발간등록번호	
11 - 1360620 - 000106 - 14	

# The report of the result on SF<sub>6</sub> Inter-Comparison Experiment, 2016 - 2017



World Calibration Centre

for SF<sub>6</sub>



National Institute of Meteorological Sciences Korea Meteorological Administration Dec, 2017

# Prepared by

Haeyoung Lee<sup>1</sup>, Sumin Kim<sup>1</sup>, Heejeong Yoo<sup>1</sup>, Hongwoo Choe<sup>1</sup>, Sang-Ok Han<sup>1</sup>, Sang-Boom Ryoo<sup>1</sup>, Brad Hall<sup>2</sup>, Grant Forster<sup>3</sup>, Yver Kwok Camille<sup>4</sup>, Frank Meinhardt<sup>5</sup>, Ingeborg Levin<sup>6</sup>, Ludwig Ries<sup>7</sup>, Cédric Couret<sup>7</sup>, Myriam Guillevic<sup>8</sup>, Simon A. Wyss<sup>9</sup>, Daniel Rzesanke<sup>10</sup>, Armin Jordan<sup>11</sup>, Rowena Moss<sup>12</sup>, Jeongsoon Lee<sup>13</sup>, Jegyu Yu<sup>14</sup>

<sup>1</sup> WMO/GAW World Calibration Centre for SF<sub>6</sub>, KMA/NIMS, Republic of Korea

<sup>2</sup> WMO/GAW Central Calibration Laboratory for SF<sub>6</sub>, NOAA/ESRL, USA

<sup>3</sup> University of East Anglia, UK

<sup>4</sup> Laboratoire des Sciences du Climat et de l'Environnement, France

<sup>5</sup> Schauinsland GAW station, UBA, Germany

<sup>6</sup>*Heidelberg University, Germany* 

<sup>7</sup> Zugspitze GAW station, UBA, Germany

<sup>8</sup> Laboratory for Gas Analysis, METAS, Switzerland

<sup>9</sup> Laboratory for Air Pollution / Environment Technology, Empa, Switzerland

<sup>10</sup> Flask and Calibration Laboratory, Integrated Carbon Observation System, EU

<sup>11</sup> Max Plank Institute for Biogeochemistry, Germany

<sup>12</sup> National Institute of Water and Atmospheric Research, New Zealand

<sup>13</sup> Korea Research Institute of Standards and Science, Republic of Korea

<sup>14</sup> Anmyeondo GAW station, KMA/NIMS, Republic of Korea

# Compiled by

World Calibration Centre for SF<sub>6</sub>

# Contents

# The result of SICE 2016-2017

Circuit 1	1
Circuit 2	3
Statistical analysis	5

# Laboratory report

1-1 WCC-SF <sub>6</sub>	7
1-2 UEA	9
1-3 LSCE	
1-4 Schauinsland GAW station	14
1-5 Heidelberg University	16
1-6 Zugspitze GAW station	
1-7 METAS	
1-8 ICOS-EU	
1-9 MPI-BGC	
1-10 NOAA	
2-1 WCC-SF <sub>6</sub>	
2-2 NIWA	
2-3 NOAA	
2-4 KRISS	
2-5 AMY GAW station	47
Appendix A. Cylinder preparation	
Appendix B. The inter-comparison experiment result betw	een WCC-SF <sub>6</sub>
and CCL	
Appendix C Cylinders and regulators information	59

# **Circuit 1: Europe with 9 labs**

Cylinder number: D339685 (High) and D339605 (Low)



### Table 1. The results of participants

	Lab	Re	sult	Repea	atability	Lab -	- WCC	Scale	Page
		(pmo	l/mol)	(0	%)	diff.(pn	nol/mol)		
		Low	High	Low	High	Low	High		
1	WCC-SF <sub>6</sub>	7.89	9.21	0.23	0.22			WMO-X2014	7
0		7.85	9.16	0.51	0.45	-0.04	-0.05	WMO-X2006	0
Ζ	UEA	(7.86)	(9.17)	(0.51)	(0.44)	(-0.03)	(-0.04)	(WMO-X2014)	9
3	LSCE	7.88	9.19	0.88	0.65	-0.01	-0.02	WMO-X2014	12
4	Schauinsland	7.96	9.20	0.03	0.03	0.07	-0.01	WMO-X2006	14
Б	Haidalbara	0 00	0.42	0.26	0.26	0 12	0.21	Heidelberg	16
5	Heidelberg	0.02	9.42	0.20	0.30	0.13	0.21	scale	10
6	Zugspitze	8.00	9.24	1.00	0.80	0.11	0.03	WMO-X2014	19
7	METAS	7.95	9.30	0.46	0.22	0.06	0.09	METAS-2016	21
8	ICOS	7.92	9.18	0.23	0.27	0.03	-0.03	WMO-X2014	30
9	MPI-BGC	7.89	9.21	0.48	0.42	0.00	0.00	WMO-X2014	33
10	NOAA	7.89	9.21	0.12	0.12	0.00	0.00	WMO-X2014	36

<sup>\*</sup>UEA also submitted figures on WMO-X2014 after the SICE. Please confirm their report.



Figure 1. The Plot shows the differences between each lab in circuit 1 and reference lab, WCC-SF<sub>6</sub>. Red plot is high level (D339685) and black plot is low level (D339605). Light blue dashed line indicates the compatibility goal,  $\pm$  0.02 ppt and light green line is for extended compatibility goal,  $\pm$  0.05 ppt. \*\* indicates WMO-X2006 scale and + is for its own scale while no mark means WMO-X2014 scale. UEA submitted two different figures on WMO-X2006 and X2014 respectively, please confirm the report.

# **Circuit 2: Asia-Pacific with 4 labs**

Cylinder number: D339688 (High) and D339629(Low)



Table 2.	The	results	of	participants
----------	-----	---------	----	--------------

	Lab	Re	sult	Repea	tability	Lab -	WCC	Casla	Daga	
	Lab	(pmo	l/mol)	()	%)	diff.(pn	nol/mol)	Scale	Page	
		Low	High	Low	High	Low	High			
1	WCC-SF <sub>6</sub>	7.88	9.20	0.11	0.18			WMO-X2014	38	
2	NIWA	7.88	9.12	1.13	0.47	0.00	-0.08	WMO-X2014	40	
3	NOAA	7.89	9.21	0.16	0.15	0.01	0.01	WMO-X2014	42	
4	KDICC	7.01	0.16	0.25	0.22	0.02	0.04	WMO-X2014	11	
4	KKI33	7.91	9.10	0.25	0.22	0.03	-0.04	KRISS primary	44	
5	AMY	7.87	9.20	0.62	0.59	-0.01	0.00	WMO-X2014	47	



Figure 2. The Plot shows the differences between each lab in circuit 2 and reference lab, WCC-SF<sub>6</sub>. Red plot is high level (D339688) and black plot is low level (D339629). Light blue dashed line indicates the compatibility goal,  $\pm$  0.02 ppt and light green line is for extended compatibility goal,  $\pm$  0.05 ppt. + is the values from its own scale while no mark means WMO-X2014 scale. KRISS submitted figures on KRISS scale with WNO-X2014 scale, please confirm the report.

# **Statistical Analysis**



Figure 3. The number of frequency according to the differences between labs and reference lab. For both of high (top) and low (bottom) concentration 5 labs are within the compatibility goal among 12 labs. NOAA participated both of circuits but was considered one lab in this analysis.



Figure 4. The number of frequency according to the differences between reference lab and labs which used WMO scale during the experiment. For both of high (top) and low (bottom) concentration 4 labs are within the compatibility goal among 8 labs. NOAA was excluded in this analysis.

# 1-1. WCC for SF<sub>6</sub>

# Cylinder number: D339685, D339605

# **Measurements and result**

Cylinder 1#: D339685

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
<u>ar</u>	08/04/2016	9.205	0.14	4
$SF_6$	19/04/2016	9.205	0.14	5
(Before)	25/04/2016	9.207	0.19	4
(After)	21/02/2017	9.209	0.26	4
(Allel)	22/02/2017	9.208	0.22	5

#### Cylinder2 #: D339605

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
<u>ar</u>	18/04/2016	7.885	0.01	3
$SF_6$	22/04/2016	7.891	0.11	5
(Before)	27/04/2016	7.890	0.02	5
(After)	26/02/2017	7.895	0.04	4
(Alter)	27/02/2017	7.890	0.23	4

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	SF <sub>6</sub>	9.207 ±0.02 ppt	0.22
D339605	$SF_6$	7.890 ±0.02 ppt	0.23

\* Before and after indicate the analysis result before and after circulating the cylinders.

\* The result value is mean average of all analysis result of each cylinder.

\* Measurement precision includes "repeatability" in ISO that it does not include uncertainties associated with the primary standards.

# **Method description**

Analytical Method:

A gas chromatography with Electron Capture Detector (Agilent 7890) was used to assign mole fractions. Configuration of analytical system used in this key comparison is as follows; Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  MFC  $\rightarrow$  Pre-concentration  $\rightarrow$ sample injection valve  $\rightarrow$  column  $\rightarrow$  detector  $\rightarrow$  integrator (Chemstation)  $\rightarrow$  area

#### comparison $\rightarrow$ results

Analytical Condition				
Detector	μECD			
Detector temperature	375.0°C			
Column	Pre: Alumina 6ft, Main: Alumina 12ft			
Loop size	5 mL			
Makeup Flow	60psi			
Sample Flow	100 mL/min			
Carrier gas, pressure	P-5 gas, 60 psi			
Oven temperature	60 °C			

#### Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards(scale):

WMO X2014 CB10895, CB10909 for D339685 WMO X2014 CB11159, CB10894 for D339605

#### Instrument calibration

Two points calibration was applied in order to assign the amount of each component. Measurement sequence was in order of CRM1- SAMPLE – CRM2 – CRM1. CRM1 and CRM2 stand for the calibration standard and SAMPLE stands for cylinders (D3396845, D339605). During whole measurements, analyzer drift was monitored and corrected based on the assumption that the detector response drifts linearly through a unit cycle of CRM1- SAMPLE – CRM2 – CRM1.

#### Sample handling

The sample cylinders were stood for more than one week at room temperature to be equilibrated.

# **1-2.** Weybourne Atmospheric Observatory

# Cylinder number: see below

#### Measurements and result

$C$ y IIII $\pi$ . D $J$	Cylinder1	#:	D339685
--	-----------	----	---------

Component	Date (dd/mm/yy)	Result (ppt)	Std. dev. (ppt)	Number of replicates
$SF_6$	27/05/2017 to 30/05/2017	9.155	0.041	14

#### Cylinder 2#: D339605

Component	Date (dd/mm/yy)	Result (ppt, pmol/mol)	Std. dev. (ppt)	Number of replicates
SF <sub>6</sub>	27/05/2017 to 30/05/2017	7.852	0.04	14

#### Results

Cylinder No.	Component	Result (ppt)	Measurement Precision* (%)
D339685	$SF_6$	9.155	0.45
D339605	SF <sub>6</sub>	7.852	0.51

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

#### Analytical Method:

Routine analysis of  $SF_6$  was performed using a modified commercial Gas Chromatograph (Clarus 500, Perkin Elmer), which comprised of gas chromatography followed by detection of  $SF_6$  using an Electron Capture Detector (ECD). The air sample was introduced to a 15 cm<sup>3</sup> sample loop held in a temperature controlled zone with a flow of 200 ml min<sup>-1</sup>. Prior to sample injection the temperature and pressure inside the sample loop was allowed to equilibrate to for 0.5 minutes.

At 0.5 minutes the contents of the sample loop were injected onto the pre-column containing Hayesep Q (80/100 mesh, stainless steel, 3/16" OD x 200 cm length)

which was operated at a constant temperature of  $65^{\circ}$  C. This stage allowed any contaminants to vent (e.g. air, oxygen). After 5.5 minutes, the sample was transferred to a second Hayesep Q column (analytical column) and the pre-column was back flushed to prevent O<sub>2</sub> from entering the analytical column. Following further separation on the analytical column the CO<sub>2</sub>, N<sub>2</sub>O and SF<sub>6</sub> eluted at 6.2 mins, 6.9 mins and 8.1 mins, respectively before entering the ECD.

The carrier gas used in this system was nitrogen N4.8 grade (99.998 % purity, BOC) with a flow rate of 60 ml min<sup>-1</sup> during chromatographic separation and 100 ml min<sup>-1</sup> during the back flushing of the pre-column. Carrier gas was further purified using a heated getter (Supelco, model no. 29546-U) and OMI purifier tube (Supelco, model no. 23909) to reduce impurities below 10 ppb. The ECD was operated at 370°C with 5 % CH<sub>4</sub>/Argon as make-up gas at a flow rate of 1 ml min<sup>-1</sup>.

The detector response was recorded and analysed using Perkin Elmer GC control software (TCNav 6.3.2). Normalised peak heights (peak height / average of bracketing working standards) measured from samples were referenced to the instruments non-linear response function of the ECD to  $SF_6$ .

Analytical condition of instrument used to measure 516		
Analytical Condition		
Detector: ECD		
Detector temperature: 370°C		
Column: Haysep Q (80/100 mesh)		
Loop size: 15 ml		
Makeup gas Flow: 60 ml min-1		
Sample Flow: 200 ml min-1		
Carrier gas, pressure: 80 psig		
Oven temperature: 65°C		

Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards(scale):

Laboratory primary reference gases are referenced on the WMO X2006 scale for  $SF_6$ , and were produced and calibrated at MPI-Jena. Concentrations in the primary reference gases range from 7.5 ppt to 15.9 ppt (5 cylinders).

The accuracy of the system is also assessed through the analysis of a target gas every 6-hours. The target gas is a cylinder of gas with accurately assigned concentrations of the target species determined at a central calibration laboratory (in this instance MPI-Jena). This target gas is introduced to the system as a sample and following analysis the deviation of  $SF_6$  concentrations from the assigned concentrations is calculated.

#### Scale conversion from X2006 to X2014

The Submitted value was on the X2006, however, when the cylinders were calibrated against X2014, the value was revised follows:

Cylinder1 # D339685 : 9.17 ± 0.04

Cylinder 2# D339605 : 7.86 ± 0.04

#### Instrument calibration

The ECD response to  $SF_6$  was calibrated on the 27/05/2016 and the SICE cylinders were analyzed every 6 hours over 4-days.

#### Sample handling

The sample cylinders were stood for 3-days at room temperature to be equilibrated.

# **1-3. LSCE**

# Cylinder number:

# Measurements and result

#### Cylinder1 #: D339685

Component	Date (dd/mm/yyyy)	Result (ppt, pmol/mol)	Std. dev. (%, relative)	Number of replicates
SF <sub>6</sub>	20/06/2016	9.19	0.65%	30

#### Cylinder 2#: D339605

Component	Date (dd/mm/yyyy)	Result (ppt, pmol/mol)	Std. dev. (%, relative)	Number of replicates
SF <sub>6</sub>	20/06/2016	7.88	0.88%	30

#### Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	$SF_6$	9.19	0.65
D339605	$SF_6$	7.88	0.88

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

#### Analytical Method:

A gas chromatography with Electron Capture Detector (Agilent 7980A) was used to assign mole fractions.

Configuration of analytical system used in this key comparison is as follows :

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  sample injection valve  $\rightarrow$  MFC  $\rightarrow$  column  $\rightarrow$  detector

 $\rightarrow$  integrator (Chemstation)  $\rightarrow$  software (developped at the lab)  $\rightarrow$  results

Analytical Condition		
Detector micro-ECD	Micro ECD	
Detector temperature	395°C	
Column	Hayesep-Q (6'x3/16"SS)	80-100mesh
Loop size	10mL	
Reference Flow	200mL/min	
Sample Flow	200mL/min	
Carrier gas, pressure	40Psi	
Oven temperature	80°C	

Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards(scale):

Calibration standard values are assigned by measuring the cylinders against a set filled and calibrated at NOAA. The scale is WMO X2014.

### Instrument calibration

A two-point calibration was applied in order to assign the amount of each component. Measurement sequence was in the order of WH-WL-WSS-TGT-A-B-AIR-WH-WL(etc.) where WH, WL and WS stand for the calibration standards and A and B stand for the two cylinders. Ambiant air is also measured. Standards are measured every hour and a half at the most. During whole measurements, analyzer drift was monitored and corrected based on the assumption that the detector response drifts linearly through a unit cycle.

#### Sample handling

The sample cylinders were equiped with regulators at their arrival and let to be equilibrated at room temperature over the next three days.

#### **Evaluation of measurement uncertainty :** 0.8%

# 1-4. Schauinsland

# Cylinder number: D339605, D339685

### Measurements and result

Cylinder1:	D339685
------------	---------

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
	160705	9.187	0.2	27
	160706	9.217	0.18	27
$SF_6$	160707	9.216	0.21	23
	160714	9.217	0.16	34
	160720	9.147	0.19	34

#### Cylinder 2: D339605

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
	160704	7.948	0.14	20
	160705	7.953	0.16	29
$SF_6$	160707	7.996	0.15	30
	160708	7.952	0.13	31
	160714	7.964	0.13	27
	160715	7.896	0.2	34

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%, relative)
D339685	$SF_6$	9.20	0.03
D339605	$SF_6$	7.96	0.03

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

Analytical Method:

A gas chromatography with Electron Capture Detector (Agilent G1533A) was used to assign mole fractions.

Configuration of analytical system used in this key comparison is as follows;

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  MFC  $\rightarrow$  sample injection valve  $\rightarrow$  column  $\rightarrow$  detector

 $\rightarrow$  integrator (Chemstation)  $\rightarrow$  area comparison  $\rightarrow$  results

Analytical Condition		
Detector	ECD Agilent G1533A	
Detector temperature	350°C	
Column	(Hayesep 80/100 mesh.)	
Sample loop size	6 feet (3/16")	
Carrier gas type and flow	Ar/CH4 95/5	
Sample flow	140 ml/min	
Make up gas type and flow	Off	
Oven temperature	80°C	

Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards (scale):

3 NOAA Laboratory standards certified also for SF<sub>6</sub>. (WMO X2006)

### ➢ <u>Sample handling</u>

The sample cylinders were stood for more than one week at room temperature to be equilibrated.

# 1-5. Heidelberg University, Institut für Umweltphysik, Germany

# Cylinder number: SICE 1 and SICE 2

### **Measurements and result**

#### Cylinder1 #: D339685

Component	Date (dd/mm/vy)	Result (ppt. pmol/mol)	Std. dev. (%, relative)	Number of replicates
	09/08/2016	9.386	0.06	3
$SF_6$	16/08/2016	9.469		2

#### Cylinder 2#: D339605

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yy)	(ppt, pmol/mol)	(%, relative)	replicates
<u>an</u>	09/08/2016	8.004	0.20	3
$SF_6$	16/08/2016	8.050		2

#### Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	$SF_6$	9.419	0.36
D339605	SF <sub>6</sub>	8.023	0.26

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

#### Analytical Method:

A gas chromatography with Electron Capture Detector (Shimadzu GC-8AIE) was used to assign mole fraction. The configuration of the analytical system used in this key comparison is as follows:

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  needle valve  $\rightarrow$  sample injection valve  $\rightarrow$  preconcentration  $\rightarrow$  pre-column  $\rightarrow$  column  $\rightarrow$  detector  $\rightarrow$  integrator (home made)  $\rightarrow$ area comparison  $\rightarrow$  results

For details, see Maiss et al. (1996)

#### Analytical condition of instrument used to measure SF<sub>6</sub>

Analytical Condition

Detector: ECD (Shimadzu GC-8AIE) Detector temperature: 330°C Pre-Column/ & Column: molecular sieve 5A Pre-concentration trap: PORAPAK-Q, -77°C/100°C Loop size: 15 ml Stripper gas Flow: N2, 1.9 bar Sample Flow through column: 20ml/min Carrier gas, pressure: N2, 1.5 bar Oven temperature: 65°C

#### Calibration Standards(scale):

Home-made secondary gravimetric standard gas processed through 1ml sample loop

#### Instrument calibration

Home made secondary gravimetric standard, non-linearity correction. The procedure of calibration and non-linearity correction is described in detail in the Supplement of Levin et al. (2010).

#### Sample handling

The sample cylinders with pressure regulators installed stood for more than one week at room temperature to be equilibrated.

#### **Evaluation of measurement uncertainty (optional)**

The estimated uncertainty is based on the reproducibility of the 5 replicates measured on each of the cylinders, but it is very well comparable with the precision of our in-house laboratory standards over a long time (over several years).

# **References** (optional)

- Levin, I., Naegler, T., Heinz, R., Osusko, D., Cuevas, E., Engel, A., Ilmberger, J., Langenfelds, R.L., Neininger, B., v. Rohden, C., Steele, L.P., Weller, R. and Worthy, D.E. 2010. The global SF<sub>6</sub> source inferred from long-term high precision atmospheric measurements and its comparison with emission inventories. *Atmos. Chem. Phys.* 10, 2655-2662.
- Maiss, M., L.P. Steele, R.J. Francey, P.J. Fraser, R.L. Langenfels, N.B.A. Trivett and I. Levin, 1996. Sulfur hexafluoride a powerful new atmospheric tracer. *Atmosph. Environment* 30, 1621-1629.

# 1-6. UBA-Zugspitze

# Cylinder number: D339685, SICE-1, 1520psi, D339605, SICE-2, 1440psi

#### **Measurements and result**

Cylinder1 #: D339685

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	27.09.2016	9,26	0,7% / 0,07	34
$SF_6$	28.09.2016	9,23	0,9% / 0,08	26

Cylinder 2#: D339605

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	27.09.2016	8,01	1,1% / 0,09	38
$SF_6$	28.09.2016	7,99	0,9% / 0,07	34

#### Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	$SF_6$	9,24	0,8%
D339605	SF <sub>6</sub>	8,00	1,0%

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

Analytical Method:

Gas chromatography with  $\mu$ ECD (Agilent HP6890) was used to assign mole fractions.

Configuration of analytical system used in this key comparison is as follows

Gas cylinder  $\rightarrow$  Pressure controller  $\rightarrow$  sample injection loop  $\rightarrow$  column  $\rightarrow$  detector

 $\rightarrow$  integrator (Chemstation)  $\rightarrow$  area comparison  $\rightarrow$  results

Analytical Condition		
Detector	μECD	
Detector temperature	350°C	
Column	Hayesep 80/100 mesh, 6 feet (3/16")	
Loop size	15mL	
Reference Flow	20,6mL/min	
Sample Flow	170mL/min	
Carrier gas, pressure	Ar/CH4, 5% CH4, 25/55 psi	
Oven temperature	80°C	

#### Analytical condition of instrument used to measure SF<sub>6</sub>

 Calibration Standards(scale): WMO X2014

#### Instrument calibration

Single point calibration was applied in order to assign the amount of  $SF_6$ . Measurement sequence was in the order of A-B-B-A-B-B-A-(etc.) where A stands for the working standard and B stands for SICE-cylinder. Moreover, the working standard was freshly calibrated with 4 different NOAA standards.

### ➢ <u>Sample handling</u>

The sample cylinders were placed for more than 3 days at room temperature to be equilibrated. The leak test didn't show any leak.

# **1-7. METAS**

Report completed by Myriam Guillevic, Laboratory for Gas Analysis, METAS and Simon A. Wyss, Laboratory for Air Pollution / Environment Technology, Empa

### Cylinder number: #D339685, #D339605

#### Measurements and result

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
SF <sub>6</sub>	18/10/2016	9.295	0.22	7

#### Cylinder 2#: D339605

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
SF <sub>6</sub>	19/10/2016	7.952	0.46	7

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	$SF_6$	9.295	0.22
D339605	SF <sub>6</sub>	7.952	0.46

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

#### Analytical Method:

The measurements were performed on a Medusa-GC/MS system at Empa, Duebendorf, Switzerland in the Laboratory for Air Pollution / Environment Technology. This system consists of a pre-concentration unit called Medusa coupled to a gas chromatograph, followed by mass detection by a quadrupole mass spectrometer. The system is further described by Miller et al. [1].

Analytical Condition		
Detector	Quadrupol Mass Spectrometer	
Detector temperature	230 °C	
Column	PoraBond Q 25 m x 0.32 mm	
Loop size	2000 ml	
Reference Flow	100 ml/min	
Sample Flow	100 ml/min	
Carrier gas, pressure	Не	
Oven temperature	40 °C to 200 °C in 420 s	

Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards(scale): METAS primary standard

#### Calibration standard (scale): METAS-2016 primary standard

The two SICE-experiment cylinders were measured at Empa vs the tertiary tank J-191 from SIO. The primary, SI-traceable  $SF_6$  standard from METAS was prepared in January 2017. The J-191 tank was then calibrated vs METAS primary standard in February 2017.

We describe here the preparation of the primary standard at METAS gas laboratory. The generation process is dynamic and made of two main steps, i) the generation of a first, high concentration  $SF_6$  mixture pressured in a cylinder as sketched on Fig. 1 and ii) the dynamic dilution of this cylinder to produce pmol/mol level SF6 reference gas mixtures (Fig. 2).

To produce the high concentration cylinder, first the matrix gas (Pangas 5.6 synthetic air) is spiked with the pure substance, using a permeation device (Fine Metrology, Italy) placed in a temperature, pressure and flow controlled atmosphere. The substance in the permeator is lost linearly over time by permeation through a membrane. The resulting permeation rate is precisely calibrated in our lab in Bern, using a magnetic suspension balance (Rubotherm, Germany).

The desired concentration is reached by dilution of the high concentration mixture flow exiting the permeation chamber with a second flow of matrix gas.

These two flows are piloted by mass flow controllers (MFCs, Red-y series, Vötglin, Switzerland). All parts in contact with the gas mixture, including the balance and MFCs, are passivated using coated surfaces (Silconert2000, SilcoTek GmbH, Germany), to reduce adsorption/desorption processes as much as possible. Finally the nmol/mol level SF<sub>6</sub> mixture is pressurized into a Silconert2000-coated stainless steel cylinders (2.25 L, Swagelok Arbor AG, SN SV4041) by cryo-filling, up to a pressure of 30 bars. Then this cylinder is homogenised during at least 48 hours.



Figure 1. Dynamic generation of high-concentration reference gas mixture for  $SF_6$ . MFM: mass flow meter. MFC: mass flow controller. PrC: Pressure controller. bPr: mechanical back pressure regulator.



Figure 2. Dynamic dilution of the high-concentration cylinder using METAS '2-stepdilutor'. The first dilution step consists in a small flow of high-concentration mixture (MFC1, 10-100 ml/min) being diluted by a larger flow of synthetic air (MFC2, 500-

5000 ml/min). For the second dilution step, a small flow of the first mixture (MFC3, 10-100 ml/min) is further diluted by a larger flow of synthetic air (MFC4, 500-5000 ml/min).

In the second step, the high concentration mixture is then diluted using METAS 'Two-step-dilutor' [2], an existing dynamic dilution system based on digital MFC (Sensirion, CMOSens series, Switzerland) and pressure controllers (El-Press, Bronkhorst, The Netherlands), see diagram on Fig. 2. We use two different flows for MFC2 to generate successively two different SF<sub>6</sub> molar fractions, that were then directly pressured in Silconert coated cylinders by cryo-filling. The generated molar fraction are:

- 8.1032 pmol/mol in cylinder SN SK5017,
- 10.0955 pmol/mol in cylinder SN SV4042.

These two cylinders constitute the METAS-2016 suite of primary reference gas mixtures for  $SF_6$ .

#### Evaluation of METAS-2016 primary standard uncertainty

We describe here the uncertainty linked to the primary reference gas mixture preparation at METAS.We evaluate the uncertainty assigned to the prepared reference mixture by taking into account the uncertainty of each component in the following equations, as listed in Table 1.

The amount of substance fraction of  $SF_6$  in the high concentration cylinder can be written as:

$$C_{high,SF_6} = X_{residual} + \frac{qmC}{M_{SF_6}} \cdot \frac{MV_{carrier}}{q_{v_{carrier}}} (1)$$

with qmC, the mass loss of SF6 from the permeator in the chamber, being:

$$qmC = \frac{\Delta m}{\Delta t} \cdot Purity_{SF_6} (2)$$

 $\Delta m$  the mass difference measured by the balance,  $\Delta t$  the time difference registered by the computer connected to METAS Network Time Protocol, and *Purity*<sub>SF6</sub> the SF<sub>6</sub> content in the permeator or substance purity. To calculate qmC we take the weighted mean of the weighting sequences done (approx. 4 days each) before and after filling the high concentration cylinder, both at precisely 32.01 °C. Unfortunately at the very beginning of the filling occurred a transient temperature drop in the permeation chamber. As permeators start to react within minutes of a temperature change, we therefore use the time-weighted mean temperature over the two hours of filling  $T_{fill}$  = 31.96 °C as best estimate, with its associated standard deviation of 0.05 °C. The temperature sensitivity of the permeation rate was additionally measured at 31.81 °C and the sensitivity curve of the permeation rate computed in between 31.81 and 32.01 °C, using an exponential function of the form  $qmC = B * exp(A * T_{fill})$ . The permeation rate at Tf ill was used as best estimate to calculate qmC.

For the second preparation step, the dilution factor f of the dynamic dilution can be written as:

with  $q_{MFCi}$  the flow of mass flow controller i, see Fig. 2.

The molar fraction in each low-concentration cylinder can be written as:

To calculate the combined uncertainty of each low-concentration cylinder, the above equations are computed by the software GumWorkBench. The expanded uncertainty of the pmol/mol level mixtures, with a coverage factor k=2 (corresponding to a confidence interval of 95%), is 1.3%. The quaternary tank J-191 at Empa is then anchored to this suite of primary gas mixtures by measuring the tanks vs each other, using the Medusa-GCMS system at Empa as comparator. From these measurements we deduce the conversion factors a and b in between the SIO and METAS standards:

• SIO value  $\_$  a + b = METAS value, with a=1.0113 and b=0.0057.

This conversion factor is then applied to all measured values of tanks #D339685 and #D339605 previously anchored to the J-191 tank on the SIO scale. (Note that the obtained values are almost not distinguishable from the values calculated using only a slope of 1.012 and no intercept.)

Finally, the value and expanded uncertainty (k=2) assigned to tanks #D339685 and #D339605, including measurement reproducibility, primary standard preparation and its transfer to the J-191 tank is:

• 9.29 ± 0.12 pmol/mol for tank #D339685 (1.3% expanded uncertainty);

• 7.95 ± 0.10 pmol/mol for tank #D339605 (1.3% expanded uncertainty).

Table 1. Generation of primary reference mixtures for  $SF_6$  at METAS: List of variables taken into account in the uncertainty budget. All flows are given at standard temperature and pressure (0 °C, 1013 hPa) and were calibrated in METAS laboratory for small volumetric flow, using the very same conditions of carrier gas type (here, synthetic air), as well as upstream and downstream pressure levels.

Variable	Description	Value	Uncertainty (k=1)	Unit	Contribution to total uncertainty, %	
	Varia	bles for both	cylinders			
Purity <sub>SF6</sub>	Purity of SF <sub>6</sub> in permeator	1	0.00289	-	21.2	
$\frac{\Delta m}{\Delta t}$	Total measured permeation rate	1210.86	14	ng/min	59.8	
X <sub>residual</sub>	SF <sub>6</sub> impurity in carrier gas	0.0065	0.00375	pmol/mol	0.5	
$M_{SF_6}$	Molar molecular mass of SF <sub>6</sub>	146.05542	0.0025	g/mol	-	
<i>MV<sub>carrier</sub></i>	Molar mass of carrier gas	22406.31	2.16	L/mol	-	
$q_{v_{carrier}}$	Flow of carrier gas	5297.74	5.30	ml/min	2.5	
$q_{MFC1}$	Flow of MFC1	29.6174	0.0444	mL/min	5.6	
$q_{MFC3}$	Flow of MFC3	39.7108	0.0596	mL/min	5.5	
$q_{MFC4}$	Flow of MFC4	1986.16	1.99	mL/min	2.4	
For cylinder SN SV4042						
$q_{MFC2}$	Flow of MFC2	1988.05	1.99	mL/min	2.5	
	For	cylinder SN S	SK5017			
$q_{MFC2}$	Flow of MFC2	2484.52	2.48	mL/min	2.5	

Table 2: Comparison of METAS-2016 primary tanks with SIO J-191 tank using the Medusa-GC-MS system at Empa: Results of  $SF_6$  molar fraction measurements.

Tonk	Date	Results (ppt,	Std dev. (%,	Number of
I dlik	(dd/mm/yyyy)	pmol/mol)	relative, k=2)	replicates
SK5017	27/02/2017	8.0069	0.22	8
SV4042	27/02/2017	9.9769	0.27	8

Table 3: Uncertainty budget of assigned value to tank #D339685 referenced vs METAS-2016 primary scale. The transfer standard is the SIO tank J-191. For measured values, we report here the uncertainty of the mean value (it is therefore lower than the standard deviation of the measurements).

Variable for tank #D339685					
Variable	Description	Value	Uncertainty (k=1)	Unit	Contribution to total uncertainty, \%
Purity <sub>SF6</sub>	Purity of SF <sub>6</sub> in permeator	1	0.00289	-	21.3
$\frac{\Delta m}{\Delta t}$	Total measured permeation rate	1210.86	14	ng/min	59.9
X <sub>residual</sub>	SF <sub>6</sub> impurity in carrier gas	0.0065	0.00375	pmol/mol	0.4
M <sub>SF6</sub>	Molar molecular mass of SF <sub>6</sub>	146.05542	0.0025	g/mol	-
<i>MV<sub>carrier</sub></i>	Molar mass of carrier gas	22406.31	2.16	L/mol	-
$q_{v_{carrier}}$	Flow of carrier gas	5297.74	5.3	ml/min	2.6
$q_{MFC1}$	Flow of MFC1	29.6174	0.0444	mL/min	5.6
$q_{MFC3}$	Flow of MFC3	39.7108	0.0596	mL/min	5.5
$q_{MFC4}$	Flow of MFC4	1986.16	1.99	mL/min	2.5
$q_{MFC2}$ SK5017	Flow of MFC2 for SK5017	2484.52	2.48	mL/min	0.3
$q_{MFC2}$ SV4042	Flow of MFC2 for SV4042	1988.05	1.99	mL/min	1
Meas-SK5017	Mean measured value of tank SK5017 vs J- 191	8.0069	0.003	pmol/mol	-
Meas-SV4042	Mean measured value of tank SV4042 vs J- 191	9.9769	0.005	pmol/mol	0.2
Meas- #D339685	Mean measured value of tank #D339685 vs J- 191	9.185	0.004	pmol/mol	0.4

Table 4: Uncertainty budget of assigned value to tank #D339605 referenced vs METAS-2016 primary scale. The transfer standard is the SIO tank J-191. For measured values, we report here the uncertainty of the mean value (it is therefore lower than the standard deviation of the measurements).

Variable for tank #D339605						
Variable	Description	Value	Uncertainty (k=1)	Unit	Contribution to total uncertainty, \%	
	Purity of SF <sub>6</sub> in permeator	1	0.00289	-	20.6	
	Total measured permeation rate	1210.86	14	ng/min	57.9	
	SF <sub>6</sub> impurity in carrier gas	0.0065	0.00375	pmol/mol	0.6	
	Molar molecular mass of SF <sub>6</sub>	146.05542	0.00250	g/mol	-	
	Molar mass of carrier gas	22406.31	2.16	L/mol	-	
	Flow of carrier gas	5297.74	5.30	ml/min	2.5	
	Flow of MFC1	29.6174	0.0444	mL/min	5.4	
	Flow of MFC3	39.7108	0.0596	mL/min	5.3	
	Flow of MFC4	1986.16	1.99	mL/min	2.4	
SK5017	Flow of MFC2 for SK5017	2484.52	2.48	mL/min	2.9	
SV4042	Flow of MFC2 for SV4042	1988.05	1.99	mL/min	-	
Meas-SK5017	Mean measured value of tank SK5017 vs J- 191	8.0069	0.003	pmol/mol	0.4	
Meas-SV4042	Mean measured value of tank SV4042 vs J- 191	9.9769	0.005	pmol/mol	-	
Meas- #D339605	Mean measured value of tank #D339605 vs J- 191	7.857	0.007	pmol/mol	1.9	

#### Instrument calibration

To assign the amount fraction of  $SF_6$  a single point calibration was applied. The measurement sequence was as followed: A-B-A-B-A-... where A stands for the calibration standard and B for the sample (D339605 and D339685). The analyser drift was corrected by the linear interpolation between to calibration standard measurements.

#### > <u>Sample handling</u>

The sample cylinders were stood for approx. a week at room temperature, before measurements, to equilibrate.

### References

- [1] B. R. Miller, R. F. Weiss, P. K. Salameh, T. Tanhua, B. R. Greally, J. Muhle, and P. G. Simmonds. Medusa: A Sample Preconcentration and GC/MS Detector System for in Situ Measurements of Atmospheric Trace Halocarbons, Hydrocarbons, and Sulfur Compounds. Analytical Chemistry, 80(5):1536–1545, 2008.
- [2] H.-P. Haerri, T. Mace, J. Walden, C. Pascale, B. Niederhauser, K. Wirtz, V. Stovcik, C. Sutour, J. Couette, and T. Walden. Dilution and permeation standards for the generation of NO, NO<sub>2</sub> and SO<sub>2</sub> calibration gas mixtures. Measurement Science and Technology, 28(3):035801, 2017.

# 1-8. ICOS-FCL, Jena, Germany

# Cylinder number: D339605, D339685

### Measurements and result

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
SF <sub>6</sub>	22/11/2016	9.199	0.300	8
	23/11/2016	9.179	0.257	17
	24/11/2016	9.178	0.308	17
	25/11/2016	9.163	0.079	3

#### Cylinder 2#: D339605

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	22/11/2016	7.921	0.110	7
	23/11/2016	7.915	0.321	17
	24/11/2016	7.914	0.177	15
	25/11/2016	7.914	0.139	3

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	$SF_6$	9.181	0.272
D339605	SF <sub>6</sub>	7.916	0.234

\* Measurement precision refers to "repeatability" in ISO

### **Method description**

Analytical Method:

A gas chromatography with Electron Capture Detector (Agilent7890A) was used to assign mole fractions.

Configuration of analytical system used in this key comparison is as follows

Gas cylinder  $\rightarrow$  regulator (provided) $\rightarrow$  sample column (MFC downstream)  $\rightarrow$ sample injection valve  $\rightarrow$  pre/main column  $\rightarrow$  detector  $\rightarrow$  integrator (GCwerks)  $\rightarrow$  peak height comparison with working tank for short term drift correction (2Point calibration) $\rightarrow$  results (calibrated by external standards)

The ECD detector is driven by 15,7% CO2 in N2 5.0 as make up gas (13ml/min).

Analytical condition of instrument used to measure SF <sub>6</sub>				
An	alytical Condition			
Detector	ECD (in Agilent7890A)			
Detector temperature	380 °C			
Column	Parapak 80-100			
Loop size	2Mx1875"OD			
Reference Flow	117 ml/min			
Sample Flow	117 ml/min			
Carrier gas, pressure	N2 5.0, 4.5bar			
Oven temperature	70 °C			

#### Calibration Standards(scale):

The lab secondary scale is calibrated against lab primaries (8 point) that have been assigned by WMO-CCL in Boulder. Range of the lab primary scale is (6.49 to 13.20) ppt  $SF_6$ , of the lab secondary scale (5.92 to 13.0) ppt, respectively.

#### Instrument calibration

Short term drift of raw values is corrected by a working tank (2 point calibration, relative, raw result correction only). The instrument for itself is calibrated on a biweekly basis on lab secondary standards (5 Points, last 5d prior analysis of the given sample). The lab secondary scale is calibrated against lab primaries (8 point). The calibration curve for 1st=>2nd standards scale transfers where retrieved from a parabolic (/w linear term) and for 2nd=>instrument/data from a linear regression.

#### Measurement sequence

WT,S1,WT,S2,WT,S1,WT,S2,WT with WT for working tank, S1 for cylinder

D339605 and S2 for cylinder D339685.

#### Sample handling

The sample cylinders were stood for one week at room temperature to be equilibrated. The regulator was mounted and flushed as stated in WCL's guidelines in annex2.

#### **Evaluation of measurement uncertainty (optional)**

Quality control time series ("targets"), running since 03/2015, indicates a reproducibility of 0.35% for the lower part (7.23ppt) and 0.22% for the upper limit (10.04ppt) of the QC-interval spanned around the SICE-RR concentrations.

#### Note (optional)

Both cylinders were analyzed with the supplied regulators. This was contrary to suggestions, but we found no irregularities of the regulators.

During the stay of the cylinders, in a parallel analysis line the GC system's "Methanizer" and FID broke. Due to hence caused temperature variations the  $SF_6$  analysis was not performed under perfect, stable conditions.

# 1-9. MPI-BGC

# Cylinder number: D339605, D339685

### Measurements and result

Cylinder 1#:	D339605
--------------	---------

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	15/11/2016	7.908	0.35	11
	16/11/2016	7.881	0.60	15
	17/11/2016	7.898	0.37	14
	18/11/2016	7.864	0.39	7

#### Cylinder2 #: D339685

Commonant	Date	Result	Std. dev.	Number of
Component	(dd/mm/yy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	15/11/2016	9.197	0.34	11
	16/11/2016	9.226	0.51	15
	17/11/2016	9.213	0.43	15
	18/11/2016	9.197	0.16	6

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	$SF_6$	9.211	0.42
D339605	SF <sub>6</sub>	7.890	0.48

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

Analytical Method:

A gas chromatograph with Electron Capture Detector (Agilent# G1533-60550) was used to quantify  $SF_6$ .

The configuration of the analytical system used in this intercomparison is as follows

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  sample selection valve (Valco 8 port MPV)  $\rightarrow$  sample injection valve  $\rightarrow$  column  $\rightarrow$  detector bypass valve (bypassing the oxygen peak)  $\rightarrow$ 

detector  $\rightarrow$  integrator (Chemstation)  $\rightarrow$  peak height comparison  $\rightarrow$  results (example)

The MFC that is regulating the sample flow at 70 mL/min is downstream of the sample loop. After filling of the sample loop the MFC opens to allow for pressure equilibration (0.X min) before injection.

Analytical condition	of instrument used to measure SF <sub>6</sub>	
Analytical Condition		
Detector	ECD Agilent G1533-60550	
Detector temperature	385 ℃	
Column	Hayesep Q (3/16", 6 ft pre-colum; 12 ft main column)	
Loop size	15 mL	
Makeup gas Flow	-	
Sample Flow	70 mL/min	
Carrier gas, pressure	4.5 bar	
Oven temperature	72 °C	

Calibration Standards(scale):

The MPI-BGC SF<sub>6</sub> measurements are linked to the WMO SF<sub>6</sub> X2014 scale using a working standard (dried ambient air with SF<sub>6</sub> at 9.185 ppt) and the following cylinders spanning the range from 3.81 to 16.85 ppt:

CA01601, CA01650, CA01675, CA01680, CA04605, CA04611, CA04639, CC121969, CA05435, CA05281, CA05290, CA05295, CA05435, CC339513.

Additional secondary laboratory standards with  $SF_6$  at 9.85 ppt, 10.55 ppt and 11.90 ppt have been calibrated at MPI-BGC based on the following cylinders with WMO assignments that had been temporarily available at MPI-BGC: CA07880, CA07842, CA07889, CB09952, CB09948, CB09955, CB09957, CB09958, CB09983.

Instrument calibration

The  $SF_6$  peak height was normalized to the peak height of a working standard (nominal  $SF_6$ : 9.185 ppt). Measurement sequence was in the order of A-B-A-B-A-(etc.) where A stands for the working reference standard and B stands for cylinders (D339605, D339685).

To assign the amount of  $SF_6$  and account for the non-linearilty of the detector a multi-point calibration based on the above listed calibration standards has been made using the same sequence order A-C-A-C- (A= working standard, C=calibration standard). A quadratic regression function was calculated and applied to the normalized peak heights.

Sample handling

The sample cylinders were kept for one day with the pressure regulator mounted and kept under pressure at room temperature to be equilibrated.

#### **Evaluation of measurement uncertainty (optional)**

The reproducibility of daily means of target gas measurements during the last five years has been 0.2 % (relative standard deviation).

# 1-10. Laboratory: NOAA

# Cylinder number: D339605, D339685

### Measurements and result

Cymuci 1#. <b>D</b> $SS90$	Cylinder	1#:	D339605	
----------------------------	----------	-----	---------	--

Component	Date (dd/mm/yyyy)	Result (ppt, pmol/mol)	Std. dev. (%, relative)	Number of replicates
SF <sub>6</sub>	20/12/2016	7.889	0.20	8
	03/01/2017	7.888	0.19	8
	04/01/2017	7.894	0.26	8
	06/01/2017	7.878	0.28	8
	10/01/2017	7.890	0.16	8

#### Cylinder2 #: D339685

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
SF <sub>6</sub>	20/12/2016	9.207	0.21	8
	03/01/2017	9.201	0.12	8
	04/01/2017	9.217	0.20	8
	06/01/2017	9.206	0.28	8
	10/01/2017	9.209	0.23	8

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339685	$SF_6$	9.21	0.12
D339605	SF <sub>6</sub>	7.89	0.12

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

Analytical Method:

Gas Chromatography with Electron Capture Detector (Agilent6890) was used to assign mole fractions.

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  sample injection valve  $\rightarrow$  column  $\rightarrow$  detector  $\rightarrow$  integrator (Gcwerks)  $\rightarrow$  peak height comparison  $\rightarrow$  results

Analytical Condition			
Detector	Agilent 6890		
Detector temperature	370 deg C		
Column	Porapak Q/Molecular sieve 5A		
Loop size	9 cc		
Reference Flow	100 cc/min		
Sample Flow	100 cc/min		
Carrier gas, pressure	32 psi		
Oven temperature	90-pre, 185-main		

#### Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards(scale): WMO-SF<sub>6</sub>-X2014

#### Instrument calibration

The response function was defined by 6 secondary standards, with mole fractions 3.3, 5.3, 7.1, 9.1, 11.9, and 17.0 ppt. The response function was determined in November 2016. A second order polynomial was used for the response function based on peak height. A target tank at 8.87 ppt  $SF_6$  was analyzed along with cylinders D339605 and D339685 to verify the response function.

#### Sample handling

Samples were unpacked and stored upright overnight. Regulators were attached and flushed 5 times and stored with gas overnight. Regulators were flushed 3 times before making measurements in ABABABA... sequence, where A=reference, B=sample. The peak height ratio B/A was determined by linear interpolation between two A measurements. The reference gas is natural air with  $SF_6 = 9.08$  ppt.

#### **Evaluation of measurement uncertainty (optional)**

Our reproducibility, based on repeated measurement of in-house standards, is 0.03 ppt at 2-sigma.

# 2-1. WCC for SF<sub>6</sub>

### Cylinder number: D339688, D339629.

#### **Measurements and result**

Cylinder 1#: D339688

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
С.Б.	14/04/2016	9.200	0.17	3
$SF_6$	25/04/2016	9.197	0.05	5
(Belole)	11/05/2016	9.191	0.11	4
(After)	23/02/2017	9.202	0.06	3
(Alter)	24/02/2017	9.209	0.06	3

#### Cylinder2 #: D339629

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
SE.	15/04/2016	7.880	0.10	2
$S\Gamma_6$	16/05/2016	7.876	0.06	4
(Belole)	18/05/2016	7.880	0.09	5
(After)	25/02/2017	7.875	0.20	4
(Alter)	26/02/2017	7.875	0.06	4

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339688	$SF_6$	9.200 ±0.02 ppt	0.18
D339629	SF <sub>6</sub>	7.877 ±0.01 ppt	0.11

\* Before and after indicated the analysis result before and after circulating the cylinders.

\* The result value is mean average of all analysis result of each cylinder.

\* Measurement precision refers to "repeatability" in ISO that it does not include uncertainties associated with the primary standards.

### **Method description**

Analytical Method:

A gas chromatography with Electron Capture Detector (Agilent 7890) was used to assign mole fractions.

Configuration of analytical system used in this key comparison is as follows;

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  MFC  $\rightarrow$  Pre-concentration  $\rightarrow$ sample injection value  $\rightarrow$ 

column  $\rightarrow$  detector  $\rightarrow$  integrator (Chemstation)  $\rightarrow$  area comparison  $\rightarrow$  results

Analytical condition	on of matument used to measure 516	
Analytical Condition		
Detector	μECD	
Detector temperature	375.0°C	
Column	Pre: Alumina 6ft, Main: Alumina 12ft	
Loop size	5 mL	
Makeup Flow	20psi	
Sample Flow	430 mL/min	
Carrier gas, pressure	P-5 gas, 60 psi	
Oven temperature	40 °C 20min → 170°C 22min	

Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards(scale):

WMO X2014 CB10895, CB10909 for D339688 WMO X2014 CB11159, CB10894 for D339629

#### Instrument calibration

Two points calibration was applied in order to assign the amount of each component. Measurement sequence was in order of CRM1- SAMPLE – CRM2 – CRM1.

CRM1 and CRM2 stand for the calibration standard and SAMPLE stands for cylinders (D339688, D339629).

During whole measurements, analyzer drift was monitored and corrected based on the assumption that the detector response drifts linearly through a unit cycle of CRM1- SAMPLE – CRM2 – CRM1.

#### Sample handling

The sample cylinders were stood for more than one week at room temperature to be equilibrated.

# 2-2. NIWA, New Zealand

### Cylinder number: D339688 and D339629

#### **Measurements and result**

Cylinder 1#: D33968	8
---------------------	---

Component	Date (dd/mm/yyyy)	Result (ppt, pmol/mol)	Std. dev. (%, relative)	Number of replicates
$SF_6$	29/6/2016	9.16 ppt	0.04 ppt	9
	1/7/2016	9.13 ppt	0.03 ppt	9
	3/7/2016	9.07 ppt	0.05 ppt	10

#### Cylinder2 #: D339629

Component	Date (dd/mm/yyyy)	Result (ppt, pmol/mol)	Std. dev. (%, relative)	Number of replicates
SF <sub>6</sub>	27/6/2016	7.92 ppt	0.05 ppt	9
	29/6/2016	7.86 ppt	0.10 ppt	10
	1/7/2016	7.91 ppt	0.06 ppt	10
	3/7/2016	7.84 ppt	0.09 ppt	9

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339688	$SF_6$	$9.12 \pm 0.04 \text{ ppt}$	0.47 %
D339629	SF <sub>6</sub>	$7.88 \pm 0.09 \text{ ppt}$	1.13%

\* Measurement precision refers to "repeatability" in ISO

### **Method description**

Analytical Method:

An Agilent 6890 GC-ECD (K3182 9/98) was used to assign mole fractions.

System configuration is as follows:

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  3 stream selection valves (samples, reference gases, instruments)  $\rightarrow$  fluorister (flow controller)  $\rightarrow$  sample injection valve  $\rightarrow$  column  $\rightarrow$  detector  $\rightarrow$  intergrator (Chemstation)  $\rightarrow$  height comparison  $\rightarrow$  results

Analytical Condition			
Detector	Agilent ECD K3182 9/98		
Detector temperature	390°C		
Column	Porapak Q		
Loop size	5ml		
Reference Flow	120ml/min		
Sample Flow	120ml/min		
Carrier gas, pressure	61psi		
Oven temperature	63°C		

#### Analytical condition of instrument used to measure SF<sub>6</sub>

### Calibration Standards(scale):

WMO X2014 Scale. 12 tanks calibrated at NOAA ranging from 2.27 ppt to 8.08 ppt.

#### Instrument calibration

Twelve standards and the two ICP reference gases were measured versus the working reference gas. The calibration of the two ICP reference gases was achieved by determining the detector response to the twelve standards and then applying the detector response to the measurements of the two ICP reference gases for each day. The influence of short term drift or noise was addressed by bracketing each standard or reference gas measurement with the working reference.

#### Sample handling

The sample cylinders were brought inside and stood with regulators attached. They were leak checked and left to equilibrate over a weekend before being measured.

# 2-3. NOAA

# Cylinder number: D339629, D339688

### Measurements and result

Component	Date	Result	Std. dev.	Number of
component	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	22/07/2016	9.215	0.13	8
	26/07/2016	9.215	0.20	8
	28/07/2016	9.212	0.14	8
	29/07/2016	9.213	0.15	8

#### Cylinder 1 #: D339688

#### Cylinder 2#: **D339629**

Component	Date	Result	Std. dev.	Number of
	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	22/07/2016	7.888	0.11	8
	26/07/2016	7.898	0.22	8
	28/07/2016	7.891	0.19	8
	29/07/2016	7.891	0.10	4

#### Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339688	$SF_6$	9.21	0.15
D339629	$SF_6$	7.89	0.16

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

> <u>Analytical Method:</u>

Gas Chromatography with Electron Capture Detector (Agilent6890) was used to assign mole fractions.

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  sample injection valve  $\rightarrow$  column  $\rightarrow$  detector  $\rightarrow$  integrator (Gcwerks)  $\rightarrow$  peak height comparison  $\rightarrow$  results

An	Analytical Condition		
Detector	Agilent 6890		
Detector temperature	370 deg C		
Column	Porapak Q/Molecular sieve 5A		
Loop size	9 cc		
Reference Flow	100 cc/min		
Sample Flow	100 cc/min		
Carrier gas, pressure	32 psi		
Oven temperature	90-pre, 185-main		

### Analytical condition of instrument used to measure SF<sub>6</sub>

Calibration Standards(scale):

#### WMO-SF6-X2014

#### Instrument calibration

- The response function was defined by 6 secondary standards, with mole fractions 3.3, 5.3, 7.1, 9.1, 11.9, and 17.0 ppt. The response function was determined prior to analysis of cylinders D339629 and D339688. A second order polynomial was used for the response function based on peak height.
- Sample handling
- Samples were unpacked and stored upright overnight. Regulators were attached and flushed 5 times and stored with gas overnight. Regulators were flushed 3 times before making measurements in ABABABA... sequence, where A=reference, B=sample. The peak height ratio B/A was determined by linear interpolation between two A measurements. The reference gas is natural air with SF<sub>6</sub> = 9.08 ppt.

#### **Evaluation of measurement uncertainty (optional)**

Our reproducibility, based on repeated measurement of in-house standards, is 0.03 ppt at 2-sigma.

# 2-4. Laboratory: KRISS

# Cylinder number: D339688, D339629

### **Measurements and result**

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(ppt, relative)	replicates
$SF_6$	2016.09.24	9.172	0.009	3
	2016.09.28	9.143	0.009	3
	2016.09.30	9.178	0.009	4

#### Cylinder 1#: D339688

#### Cylinder2 #: D339629

Component	Date	Result	Std. dev.	Number of
Component	(dd/mm/yyyy)	(ppt, pmol/mol)	(ppt, relative)	replicates
$SF_6$	2016.09.26	7.914	0.008	3
	2016.09.26	7.905	0.008	3
	2016.09.28	7.922	0.008	4
	2016.09.30	7.909	0.008	3

Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (ppt)
D339629	$SF_6$	7.91	0.02
D339688	$SF_6$	9.16	0.02

\* Measurement precision refers to "repeatability" in ISO

### **Method description**

Analytical Method:

A gas chromatography with Electron Capture Detector (Agilent#6890) was used to assign mole fractions.

Flow scheme of analytical system used in this key comparison is as follows;

[Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  MFC  $\rightarrow$  pre-concentrator device  $\rightarrow$  injection value  $\rightarrow$  column  $\rightarrow$  detector  $\rightarrow$  vent]

For concentrating sample gas, we used a carboxen trap with cooled down up to low temperature (-30  $^{\circ}$ C) before introduction to the main Alumina column

Analytical Condition			
Detector	μECD		
Detector temperature	375 °C		
Column	Alumina 18ft		
sample size	200		
Reference Flow	40 ml/min		
Sample Flow	40 ml/min		
Carrier gas, pressure	P5, 85 psi		
Oven temperature	50 °C		

#### Analytical condition of instrument used to measure SF<sub>6</sub>

#### Calibration Standards(scale):

For the assignment of  $SF_6$ , we used 3-5 cylinders, three of them are from WMO's scale FB04070, FB04082, FB04097) and the others are traceable to KRISS gravimetric values. Followings are the details of the cylinders for the comparison.

Cylinder #	D155867	FB04070	FB04082	FB04097	D155873
Amount [pmol/mol]	7.01	8.11	8.50	9.16	9.22
Unc [pmol/mol]	0.01*	0.01**	0.01**	0.02**	0.01*

\*: gravimetric preparation uncertainty, \*\*: WMO calibration uncertainty

#### Instrument calibration

Single (or multi) point calibrations were applied in order to assign the amount of each component. Measurement sequence was in the order of A-S1-A-S1-A for single point calibration (or A-B-A-S1-A-C-A-D-A-S2-A-E-A for multi calibration), where S1 and S2 mean mixtures given for the RRT comparison and A, B, C are those of WMO scale, D and E are those of KRISS scale. During whole measurements, analyzer drift was monitored with A mixture and corrected based on the assumption that the detector response drifts linearly through a unit cycle of A-B-A.

#### Sample handling

The all cylinders used for the comparison were stood in the analysis laboratory for more than one week before starting analysis. It means that their temperature had been equilibrated (to reach at the same temperature with the room temperature). All analysis of sample and calibration mixtures was conducted under the same environmental condition of the laboratory.

### **Evaluation of measurement uncertainty (optional)**

Uncertainty factors were measurement precision and mixture's uncertainty used for assignment of amount of mole fraction.

# 2-5. AMY

### Cylinder number: D339688, D339629.

### Measurements and result

Cymider 11. D3	57000			
Component	Date	Result	Std. dev.	Number of
	(dd/mm/yyyy)	(ppt, pmol/mol)	(%, relative)	replicates
$SF_6$	30/11/2016	9.200	0.45	3
	30/11/2016	9.211	0.13	3
	01/12/2016	9.202	0.28	4

### Cylinder 1#: D339688

#### Cylinder2 #: D339629

Component	Date (dd/mm/yyyy)	Result (ppt, pmol/mol)	Std. dev. (%, relative)	Number of replicates
$SF_6$	02/12/2016	7.872	0.43	3
	05/12/2016	7.867	0.45	5
	06/12/2016	7.879	0.52	4

#### Results

Cylinder No.	Component	Result (ppt, pmol/mol)	Measurement Precision* (%)
D339688	SF <sub>6</sub>	9.204	0.59
D339629	SF <sub>6</sub>	7.872	0.62

\* Measurement precision refers to "repeatability" in ISO

# **Method description**

#### Analytical Method:

A gas chromatography with Electron Capture Detector (Agilent 6890) was used to assign mole fractions.

Configuration of analytical system used in this key comparison is as follows;

Gas cylinder  $\rightarrow$  regulator  $\rightarrow$  MFC  $\rightarrow$  Pre-concentration  $\rightarrow$ sample injection valve  $\rightarrow$ 

column  $\rightarrow$  detector  $\rightarrow$  integrator (Chemstation)  $\rightarrow$  area comparison  $\rightarrow$  results

mary treat condition of instrainent used to incusate of 8					
Analytical Condition					
Detector	μECD				
Detector temperature	375.0°C				
Column	Pre: Alumina 6ft, Main: Alumina 12ft				
Loop size	Trap (pre-concentrator)				
Makeup Flow	20 psi				
Sample Flow	375 mL/min				
Carrier gas, pressure	P-5 gas, 70 psi				
Oven temperature	65 °C 30min				

Analytical condition of instrument used to measure SF<sub>6</sub>

 Calibration Standards(scale): WMO X2014 FB04081
 WMO X2014 CB11159

#### Instrument calibration

One point calibration was applied in order to assign the amount of each component.

Measurement sequence was in order of CRM1- SAMPLE - CRM1.

CRM1 stands for the calibration standard and SAMPLE stands for cylinders (D339688, D339629).

During whole measurements, analyzer drift was monitored and corrected based on the assumption that the detector response drifts linearly through a unit cycle of CRM1- SAMPLE – CRM1.

➢ <u>Sample handling</u>

The sample cylinders were stood for more than one week at room temperature to be equilibrated.

# **APPENDIX A. Cylinder Preparation**

- 1. Sampling with a compressed gas cylinder
- 1.1 Sampling site

Anmyeondo (36.54°N, 126.33°E, 46 m a.s.l.) is located in the western part of the Korean Peninsula and has monitored SF<sub>6</sub> since 2007. It has seen a dynamic and wide range of SF<sub>6</sub> concentrations according to wind direction. The average concentration of SF<sub>6</sub> at the Anmyeondo GAW station was 9.5 ppt in 2016.



Figure A. Air sampling site in Korea and SF<sub>6</sub> concentration according to wind direction

The station has a 40 m tower behind the main building, and it is connected to a gas sampling system with a decabon tube for tertiary standard gases. Samples are collected when the air mass comes from the south or the west.

1.2 Cylinders

A high-pressure aluminum cylinder (30 L) is used because aluminum has low absorptivity and reactivity towards gas. More detailed information about the cylinder used in this comparison is given in APPENDIX C.

1.3 Cylindrical vacuum pumping system

The cylindrical vacuum pumping system is capable of vacuum processing up to 10-3, which is the Pa level inside the cylinder used for ambient air sampling. The system includes a turbo molecular pump and a heating jacket that can remove moisture inside the cylinder by keeping the temperature at a constant  $\sim 60^{\circ}$ C.

1.4 Compressor

When sampling in a high-pressure cylinder, an SA-3E series air compressor (RIX Industries, Benicia, CA, U.S.A.) is used as an oil-free piston-type pump. Additionally, a pressure sensor is embedded in the compressor so that it can be turned off when the pre-determined pressure level has been reached (1500 psi), thus preventing collection of samples under excessively high pressure. As a safety measure, a relief valve that releases gas when pressure exceeds 1700 psi should also be mounted to the compressor.

1.5 Dry air collection system

The dry air collection system is mounted between the compressor and the cylinder. Its components include a moisture trap, which removes atmospheric moisture; a pressure gauge, which can measure the filling pressure of a cylinder or canister; a relief valve for safety; and a check valve, which prevents samples from reflowing.

- Moisture trap and compressor: Moisture traps are made by filling a stainless steel tube with a moisture absorbent, such as magnesium perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>), and mounting a dust filter (7  $\mu$ m) at the bottom of the trap. A granule-type moisture absorbent of 8–12 mesh Mg(ClO<sub>4</sub>)<sub>2</sub> is used. We do not use Mg(ClO<sub>4</sub>)<sub>2</sub> for more than 24 hours after the moisture absorbent is filled. Also, we change the VCR gaskets, which are used at the inlet and the outlet of the moisture trap.
- Pressure gauge and relief valve: The pressure gauge monitors internal pressure in the collection system and cylinder during sampling and keeps the sampling pressure below the maximum pressure allowable for high-pressure cylinders. The relief valve controls the pressure in high-pressure cylinders so they do not exceed their respective maximum pressures.



Figure B. Schematic diagram of the dry air collection system



Figure C. The WCC-SF6 laboratory's dry air collection system

- 2. Adjusting  $SF_6$  gas levels
- 2.1 How to produce a mixture gas using the pressure method

The concentration of gases to be produced depends on their respective pressures, which is measured when a compensating gas mixture (high concentration of SF<sub>6</sub> or zero air) continues adding those component gases into an evacuated container. When Pi is the partial pressure of each component gas to be injected and Ci is its molarity, the container volume (V) is constant; then  $P_i$  can be expressed using the ideal gas equation at the temperature T as below:

$$\overline{\Sigma P}$$
  $\overline{\Sigma}$ 

where *P* is the pressure, *V* is the volume, *n* is the number of moles, and *R* is the gas constant (8.3144598 L·kPa·K<sup>-1</sup>·mol<sup>-1</sup>). However, in this case, unless the temperature (*T*) is constant and each component gas behaves like an ideal gas, there will be significant errors for real gases. Such error factors are corrected by using compressibility factor  $Z_i$  at the temperature and the pressure accurately measured when each component gas is injected.

2.2 How to produce a gas mixture with the same composition as the atmosphere

In order to produce a gas mixture with an SF<sub>6</sub> concentration lower than that of the background air, the component gases must contain major elements of  $SF_6$ , oxide and nitrogen whose composition is the same as that of the atmosphere. To produce a gas mixture with a higher concentration of SF<sub>6</sub>, the gas mixture needs to contain an SF<sub>6</sub> concentration that is 10% higher than that of the background air. In this experiment, the SF<sub>6</sub> concentration in the atmosphere at Anmyeondo was higher than that recorded at other observatories, so dry air was sampled and used as an SF<sub>6</sub> gas mixture after the dry air was certified that it was used the high concentration cylinders during the experiment, and the gas mixture with a lower SF<sub>6</sub> concentration was created by diluting the sampled air for low concentration cylinders. The zero gas (Ar 0.93 % +  $O_2$  20.0 % in  $N_2$ ) purchased and used should be pure with a certified ultralow  $SF_6$ concentration, and its composition of major component gases should be equivalent to that of the atmosphere. To produce a concentration lower than that of the atmosphere, a gas mixture with the same composition as the atmosphere is filled into a container according to predetermined calculations; zero gas is then added until the pressure reaches the predefined level. The mixture ratio of component gases to produce the standard  $SF_6$  gas with the target concentration can be calculated by the following formula:

- A: SF<sub>6</sub> concentration in component gases (ppt)
- B: Injected amount of component gases (psi)
- C: SF<sub>6</sub> concentration in the zero gas (ppt)
- D: Injected amount of the zero gas (psi)

Since gas injecting generates heat due to compression, gas should be injected slowly (for 30-40 minutes). However, the pressure calculated above is the pressure in a state of equilibrium, so even slow injection generates heat. Therefore, the current pressure is checked according to both Boyle's Law and Charles' Law when injecting gases, and gases should be injected in accordance with the following formula:

P: Injecting pressure (psi), P': Injecting pressure (psi)

V: Container volume (L), V': Container volume (L)

*T*: Current Temperature ( $^{\circ}$ C), *T*': Current Temperature ( $^{\circ}$ C)

The injecting pressure slightly expands the volume of a container, but such expansion is negligible, and it may be assumed that the volumes of the two cylinders are expanded equally. Therefore, PT=P'T', and the formula is also expressed as below:

For example, where a pressure of 100 atm is injected, the current temperature is  $2^{\circ}$ C; and if the current temperature is  $30^{\circ}$ C, the injecting pressure will be about 110 atm.

#### 2.3 Spiking/diluting system



Figure D. Schematic diagram of the spiking/diluting system



Figure F. The WCC-SF<sub>6</sub> laboratory's spiking/diluting system

The WCC-SF<sub>6</sub> spiking/diluting system is able to safely control pressure of up to 100 atm (1,470 psi) with displays attached for a high pressure sensor (④, Max. 0-3000 psia) and a low pressure sensor (③, Max. 0-500 psia), respectively. As seen in Figure D, four pressure control valves (⑦ V1, ⑩ V2, ⑧ V3, and ⑨ V4) and a purge vent valve (⑪) have been attached. Since the s.s.lines of most gas mixture producers are 1/8" in diameter, the use of long lines with such a narrow inlet diameter makes it hard to remove polluted air from the lines even when a vacuum pump is used to evacuate the air. The WCC-SF<sub>6</sub> system, however, has a purge valve to allow mother gas (①) gradually to flow into and out of the purge valve attached to the end of the sampling cylinder valve (②), easily eliminating polluted air. In addition, improper operation may generate high pressure that can burst or break the low-pressure sensor since it can handle a maximum pressure of 0-500 psia. Accordingly, a safety valve has been installed in front of the pressure sensor so that the valve will open at a pressure of about 400 psia, while closing the V3 valve (⑧) and allowing high pressure to be used if low pressure is not used.

3. Certifying the  $SF_6$  in gas cylinders

After adjusting the SF<sub>6</sub> level in the cylinder, the SF<sub>6</sub> mole fraction was assigned by GC- $\mu$ ECD (Agilent 7890A). The analysis was conducted in the following order: certified reference material 1, unknown sample, certified reference material 2, and certified reference material 1 again (*CRM1-sample-CRM2-CRM1*). Here, the certified reference materials were WMO-X2014 scale and those sequences were based on the result that equipment responses showed linearity in a given range of *CRM*.

$$C_{sample} = C_{CRM1} + (C_{CRM2} - C_{CRM1}) \times \frac{R_{corr.} - R_{CRM1}}{R_{corr.CRM2} - R_{CRM1}}$$
(1)

Here,  $R_{corr.CRM2}$  is the response of the equipment to certified reference material 2 (*CRM2*) with the drift corrected.

Assuming that equipment drift is linear with time,  $f_{drift}(i)$  can be obtained as follows:

$$f_{drift}(i) = \left\{ \frac{(3 \times R_{CRM1'})}{3 R_{CRM1'} + (R_{CRM1^*} - R_{CRM1'})i} \right\}$$
(2)

Here,  $R_{CRMI'}$  is the average (mean value) of the responses of the certified reference material 1 (*CRM1'*) from the first set of repeated measurements, and  $R_{CRMI''}$  (*CRM1''*) is the average of the responses for the certified reference material 1 from the second set of repeated measurements. Thus, the response of the unknown sample with corrected drift,  $R_{corr.}$  (= $R_{corrected}$ ), and the response of certified reference material 2,  $R_{corr.CRM2}$ , respectively, are as follows:

$$R_{corr.} = f_{drift}(i) \times R_{sample} \tag{3}$$

$$R_{corr.CRM2} = f_{drift}(i+1) \times R_{CRM2}$$
(4)

If the drift value defined as follows is smaller than the RSD (%) of the subset of repeated measurements,  $f_{drift}$  is 1.

$$drift(\%) = (R_{CRM''} - R_{CRM'}) / R_{CRM''} \times 100$$
(5)

A sample comparison analysis with two-point calibration of  $SF_6$  is shown in Table 1. According to the equation (1), the concentration was determined as follows:

To evaluate the uncertainty of analysis for two-point calibration, we considered the drift increase in the two-point calibration formula.

$$\begin{aligned} u(C_{sample})^{2} &= \left[ \left| \frac{R_{sample} - R_{CRM1}}{R_{CRM2} - R_{CRM1}} \times (C_{CRM2} - C_{CRM1}) \right| \\ &\times \sqrt{\left( \frac{u(R_{sample} - R_{CRM1})}{R_{sample} - R_{CRM1}} \right)^{2} + \left( \frac{u(R_{CRM2} - R_{CRM1})}{R_{CRM2} - R_{CRM1}} \right)^{2} + \left( \frac{u(C_{CRM2} - C_{CRM1})}{C_{CRM2} - C_{CRM1}} \right)^{2}} \right]^{2} + u(C_{CRM1})^{2}} \end{aligned}$$
(6)  
Here,  $u(R_{i} - R_{j}) = \sqrt{u(R_{i})^{2} + u(R_{j})^{2}}$ 

However, we assume that all participants attended with the same scale, so we did not consider uncertainty from the reference scale and only considered repeatability and drift in this formula.

$$u(C ) |(----) )| \qquad (7)$$

According to the formula above, the uncertainty was determined to be  $\pm 0.01$  to  $\pm 0.02$  ppt in a set, while taking into consideration the uncertainty of the reference gases it was increased to  $\pm 0.02 \sim 0.03$  ppt (Equation (6)).

Final uncertainty was decided by the standard deviation of all sets, taking into consideration analysis results pre- and post-circulating, and by the largest uncertainty which took into consideration repeatability and drift in a set among all sets.

2016.5.16	CRM1'	D339629	CRM2	CRM1"
1	11140	11209	11422	11142
2	11148.4*	11199	11425	11147
3	11148*	11195.9*	11426	11151
4	11142	11197	11433	11146
5	11142	11203	11436	11152
Mean Response	11141.1	11201.9	11428.4	11147.3
Standard deviation	1.34	6.64	4.86	3.67
Relative S.D. (%)	0.01	0.06	0.04	0.03
f-drift		1.0002	1.0004	
R-corrected response (Corrected peak area)		11199.8	11424.1	
Certified mole fraction (pmol/mol)	7.83		8.05	7.83
Sample mole fraction (pmol/mol)		7.88 (Eq. 1)		
Drift (%)				0.06
Sample uncertainty (pmol/mol)		0.01 (Eq. 7)		

Table 1. Sample comparison analysis for two-point calibration of  $SF_6$  in this comparison

experiment

# APPENDIX B. Inter-comparison Results between WCC-SF<sub>6</sub> and CCL

One of the activities requested by the WMO in the operation of a World Calibration Centre for  $SF_6$  is to maintain  $SF_6$  gas standards that are traceable to their respective primary standards. In this context, we signed a memorandum of understanding with the U.S. National Oceanic and Atmospheric Administration (NOAA), which serves as Central Calibration Laboratory under the WMO/GAW, regarding the biennial inter-comparison experiment for  $SF_6$ .

Since 2013, we have implemented this comparison with CCL (NOAA/ESRL) and shown the results in 2017 with this report.

The inter-comparison experiment was implemented between WCC-SF<sub>6</sub> (KMA) and CCL-SF<sub>6</sub> (NOAA/ESRL) from May to June 2017, according to the following procedure: 1) WCC-SF<sub>6</sub> prepared two different levels of cylinders and analyzed them according to the WMO-X2014 scale; 2) WCC-SF<sub>6</sub> sent two tanks to CCL-SF<sub>6</sub>; 3) CCL analyzed them; 4) and compared the results with WCC-SF<sub>6</sub>.

We used the analytical system and method described in APPENDIX A.

For this report, we analyzed 4 sets and the results are shown in Table 2. The differences between WCC and CCL were -0.02 ppt at low level (7.37 ppt) and 0.00 ppt at high level (9.29 ppt) indicating they were in WMO/GAW DQO,  $\pm 0.02$  ppt.

Cylinder #	1 Set	2 Set	3 Set	4 Set	Mean	WCC	CCL	Differences (WCC- CCL)
SA(D376125)	7.36 ± 0.002	7.34 ± 0.01	7.35 ± 0.01	7.34 ± 0.01	7.35 ± 0.01	7.35 (±0.015)	7.37 (±0.01)	-0.02
SB (D376130)	9.28 ± 0.015	9.29 ± 0.004	9.29 ± 0.01	9.29 ± 0.01	9.29 ± 0.01	9.29 (±0.018)	9.29 (±0.01)	0.00

Table 2. Results of inter-comparison experiment between WCC-SF<sub>6</sub> and CCL

# **APPENDIX C. Cylinders and regulators**

1 Cylinder:

- > Quantity : 2 cylinders (29.5 L) at each circuit
- Contents: High level (Dry ambient air), Low level (Diluted dry ambient air with pure air)
- Initial Volume: 1500 psi
- Cylinder No.: D339688, D339605, D339688, D339629
- Manufacturer: Luxfer

#### 2. Regulator

- > Quantity : 2 regulators with gaskets at each circuit
- ➢ Type: Two-stage, stainless steel, SG2 Series
- > Manufacturer: Tescom