

Current Activities of World Calibration Center for SF₆

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Outline

⊕ Introduction of WCC-SF₆

- ◆ What is WCC and sulfur hexafluoride (SF₆)?
- ◆ History and Infrastructures of WCC-SF₆

⊕ Intercomparison between CCL and WCC-SF₆

- ◆ Outline of intercomparison
- ◆ Sample Analysis (analysis condition, etc.)
- ◆ Intercomparison Result

⊕ Future Plans of WCC-SF₆

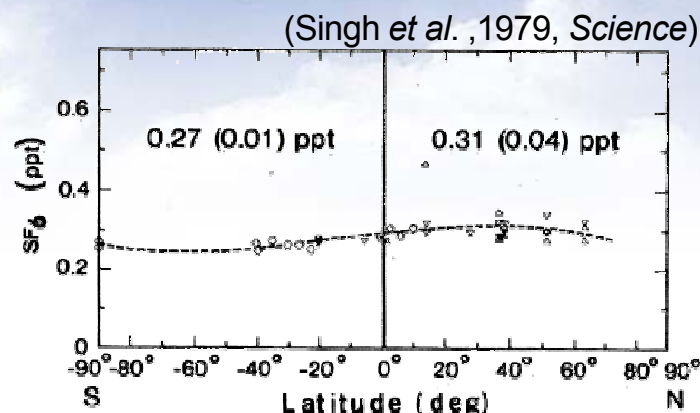


Korea Global Atmosphere Watch Center,
the regional GAW station in Anmyeon island, Rep. of Korea

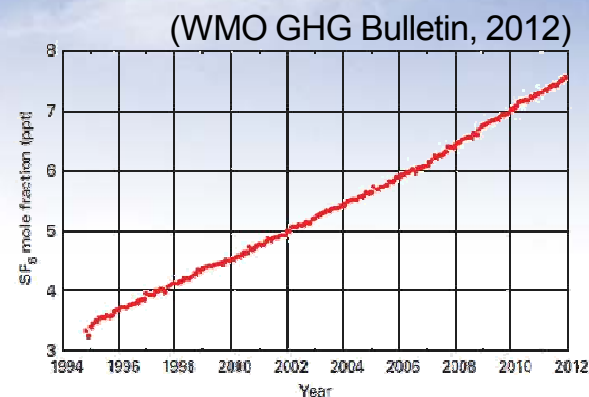
1. Introduction of WCC-SF₆

- What is sulfur hexafluoride (SF₆) and
World Calibration Center?
- History and Infrastructure

Sulfur Hexafluoride, SF₆



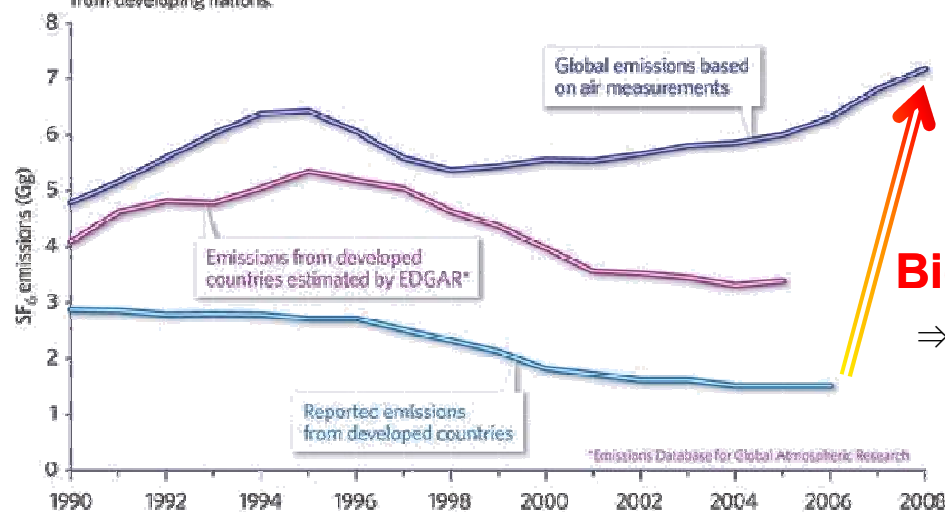
0.3 ppt in 1970s



7.5 ppt in 2011

KEEPING TABS ON A GREENHOUSE GAS

Developed countries may be reporting only about half of their emissions of sulphur hexafluoride (SF₆), a potent greenhouse gas. Much of the recent global increase may be due to rising emissions from developing nations.



(Levin *et al.*, 2010, *Atmos. Chem. Phys.* & Tollefson, 2010, *Nature*)

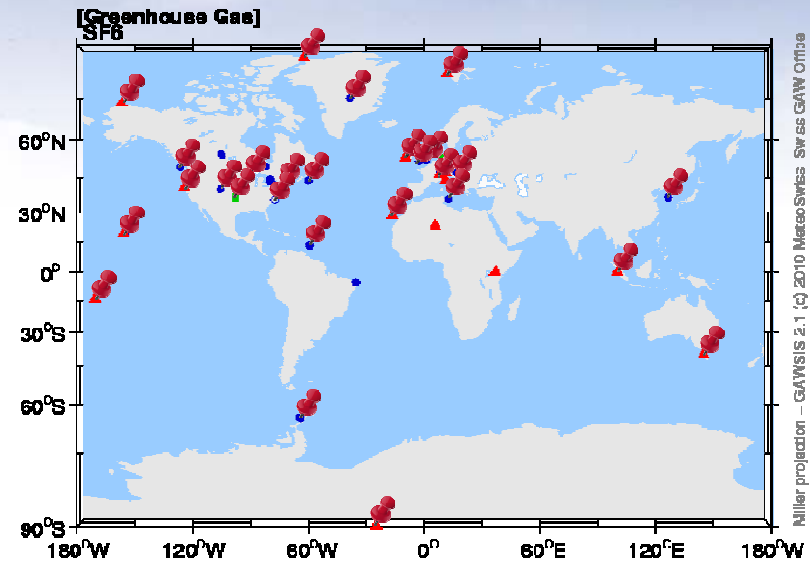
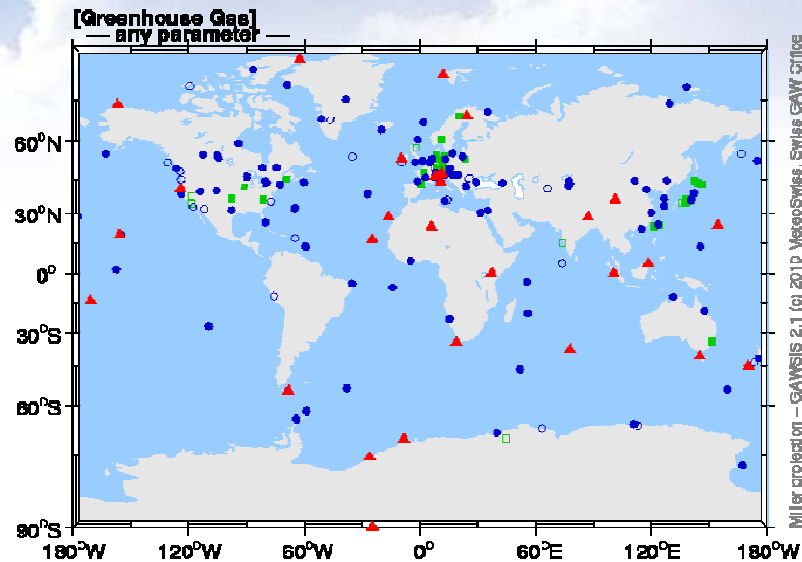
Aluminum industry
Semiconductor manufacturing
Electrical transmission equipment

Big difference of SF₆ emissions

⇒ Observation is important
to verify the global and regional emissions



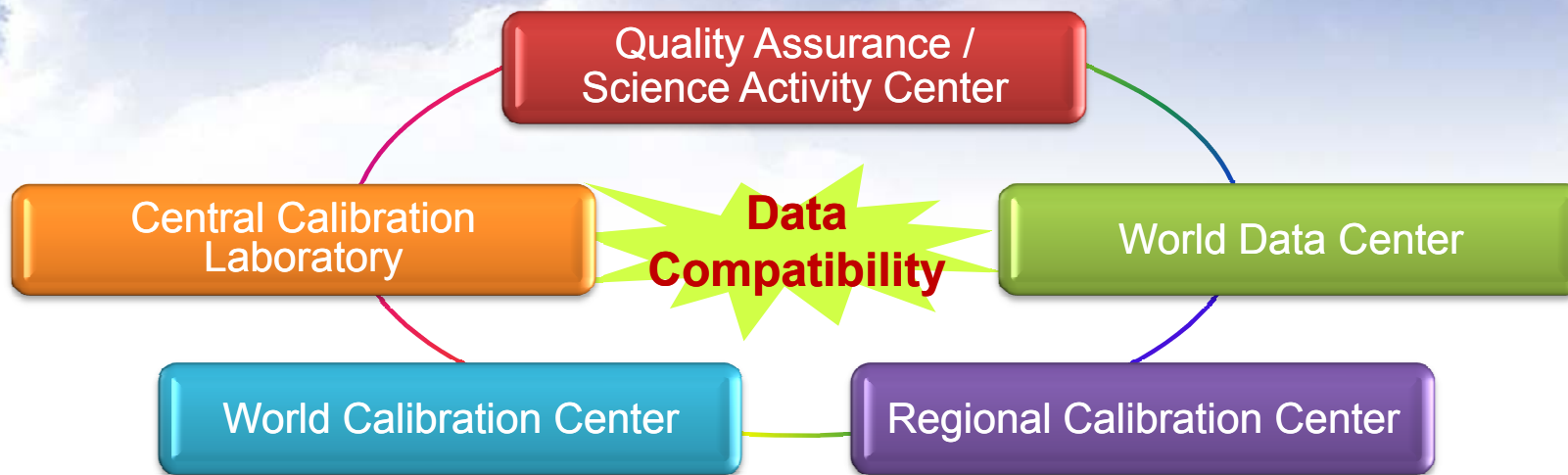
Observation Stations in WMO/GAW Programme



Region Species	Total	Africa	America	Asia	SW Pacific	Europe	South Pole
Greenhouse Gases	189	13	48	40	16	59	13
SF ₆	40	3	16	1	5	12	3

(GAW Station Information System at <http://gaw.empa.ch/gawsis/>)

WMO/GAW Quality Assurance System



Missions of WCC

- ✓ To develop and publish **quality control procedures** required to support the quality assurance of measurements
- ✓ To prepare and maintain **laboratory standards** which are traceable to the **WMO reference scale**
- ✓ To perform **intercomparison campaigns, system/performance audits**, and provide a training and long-term **technical help** for those who work for WMO/GAW stations

History of WCC-SF₆

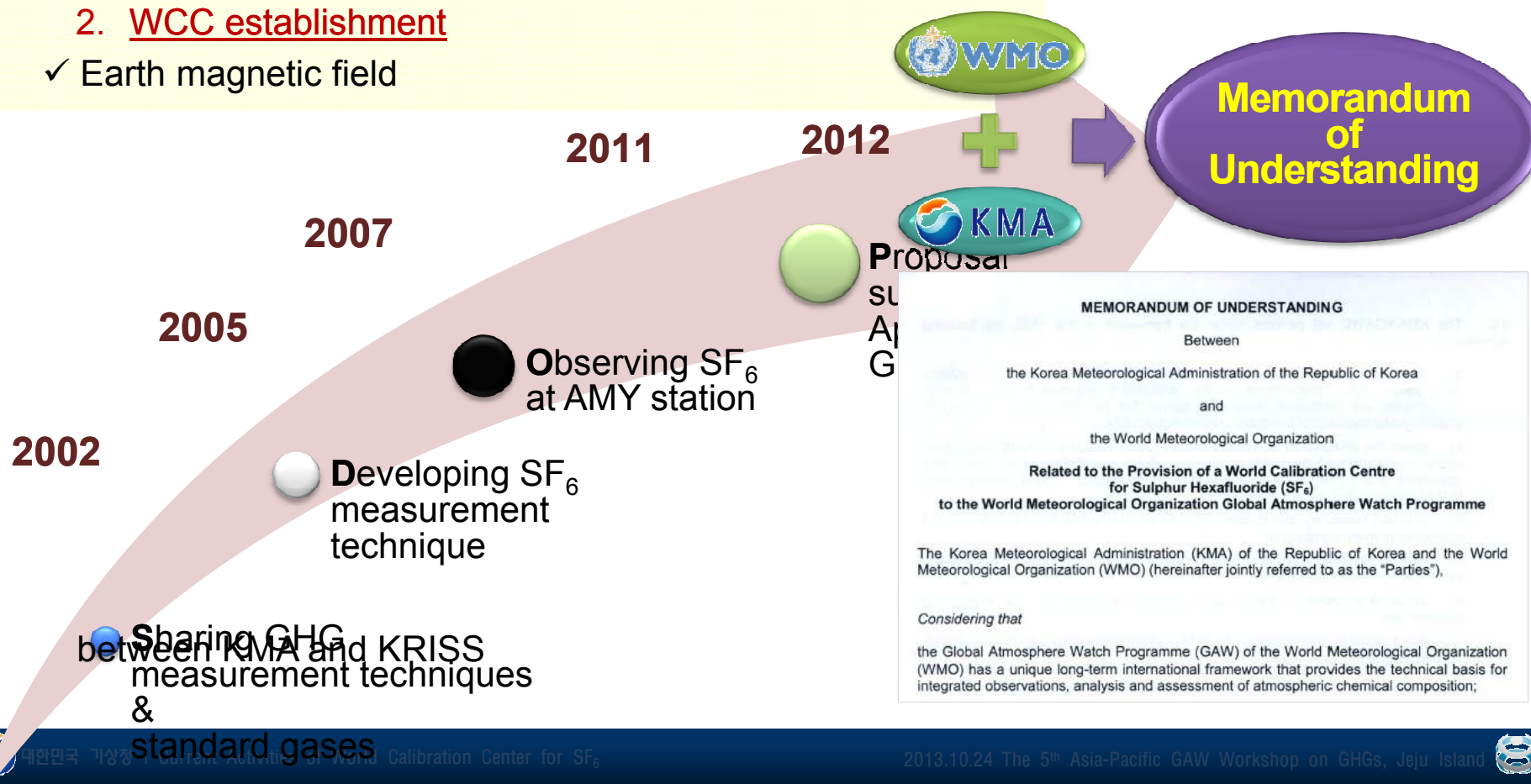
➤ Agreement with mutual cooperation between KMA and KRISS (2010)

✓ Climate change

1. Greenhouse gas analysis for aircraft air samples (NIMR)

2. WCC establishment

✓ Earth magnetic field



Infrastructure

Cylinder and evacuation system



Cylinders

Evacuation system

Analysis system and standard gases



Analysis system(GC/ECD)

Standards (NOAA-2006)

Preparation of compressed dry air



Sampling tower



Air compressor



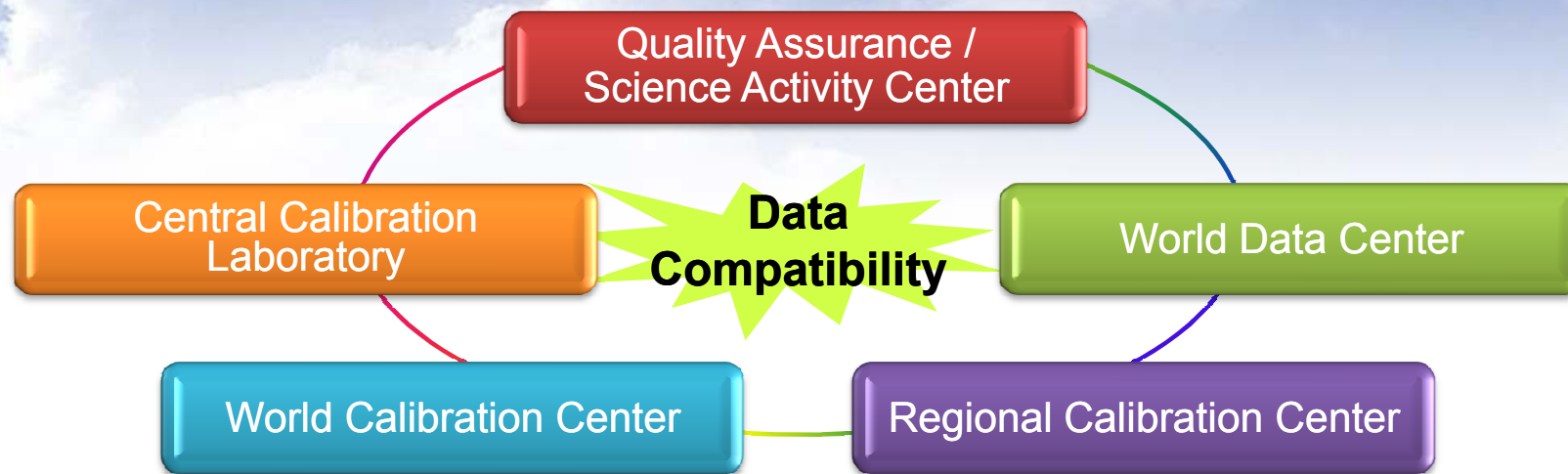
Sampling system



Mixing system



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2. Intercomparison between CCL and WCC-SF₆

- Outline
- Sample analysis
- Result of intercomparison

Outline of Intercomparison

➤ Schedule

- ✓ Suggestion of comparison by CCL: 28 Nov., 2012
- ✓ Sending samples to WCC: Last week of Jan., 2013
- ✓ Arrival of samples at WCC: 5 Feb., 2013
- ✓ Sample analysis by WCC: 6~27 Feb., 2013
- ✓ Submission of result to CCL: 15 Mar., 2013
- ✓ Sending back sample to CCL: 9 May, 2013



FB03560 & FB03054

➤ Reference Gases

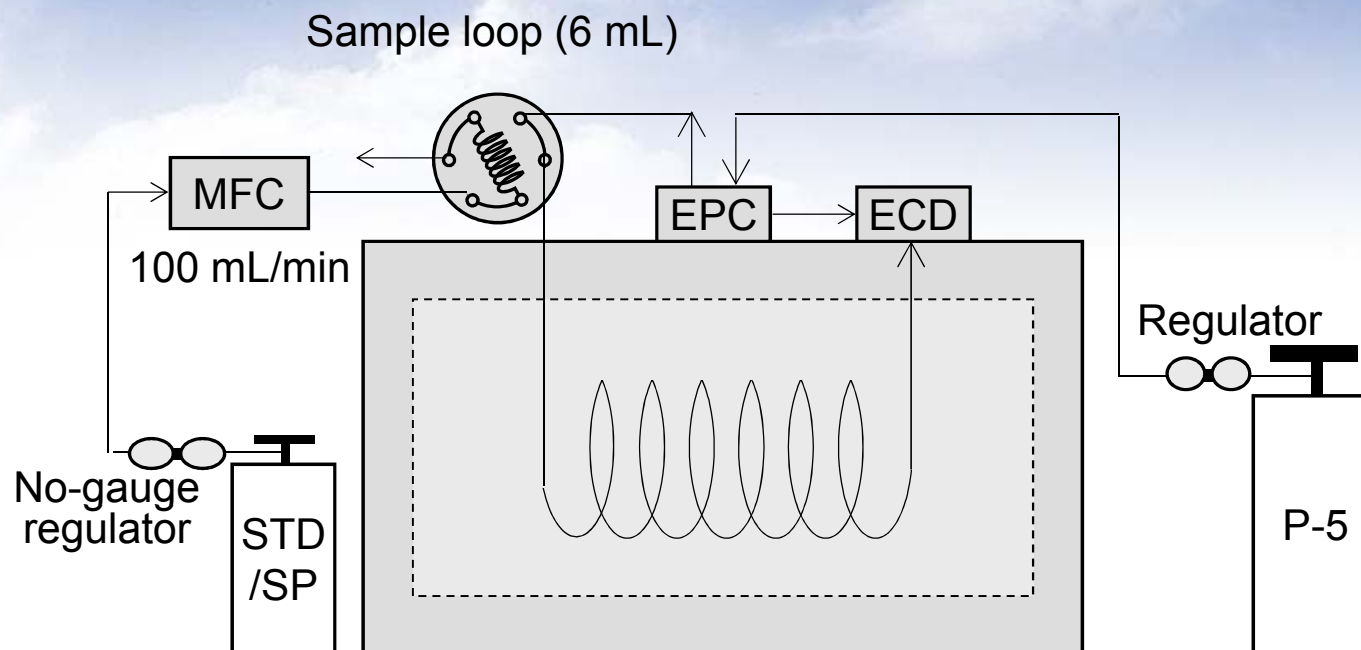
- ✓ Traceable to the WMO mole fraction scale (NOAA-2006)

Cylinder Number	FB03443	FB03444	FB03447	FB03450
SF ₆ Conc. (ppt)	5.920	7.972	9.595	11.887
SD (ppt)	0.017	0.023	0.018	0.020



SF₆ standard gases

Schematic Diagram of Analysis System



GC/Electron Capture Detector
(7890A/G3440A, Agilent, USA)

➤ Analysis Condition

- ✓ Oven temp.: 50 °C (or 60 °C), isothermal
- ✓ Column: Activated Alumina F-1 (80/100),
4 m length, 1/8" OD (Restek, USA)
- ✓ Carrier gas: 20 mL/min of P-5 (CH₄ 5 % in Ar)
with makeup 30 mL/min
- ✓ GC injection method: 6-port gas sampling valve

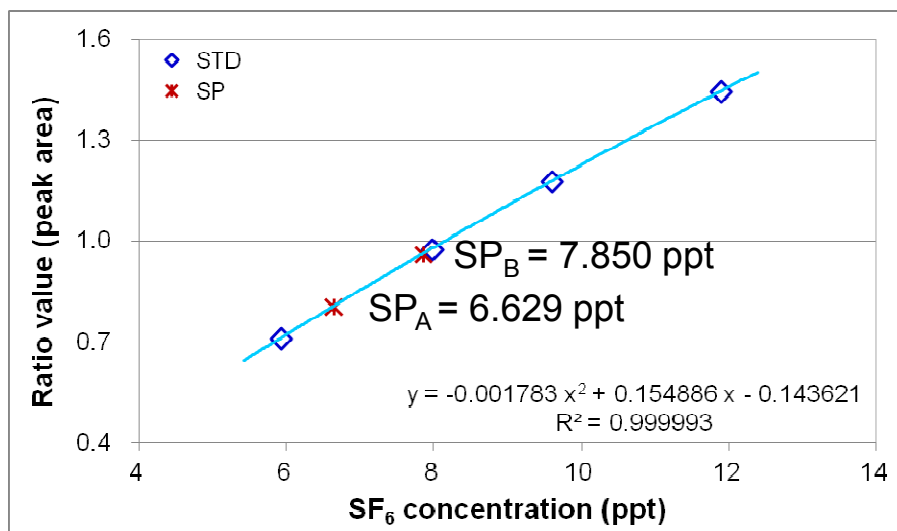
Measurement Result (4-point calibration)

A → B → A' method

* Ratio value of SP(or STD) = $2 \cdot B / (A + A')$

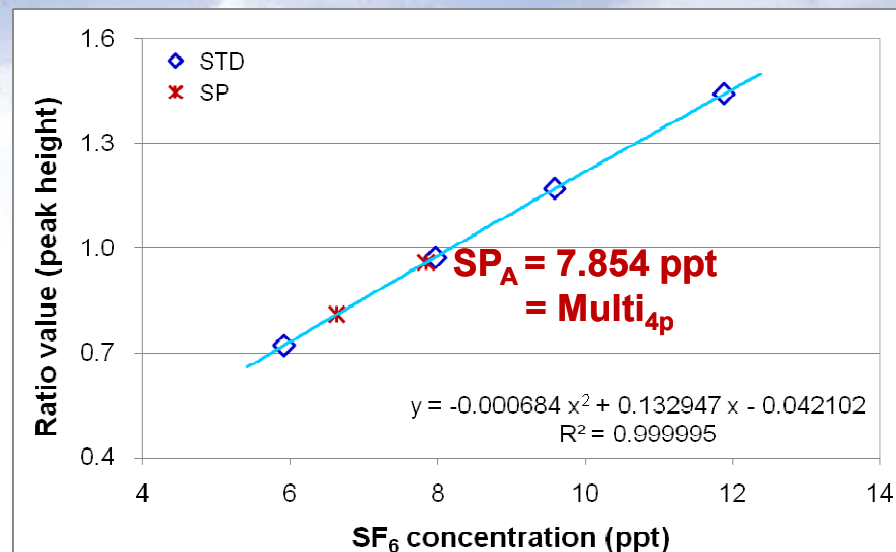
Cylinder	WS	SP _A	WS	STD _{8 ppt}	WS	SP _B	WS
Peak area	160.57	128.66	159.17	156.04	160.32	154.54	160.84
Ratio value		0.8048		0.9768		0.9624	

Cylinder	STD _{6 ppt}	WS	STD _{10 ppt}	WS	WS	STD _{12 ppt}	WS
Peak area	113.92	159.58	187.94	159.18	159.28	230.43	159.58
Ratio value	0.7111		1.1793			1.4453	



Cylinder	SF ₆ (ppt)	Ratio value	Cal. SF ₆ (ppt)	Difference (Cal-Ref)
FB03443	5.920	0.7111	5.922	0.002
FB03444	7.972	0.9768	7.964	-0.008
FB03447	9.595	1.1793	9.603	0.008
FB03450	11.887	1.4453	11.885	-0.002
FB03054	6.629	0.8048	/	/
FA03560	7.850	0.9624	/	/

Selection of Calibration Method



1-point Calibration

Standard gas	6 ppt	8 ppt	10 ppt	12 ppt
Cal. SF ₆ (ppt)	7.879	7.861	7.863	7.916
Difference (single-multi _{4p})	0.025	0.007	0.009	0.062

2-point Calibration

Standard gases	6 ppt, 8 ppt	8 ppt, 10 ppt	6 ppt, 10 ppt	6 ppt, 12 ppt
Cal. SF ₆ (ppt)	7.861	7.860	8.869	7.898
Difference (multi _{2p} -multi _{4p})	0.007	0.006	0.015	0.044

3-point Calibration

Standard gases	6 ppt, 8 ppt, 10 ppt	8 ppt, 10 ppt, 12 ppt
Cal. SF ₆ (ppt)	7.861	7.862
Difference (multi _{3p} -multi _{4p})	0.007	0.008

Intercomparison Result

Multi-point calibration (4 standard gases ranged 6~12 ppt)
(unit: ppt)

# of meas. Sample	1	2	3	4	5	SF ₆ from WCC [SD]	SF ₆ from CCL [SD]	Difference (WCC-CCL)
FB03054	6.651	6.649	6.629	6.636	6.612	6.635 [0.016]	6.633 [0.012]	+0.002
FB03560	7.841	7.833	7.851	7.828	7.901	7.851 [0.029]	7.885 [0.019]	-0.034

WMO recommended measurement target for SF₆: 0.02 ppt

Two-point calibration (6, 8 ppt)

(unit: ppt)

# of meas.	1	2	3	4	5	SF ₆	SD
Working Standard	8.169	8.212	8.148	8.224	8.165	8.179	0.033

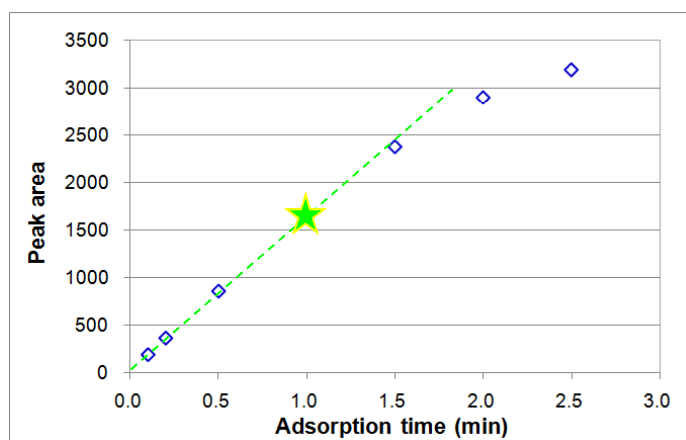


Pre-concentration System

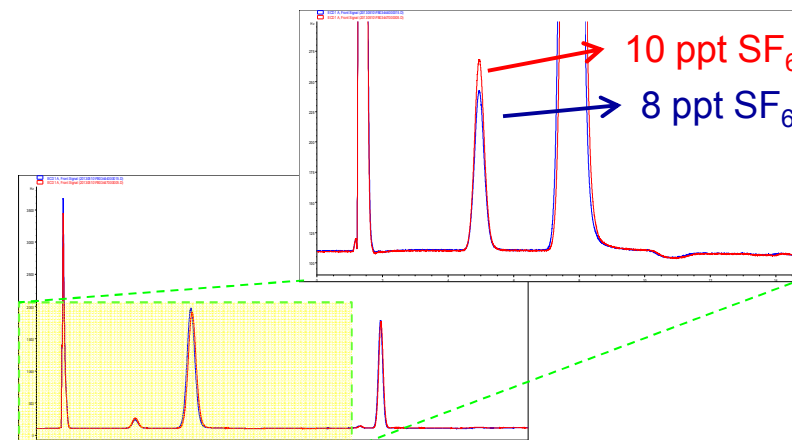


➤ Analysis Condition

- ✓ Adsorption/Heating temp.: -40 °C / 200 °C
- ✓ Adsorbent: 100 mg of HayeSep D
(80/100, Hayes Separation Corp.)
- ✓ Sample/Standard gas flow: 50 mL/min
- ✓ Adsorption time: 1 minutes



GC without this system



GC with this system

(unit: ppt)

# of meas.	1	2	3	4	SF ₆	SD
WS	8.374	8.388	8.323	8.354	8.339	0.022

3. Future plans of WCC-SF₆

Challenges of SF₆



Future Plans

- ✓ To prepare standard operation procedures to **maintain laboratory standard gases** traceable to the WMO reference scale
- ✓ To develop the **measurement guideline** for SF₆ observation in cooperation with KRISS
- ✓ To provide the **technical training** course for GAW stations to enhance their capability building for SF₆ observation
- ✓ To conduct **intercomparison campaigns** and **system/performance audits** for stations to improve the quality of observation data
- ✓ To expand the SF₆ **observation network** including the *in-situ* and/or flask sampling analysis supported by several funding sources



Thank you for your attention!

