



**EURAMET Project 1329
Comparison of sulphur dioxide (SO₂) in synthetic air**

Final report

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Table of contents

1	BACKGROUND.....	2
2	OBJECTIVES.....	2
3	PARTICIPANTS	2
4	COMPLETION DATE	3
5	COMPARISON PROTOCOL.....	3
6	DETERMINATION OF THE REFERENCE VALUES OF THE TRAVELLING STANDARDS AT THE TIME OF ANALYSIS AND THEIR EXPANDED UNCERTAINTIES.....	3
6.1	DETERMINATION OF THE REFERENCE VALUES.....	3
6.2	DETERMINATION OF THE ASSOCIATED UNCERTAINTIES.....	7
7	RESULTS SUBMITTED BY PARTICIPATING LABORATORIES	8
8	CALCULATION OF DEGREES OF EQUIVALENCE	9
9	DISCUSSION AND CONCLUSIONS.....	11
10	ANNEXES	12
10.1	DETERMINATION OF THE LNE'S UNCERTAINTY CALCULATION	12
10.2	RESULTS AND REPORTS AS SUBMITTED BY PARTICIPATING LABORATORIES	14

1 BACKGROUND

In the framework of JRP ENV01 “Metrology for Chemical Pollutants in Air” (MACPoll) an inter-laboratory comparison was organized to evaluate the comparability between different dilution methods used for generating standard gas mixtures for calibration, quality control and application to field measurements.

The results of this interlaboratory comparison show that for sulphur dioxide (SO₂) at 40 and 150 nmol/mol the degrees of equivalence which are around 5% don't satisfy the requirement for the 2% set within this JRP for all participant laboratories except LNE. Positive deviations between the reference amounts of substance fraction (LNE) and the amounts of substance fraction measured by the participants were observed.

In the framework of EURAMET a comparison for SO₂ at 100 nmol/mol was conducted to understand and improve the sulphur dioxide results obtained in the MACPoll project.

2 OBJECTIVES

The objective of this analytical comparison was to compare analytical results obtained by the participating laboratories on the respective gas mixtures to their reference values.

The comparison is aimed at typical amount fractions used to calibrate analysers carrying out automatic measurements of SO₂ in ambient air (cf. Table 1).

Table 1: Nominal amount of substance fraction

Component	Amount of substance fraction x (nmol.mol ⁻¹)
Sulphur dioxide	100
Synthetic air	Balance

3 PARTICIPANTS

LNE acted as coordinating laboratory for this comparison which was led in the EURAMET framework.

The National Metrology Institutes which participated in this comparison are: NPL, LNE, VSL, FMI, BEV/EAA and UBA.

4 COMPLETION DATE

The comparison was completed in March 2015.

5 COMPARISON PROTOCOL

This comparison involved a batch of 6 gas mixtures which were prepared in 20 litre aluminium cylinders (Luxfer) by a specialty gases company (Air Liquide).

On arrival at the coordinating laboratory (LNE), the batch of gas mixtures was analyzed with permeation method as reference method over a 4 month period.

After the 4 month period, 5 gas mixtures were circulated by LNE to the participant laboratories and one gas mixture was kept at LNE as a control while the laboratories were making measurements. The amount fraction of this gas mixture was then measured during this period to monitor stability.

After the measurements, the participants returned the cylinders to LNE. Each gas mixture was re-analysed by LNE.

The amount fractions as calculated from the reference method (permeation method) are used to estimate the reference values. Each cylinder has its own reference value and associated expanded uncertainty.

The participating laboratories made at least three measurements of the amount fraction of the component in the gas mixtures. The results of these measurements were combined to provide the final result. The expanded uncertainties reported for the analysis by each participant include the estimated uncertainties from the analysis and the reference standards used.

6 DETERMINATION OF THE REFERENCE VALUES OF THE TRAVELLING STANDARDS AT THE TIME OF ANALYSIS AND THEIR EXPANDED UNCERTAINTIES

6.1 DETERMINATION OF THE REFERENCE VALUES

The batch of the 6 gas mixtures was analyzed with permeation method as reference method over a 4 month period and after the comparison. In this way, 5 analytical amount fractions were determined for each gas mixture by LNE over a total period of 6 months.

One of the 6 gas mixtures (N°4465) was kept at LNE as a control while the laboratories are making measurements. The amount fraction of this gas mixture was then measured during this period to account for any unexpected stability issues. The results obtained for the cylinder N°4465 are represented on the Figure 1.

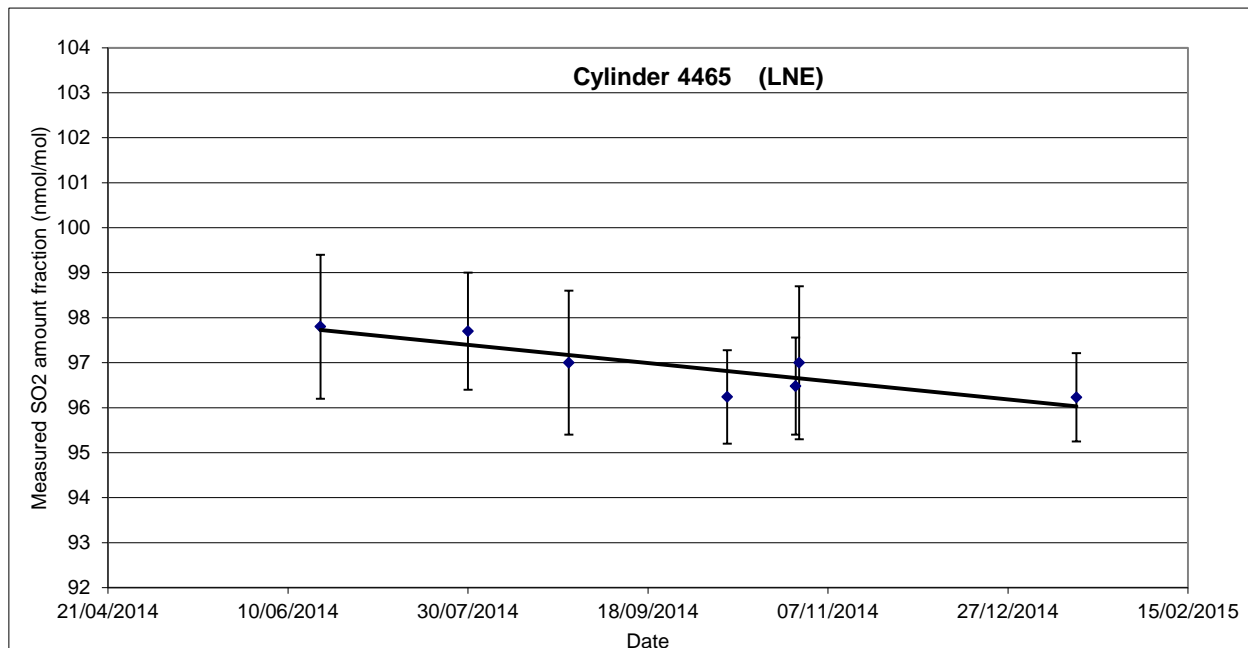


Figure 1: Drift of the travelling standard kept at LNE as a control while the laboratories are making measurements. The measurements shown were carried out by the coordinating laboratory. The error bars indicate the expanded uncertainties of the measurements. The regression line has been fitted by ordinary least squares.

The results obtained for the cylinder N°4465 show a drift of the amount fractions over the time. This was also observed for some of the other gas mixtures used, so in order to compensate, the drift of each travelling standard was determined and used to calculate the reference value at the time when it was analysed by the relevant participating laboratory.

The drift of each travelling standard was estimated by plotting the different amount fractions obtained over 6 months versus time and by calculating the slope (m) and the intercept (b) of the straight line fitted by ordinary least squares for each travelling standard using XLGenline software.

The analytical standard uncertainty on the amount fraction is calculated by taking into account the uncertainty on the permeation rate of the SO₂ permeation tube and the uncertainty on the flow measured with a high accuracy flowmeter (Molbloc/molbox) (cf. annex 1). Moreover 3 measurements are always performed to determine the amount fractions: consequently the repeatability standard deviation on these 3 measurements is also added to estimate the analytical standard uncertainty. In this comparison the values of the analytical standard uncertainty were in a range between 0.5 and 0.85 nmol/mol because it depends on the stability of the measurements and the permeation rate. It was decided to maximize the analytical standard uncertainty and to use the higher value, i.e. 0.85 nmol/mol for each amount fraction. No uncertainty on the time is applied as it is negligible.

The reference values are then calculated using the time when the laboratories perform their measurement and the equation of the straight line fitted by ordinary least squares (slope and y-intercept). A standard uncertainty of 0.85 nmol/mol was applied in the analysis for each point.

$$Z_i^{ref} = (D_2 - D_1) \times m + b \quad (1)$$

With

- Z_i^{ref} the reference value
- D_2 the date of the participant measurement
- D_1 the date of the first measurement performed by LNE
- m the slope of the straight line fitted by ordinary least squares
- b the intercept of the straight line fitted by ordinary least squares

The table 2 summarizes the values of the slope and the intercept calculated for each travelling standard, the reference values and associated expanded uncertainties explained in paragraph 6.2.

Table 2: Reference values determined for each participating laboratory and associated uncertainties

NMI	Standard Identifier	Slope m (nmol.mol ⁻¹ . day ⁻¹)	$u(m)$ (nmol.mol ⁻¹ . day ⁻¹)	y-intercept b (nmol.mol ⁻¹)	Date of the first measurement D_1	Date of the participant measurement D_2	Reference value Z_i^{ref} (nmol.mol ⁻¹)	$u(m)x(D_2 - D_1)$ (nmol.mol ⁻¹)	r (nmol.mol ⁻¹)	$u(Z_i^{ref})$ (nmol.mol ⁻¹)
NPL	842745	-0.00008	0.00554	84.25	26/06/2014	18/12/2014	84.23	0.97	0.39	1.05
UBA	842748	0.00108	0.00694	84.18	25/06/2014	21/11/2014	84.35	1.03	0.09	1.04
BEV/EAA	4499	-0.00360	0.00543	99.21	17/06/2014	12/12/2014	98.57	0.97	0.29	1.01
VSL	4498	-0.01088	0.00503	96.81	24/06/2014	11/12/2014	94.96	0.85	0.22	0.88
LNE	4465	-0.00807	0.00501	97.73	19/06/2014	29/10/2014	96.66	0.66	0.33	0.74
FMI	842678	0.00289	0.00479	84.75	18/06/2014	16/12/2014	85.28	0.87	0.45	0.98

6.2 DETERMINATION OF THE ASSOCIATED UNCERTAINTIES

The expanded uncertainties on the reference values $u(Z_i^{ref})$ are defined as:

$$u(Z_i^{ref}) = \sqrt{u(m) \times (D_2 - D_1) + r^2} \quad (2)$$

With

- $u(m)$ the standard uncertainty from the drift in the travelling standard
- D_2 the date of the participant measurement
- D_1 the date of the first measurement performed by LNE
- r the repeatability of the drift measurements

An additional uncertainty component, r , is required to account for the repeatability of the drift measurements over the time period of the comparison. This was obtained by calculating the standard deviation of the analytical amount fractions for each travelling standard after making correction for drift as this influences the repeatability of the measurement.

The process to calculate the repeatability standard uncertainty is illustrated by an example based on NPL's raw data (see table 3).

Table 3: Example of the calculation of the repeatability standard uncertainty with NPL's raw data

Day (D)	Analytical amount fraction w_i (nmol/mol)	Fitted result Z_i (nmol/mol)	Correction Corr (nmol/mol)	Corrected measurement $w_{i,corr}$ (nmol/mol)	r (nmol/mol)
0	84.50	84.25	0.00	84.50	0.39
26	84.50	84.25	0.00	84.50	
69	83.60	84.24	-0.01	83.61	
105	84.12	84.24	-0.01	84.13	
196	84.49	84.23	-0.02	84.50	

Each gas mixture was analyzed by comparison to a reference standard generated by permeation over a 4 month period. In this way, 5 analytical amount fractions w_i were determined for each gas mixture by LNE over a total period of about 6 months (column 2 of the table 3).

The fitted results Z_i (column 3 of the table 3) are calculated with the equation of the straight line fitted by ordinary least squares (slope and intercept).

$$Z_i = p \times m + b \quad (3)$$

The corrections $Corr$ (column 4 of the table 3) are given by making the difference between each fitted result Z_i and the first fitted result.

$$Corr = Z_i - Z_1 \quad (4)$$

The corrected measurements (column 5 of the table 3) are defined as

$$w_{i,corr} = w_i - Corr \quad (5)$$

The column 6 of the table 3 gives the standard deviations of the 5 corrected measurements which is the repeatability of the drift measurements.

7 RESULTS SUBMITTED BY PARTICIPATING LABORATORIES

The results submitted by the participating laboratories (cf. annex 2) are listed in Table 4. All of the uncertainties represent 95 % confidence intervals (expanded using a coverage factor k of 2).

Table 4: Results submitted by the participating laboratories for Euramet project 1329

NMI	Standard Identifier	Submitted result x_i (nmol/mol)	Submitted expanded uncertainty $U(x_i)$ (nmol/mol)	Date of participant measurement
NPL	842745	87.3	2.0	05 to 18/12/2014
UBA	842748	81.97	1.30	19 to 21/11/2014
BEV/EAA	4499	99.50	2.67	04 to 12/12/2014
VSL	4498	96.38	0.96	10 to 11/12/2014
LNE	4465	96.48	1.08	29/10/2014
FMI	842678	88.7	1.6	12 to 16/12/2014

The reference standards and the analytical methods used by the participating laboratories to analyse the gas mixtures are summarized in Table 5 and Table 6 respectively.

Table 5: Reference standards used by the participating laboratories

NMI	Reference standards used
LNE	Permeation method
NPL	Dilution of a NPL gravimetric standard of SO ₂ in N ₂ at 5 µmol/mol with thermal mass flow controllers (Brooks)
VSL	Dilution of a VSL gravimetric standard of SO ₂ in N ₂ in the range of 1 – 6 µmol/mol with Bronkhorst low Δp-flow Mass flow controllers
FMI	Dilution of a NPL gravimetric standard (50.03 µmol/mol ± 0.25 µmol/mol) with a dynamic dilution calibrator LNI Sonimix 6000 A1 s/n 1585
UBA	Static dilution
BEV/EAA	Dilution of a VSL gravimetric standard (90.02 µmol/mol ± 0.36 µmol/mol in nitrogen) with a dynamic dilution calibrator Horiba ASGU 364

Table 6: Analytical methods used by the participating laboratories

NMI	Analytical methods used
LNE	43C (TEI) analyser (UV fluorescence)
NPL	43i (TEI) analyser (UV fluorescence)
VSL	43A (TEI) analyser (UV fluorescence)
FMI	43i (TEI) analyser (UV fluorescence)
UBA	APSA 370 (HORIBA) analyser (UV fluorescence)
BEV/EAA	43C trace level (TEI) analyser (UV fluorescence)

8 CALCULATION OF DEGREES OF EQUIVALENCE

The degree of equivalence of the participating laboratory in the comparison D_i is defined as

$$D_i = x_i - Z_i^{ref}$$

Where x_i denotes the result of each participating laboratory and Z_i^{ref} the reference value.

The standard uncertainty of D_i can be expressed as

$$u(D_i) = \sqrt{u^2(x_i) + u^2(Z_i^{ref})}$$

Where $u(Z_i^{ref})$ and $u(x_i)$ are standard combined uncertainties of reference value and participating laboratory, respectively, assuming that the error terms associated with the laboratory result and the reference value are uncorrelated.

The expanded uncertainty of D_i , at 95% level of confidence, is given by

$$U(D_i) = 2 \times u(D_i)$$

The degrees of equivalence are listed in Table 7 and shown in Figure 2.

Table 7: Calculation of the degrees of equivalence

NMI	Standard Identifier	Submitted result x_i (nmol/mol)	Submitted standard uncertainty $u(x_i)$ (nmol/mol)	Z_i^{ref} (nmol/mol)	$u(Z_i^{ref})$ (nmol/mol)	D_i (nmol/mol)	$U(D_i)$ (nmol/mol)
NPL	842745	87.3	1.0	84.23	1.05	3.1	2.9
UBA	842748	81.97	0.65	84.35	1.04	-2.4	2.4
BEV/EAA	4499	99.50	1.34	98.57	1.01	0.93	3.35
VSL	4498	96.38	0.48	94.96	0.88	1.4	2.0
LNE	4465	96.48	0.54	96.66	0.74	-0.18	1.83
FMI	842678	88.70	0.80	85.28	0.98	3.4	2.5

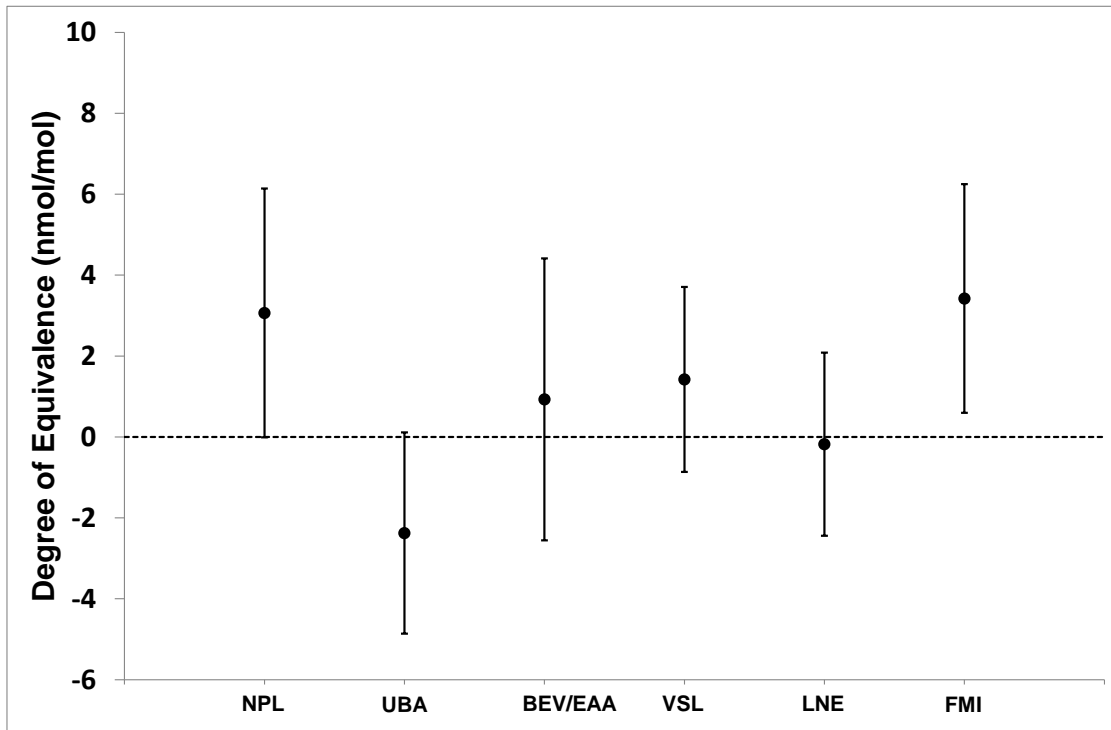


Figure 2: Representation of the degrees of equivalence

9 DISCUSSION AND CONCLUSIONS

The results obtained in the Euramet comparison 1329 on sulphur dioxide at 100 nmol/mol are consistent for NPL, UBA, BEV/EAA and VSL. One laboratory (FMI) reports result that is slightly inconsistent with the reference value.

This new comparison on sulphur dioxide at 100 nmol/mol led to results within $\pm 4\%$ of the reference values. In the framework of JRP ENV01 "Metrology for Chemical Pollutants in Air" the degrees of equivalence were around 5%. Consequently this new comparison didn't allow to understand and improve the sulphur dioxide results obtained in the JRP ENV01 project because the two sets of results are similar.

The observed results obtained in this Euramet comparison 1329 could be explained by the lack of stability of the SO₂ amount fractions for the gas mixtures in cylinders over the time. In this case, the reference amount fractions are difficult to determine and the deviations between the reference amount fractions and those determined by the participant laboratories could be not accurate.

Another explanation could come from the reference methods used by the participant laboratories and the pilot laboratory because as in the JRP ENV01 it was observed positive deviations between the reference amount fraction (LNE) and the amount fractions measured by the participant laboratories. LNE calibrated the analysers with SO₂ reference gas mixtures generated by the permeation method whereas four of the five participant laboratories calibrated their analysers with SO₂ reference gas mixtures generated by the dynamic dilution of gravimetric standards and one by the static dilution. This hypothesis based on the use of different methods for preparing reference standards has already been raised in a former EURAMET comparison led by NPL (CCQM-K26b).

10 ANNEXES

10.1 DETERMINATION OF THE LNE'S UNCERTAINTY CALCULATION

Travelling standard: 4465

NOMINAL COMPOSITION

- Sulphur dioxide: 100 nmol/mol
- Synthetic air: balance

Component	Date	Result (nmol/mol)
SO ₂	29.10.2014	96.37
	29.10.2014	96.33
	29.10.2014	96.72

Results:

Analyte	Date	Result (nmol/mol)	Coverage factor	Expanded Uncertainty (nmol/mol)
SO ₂ 100 nmol/mol	29.10.2014	96.48	2	1,08

Reference Method:

A Fluorescence UV analyzer Model 43C from Thermo Fischer is used for the analysis.

Calibration Standards:

Standard gas mixtures of SO₂ in air are generated by permeation method. The permeation rate (about 800 ng/min) is determined by weighing the tube once per month. The total dilution flow is measured by Molbloc/Molbox 10 slm full scale calibrated at LNE.

Instrument Calibration:

For each concentration, calibration of the analyser is done at zero and the target concentration with the standard gas mixtures obtained by permeation method.

Sample Handling:

The cylinder is connected to the analyser with stainless steel tube with a sulfiner treatment. A T-connector was added at the analyser entry to bypass the excess flow.

Value assignment:

After stabilization an average of the analyser values during twenty minutes is done to calculate the average of each point.

Uncertainty Budget:

Uncertainty source	Value	Standard uncertainty $u(x_i)$	Assumed distribution	Sensitivity coefficient c_i	Contribution (%)
Permeation rate	785.0 ng/min	2.5 ng/min	-	0.12	32.9
SO ₂ molar mass	64.0638 g/mol	0.060 g/mol	-	-1.5	0.03
Volume of one mole of gas	22.414 l	0,00019 l	-	4.3	0.0
SO ₂ concentration in dilution gas	0 nmol/mol	0.5 nmol/mol	rectangular	1.0	29.1
Dilution gas flow (reading)	2851.5 sccm	7.2 sccm	-	-0.034	20.3
Reading of analyser for the standard gas mixture	96.5 nmol/mol	0.1 nmol/mol	rectangular	-1.0	1.2
Average of analyser for the cylinder	96.66 nmol/mol	0.22 nmol/mol	-	1.0	16.5

Results : C(SO₂) = 96.48 nmol/mol

Expanded uncertainty (k=2): U = 1.08 nmol/mol

10.2 RESULTS AND REPORTS AS SUBMITTED BY PARTICIPATING LABORATORIES

Final report - Finnish Meteorological Institute (FMI)

Cylinder number: 842678
 Nominal composition
 - Sulphur dioxide: 100 nmol/mol
 - Synthetic air: balance

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	12.12.2014	88.77	0.31	10
		88.68	0.28	10
		88.93	0.51	10

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	15.12.2014	88.59	0.58	10
		88.82	0.52	10

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	16.12.2014	88.23	0.36	10
		88.98	0.42	10
		88.69	0.33	10

Results

Component	Result (nmol/mol)	Standard deviation (% relative)
Sulphur dioxide	88.7	0.3

Calibration standards

Calibration standard was from NPL, concentration 50.03 µmol/mol with expanded uncertainty of 0.25 µmol/mol. The dilution air was from AGA (instrument air 5.0). The gas standard was diluted by dynamic dilution method at the concentrations of 70.8, 94.4 and 121.2 nmol/mol.

Instrumentation

Gas dilutor of Sonimix 6000 A1 s/n 1585 by LNI, Switzerland, was used for preparation of calibration gas mixtures to calibrate the analyzer. The analyzer, Thermo Environment 43 iTLE s/n *354 by Thermo Fisher, was used to measure the concentration of SO₂.

Calibration method and value assignment

The analyser TEI 43i TLE (s/n *354) used for the analysis was calibrated according to the standard operation procedure of the laboratory (SOP). The calibration concentrations for the analyser was 0 70.8, 94.4 and 121.2 nmol/mol (zero + 3 concentration) obtained from Sonimix 6000A1 (s/ 1585) gas dilutor. Synthetic air from AGA (Instrument air 5.0) was used as a dilution gas. The calibration of the analyser took place before and after the analysis of the sample.

The gas dilutor, Sonimix 6000A1 by LN-Industries Switzerland, is based on the 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 and the carbon monoxide analyser, APMA-370 s/n F010A60V. To verify the correct dilution of the Sonimix 6000A1 dilutor the primary gas standard of the National Physical Laboratory of the concentration of 20 ± 0.10 µmol/mol was used.

During the operation of the dilutor the pressure of the dilution line was controlled by the reference pressure meter of the laboratory.

The comparison result was calculated based on the average of the results gained from both calibration (prior and after comparison) by bracketing the upper and lower calibration concentration compared to comparison concentration.

Uncertainty evaluation

The standard uncertainty of the Sonimix 6000A gas dilutor for dilution step P4 = 94.4 nmol/mol can be expressed by:

$$u(C(4))^2 = \left(\frac{C_{ST}}{f(bs1) + f(bs2)} \right)^2 u(bs5)^2 + \left(\frac{f(bs5) \cdot C_{ST}}{(f(bs1) + f(bs2))^2} \right)^2 (u(bs1)^2 + u(bs2)^2) + \left(\frac{f(bs5)}{f(bs1) + f(bs2)} \right)^2 u(C_{ST})^2 + u(C_{dil})^2 \quad \text{Eq(1)}$$

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 ... 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)

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 only those performance characteristics of the analyser that are important in this case are included into the uncertainty budget. The following performance characteristics have been included into the uncertainty budget of the analyser according to EN 14212:2012:

- Linearity of the analyser in the range of 0 to 150 nmol/mol
- Sensitivity coefficient of sample gas pressure
- Sensitivity coefficient of sample gas temperature
- Sensitivity coefficient of surrounding temperature
- Sensitivity water content
- Uncertainty of the zero air

Uncertainty source	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Preparation of gas mixture					
Uncertainty of sonic nozzle	3.79 ml/min	Rectangular	0.011 (ml/min)	28.45 nmol/mol ml/min	0.324 nmol/mol
	3454 ml/min	Rectangular	10.36 (ml/min)	0.031 nmol/mol ml/min	0.318 nmol/mol
	49.92 ml/min	Rectangular	0.15 ml/min	0.031 nmol/mol ml/min	0.0046 nmol/mol
	50.03 umol/mol	Normal	125 nmol/mol	0.0022	0.27 nmol/mol
	0.5 nmol/mol	Normal	0.25 nmol/mol	1	0.25 nmol/mol
Analysis of gas mixture					
Lack of fit	0.1 %	Rectangular	0.05	1	0.05 nmol/mol
Sensitivity to sample pressure	0.05 nmol/mol/kPa	Rectangular	0.01	1	0.01 nmol/mol
Sensitivity to sample temperature	0.21 nmol/mol/K	Rectangular	0.25	1	0.25 nmol/mol
Sensitivity to variation of surrounding temperature	0.2 nmol/mol/K	Rectangular	0.24	1	0.24 nmol/mol
Sensitivity to water content	-2.33	Rectangular	-0.35	1	-0.35 nmol/mol
Uncertainty of the zero air	0.25 nmol/mol	Rectangular	0.25	1	0.25 nmol/mol
Combined standard uncertainty u_c (nmol/mol)					0.81 nmol/mol
Expanded uncertainty U (nmol/mol)					1.6 nmol/mol

Coverage factor: $k = 2$

Expanded uncertainty: $U = 1.6$ nmol/mol

Authorship

Jari Waldén, Sisko Laurila, Kaisa Lusa

Final report – National Physical Laboratory (NPL)

Cylinder number: D842745
 Nominal composition
 Sulphur dioxide: 100 nmol/mol
 Synthetic air: balance

Measurement 1: pulsed fluorescence spectroscopy

Component	Date (dd/mm/yy)	Result (nmol/mol)	standard deviation (% relative)	No. of replicates
SO ₂	05/12/2014	87.8	0.6	4

Measurement 2: pulsed fluorescence spectroscopy

Component	Date (dd/mm/yy)	Result (nmol/mol)	standard deviation (% relative)	No. of replicates
SO ₂	16/12/2014	87.0	0.4	10

Measurement 3: pulsed fluorescence spectroscopy

Component	Date (dd/mm/yy)	Result (nmol/mol)	standard deviation (% relative)	No. of replicates
SO ₂	18/12/2014	87.2	1.1	5

Final Result:

Component	Date (dd/mm/yy)	Result (nmol/mol)	expanded uncertainty (nmol/mol)	Coverage Factor
SO ₂	09/01/2015	87.3	2.0*	2

*The reported uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of 95 %. The result assumes an oxygen content in the travelling standard of 20.9 cmol/mol.

Calibration standards

The calibration gas mixture was produced dynamically by blending a 5 μ mol/mol primary reference gas mixture (PRGM) of sulphur dioxide with synthetic air (BOC, metrology grade). The diluent gas was passed through three filters containing silica gel, purafil and charcoal (Thermo Fisher Scientific) to ensure it was free from the target gas and other impurities such as water. The flows of the diluent and the PRGM were regulated by 20 mg/s full-scale viton seal (Brooks

SLA5850SE1AB1B2A1) and 2 mg/s full scale metal seal (Brooks SLA7950-S1EGG1B2A1) thermal mass flow controllers respectively. The mass flow of each gas was measured accurately with Molbloc-L laminar mass flow elements (DHI, model 1E3-VCR-V-Q for the diluent gas and 1E2-VCR-V-Q for the PRGM), located upstream, and matched to the full scale setting of the mass flow controllers. These devices estimate the flow by means of Poiseuille's law [1].

Instrumentation

A pulsed UV fluorescence analyser (Thermo 43i) was used for analysis.

Calibration method and value assignment

Reference mixtures were generated with amount fractions that differed by less than 2 % from the nominal composition of the travelling standard. This ensured that the uncertainty contribution from any deviation from the linearity of the analyser response was negligible.

The analyser response to the matrix gas was recorded. The analyser was then used to sample the generated reference mixture. A period of 2 minutes was allowed for the response to reach steady state. The analyser response was then recorded for 2 minutes. This process was then repeated for the travelling standard. The amount fraction of sulphur dioxide in the travelling standard was determined using the amount fraction of the generated reference mixture and the ratio of the analyser response to the reference and travelling standard. Cylinders were maintained at a laboratory temperature of (20 ± 3) °C throughout the period of analysis. Samples were introduced into the analyser at atmospheric pressure (excess flow was passed to vent) using a low volume gas regulator.

Uncertainty evaluation

The amount fraction of the generated reference standard is determined by:

$$x_r = \frac{f_s}{(f_s + f_d)} \times x_s$$

Where x_r is the amount fraction of the generated reference mixture, f_s and f_d represent the flow rate of the nominal 5 $\mu\text{mol/mol}$ PRGM and diluent gas respectively and x_s is the amount fraction of the PRGM.

The ratio of the analyser response from the travelling standard and the generated reference mixture was calculated using:

$$r = \frac{(y_u - y_z)}{(y_r - y_z)}$$

Where y_r , y_u and y_z represent the analyser response to the generated reference mixture, the travelling standard and the zero gas respectively.

And the average ratio (\bar{r}) is calculated by:

$$\bar{r} = \frac{\sum r}{n}$$

Where n is the number of ratios. The amount fraction of the sulphur dioxide in the travelling standard, x_u , is then calculated by:

$$x_u = x_r \bar{r}$$

Where x_r is the amount fraction of sulphur dioxide in the generated standard. The standard uncertainty of the measurand, $u(x_u)$, is calculated by:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_r)^2}{x_r^2} + \frac{u(\bar{r})^2}{\bar{r}^2}}$$

The table which follows details the uncertainty analysis for an example measurement.

quantity	unit	example value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_s	nmol/mol	5001	50	0.02	0.89	A	normal
f_s	mg/s	0.4	0.001	227.272	0.26	A	normal
f_d	mg/s	21.2	0.064	4.111	0.26	A	normal
x_z	nmol/mol	0.0	0.7	1.0	0.7	A	normal
x_r	nmol/mol	88.9					
$u(x_r)$	nmol/mol	1.2					
$U(x_r)$	nmol/mol	2.4					

quantity	unit	example value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_r	nmol/mol	88.9	1.2	1.0	1.2	A	normal
\bar{r}	-	0.979	0.004	88.9	0.4	A	normal
x_u	nmol/mol	87.0					
$u(x_u)$	nmol/mol	1.2					
$U(x_u)$	nmol/mol	2.5					

To obtain the final result for the comparison, an average was taken for the three measurements.

The following table shows the calculation of the final results and its uncertainty.

quantity	unit	value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_1	nmol/mol	87.8	1.8	0.3	0.6	A	normal
x_2	nmol/mol	87.0	1.2	0.3	0.4	A	normal
x_3	nmol/mol	87.2	2.1	0.3	0.7	A	normal
x_f	nmol/mol	87.3					
$u(x_f)$	nmol/mol	1.0					
$U(x_f)$	nmol/mol	2.0					

Where x_1 - x_3 is the measurement number and x_f is the final value of the amount fraction of sulphur dioxide in the travelling standard.

References

[1] P. Delajoud and M. Girard, A high accuracy portable calibration standard for low mass flow. Presented at the XIII IMEKO world Congress of Metrology, Torino (Italy), 1994.

Authorship

Paul J Brewer, Marta Doval Miñarro, Richard J C Brown.

Final report – Umweltbundesamt (UBA)

Cylinder number: 842748
 Nominal composition
 - Sulphur dioxide: 100 nmol/mol
 - Synthetic air: balance

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	19/11/2014	81.92	0.17	10
		81.98	0.12	10
		81.92	0.17	10

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	20/11/14	81.51	0.35	10
		81.93	0.23	10
		81.74	0.15	10

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	21/11/14	82.27	0.18	10
		82.22	0.20	10
		82.30	0.17	10

Results

Component	Result (nmol/mol)	Standard deviation (% relative)
Sulphur dioxide	81.97	0.3

Calibration standards

Calibration standard is prepared by volumetric static dilution
 Known volume of the pure gas compound is added to the complementary gas in a vessel of well-defined volume.
 The method is described at ISO 6144.

Equipment:

cast iron vessel coated with enamel inside	0.014736 m ³
pressure gauge	PACE 1000 Druck
Temperature gauge	Fluke 1529-Thermistor
Vacuum pump	MV2 vacuubrand

Operating material:

Microliter syringe	1000µl Hamilton series 1001 LTN
Synthetic air (balance gas)	5.0 Air Liquide
Sulphur dioxide (pure gas)	3.8 VSL; certified by VSL

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.

Instrumentation

For analysing sulphur dioxide at the UBA laboratory an UV-fluorescence method based monitor HORIBA APSA 370 was used.

Calibration method and value assignment

Bracketing -Two-point Calibration

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

Measurement result: 82 nmol/mol
High standard: 90 nmol/mol
Low standard: 78 nmol/mol

The concentrations were prepared in three steps by pressure reduction and refilling the vessel.

1. Static dilution to 7,16 µmol/mol (p_1/p_2)
2. Static dilution to 750 nmol/mol (p_3/p_4)
3. Static dilution to 78 or 90 nmol/mol (p_5/p_6)

The value was calculated by interpolation between the both bracketing points.

Uncertainty evaluation

$$u_c^2 = u_1^2 + s^2(\bar{q}) \quad (1)$$

u_c = Combined uncertainty

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

$s^2(\bar{q})$ = Estimate of the variance of the mean

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.

$$u_1 = 0,55 \text{ nmol/mol}$$

$$s^2(\bar{q}) = 0,3 \text{ nmol/mol}$$

$$u_c = 0,63 \text{ nmol/mol} \quad (1)$$

Coverage factor: $k = 2$

Expanded uncertainty: $U = \pm 1,3 \text{ nmol/mol}$

EURAMET 1329 SO₂ 100 nmol/mol

Uncertainty calculation of the Static Dilution Method for the preparation of SO₂ gas mixtures by GUM workbench. The procedure is described in ISO 6144.

Model Equation:

$$C = 1/Z * C_p * V_s / V_d * p_1 / p_2 * p_3 / p_4 * p_5 / p_6 * T_2 / T_1 * T_4 / T_3 * T_6 / T_5$$

List of Quantities:

Quantity	Unit	Definition
C	mol/mol	Concentration of Calibration Gas
Z		Real Gas Factor
C _p	mol/mol	Pure Gas Concentration SO ₂
V _s	l	Syringe Volume
V _d	l	Vessel Volume
p ₁	kPa	Ambient Pressure
p ₂	kPa	Final Pressure 1. Dilution Step
p ₃	kPa	Start Pressure 2. Dilution Step
p ₄	kPa	Final Pressure 2. Dilution Step
p ₅	kPa	Start Pressure 3. Dilution Step
p ₆	kPa	Start Pressure 3. Dilution Step
T ₂	K	Final Temperature 1. Dilution Step
T ₁	K	Start Syringe Temperature
T ₄	K	Final Temperature 2. Dilution Step
T ₃	K	Start Temperature 2. Dilution Step
T ₆	K	Final Temperature 3. Dilution Step
T ₅	K	Start Temperature 3. Dilution Step

Z:

Constant

Value: 0.981

C_p:

Type B rectangular distribution
Value: $99.9797 \cdot 10^{-2}$ mol/mol
Halfwidth of Limits: $0.004 \cdot 10^{-2}$ mol/mol
VSL- certified Cylinder NS 7080

V_s:

Type B rectangular distribution
Value: $1000 \cdot 10^{-6}$ l
Halfwidth of Limits: $10 \cdot 10^{-6}$ l
Syringe is validated by weighing with certified balance

V_d:

Type A
Method of observation: Direct
Number of observations: 5

No.	Observation
1	14.736 l
2	14.733 l
3	14.738 l
4	14.734 l
5	14.737 l

Arithmetic Mean: 14.735600 l
Standard Deviation: $2.1 \cdot 10^{-3}$ l
Standard Uncertainty: $927 \cdot 10^{-6}$ l
Degrees of Freedom: 4

p₁:

Type B rectangular distribution
Value: 99.4 kPa
Halfwidth of Limits: 0.02 kPa
certified Pressure Indicator PACE 1000

p₂:

Type B rectangular distribution
Value: 950 kPa
Halfwidth of Limits: 0.05 kPa
PACE

p₃:

Type B rectangular distribution
Value: 100 kPa
Halfwidth of Limits: 0.02 kPa

p₄:

Type B rectangular distribution
Value: 950 kPa
Halfwidth of Limits: 0.05 kPa

p₅:

Type B rectangular distribution

Value: 110 kPa

Halfwidth of Limits: 0.02 kPa

p₆:

Type B rectangular distribution

Value: 956 kPa

Halfwidth of Limits: 0.05 kPa

T₂:

Type B rectangular distribution

Value: 295 K

Halfwidth of Limits: 0.5 K

certified Thermometer FLUKE 1529 Thermistor

T₁:

Type B rectangular distribution

Value: 295 K

Halfwidth of Limits: 0.5 K

T₄:

Type B rectangular distribution

Value: 295 K

Halfwidth of Limits: 0.5 K

T₃:

Type B rectangular distribution

Value: 295 K

Halfwidth of Limits: 0.5 K

T₆:

Type B rectangular distribution

Value: 295 K

Halfwidth of Limits: 0.5 K

T₅:

Type B rectangular distribution

Value: 295 K

Halfwidth of Limits: 0.5 K

Uncertainty Budgets:**C: Concentration of Calibration Gas**

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
Z	0.981					
C _p	0.9997970 mol/mol	23.1·10 ⁻⁶ mol/mol	rectangular	88·10 ⁻⁹	2.0·10 ⁻¹² mol/mol	0.0 %
V _s	1.00000·10 ⁻³ l	5.77·10 ⁻⁶ l	rectangular	88·10 ⁻⁶	510·10 ⁻¹² mol/mol	85.2 %
V _d	14.735600 l	927·10 ⁻⁶ l	normal	-5.9·10 ⁻⁹	-5.5·10 ⁻¹² mol/mol	0.0 %
p ₁	99.4000 kPa	0.0115 kPa	rectangular	880·10 ⁻¹²	10·10 ⁻¹² mol/mol	0.0 %
p ₂	950.0000 kPa	0.0289 kPa	rectangular	-92·10 ⁻¹²	-2.7·10 ⁻¹² mol/mol	0.0 %
p ₃	100.0000 kPa	0.0115 kPa	rectangular	880·10 ⁻¹²	10·10 ⁻¹² mol/mol	0.0 %
p ₄	950.0000 kPa	0.0289 kPa	rectangular	-92·10 ⁻¹²	-2.7·10 ⁻¹² mol/mol	0.0 %
p ₅	110.0000 kPa	0.0115 kPa	rectangular	800·10 ⁻¹²	9.2·10 ⁻¹² mol/mol	0.0 %
p ₆	956.0000 kPa	0.0289 kPa	rectangular	-92·10 ⁻¹²	-2.6·10 ⁻¹² mol/mol	0.0 %
T ₂	295.000 K	0.289 K	rectangular	300·10 ⁻¹²	86·10 ⁻¹² mol/mol	2.4 %
T ₁	295.000 K	0.289 K	rectangular	-300·10 ⁻¹²	-86·10 ⁻¹² mol/mol	2.4 %
T ₄	295.000 K	0.289 K	rectangular	300·10 ⁻¹²	86·10 ⁻¹² mol/mol	2.4 %
T ₃	295.000 K	0.289 K	rectangular	-300·10 ⁻¹²	-86·10 ⁻¹² mol/mol	2.4 %
T ₆	295.000 K	0.289 K	rectangular	300·10 ⁻¹²	86·10 ⁻¹² mol/mol	2.4 %
T ₅	295.000 K	0.289 K	rectangular	-300·10 ⁻¹²	-86·10 ⁻¹² mol/mol	2.4 %
C	87.649·10 ⁻⁹ mol/mol	548·10 ⁻¹² mol/mol				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
C	87.6·10 ⁻⁹ mol/mol	1.3 % (relative)	2.00	manual

References

EN ISO 6144 (2006) Gas analysis-Preparation of calibration gas mixtures-Static volumetric method

VSL - Certificate 3222042A purity analysis SO₂ cylinder number NS 7087

Authorship

Dr. Klaus Wirtz

Volker Stummer

Rita Meyer-Arnold

Falko Braak

Final report – Dutch Metrology Institute (VSL)

Cylinder number: 4498

Nominal composition

- Sulphur dioxide : 100 nmol/mol
 - Synthetic air : balance

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	10-12-2014	95.06	0.6	3

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	10-12-2014	96.22	0.6	3

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	11-12-2014	97.24	0.6	3

Measurement #4

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	11-12-2014	97.01	0.6	3

Results

Component	Result (nmol/mol)	Standard deviation (% relative)
Sulphur dioxide	96.38	0.5

Calibration standards

Gravimetrically prepared standards of SO₂ in N₂ in the range of 1 – 6 µmol/mol were diluted with synthetic air to prepare a calibration curve. Dilution factors 10, 30 and 40 were used to prepare dynamic standards in the range of 60 to 145 nmol/mol SO₂ in air.

Instrumentation

A Thermo electron 43A UV pulsed fluorescence SO₂ analyser was used for analysis. Bronkhorst low Δp-flow Mass flow controllers were used and the individual flows were measurement with a Bronkhorst model FPPT flow meter.

Calibration method and value assignment

Gravimetrically prepared standards of SO₂ in N₂ in the range of 1 – 6 µmol/mol were diluted with synthetic air to prepare a calibration curve. Dilution factors 10, 30 and 40 were used to prepare dynamic standards in the range of 60 to 145 nmol/mol SO₂ in air. The uncertainty of the dynamically prepared mixtures is dominated by the uncertainty of the flow measurement (0.3% rel.) As 2 flows are mixed (flow from standard and diluting flow) the uncertainty on the dynamically generated mixtures is 0.42% rel. The uncertainty on the responses of the analyser is 0.5% rel.

A first order linear regression curve was used to determine the amount fraction of the unknown according to ISO6143. The measurement was repeated for 4 times with different diluting flows and standard gas mixtures so that 4 independent measurement results were acquired. The assigned value is the average of those 4 results.

Uncertainty evaluation

As the uncertainty of the standards and the uncertainty of the flow measurement are input parameters for ISO6143, the uncertainty given by the regression analysis gives the uncertainty for each individual amount value. The uncertainty on the assigned value is the uncertainty of the average of the 4 individual measurement results.

Coverage factor: $k = 2$

Expanded uncertainty: $U = 0.96 \text{ nm/mol}$

Authorship

J.I.T. van Wijk

Final report – Umweltbundesamt GmbH (BEV/EAA)

Laboratory name: BEV/EAA (Umweltbundesamt)

Cylinder number: 4499

Nominal composition

- Sulphur dioxide : 100 nmol/mol

- Synthetic air : balance

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	04/12/2014	99.0	0.31	1

Standard deviation of the signal of the monitoring instrument during measurement of cylinder number 4499.

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	05/12/2014	99.8	0.10	1

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	09/12/2014	99.8	0.22	1

Measurement #4

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	10/12/2014	99.8	0.26	1

Measurement #5

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	11/12/2014	99.0	0.15	1

Measurement #6

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
Sulphur dioxide	12/12/2014	99.3	0.19	1

Results (average of 6 measurements)

Component	Result (nmol/mol)	Standard deviation (% relative) Average of 6 above
Sulphur dioxide	99.5	0.21

Expanded combined uncertainty: 2.67 nmol/mol

Calibration standards

Dynamic dilution of PRM

PRM: VSL, 90.02 $\mu\text{mol/mol}$ SO₂, U: 0.36 $\mu\text{mol/mol}$, in nitrogen.

Cylinder No: D249666, Certificate No: 32217802

Molbox No 926, calibration valid to July 2015,

Molbloc 3322 (mid flow, N₂), calibration valid to Dec 2015,

Molbloc 3283 (high flow, synthetic air), calibration valid to Feb 2016.

Instrumentation

Monitoring Instrument (ultraviolet fluorescence): Thermo 43C trace level, Serial No 61892-333.

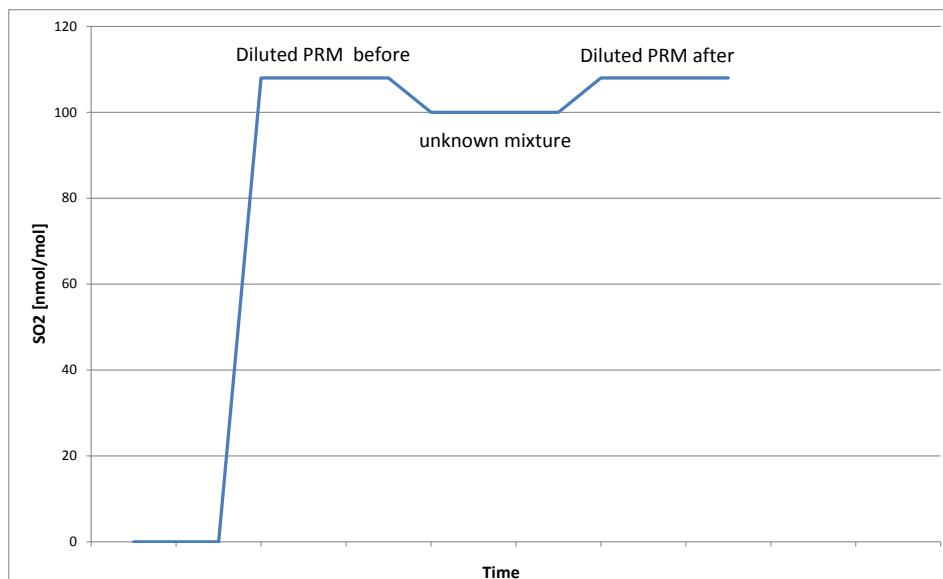
Dynamic dilution calibrator (with MFC): Horiba ASGU 364, Serial No HA214

Calibration method and value assignment

Monitoring instrument is calibrated with a gas mixture produced by dynamic dilution of PRM with an amount of substance close to the mixture under investigation. The diluted PRM is measured by the monitoring instrument before and after the mixture under investigation.

The actual flows produced by the dynamic dilution calibrator are measured with a Molbloc/Molbox system before and after measurement of the unknown mixture and are used to calculate the actual amount of substance of the diluted PRM.

The monitoring instrument is not adjusted, all corrections necessary are calculated.



Uncertainty evaluation

Numbers given in this example are valid for the 1st of the 6 measurements.

Uncertainty source	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
PRM	Type B	normal	0.18	0.0012	$2.18 \cdot 10^{-4} \mu\text{mol/mol}$
Traces of SO ₂ in dilution gas	Type B	normal	$5.77 \cdot 10^{-4}$	0.999	$5.77 \cdot 10^{-4} \mu\text{mol/mol}$
Volume flow PRM	Type A, B		$1.080 \cdot 10^{-2}$	$2.40 \cdot 10^{-2}$	$2.58 \cdot 10^{-4} \mu\text{mol/mol}$
Volume flow dilution gas	Type A, B		3.755	$2.9 \cdot 10^{-5}$	$1.09 \cdot 10^{-4} \mu\text{mol/mol}$
Reproducibility of calibrator	Type A	normal	$4.1 \cdot 10^{-4}$	1	$4.1 \cdot 10^{-4} \mu\text{mol/mol}$
Uncertainty of diluted PRM (sum of uncertainties above) in nmol/mol					0,8 nmol/mol
Standard deviation of signal during calibration	Type A	normal	0.19	1	0.19 nmol/mol
Reproducibility of monitoring instrument	Type A	normal	0.9	1	0.9 nmol/mol
Standard deviation of signal during measurement of mixture	Type A	normal	0.31	1	0.31 nmol/mol
Short time stability of mixture	Type B	normal	0.5	1	0.5 nmol/mol

Coverage factor: $k = 2$

Expanded uncertainty: $U=2.67$ nm/mol (average of uncertainties calculated for each measurement)

Authorship

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