBA laboratory a UV-fluorescence method based monitor HORIBA APSA 360 is used.

Calibration Standards:

Calibration standard is prepared by volumetric static injection. Known volumes of the pure gas compound are added to the complementary gas in a vessel of well-defined volume .

The method is described at ISO 6144 and VDI 3490. p. 14

Equipment:

cast iron vessel coated with enamel inside Pressure gauge	0.014736 m ³ max. pressure 1000 kPa 0-1000hPa Diptron 3 Wallace&Tiernan	
Temperature gauge	SPE-Pt 100 Schwille	
Vacuum pump	vacuubrand	
Operating material:		
Digital microliter syringe 1710	50 µl Hamilton series	
Synthetic air (balance gas)	5.0 Messer	
Sulphur dioxide (pure gas)	3.8 Messer; certified by NMI Netherlands	

After evacuation the vessel is filled with synthetic air at ambient air pressure and temperature. The pure gas is injected by syringe. After that the pressure is increased by introducing additional complementary gas (9-fold ambient air pressure e.g.). The mixture have to re-equilibrate to ambient temperature.

The whole procedure is done in accordance with ISO 6144.

Instrument Calibration:

Bracketing - Two-point Calibration

The low and the high standards were prepared by static volumetric injection method .The concentrations were chosen after measuring (estimate) the unknown gas by our reference analyzer.

Measurement result: 282 nmol/mol High standard: 295 nmol/mol Low standard: 265 nmol/mol

The concentrations were prepared in three steps by pressure reduction and refilling of a base standard.

- 1. Preparing base concentration 375 nmol/mol (p_{11}/p_{21})
- 2. Static dilution to 295 nmol/mol (p_{12}/p_{22})
- 3. Static dilution to 265 nmol/mol (p_{13}/p_{23})

$$C = C_{\text{Vessel}} \cdot \prod_{i=1}^{n} \frac{p_{1i}}{p_{2i}}$$
(1)

 p_1 = Pressure after reduction

 $p_2 = Pressure after refilling$

Sample Handling:

After arriving the cylinder was kept three weeks in the laboratory (stabilization).In order to take samples at ambient air pressure a pressure regulator was used and via T-piece a little overflow was controlled by a valve. For connecting with the monitor sample inlet ¹/₄" Teflon tubes and stainless steel fittings were used.

The gas flow was about 1.3 l/min.

For this intercomparison we took after a running in period of the pressure regulator (45min.)

4 samples (5 min.) for each measurement result.

Uncertainty:

 $u_{c}^{2} = u_{1}^{2} + s_{R}^{2} + s^{2}(\bar{q})$ (1)

u_c = Combined uncertainty

 u_1 = Combined uncertainty given by static injection method valid for both bracketing points

 s_R = Reproducibility of the static injection method in UBA laboratory

 $s^{2}(\bar{q}) = \text{Estimate of the variance of the mean}$ $s^{2}(\bar{q}) = \frac{s^{2}(q_{k})}{4}$ (2)

Calculation of u_1 according to ISO Guide GUM supported by GUM Workbench software.

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

 $u_1 = 2,51 \text{nmol/mol}$

 $s_R = 1,2 \text{ nmol/mol}$

 $s^{2}(\bar{q}) = 0,22 \text{ nmol/mol}$ (2)

$u_c = 2,78 \text{ nmol/mol}$ (1)

Coverage factor: 2 Expanded uncertainty: ± 5,6 nmol/mol

Uncertainty calculation of the Static Volumetric Method for the preparation of SO2 standard gas mixtures

The procedure is described in ISO 6144 Bracketing high

Model Equation:

 $C = C_p * V_s / V_d * p_1 / p_2 * p_3 / p_4$

List of Quantities:

Quantity	Unit	Definition
С		Volume fraction in the resulting mixture of SO2
C _p		Volume fraction of the pure gas SO2
Vs	1	Injected volume by syringe
V_d	1	Volume of the vessel (complementary gas)
p ₁	kPa	Pressure in the syringe
p ₂	kPa	Final pressure in the vessel
p3	KPa	Pressure static dilution
p ₄	KPa	Final Pressure static dilution

C: Result C_p : Type B rectangular distribution Value: 0.992 Halfwidth of Limits: 0.004 V_s : Type B triangular distribution Value: 51·10⁶1 Halfwidth of Limits: 0.0000011 It is taken into account the real gas factor with 0,976 (±2%) V_d : Type A Method of observation: Direct Number of observation: 5

No.	Observation
1	14.730
2	14.741
3	14.735
4	14.740
5	14.737

Arithmetic Mean: $14.73660 \ 1$ Standard Deviation: $4.4 \cdot 10^{-3} \ 1$ Standard Uncertainty: $1.96 \cdot 10^{-3} \ 1$ Degrees of Freedom: 4 **p₁:** Type B rectangular distribution Value: 101.3 kPa Halfwidth of Limits: 0.04 kPa **p₂:** Type B rectangular distribution Value: 911.7 kPa

Halfwidth of Limits: 0.36 kPa **p3:** Type B rectangular distribution

Value: 600 KPa Halfwidth of Limits: 0.24 KPa

p4:

Type B rectangular distribution Value: 762.7 KPa Halfwidth of Limits: 0.30 KPa **Uncertainty Budget:**

Standard **Degrees** of Distribution Sensitivity Index Quantity Value Uncertainty Freedom Coefficient $2.31 \cdot 10^{-3}$ 300.10-9 0.99200 rectangular 7.8 % Cp ∞ $408 \cdot 10^{-9}1$ $5.9 \cdot 10^{-3}$ V_s 51.000.10-61 triangular 91.9 % ∞ 1.96.10-31 -20·10⁻⁹ V_d 14.736601 4 0.0 % normal 23.1·10⁻³ kPa 3.0.10-9 101.300 kPa rectangular 0.0 % ∞ p_1 -330·10⁻¹² 911.700 kPa 0.208 kPa 0.0 % rectangular $p_{2} \\$ ∞ 500·10⁻¹² 600.000 KPa 0.139 KPa rectangular 0.0 % p3 ∞ -390·10⁻¹² 762.700 KPa 0.0 % p_4 0.173 KPa ∞ rectangular С 300.08.10-9 2.51.10-9 s

Result:

Quantity: C Value: 300.1·10⁻⁹ Expanded Uncertainty: ±5.0·10⁻⁹ Coverage Factor: 2.00 Coverage: manual

Final Report - VNIIM

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

Key Comparisons CCQM-K26 b Sulphur dioxide at the ambient level

REPORT 17.04.06

Authors:	L.A. Konopelko
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Reference method

Sulphur dioxide mole fraction in synthetic air was determined by fluorescent method. The analysis was carried out on gas analyzer "AF/SH 20M" (Environnement S.A., France), which is a part of apparatus of State primary standard of the units of components' mole fraction and mass concentration in gas media GET 154.

Calibration standards

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

Substance	Molar fraction,	Standard	Relative standard
	ppm	uncertainty, ppm	uncertainty, %
Sulphur dioxide	999750	68	0,007
Nitrogen	999988,5	0,812	0,00008
Oxygen	999990	2	0,0002

Preparation of standard gas mixture was carried out with the help of the standard calibration gas generator TDG-01 and the sulphur dioxide permeation tube, which was certified on standard thermo-gravimetrical complex. Synthetic air was used as diluent gas.

The uncertainty budget of sulphur dioxide mole fraction in the calibration standard is shown in Appendix A.

The characteristics of calibration standard are shown in table 2.

Table 2 – Characteristics of calibration standard

Substance Molar fraction, nmol/mol		Relative standard uncertainty, %
Sulphur dioxide	260,1	0,81
Synthetic air	balance	

Instrument calibration

The method of absolute calibration (comparison method) was used.

There were made 4 independent measurements under repeatability conditions with 4 independent calibrations (in 4 days during 8 days). One single measurement consisted of 3 sub-measurements. The measurement sequence was "calibration→measurement".

Sample handling

Prior to measurements cylinders were stabilized to room temperature. Measurements of sulphur dioxide mole fraction in cylinder N_{2} 172467 are shown in the table 3

Table 3 - Results of measurements of sulphur dioxide mole fraction in cylinder N_{2} 172467

N⁰	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
1	06.10.04	259,4 256,6 259,5	258,5	0,57

N⁰	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
2	08.10.04	259,5	259,7	0,60
		261,3		
		258,2		

N⁰	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
3	11.10.04	261,4	262,3	0,34
		262,4		
		263,2]	

N⁰	Date $(d/m/y)$	Measured value, nmol/mol	Mean value,	Standard deviation
4	13.10.04	261,4	261,1	0,55
		259,5	,	,
		262,3		

Evaluation of uncertainty of measurements

Total standard uncertainty of sulphur dioxide mole fraction was calculated on the base of the following components:

- total standard uncertainty of sulphur dioxide mole fraction in standard gas mixture (including uncertainty of permeation tube gravimetrical certification, uncertainty of measurement and keeping of flow rate and thermostatting temperature of permeation tube);

- standard deviation of the measurement results of sulphur dioxide mole fraction in gas mixture in cylinder № 172467.

Uncertainty budget for sulphur dioxide mole fraction in investigated gas mixture is shown in the table 4.

Table 4 – Estimation of uncertainty of sulphur dioxide mole fraction in gas mixture in cylinder №172467, presented for comparison

N⁰	Source of unce	ertainty	Relative
			standard
			uncertainty,%
1	Preparation	Permeation rate gravimetric certification	0,636
	of standard	Measurement and keeping of permeation	0,405
	gas mixture	tube thermostatting temperature	
		Measurement and keeping of diluent gas	0,289
		flow rate	
2	Standard devia	ation of the measurement result	0,31
	Total standa	rd uncertainty 0,	87
	Expanded un	certainty 1,7	'5

Result of measurements of sulphur dioxide mole fraction in investigated gas mixture is shown in the table 5 (this result was sent to NPL 15.10.04)

Table 5– Obtained value of sulphur dioxide mole fraction in gas mixture in cylinder N_{2} 172467 and expanded uncertainty

Substance	Result, nmol/mol	Expanded uncertainty, %	Coverage factor
Sulphur dioxide	260,4*	1,75*	2,0
Synthetic air	balance		

* Note – The result does not take into account the amendment due to different humidity of air during calibration of flowmeter and during measurements of gas flow on the outlet of TDG-01 in carrying out of comparison.

Corrected values due to the amendment for humidity are shown in the Appendix A

Appendix to Final report from VNIIM

Supporting material for the necessity of amendment insertion and

calculations of the corrected values

The flowmeter (Wet-gas meter "Ritter", $\delta = 0.5$ %), which was used for standard gas flow control, was calibrated with the help of "Bell-prover" ($\delta = 0.2$ %), with humid air (with approximately 100% humidity at temperature of performing calibration). But while preparing of the standard gas mixture with the help of TDG-01 and the SO₂ permeation tube dry air was used. Therefore, using of "Ritter" for dry gas flow control requires application of corrections to design formula of analyte concentration in the standard gas mixture - the amendment on water vapor pressure should be inserted for recalculation of humid gas flow rate to the real dry gas flow rate on the outlet of TDG-01.

<u>I Calculations of SO₂ mass concentration in standard gas mixture without</u> <u>amendment (C, mg/m³) and with it (C', mg/m³)</u> are shown below.

1 Mass concentration of SO_2 in standard gas mixture is calculated according to formula (1)

$$C = \frac{G}{Q} = \frac{G}{Q_{R} \cdot \frac{p \cdot 293,2}{101,3 \cdot (t+273,2)}}$$
(1),

where

G – permeation rate of SO₂ standard permeation tube (G=0,696 μ g/min);

 \mathbf{Q} – gas flow rate through Calibration gas generator, dm³/min;

 Q_R – gas flow rate in accordance with flowmeter «Ritter», dm³/min;

t, p – ambient temperature and pressure in measurements, °C and kPa.

Thus SO_2 mass concentration (and molar fraction) in standard gas mixture without amendment

C=0,693 mg/m³ = 260,1 nmol/mol (At t = 19,0°C, p = 102,7 kPa, Q_R =0,987 dm/min)

2 Formula (1) with amendment turns to

$$C' = \frac{G}{Q_{R}' \cdot \frac{p \cdot 293,2}{101,3 \cdot (t+273)}} = \frac{G}{Q_{R} \cdot \frac{(p-p_{w}) \cdot 293,2}{101,3 \cdot (t+273,2)}}$$

where

 \mathbf{p}_{w} – partial pressure of water vapor under measurement conditions, kPa.

In order to determine partial pressure of water vapor under measurement conditions we have performed the special experiments – measurements of relative humidity in the gas flow at the "Ritter" outlet.

Thermohygrometer Vaisala HMP 233, was used for this purpose (U = 1,0 %(abs.) at k=2)

At t=18,3 °C and Q_R =0,987 dm/min relative humidity at the outlet of the Ritter flow meter Rh=89,3%.

At t=24,1 °C and $\rm Q_R$ =0,987 dm/min relative humidity at the outlet of the Ritter flow meter Rh=87,7%

We can extrapolate relative humidity at $\mathbf{t} = 19,0^{\circ}$ C as 89 % and the appropriate \mathbf{p}_{w} will be

 $p_w = 1,955 \text{ kPa}$

With the amendment $C' = 0,704 \text{ mg/m}^3 = 264,5 \text{ nmol/mol}$

In presenting of the preliminary result (15.10.04) p_w was not taken into account.

Taking into account the above amendment, final result of measurements of SO_2 molar fraction in investigated gas mixture in cylinder No 172467 is **264,8 nmol/mol.**

II Calculations for standard uncertainty of diluent gas flow rate

$$Q = Q_{R} \cdot \frac{293, 2 \cdot (p - p_{w})}{(t + 273, 2) \cdot 101, 3}$$

$$\mathbf{u}_{Q}^{rel} = \frac{\mathbf{u}_{Q}}{Q} = \sqrt{\frac{\mathbf{u}_{QR}^{2}}{Q_{R}^{2}} + \frac{\mathbf{u}_{p}^{2} + \mathbf{u}_{pw}^{2}}{(p - p_{w})^{2}} + \frac{\mathbf{u}_{t}^{2}}{(t + 273)^{2}}}$$

1)
$$\mathbf{U}_{\mathbf{Q_R}}^{\text{rel}} = \boldsymbol{\delta}_{\mathbf{Q_R}} = 0.5 \%$$

 $\mathbf{u}_{\mathbf{Q_R}}^{\text{rel}} = 0.5 / \sqrt{3} = 0.289 \%$

2) $U_p = 0,2 \text{ kPa}$ $u_p = 0,2/\sqrt{3} = 0,12 \text{ kPa}$

3)
$$U_{p_w} = 0,044 \text{ kPa}$$

 $u_{p_w} = 0,044/\sqrt{3} = 0,025 \text{ kPa}$

4)
$$U_t = 0.2^{\circ}C$$

 $u_t = 0.2/\sqrt{3} = 0.12^{\circ}C$

$$\mathbf{u}_{Q}^{\text{rel}} = \sqrt{0,289^{2} + \frac{(0,12^{2} + 0,025^{2}) \cdot 100^{2}}{(102,7 - 1,955)^{2}} + \frac{0,12^{2} \cdot 100^{2}}{(19 + 273,2)^{2}}} = 0,316\%$$

<u>III The corrected uncertainty budget for sulphur dioxide mole fraction in</u> <u>standard gas mixture</u> is shown in the table 6.

Table 6 – Estimation of uncertainty of sulphur dioxide mole fraction in standard gas mixture of SO_2 in synthetic air

No	Source of uncertainty	Relative standard uncertainty,%
1	Permeation tube gravimetric certification	0,636
2	Measurement and keeping of permeation tube thermostatting temperature	0,405
3	Measurement and keepinq of diluent gas flow rate	0,316
	Total standard uncertainty	0,82

IV The corrected final result of measurements

Corrected uncertainty budget for measurements of sulphur dioxide mole fraction in gas mixture in cylinder $N_{2}172467$

Source of uncertainty	Type of valuation	Standard uncertainty $u(x_i)$, %	oefficient sensitivity	ontribution $U_i(y, \%)$
paration of standard gas mixture vimetry)	В	0,81	1	0,82
idard deviation of the results of surements	A	0,31	1	0,31
Total standard uncertainty				0,88
Expanded uncertainty (<i>k</i> =2)				1,8

• The final result of measurements (cylinder № 172467)

Substance	Result, nmol/mol	Expanded uncertainty (k=2), nmol/mol	Relative expanded uncertainty (k=2), %	Coverag e factor
Sulphur dioxide	265	5	1,8	2,0
Synthetic air	balance			

<u>Pilot study participants:</u>

Final Report - Umweltbundesamt GmbH [UBA(A)]

Laboratory: Umweltbundesamt GmbHCylinder number: BOC 172703, connectot No: 11, DIN 477

NOMINAL COMPOSITION

- Sulphur dioxide	:	240 to 320 .10 ⁻⁹ mol/mol
- synthetic air	:	balance

- synthetic air :

Measurement	Date	Result	stand. deviation	number of sub-
No. 1		(mol/mol)	(% relative)	measurements
SO_2	27.8.04	279 E-9	0,2	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 2		(mol/mol)	(% relative)	measurements
SO_2	30.8.04	278 E-9	0,2	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 3		(mol/mol)	(% relative)	measurements
SO ₂	30.8.04	279	0,3	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 4		(mol/mol)	(% relative)	measurements
SO ₂	31.8.04	278	0,3	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 5		(mol/mol)	(% relative)	measurements
SO ₂	1.9.04	281	0,2	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 6		(mol/mol)	(% relative)	measurements
SO ₂	17.9.04	280	0,3	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 7		(mol/mol)	(% relative)	measurements
SO ₂	22.9.04	280	0,1	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 8		(mol/mol)	(% relative)	measurements
SO ₂	22.9.04	279	0,1	5

Measurement	Date	Result	stand. deviation	number of sub-
No. 9		(mol/mol)	(% relative)	measurements
SO_2	23.9.04	280	0,2	5

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
SO ₂	279	2	4,0 ppb

Reference Method:

UV fluorescence, monitor: TE 43 C (range 0-500 ppb)

Calibration Standards:

Dynamic dilution of NMi primary reference material, 8610 E, 90,2±0,5 E-6mol/mol

Instrument Calibration:

2 point calibration with dynamic dilution of prim. ref. material at (229 E-9 mol/mol) by a Horiba ASGU 364 Calibrator, linearity tested up to 400 E-6 mol/mol

Sample Handling:

all gases through same sample port, with particle filter

Uncertainty:

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c ₁	Contribution to standard uncertainty $u_l(y)$
primary reference material	500 ppb		1,6 ppb		1,6
Dilution by massflow controllers	0,4% and 0,5% rel.		1,0 ppb 0,6 ppb		1,0 0,6
repeatability of analyser			0,4 ppb		0,4
combined standard uncertainty					2,0 ppb

Coverage factor: 2 Expanded uncertainty: 4,0 ppb

Annex E – Contact details for participating laboratories

Laboratory	Country	Contact name	Delivery address				
0551 // 10/01	Key comparison participants						
CERI [for NMIJ]	Japan	Masaaki Maruyama	Chemical Standards Department Chemicals Evaluation and Research Institute, Japan (CERI) 1600,Shimo-Takano Sugito-machi, Kitakatsushika-gun Saitama 345-0043 Japan				
СНМІ	Czech Republic	Jiri Novak	Czech Hydrometeorological Institute Na Sabatce 17 143 06 Praha 4 Czech Republic				
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