



Ambient SF₆ measurement and WCC Invitation

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Contents

- ❖ Proposal for WCC-SF₆
 - Background
 - WCC scope
 - Operation plan of WCC-SF₆
- ❖ Summary
- ❖ GAW activity for WCC preparation



Current status towards WCC-SF₆

- Feb. 2011: Submission of WCC-SF₆ proposal to WMO
- Aug. 2011: re-submission
- Oct. 2011: presentation at the 16th expert meeting
- Nov. 2011: secure funding for WCC-SF₆ by KMA after decision
- 2012 ~: operation of WCC-SF₆



Background

- KMA has observed several greenhouse species since 1998 and contributes to the GAW program as a regional GAW station.
- To build up their technical ability for observation, KMA has cooperated with KRISS since 2002. KMA would like to contribute more to WMO-GAW activity.
- CCL for SF₆ was established in 2010 and it is time to designate WCC for SF₆. KMA now want to offer the service to GAW stations by systematically supporting their traceability and quality system through WCC activities.



For global observation

- Need for quality control

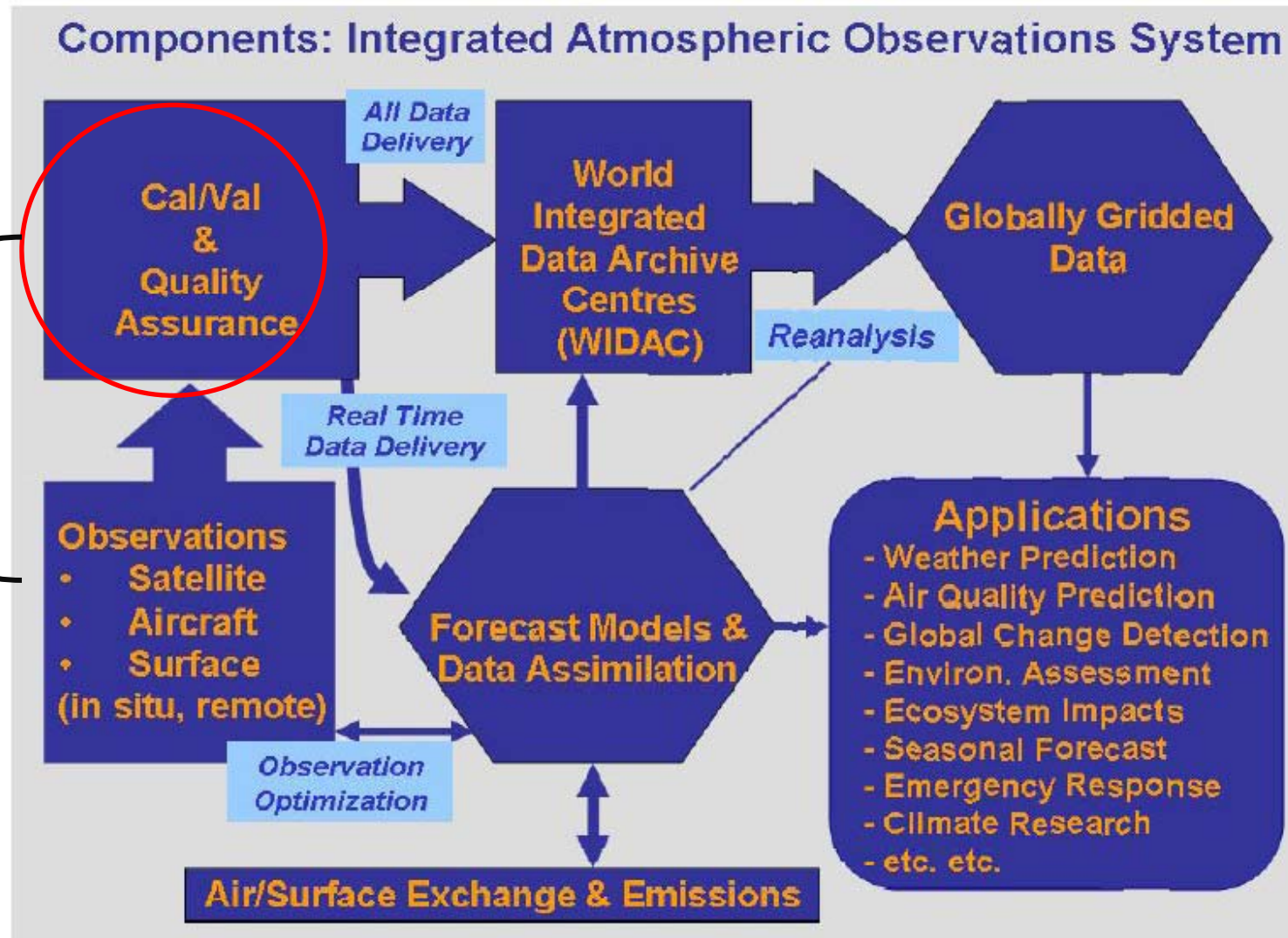
- Detect small trends (through DQO)
- Detect small spatial gradients
- Ensure long-term stability of observations
- Data comparability (on the same scale)

>>> No. 172 (2008). WMO/GAW Strategic Plan: 2008-2015 - A Contribution to the Implementation of the WMO Strategic Plan: 2008-2011 (WMO TD No. 1384), 108 pgs, August 2008



Framework of a global atmospheric observations system

WCC





SF₆ WCC scope

- ToR in GAW report #172

- Development of quality control procedures (in co-operation with the respective QA/SAC and SAG)
- Maintaining laboratory and transfer standards that are traceable to the WMO scale
- Conducting performance and system audits at stations
- Conducting round-robin experiments (coordination of intercomparisons) and participation in international intercomparisons
- Providing training and long-term technical assistance for station scientists and technicians
- To assist members operating GAW stations to link their observations to the GAW scale

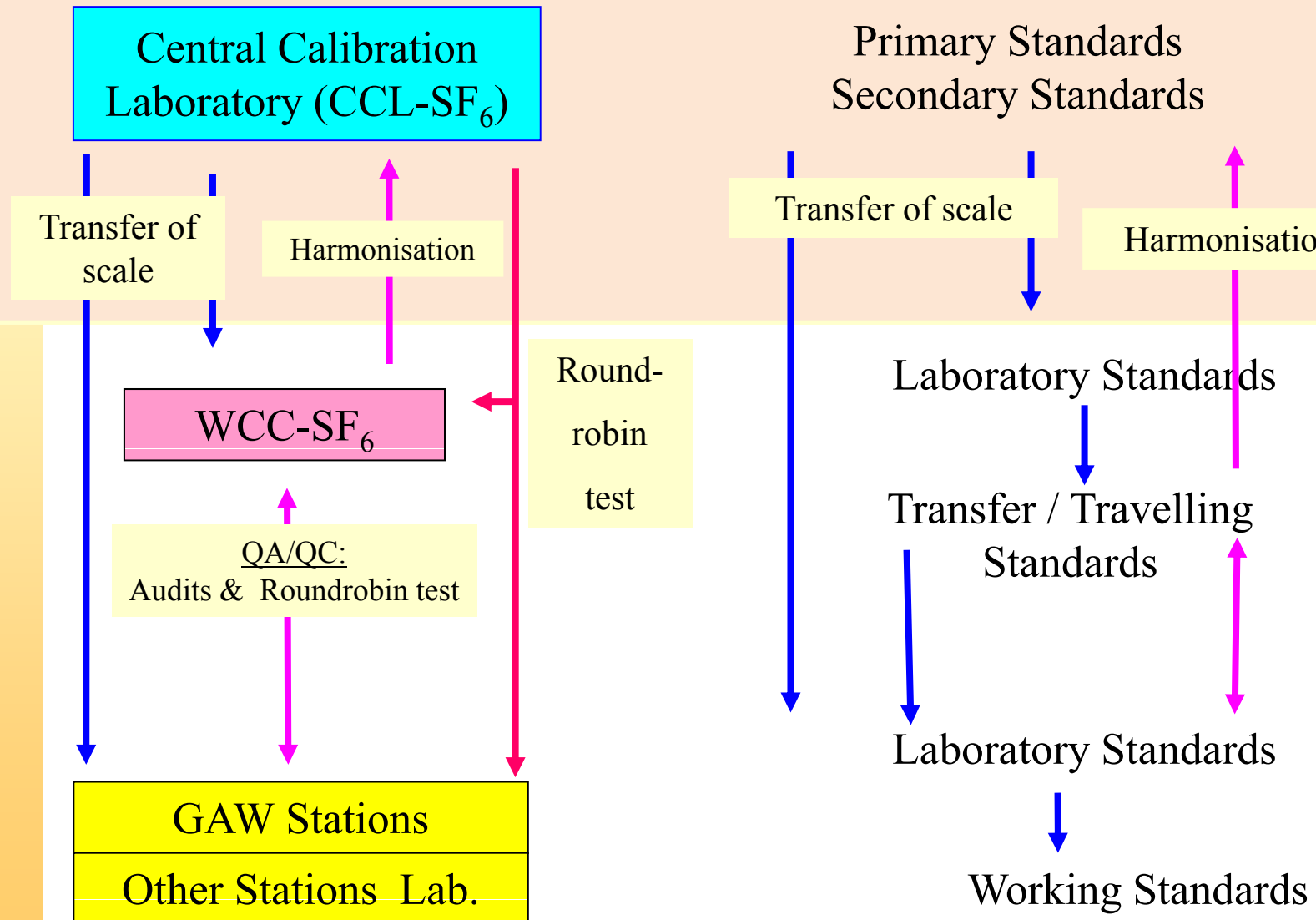


Recommended compatibility of GHG measurements in the GAW programme (DQOs)

| Component | Compatibility goal | range in the unpolluted troposphere |
|-----------------------------------|--|-------------------------------------|
| CO ₂ | ± 0.1 ppm ± 0.05 ppm: southern hemisphere | 360 ... 420 ppm |
| δ ¹³ C-CO ₂ | ± 0.01 ‰ | -7.5 ... -9 ‰ vs. VPDB |
| δ ¹⁸ O-CO ₂ | ± 0.05 ‰ | -2 ... +2‰ vs. VPDB |
| Δ ¹⁴ C-CO ₂ | ± 1 ‰ | 0 ... 70‰ |
| O ₂ /N ₂ | ± 2 per meg | -250 ... -550 per meg |
| CH ₄ | ± 2 ppb | 1700 ... 2000 ppb |
| CO | ± 2 ppb | 30 ... 300 ppb |
| N ₂ O | ± 0.1 ppb | 320 ... 335 ppb |
| H ₂ | ± 2 ppb | 450 ... 600 ppb |
| SF ₆ | ± 0.02 ppt | 5 ... 9 ppt |



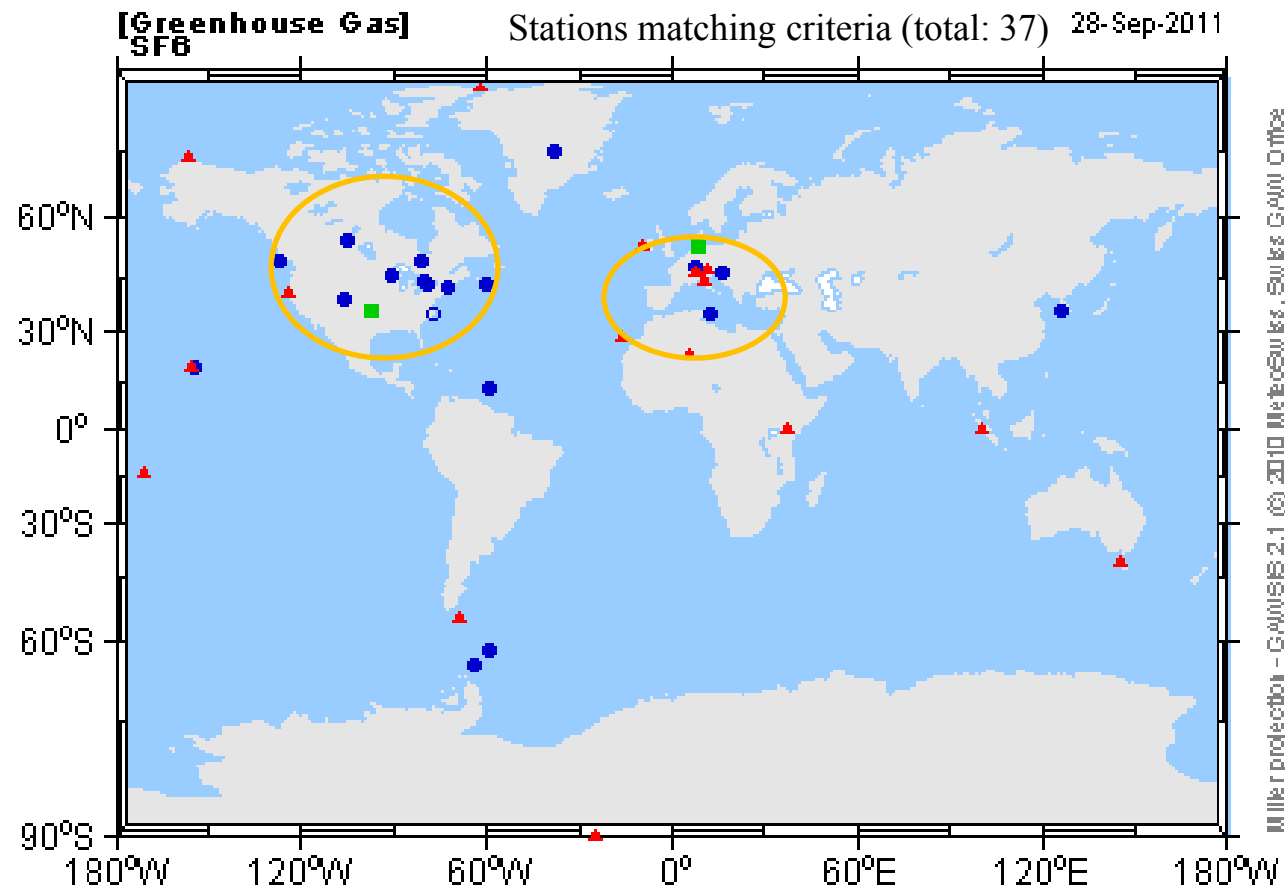
Traceability of Calibrations and Audits





Global network of SF₆ observations

<http://gaw.empa.ch/gawsis/default.asp>



▲ GAW Global Station ● GAW Regional Station ■ Contributing Station
Open symbols denote closed or inactive stations.



Plan for performing WCC-SF₆

| year | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 |
|----------------------------------|---|------|------|------|------|------|------|
| Traceability | - Purchase of WMO scale (every 5 year) | | | | | | |
| | <ul style="list-style-type: none"> - Procedure document for Working standard preparation - Procedure document for instrument calibration | | | | | | |
| Quality system Assistance | <ul style="list-style-type: none"> - Audit : Procedure (2012) then audit report after finishing 1 cycle - system audit: based on GAW report on quality assurance or some recommendation of SAG - performance audit (RRT): SF₆ measurement stations (39,(26WDCGG): every 4 year) | | | | | | |
| Technical assistance | <ul style="list-style-type: none"> -WMO/IAEA expert meeting - GAW workshop (bi-annually: SF₆)>>> training - visiting GAW station | | | | | | |
| Operation (KMA) | <ul style="list-style-type: none"> - KMA: Develop WCC program for financial support and provide budget for Manpower and all infra - KRISS: technical support by long term project (RRT, development of procedure, maintenance) | | | | | | |
| Cooperation | <p>———— Cooperation with KRISS to satisfy the recommendation of WMO/GAW, SAG-GG —————></p> | | | | | | |
| equipment | <ul style="list-style-type: none"> - WMO scale, analysis system (GC/ECD), Air compression device - cylinders, cylinder evacuation system | | | | | | |
| documents | <ul style="list-style-type: none"> -procedure: Analysis, Air sampling: 2011 - Audit procedure: 2012-2013 - preparation of working standard, annual report | | | | | | |



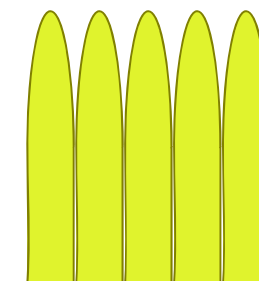


SF₆ analytical capability

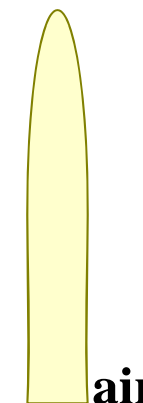
<< GC/ECD Analytical Condition >>

- * Detector : μ ECD (6890A, Agilent)
- * Heater temp. : 375 °C
- * Oven temp. : 57 °C, 16.5 min
25 °C/min to 165 °C, 7.7 min
25 °C/min to 170 °C, 16.5 min
- * Carrier gas : P5 (CH₄ 5 % in Ar), 80 psi (~28 mL/min)
- * Column : RESTEK Alumina F-1 12 ft*2 ea, 1/8 inch SS
- * Valve box temp. : 110 °C
- * Sample loop size : 7 mL
- * Sample flow : ~200 mL/min (MFC 1000)
- * New regulator without gauge, outlet P. 40 psig
- * Integration : slope 2, width 0.35 Reject(1,1)

but manually integrated, 7.5 min-9.5min



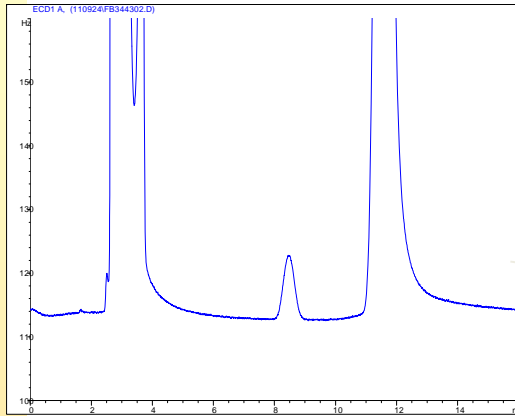
WMO scale



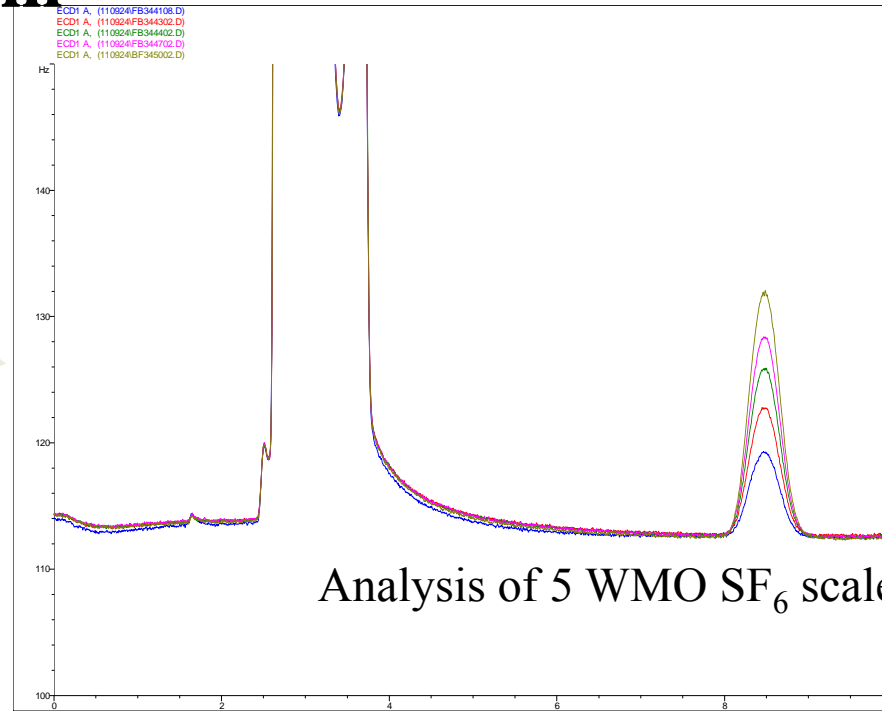
air



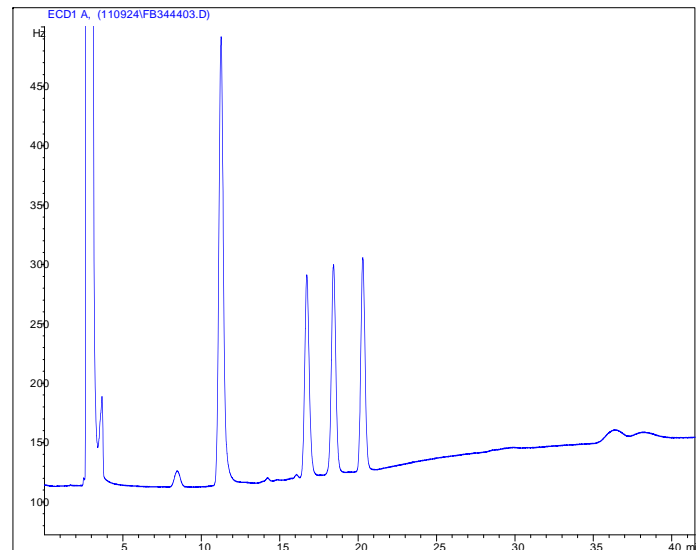
SF₆ chromatogram



Separation: SF₆ and N₂O peaks



Analysis of 5 WMO SF₆ scale



Baking Column after three injections



Internal Consistency

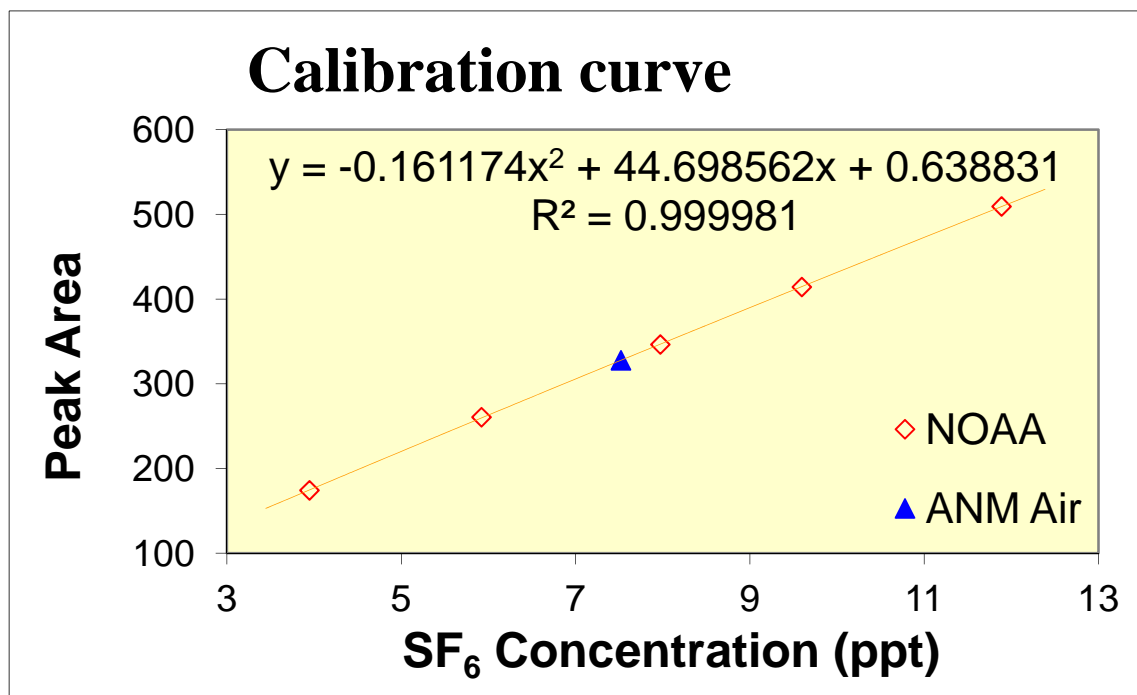
- between cylinders of WMO scale

NOAA/ESRL sent 5 cylinders to KRIS in Sep. 2011

| Cyl # | C_{prm} (ppt) | SD | Area By GC/ECD | $C_{\text{Calibrated}}$ (ppt) | Difference (ppt) |
|---------|---------------------------|-------|-------------------|----------------------------------|---------------------|
| FB03441 | 3.946 | 0.015 | 174.12 | 3.937 | -0.009 |
| FB03443 | 5.920 | 0.017 | 260.51 | 5.941 | 0.021 |
| FB03444 | 7.972 | 0.023 | 346.38 | 7.964 | -0.008 |
| FB03447 | 9.595 | 0.018 | 414.28 | 9.585 | -0.010 |
| FB03450 | 11.887 | 0.020 | 509.43 | 11.893 | 0.006 |



Preparation of working standard - traceable to WMO scale



KRIS prepared working cylinder (#CC315007) based on WMO SF₆ scale

-By multi position calibration C_{ANM} is 7.520 ± 0.02 ppt

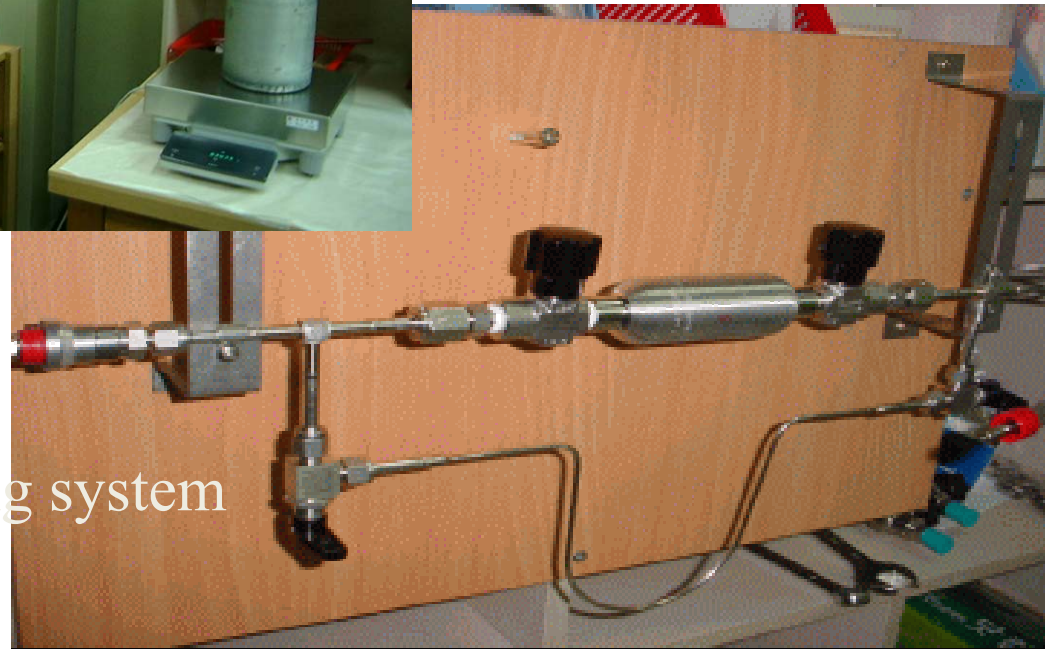
-By two points calibration (near bracketing) C_{ANM} is 7.524 ± 0.02 ppt



Filling System for mixing



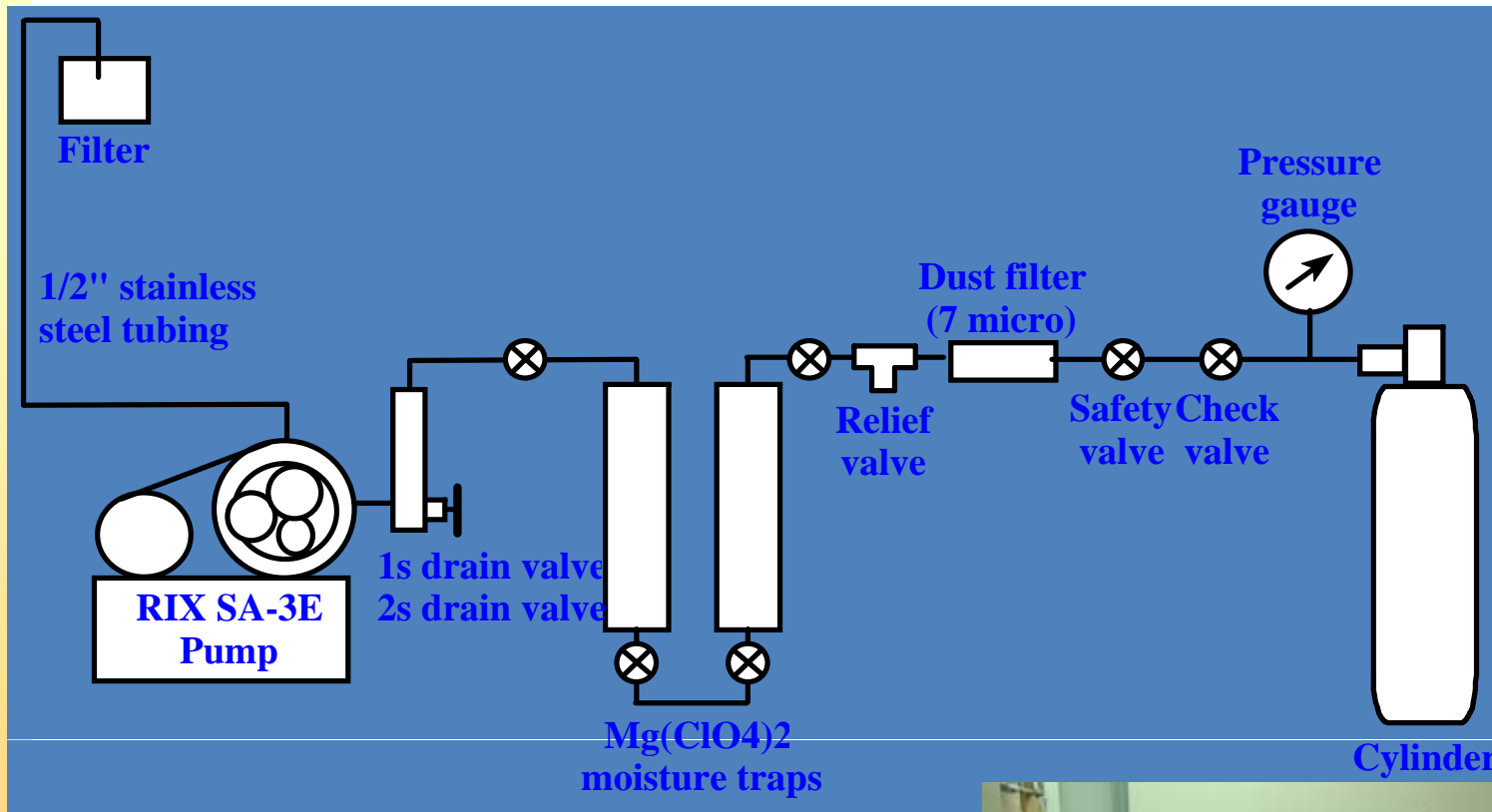
Cylinder filling system



75 mL Mini-Cyl. filling system



Oil free Air Sampling System





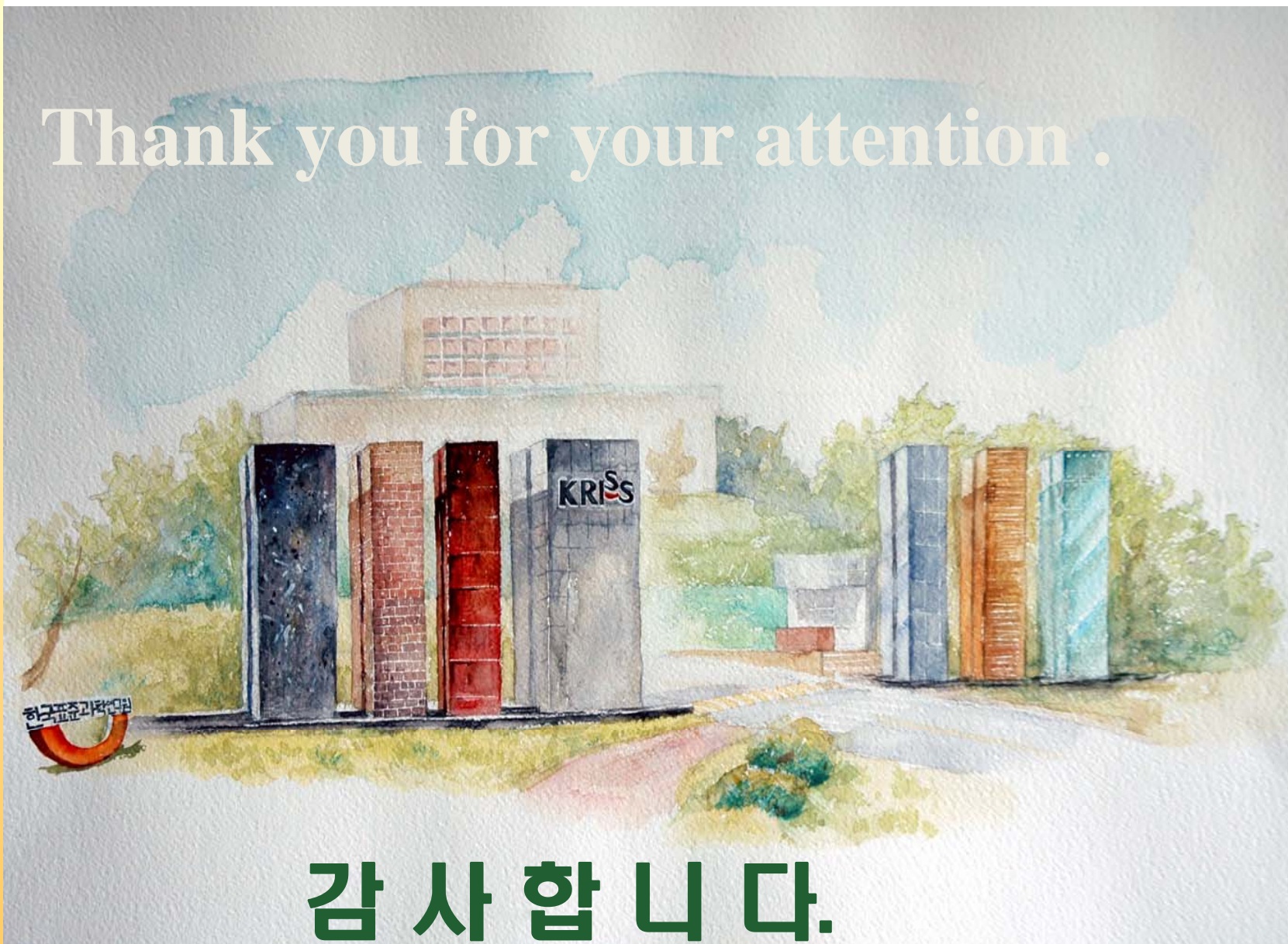
Summary

- Submission of proposal for World Calibration Center (WCC)
 - variable : SF₆
 - Technical support that measurement scale should be traceable and data quality should satisfy DQO
 - KMA has a role as a responsible organization of the WCC - SF₆.
- 1st, 2nd and 3rd East Asia workshop annually since 2009
- Participation RRT and Performing Proficiency test
- For the purpose KRISS/KMA have been cooperating continuously.





Thank you for your attention .



감사합니다.

