Why Standard Gases?

-WCC-SF_6 activities at AMY-

Haeyoung Lee[1], Hee-Jung Yoo[1], Jeong-Sik Lim[2], Jeong-Soon Lee[2] , Chulkyu Lee[1], Bok-Haeng Heo[1]

1. Korea GAW Center, KMA, Korea
2. KRISS, Korea

1. Why Standard Gases?

What is the standard?

Liberty leading the people, 1830, Ferdinand Eugene Victor Delacroix

Etymology: Stand + Hard

-Flag or conspicuous subject to serve as a **rallying point** for a military force

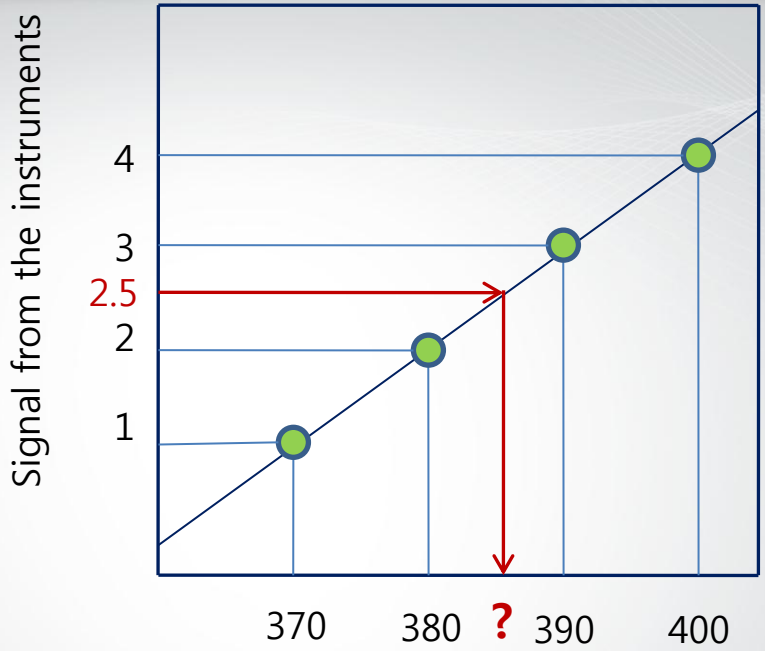
-it is derived from Frankish word "**standhard**"

-it was called because a flag was fixed to a pole
-And pole stuck in the ground to stand upright.

What is the standard gas?

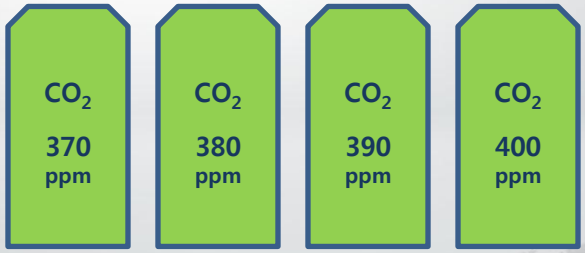
Korea
Global Atmosphere
Watch Center

Unknown
Samples



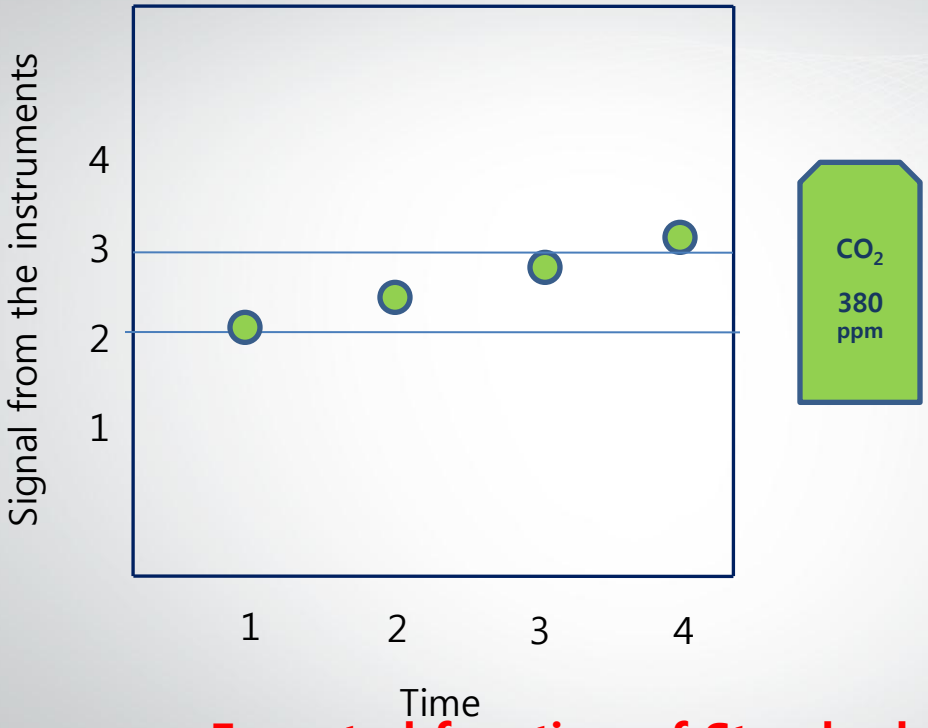
385 ppm

known
Samples



- Standard gases establish known analyzer responses to a certified chemical component
- Sample is only determined by calibration with reference standard

What is the standard gas?



Expected function of Standard gas

-Injection of same concentration but difference response from Instrument

-Because we know it should have same response,

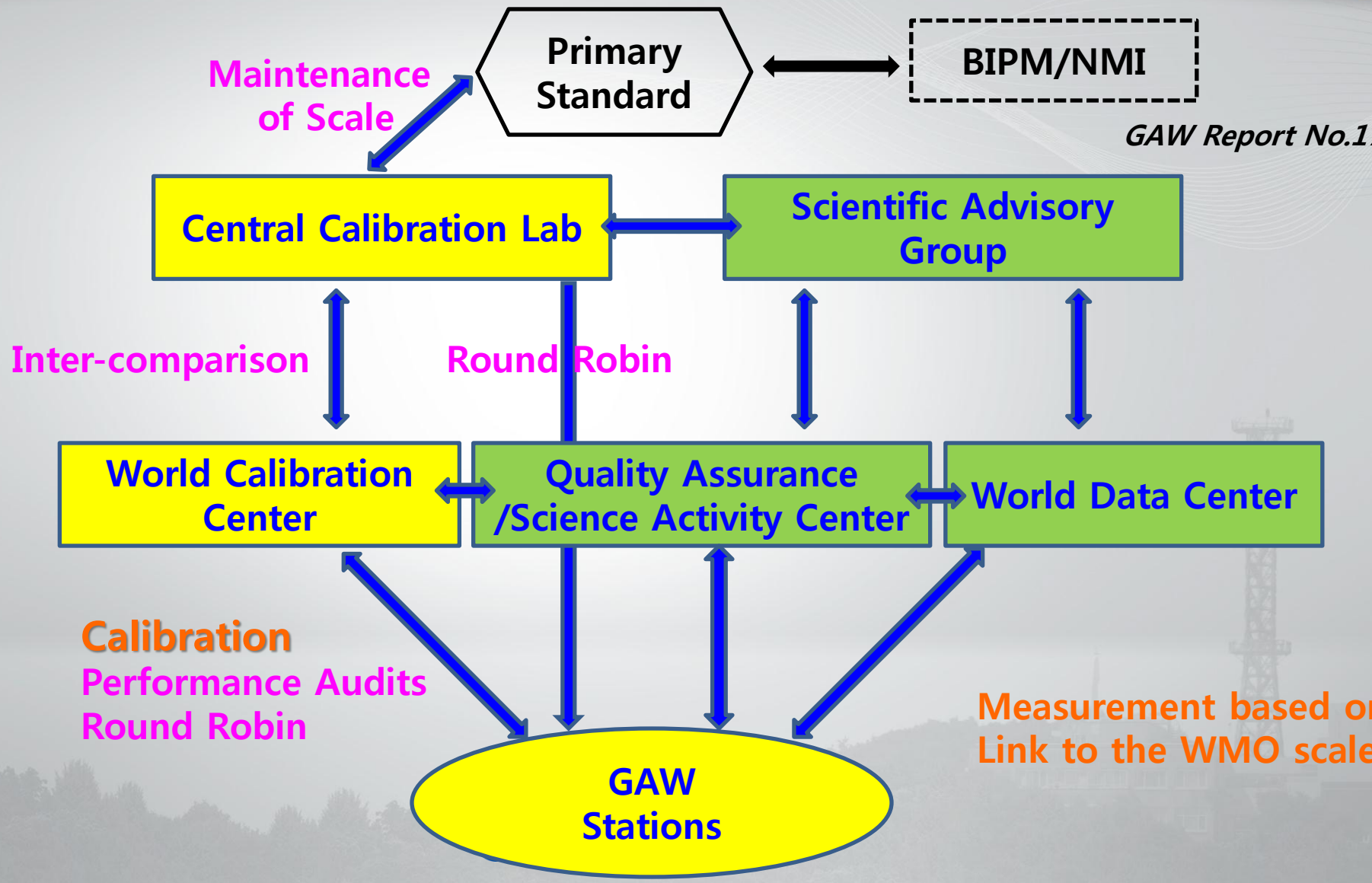
We can use it to check repeatability, reproducibility, bias…

1) Standard gases make unknown samples known
2) Standard gases can check monitoring system and analysis performance

} **Traceability**
Compatibility

Traceability and compatibility

Korea
Global Atmosphere
Watch Center



Compatibility goal in GAW

Korea
Global Atmosphere
Watch Center

Liberty leading the people, 1830, Ferdinand Eugene Victor Delacroix

New compatibility goal, Beijing 2013

Compatibility:

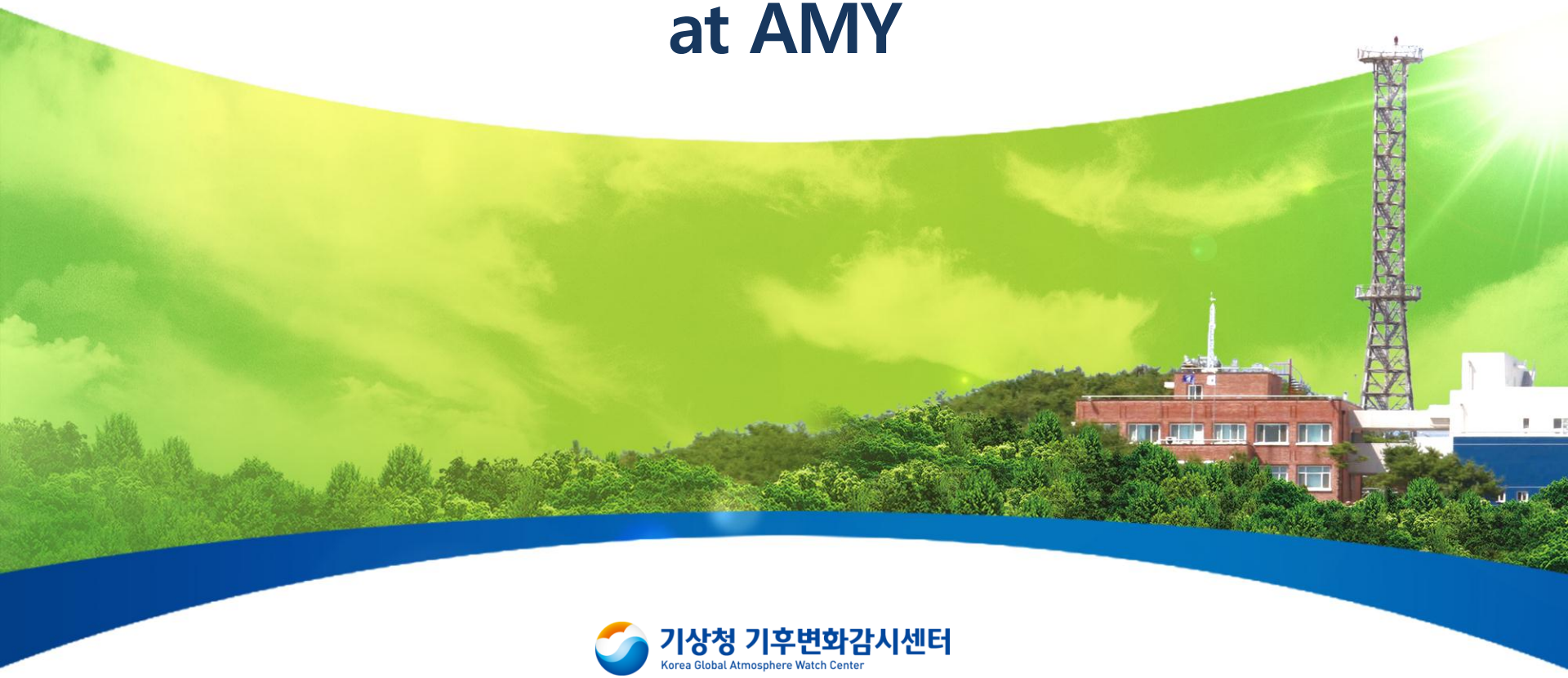
Comparison results are compatible, within a specified numerical value

Components	Compatibility goal	Extended Compatibility goal	Range in unpolluted troposphere
CO_2	± 0.1 ppm (N.H.) ± 0.05 ppm (S.H.)	± 0.2 ppm	360-450 ppm
CH_4	± 2 ppb	± 5 ppb	1700-2100 ppb
CO	± 2 ppb	± 5 ppb	30-300 ppb
N_2O	± 0.1 ppb	± 0.3 ppb	320-335 ppb
SF_6	**± 0.02 ppt**	**± 0.05 ppt**	**6-10 ppt**
H_2	± 2 ppb	± 5 ppb	450-600 ppb
.	.	.	.
.	.	.	.
.	.	.	.

Main aims WCC-SF_6 pursue are

Traceability and compatibility

2. Experiments using Standard gases at AMY



History of SF_6 monitoring activities at AMY

Korea
Global Atmosphere
Watch Center

1) SF_6 has been monitored from 2007 at AMY

→ not that long

2) Western part of Korea downwind area from China and affected by industrial area in Korea

→ can show high concentrations

3) one point calibration every 6 hour with KRISS scale

→ not link to WMO scale,

→ not have enough STD to cover the range

4) But it has been changed to WMO scale from 2013

→ can have problem of continuity from previous data

5) using GC-μECD

→ can show non-linear performance

6)Data has been uploaded to WDCGG from 2012

→ can be tracked and changed easily

Instruments performance

Korea
Global Atmosphere
Watch Center

WMO scale
FB03447
9.595 ppt

And

Sample
Collected by
AMY

Number of measurements*	Peak area	Ratio Value $S_i \cdot 2/(R_i + R_{i+1})$	Instrumental Drift [%]
STD1	473.04		
S1	541.89	1.1454	0.03
STD2	473.17		
S2	541.80	1.1439	0..20
STD3	474.10		
S3	541.31	1.1427	-0.17
STD4	473.29		
S4	541.72	1.1465	-0.34
STD5	471.70		
S5	541.99	1.1483	0.12
STD6	472.27		
Average		**1.1454**	
Standard deviation		**0.0022(0.19%)**	
		0.018 ppt	

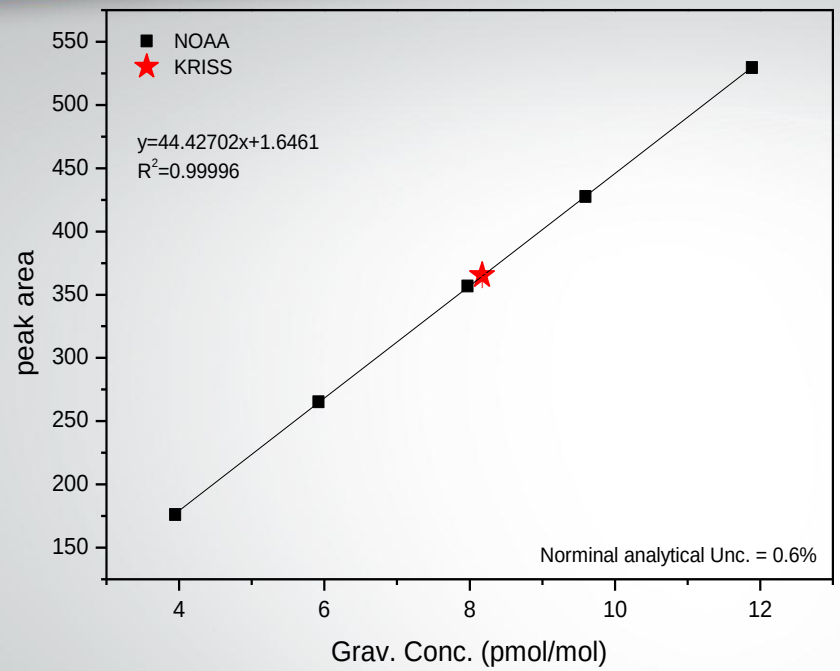
The operating sequence alternated between stan dard gas and ambient measurement.

* 3 injection per a measurement

기상청 기후변화감시센터
Korea Global Atmosphere Watch Center

Link to WMO scale?

Korea
Global Atmosphere
Watch Center



Specification	Condition
Detector	μECD
Detector temp.	350 ℃
Oven temp.	35℃ 75min 30℃/min 170℃ 10min
Column	Alumina-F1 80/100 12ft*1/8 inch SUS
Sample loop	10 mL
Carrier flow	P-5, 95 mL/min
Sample flow	100 mL/min

Scale	Cyl. No.	$C_{NOAA\text{-}scale}$ [pmol/mol]	$C_{calibrated}$ [pmol/mol]	Residual [pmol/mol]	Residual [%]
NOAA Scale	FB03441	3.946	3.929	0.017	0.44
	FB03443	5.920	5.933	-0.013	-0.22
	FB03444	7.972	7.992	-0.020	-0.25
	FB03447	9.595	9.587	0.008	0.09
	FB03450	11.887	11.879	0.008	0.07
KRISS standard	D068069	8.164	8.186	**-0.022**	-0.27

The difference between WMO and KRISS is within the compatibility goal 0.05 ppt

One point calibration?

Calibration method	Multi-point (nominal value)	Two-point	One-point [KIT]	Difference	
				multi-1point	multi-2point
Concentration of CRMs (NOAA)	3.9~11.9	8, 9.6	8 [9.6]		
#D068069 (KRISS)	8.173	8.169	8.164	0.009 [0.12%]	0.005 [0.06%]
DS-13 (KIT)	10.019		[10.026]	-0.007 [-0.07%]	
DS-19 (KIT)	10.166		[10.173]	-0.007 [-0.07%]	

One point calibration is reliable but

Pros and Cons

-get more samples (because AMY operating sequence CRM-S1-S2-S3-S4-S5-CRM..)

-use as a target tank concept

-chose the standard gas which has similar with targeting value

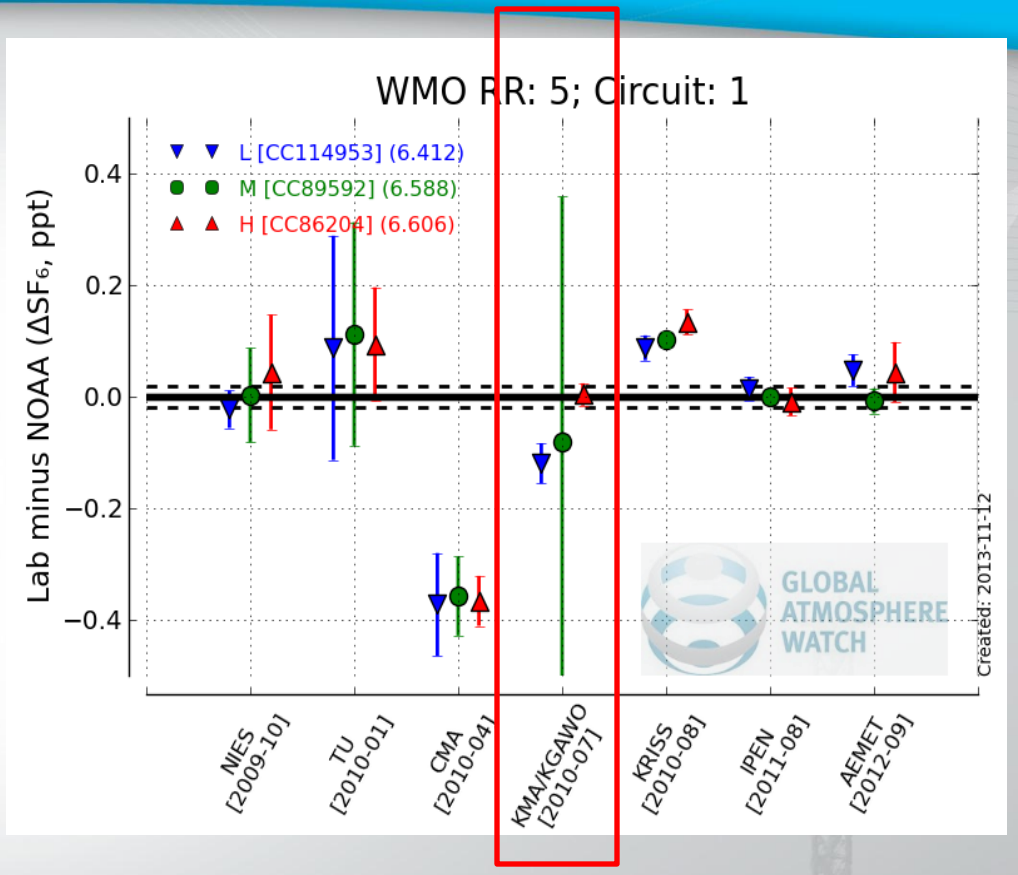
-miss certain level high or low

Example of an wrong calibration case

Korea
Global Atmosphere
Watch Center

	Low	Mid	High
NOAA	6.412	6.588	6.606
KMA	6.3	6.5	6.6
KMA-NOAA	-0.112	-0.088	-0.006

Specification	Condition
Detector	μECD(G1530A)
Detector temp.	350 ℃
Oven temp.	35℃
Column	Alumina-F1 80/100 12ft*1/8 inch SUS
Sample loop	20.5 mL
Carrier flow	P-5, 95 psi
Sample flow	100 mL/min



But one point calibration with 8.50 ± 0.03ppt
Targeting levels are between 6.4 to 6.7 ppt though

기상청 기후변화감시센터
Korea Global Atmosphere Watch Center

These results were published..

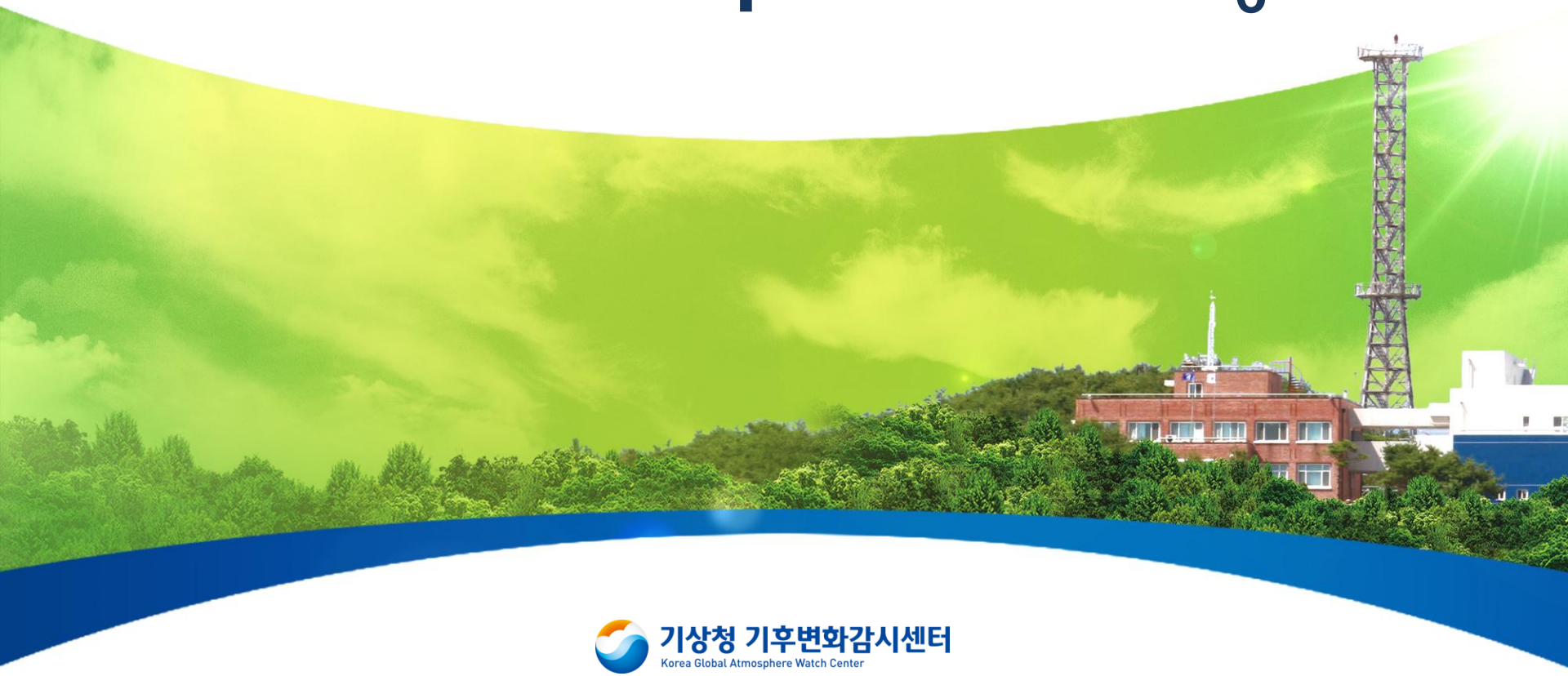
-as "Guideline for the analysis of SF_6 at ambient level using GC-micro ECD(Korean version)

To check your system performance and analysis method

1)The diagnostic procedure of the analysis system to secure test conditions
2)Test method

-English version will be published within this year

3. Next Step of WCC-SF_6



Main aims WCC-SF_6 pursue are

Traceability and compatibility

-**comparison(next presentation from KRISS)**
Various monitoring method
Calibration method
Log book

-**Round Robin Test/ Inter-comparison experiments**
Check your system and performance

-**Education courses(discussion session)**
Improve your system and performance


Thank you
기상청 기후변화감시센터
Korea Global Atmosphere Watch Center
WMO
GAW