Report on the system and performance audit of Sulfur Hexafluoride

Global GAW station Mauna Loa (MLO) USA October 2018

Submitted to the World Meteorological Organization by

Haeyoung Lee, Sangsam Lee, and Sang-Boom Ryoo

World Calibration Centre for SF_6
Environmental Meteorological Research Division
National Institute of Meteorological Sciences
Korea Meteorological Administration
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WCC-SF_6 Report 2019-1

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GLOBAL ATMOSPHERE WATCH

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1. Summary and recommendations

1.1 General

The first system and performance audits for sulfur hexafluoride (SF_6) by the World Calibration Centre for SF_6 (WCC-SF_6) at Mauna Loa Observatory (MLO) Global GAW station in the USA were conducted from 22 to 26 October, 2018.

WCC-SF_6 is responsible for quality assurance measures through audits and inter-comparison experiments. Audits consist of two parts: a system audit and a performance audit. The system audit is more generally defined as a check of the overall conformity of a station with the principles of the GAW system, while the performance audit is a voluntary check of the conformity of a measurement where the audit criteria are the data quality objectives (DQOs) for the specific parameter. In the absence of formal DQOs, an audit will at least involve ensuring the traceability of measurements to the reference standards [1]. For SF_6, the DQO is ± 0.02 ppt, while extended compatibility is ± 0.05 ppt [2].

For this audit, WCC-SF_6 used the check list, which refers to [3] and was modified to match the SF_6 system, and the inter-comparison experiment with four different level cylinders.

This report includes the results from system and performance audits and will be distributed to the MLO station and the WMO/GAW secretariat. The report also will be posted on the WCC-SF_6 webpage.

1.2 System audit of the observatory

The Mauna Loa GAW station is well operated and supported by the National Oceanic and Atmospheric Administration (NOAA)-Earth System Research Laboratory (ESRL)-Global Monitoring Division (GMD) with great facilities for atmospheric monitoring and research. It is located on the northern slope of Mauna Loa (19.54°N, 155.58°W, 3397 m). The administration and data processing for MLO are implemented at the Hilo Office, which is located 73 km east of the station.

Since MLO is a premier atmospheric research facility that has been continuously monitoring and collecting data related to atmospheric change from the 1950's, the consortium of several institutes and universities monitors various atmospheric species in order to share scientific knowledge in a supportive environment.

Due to its location on the highest mountain on the island in the North Pacific Ocean, this station is suited to monitor Northern Hemisphere atmospheric levels. The instrumentation systems and facilities of the station are good enough to monitor activities as part of the GAW network. It is a very suitable station for other monitoring programs and projects, and capable of a wide scope of atmospheric research activities.

The installation for the ambient air sampling and measurement of SF_6 was good enough. All systems including SF_6 were operated with great care and efficiency. The operator and staff are responsible for measurement and data evaluation and are well experienced.

1.3 Performance audit of the SF_6 measurement

During the audit periods, the individual procedures from operation to data management were considered and generally followed the WMO/GAW requirements.

The developed four channel gas chromatograph at MLO, which is called CATS (Chromatograph for Atmospheric Trace Species), is deployed and makes hourly measurements of SF_6 and 16 other species of halogens.

The inter-comparison experiment with WCC-SF_6 travelling standards that are traceable to WMO-X2014 scale was performed as part of the audit. According to the results, it was assumed that the detector has a non-linear characteristic. The SF_6 value, which is bracketed by standard gases (8.636 ppt and 9.344 ppt), is within the WMO/GAW compatibility goal while other levels were behind the DQO. A CATS was so unstable that the value of repeatability was large during the audit period. After the audit, MLO made a decision to change the detector since its performance had degraded over the previous years.

1.4 Recommendations

- GAWSIS information about staff and the SF_6 monitoring system should be updated.
- SF_6 values for the calibrations can be adjusted according to the atmospheric SF_6 level due to the non-linear characteristics of the detector.
- MLO will change the detector due to its degraded performance.

1.5 Conclusion

		Inadequate·········adequate						
Site access		□	□	□	□	□	□	■
Facilities	Laboratory and office space/equipment	□	□	□	□	□	□	■
	Air conditioning	□	□	□	□	□	□	■
	Power supply for the station	□	□	□	□	□	■	□
General Management and Operation	Organization	□	□	□	□	□	□	■
	Competence of staff	□	□	□	□	□	□	■
Air inlet system		□	□	□	□	□	□	■
Instrumentation		□	□	□	□	□	■	□
Calibration and Maintenance		□	□	□	□	□	□	■
Standards		□	□	□	□	□	□	■
Data Management	Data acquisition	□	□	□	□	□	□	■
	Data processing	□	□	□	□	□	□	■
	Data submission	□	□	□	□	□	□	■
Documentation		□	□	□	□	□	□	■

Audit completed 24 Nov 2017
Submitted to WMO Aug 2018

Scientist of WCC-SF_6 Haeyoung Lee

Head of WCC-SF_6 Sangsam Lee

Director of the division Sang-Boom Ryoo

2. Introduction

The Korea Meteorological Administration (KMA) has performed the role of World Calibration Centre for SF_6 (WCC-SF_6) since 2012. Under the MoU with the World Meteorological Organization, WCC-SF_6 started conducting the audit.

According to the WMO/GAW Glossary of QA/QC-Related Terminology [1], "*System audit*" is more generally defined as a check of the overall conformity of a station with the principles of the GAW system, while "*Performance audit*" is a voluntary check of the conformity of a measurement where the audit criteria are the DQOs for the specific parameter.

In this context, the compatibility goal, which is considered DQOs, of SF_6 was ± 0.02 ppt under the background condition and the extended level was ± 0.05 ppt in 2016 [2]. The WMO/GAW Central Calibration Laboratory (CCL, NOAA/ESRL) updated the scale NOAA-X2014 as the expanded primary standard levels reflecting non-linearity characteristics of the Electronic Capture Detector.

The Mauna Loa GAW global station (MLO), which is one of the important background stations as the premier long-term atmospheric monitoring facility on earth, is run by NOAA/ESRL, one of main facility as CCL under the WMO/GAW Programme. Therefore, the standards and calibration were suitably carried out according to the WMO/GAW guidelines.

In agreement with NOAA/ESRL, WCC-SF_6 conducted the first system and performance audit of SF_6 at the MLO GAW station from 22 to 26 October, 2018.

During this period, the checklist, which was modified from the N_2O audit checklist, was completed in detail and an inter-comparison experiment was conducted using 4 traveling standards (TS) of the WCC-SF_6. The linearity test was also confirmed with lab standard gases which are tertiary WMO-X2014 scale.

Finally, WCC-SF_6 appreciates all Mauna Loa staff and NOAA for their cooperation in WCC-SF_6 activities.

3. System and performance audit for sulfur hexafluoride

3.1 Description of the site environment

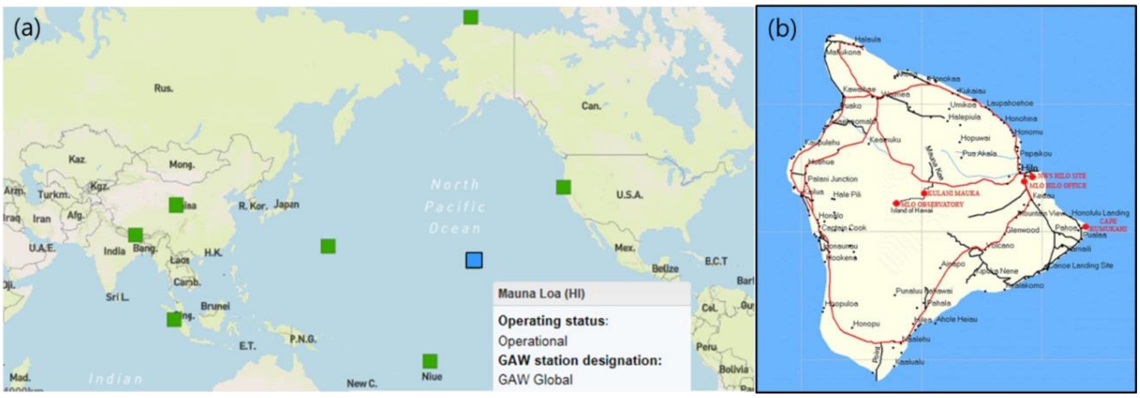


Figure 1. (a) The location of MLO Global GAW stations and (b) the big island where MLO is established (source: https://gawsis.meteoswiss.ch and https://www.esrl.noaa.gov/gmd/obop/mlo/aboutus/siteInformation/siteinformati on. html, last access: 18 Feb. 2019).

The northern hemisphere GAW Global Station MLO (19.5362°N, 155.5763° W) is located on the island of Hawaii at an elevation of 3397 m on the northern flank of Mauna Loa volcano at 200 m north (Figure 1). The time zone is UTC -10 and all records and log books are written with UTC and local times simultaneously. More detailed information can be obtained from GAWSIS (https://gawsis.meteoswiss.ch). MLO's elevation and isolation in the mid-Pacific make it a favorable site for tracking background atmospheric levels.

MLO has a tropical climate with warm temperatures at lower elevations and cool to cold temperatures at higher elevations year-round. Trade winds blow from east to west across the Hawaiian Islands, and the presence of Mauna Loa strongly affects the local climate. At low elevations, the eastern (windward) side of the volcano receives heavy rain; the city of Hilo is the wettest in the United States. The rainfall supports extensive forestation. The western (leeward) side has a much drier climate. At higher elevations, the amount of precipitation decreases, and skies are very often clear. Very low temperatures mean that precipitation often occurs in the form of snow, and the summit of Mauna Loa is described as a periglacial region, where freezing and thawing play a significant role in shaping the landscape.

At night, the observatory is above the inversion layer, in the free-tropospheric atmosphere with minimal influence from local emissions. Around the stations, there are dark rocks with basalt and mantle minerals, which are derived from the lava flows.

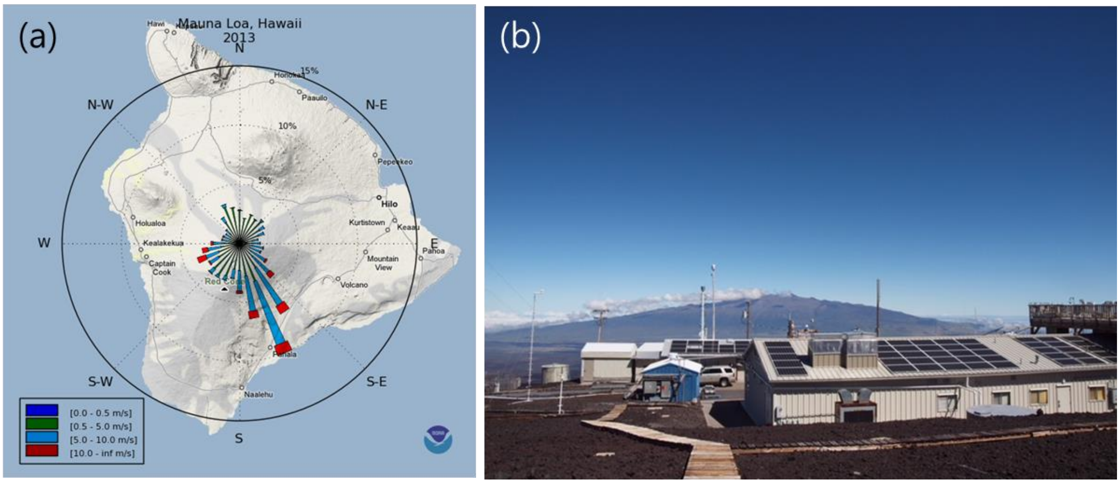


Figure 2. (a) Observed meteorological pattern at MLO (https://www.esrl.noaa.gov/gmd/obap/mlo) and (b) the backside of the NACC building.

3.2 Description of the observatory

Established in 1957, MLO has grown to become the premier long-term atmospheric monitoring facility on earth and is the site where the ever-increasing level of global atmospheric carbon dioxide was determined. The observatory consists of 10 buildings at which up to 250 different atmospheric parameters are measured by a complement of 12 NOAA/ESRL and other agency scientists and engineers.

The CATS system is installed in the building named Network for the detection of Atmospheric Composition Change (NACC) which was built in 1995. The Keeling Building, where carbon dioxide was monitored for the very first time on earth, is used for aerosol and reactive gas monitoring.

The laboratory is prepared only for CATS and offers a spacious and clean environment. Lab conditions, such as temperature and humidity, are controlled through monitoring.

3.3 Staff/operator

Eight people are involved in MLO station monitoring activities, including the station manager and IT expert. Most staff have been working at MLO for almost 10 years or more so they have a lot of experience and are proficient in the monitoring program.

Staff work at the Hilo office three days a week and visit the MLO station two days a week. All the species at MLO can also be monitored by scientists at NOAA in Boulder remotely.

The operation and maintenance of the station are well organized with clear assignments of responsibilities (Table 1). With respect to SF_6 measurements and instruments, the staff were well trained and have expertise.

Table 1. Staff responsible for the SF6 measurements at the MLO station and at Boulder

Name/duty	**Responsibility**	**Email**
Darryl Kuniyuki/ Station Chief	Station managing at MLO	*Darryl.t.kuniyuki@noaa.gov*
Aidan Colton /Atmospheric Scientist	CATS system at MLO	*Aidan.colton@noaa.gov*
Geoff Dutton /Scientist	NOAA CATS network	Geoff.dutton@noaa.gov

Table 2. The staff who were involved in the audit from 22 to 26, Dec. are listed below.

WCC-SF_6	Haeyoung Lee	Research scientist (Auditor)
NOAA at Boulder	Geoff Dutton	Scientist
MLO station	Aidan Colton	Scientist

3.4 Monitoring set-up and procedure

3.4.1 Air inlet system

The location of the 40 m high inlet tower is left of the NACC building. The length of the inlet line from the top to the lab is ~ 120 m.

The air is sampled by KNF pump via Dekabon (Synflex 1300, 3/8”) line from 40 m and 20 m. The pumps are installed on the manifold so that even if the humidity is high, the water can be dropped to the floor.

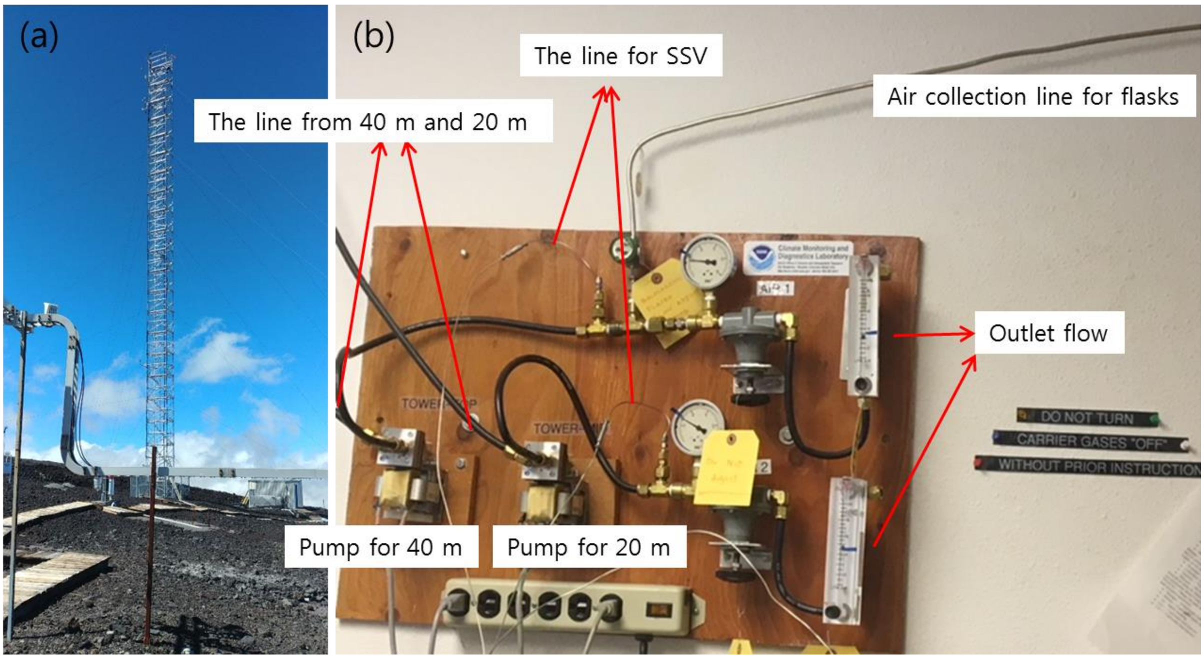


Figure 3. (a) The 40 m inlet tower and (b) the manifold inside the lab.

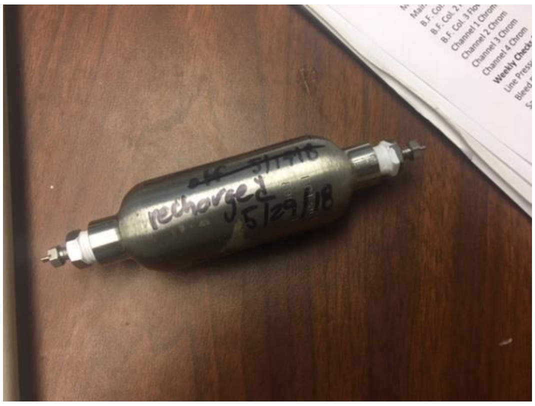


Figure 4. The chemical trap filled with $Mg(ClO_4)_2$ for drying air.

To dry the sampled air, $Mg(ClO_4)_2$ is used in a 7 cm trap and exchanged every 6 months. It is installed between the Streamline Selection Value (SSV) and CATS. Therefore, the system diagram consists of inlet – pump – SSV – drying trap – and sampling loop of CATS.

3.4.2 Gas chromatography system

Chromatograph for Atmospheric Trace Species (CATS): The CATS system was developed by NOAA and has been in continuous operation at MLO since 1998. This system consists of 4 different channels to monitor 16 different species. Each channel consists of a different valve system, different columns and detectors according to the target species. For SF_6, it is detected in Channel 1 with N_2O while CFCs and other halocarbons are detected in channels 2 to 4 (Fig.5).

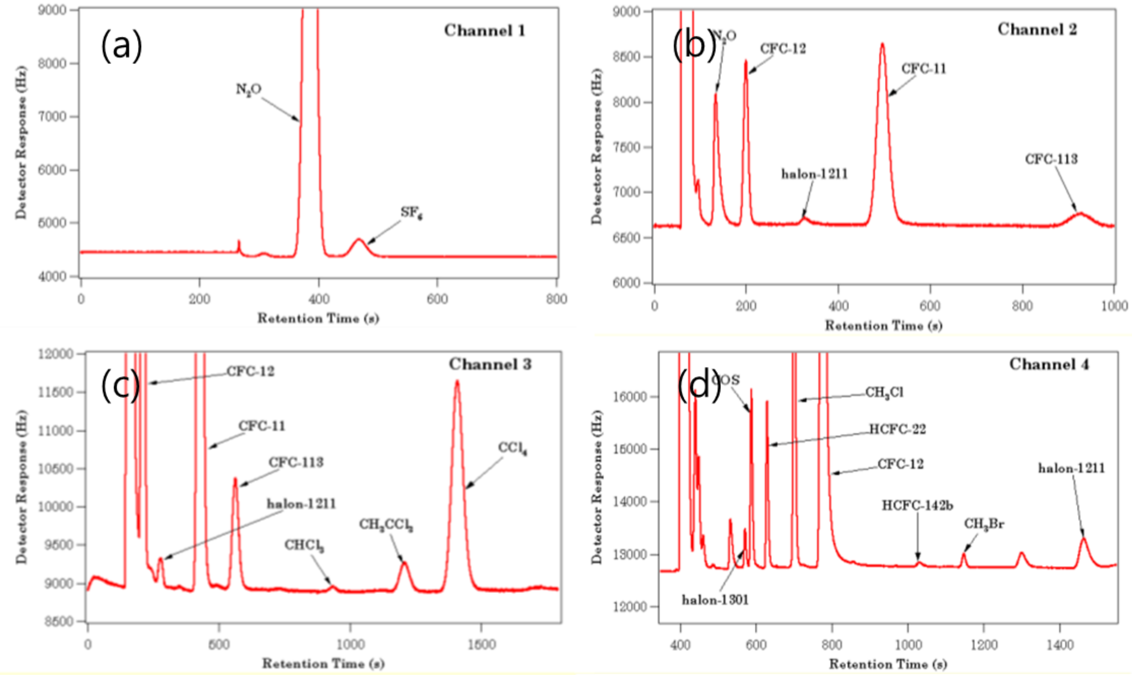


Figure 5. The identified compounds in channel (a) 1, (b) 2, (c) 3, and (d) 4 in CATS (http://www.esrl.noaa.gov/gmd/hats/insitu/cats/stations/index.html)

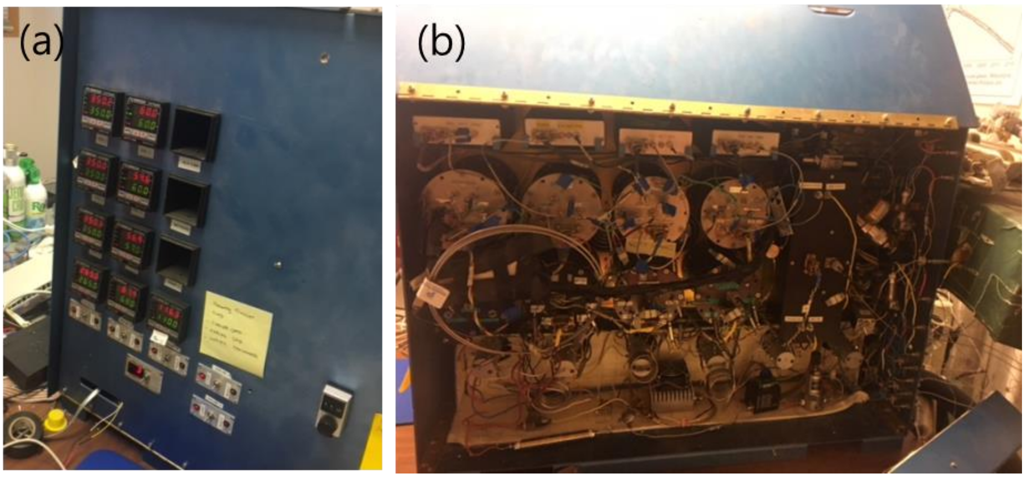


Figure 6. (a) the exterior and (b) interior of the CATS installed at MLO.

The stream selection valve (SSV): After the pump, the sample air moves to the SSV (VICI, 8 ports) through 1/8″ tubing of stainless steel. Positions 2 and 6 are used for the calibration tanks. At position 4, air is sampled from 40 m and at position 8 air is sampled from 20 m. After selecting the sampled air, it is injected to the CATS.

The injection valve: In channel 1 in CATS, the injection valve is VICI with 12 ports. However, it is plumed as a 10 port valve with a 10 mL sample loop (Figure 7). The back-flush method is applied for N_2O and SF_6 with pre-column (Porapak Q, 6 feet, 3/16” O.D.) and main-column (Porapak Q, 10 feet, 3/16” O.D.).

The carrier gas: Commercial high purity N_2 is used as the carrier gas. Pure CO_2 is added to the N_2 carrier gas as a dopant.

The analytical condition is shown in Table 3. The SF_6 signal was detected around 7.7 min (460 sec) and separated enough from the N_2O peak .

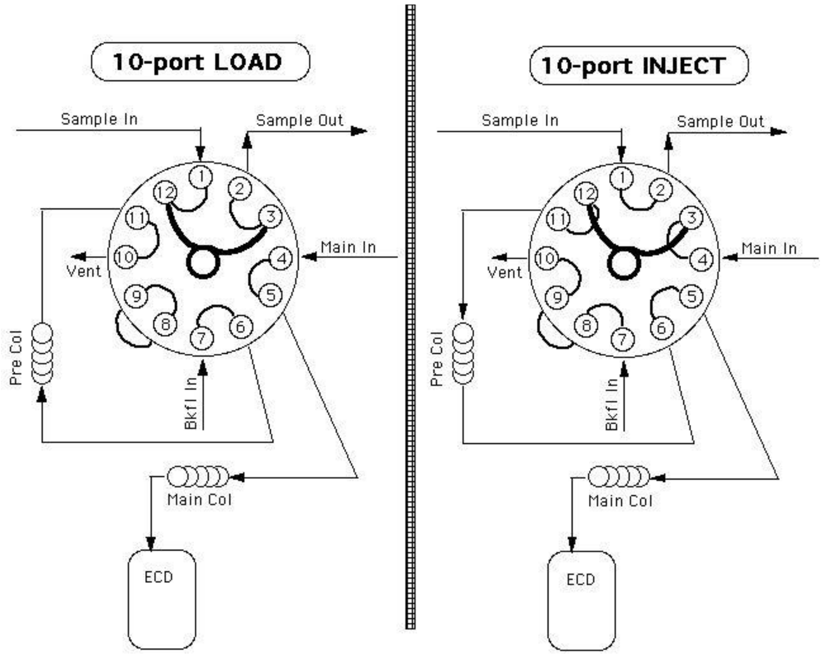


Figure 7. The injection valve system installed in CATS at MLO.

Table 3. Analytical condition at MLO

Analytical Condition	
Detector	μECD (Valco)
Detector temperature	350℃
Column	Pre: Porapak Q, 6 feet (3/16") Main: Porapak Q, 10 feet (3/16")
Loop size	10 mL
Makeup Flow	No makeup gas
Sample Flow	70 mL/min
Carrier gas, pressure	CO_2 doped N_2 gas, 80 psi
Oven temperature	60 ℃

3.5 Calibration and maintenance

3.5.1 General

The station has been operated by eight staff under the NOAA/ESRL and they work at the station 2 days a week to maintain the whole system. The entire system can be monitored remotely by the scientists in Boulder and at the office in Hilo, Hawaii.

3.5.2 Sampling and calibration

A leak check: The gas leakages check is performed when cylinders are exchanged.

Sequence of analyses and calibration method: The sequence of the working standard (W) and ambient air (A) is: W1-A1-W2-A2. W1 stands for the lower level of working standard and W2 for a higher level than the target level, which is bracketed by both working standards. A1 stands for the ambient air from the 40 m tower while A2 stands for the ambient air from the 20 m tower. The working standard levels are 8.636 ppt (AAL072099C) and 9.344 ppt (CC456872) to bracket the target ranges. Each sample is injected every hour.

When we compare the analysis results of the same cylinders between WCC-SF6 and MLO (see 3.10), we assumed that the instrument response can be non-linear so that using two tanks for the data calibrations is very appropriate.

The repeatability was reported as the standard deviation with 7 to 20 duplicates for each cylinder and those values were from 0.228 to 0.350 ppt during the audit period due to the bad instrument condition (Table 4).

3.5.3 Maintenance

The staff checks the cylinder pressure and detector, etc. and records it in the electronic log book. When the analytical system has malfunctions/problems, the instrument is sent to Boulder, the central lab.

3.6 Standard

3.6.1 Regulators and connections

The pressure regulators are Scott specialties with single stages. Between the cylinder and the regulator, there is tubing made of brass while the tubing from the cylinders to the valve is made out of stainless steel.

3.6.2 Laboratory and working standards

Since NOAA ESRL runs CCL for SF_6, there is no laboratory standard at the station. The central laboratory located in Boulder keeps the laboratory standard and propagates the working standards for the NOAA network directly.

3.7 Data acquisition and processing

3.7.1 General

Data acquisition of the gas chromatographic signals and parameters are controlled by custom software developed at NOAA for the QNX operating system. The GC can be controlled remotely as well. The data is synchronized in the UTC time zone. All data and its information are delivered to Boulder every 24 hours and the scientists in Boulder implement data quality checks and decide observed SF_6 values.

Notes on cylinder changes (carrier gas and working standards) and instrument maintenance are recorded in an electronic log which is delivered to Boulder daily.

3.7.2 Chromatogram evaluation

Chromatograms and engineering data such as sample flow, column flows and temperatures are uploaded to data servers in Boulder daily. The peaks in the chromatograms are automatically integrated. Retention times, peak area, width and height are saved. Chromatograms are evaluated with statistical filters as well as inspected manually.

3.8 Data management and submission

All data from MLO station are delivered to storage in Boulder every 24 hours along with metadata.

The flagging consists of large outliers relative to the working standards being flagged and manually reviewed. Conditions in which poor sample flows or large detector temperature fluctuations are found are also flagged.

The IT group at NOAA regularly backup data servers. Backups are maintained locally and remotely from the Boulder NOAA facility.

The high quality data have been submitted to the World Data Centre for Greenhouse Gases.

3.9 Documentation

The WMO GAW Measurement guidelines and instrument manuals are available to the operators. The field logbooks and instrument logbooks with hand-written entries are maintained on the site in an orderly manner. In the logbook, instrumental manipulations, changes, and the reasons for questionable data are included.

3.10 Inter-comparison experiment of SF_6 standards

3.10.1 Experimental procedure

Before conducting the audit, WCC-SF_6 sent four traveling standards with four pressure regulators to the MLO station. They arrived at the station before the audit.

The four traveling standards for this inter-comparison experiment are listed in Table 4. The WCC-SF_6 analysis method is described [4]. For WCC-SF_6, four traveling standards were calibrated against laboratory standards of WMO-X2014 scale with a two-point analysis method. The standards to certify them were selected at a level similar to that which covers the target range for the calibrations. The analysis results are shown in Appendix A.

Table 4. Cylinder information on the SF_6 traveling standards

Manufacture	Luxfer Gas cylinders (UK)
Cylinder #	D376130, D376143, D056072, D056078
The level of SF_6	Between 8 and 12 ppt in natural dry air
Material	Aluminum 10 L cylinders

During the audit period, four traveling standards were analyzed against laboratory standards, which are traceable to WMO-X2014 scale with the same sequence described in 3.5.2. Flushing and leak checks were performed before with this experiment. There were no modifications of the GC system for the inter-comparison experiment.

3.10.2 Results of the SF_6 inter-comparisons

As described in 3.5.2, MLO used two standard gases with 8.636 and 9.344 ppt. The differences (MLO-WCC) of D056078 and D376130 were in the WMO extended compatibility goal (±0.05 ppt) while the others were out of the DQO. This is definitely derived from the nonlinear characteristics of ECD and could appear outside of the range covered by standard gases.

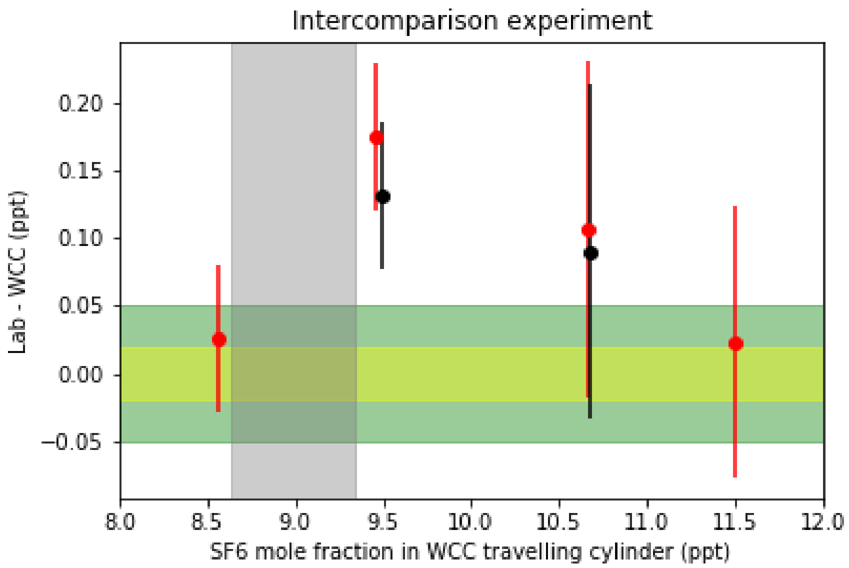
Therefore, MLO is using the working standard gases with very narrow range to decide the target level. The target range seems to compensate the drift by the bracketing methods that the calibration strategy of MLO applies and that are suitable for this condition.

When we compared the analysis results for the same cylinders (D376143 and D056072) at the Central Calibration Laboratory in NOAA, it showed differences of -0.016 ppt and -0.044 ppt, respectively. We show the results in Appendix B.

In Figure 6, we display the differences between MLO and WCC (red dots) and between MLO and CCL (black dots). The differences decreased when MLO and CCL compared the same cylinder values.

Table 5. Summary results for the inter-comparison as reported by WCC-SF_6 and MLO. MLO decided SF_6 values with two standards, 8.636 ppt and 9.344 ppt. All units are ppt. WCC uncertainty was decided according to the Annex 1 while MLO uncertainty was assigned by the standard error (1-std/sqrt(N)). Repeatability is standard deviation.

Cylinder: WCC Result	MLO Result	Repeatability	Differences (Lab-WCC)
D376130 : 11.497 ± 0.034	11.52 ± 0.1	0.275 (N=7)	0.023
D376143 : 10.664 ± 0.035	10.77 ± 0.124	0.350 (N=8)	0.106
D056072 : 9.455 ± 0.027	9.63± 0.054	0.236 (N=20)	0.175
D056078 : 8.564 ± 0.02	8.59 ± 0.054	0.228 (N=19)	0.026



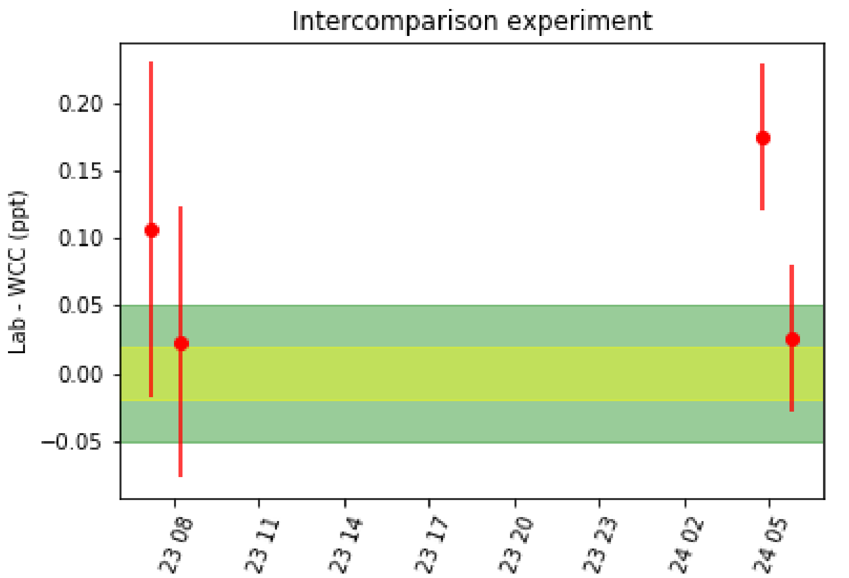


Figure 6. The differences between MLO and WCC. Two labs used WMO-X2014 scale for the calibrations. The error bars show reported uncertainties of individual measurement points. Yellow and green areas correspond to WMO compatibility and extended compatibility goal. (Top) Red dots represent the differences between two labs with respect to the WCC traveling standards, while the black dots represent the differences between CCL and MLO. Grey indicates the range covered by the two standards at MLO during the audit period. (Bottom) The differences in time dependence.

4. References

[1] J.Klausen, H.E.Scheel, M. Steinbacher, 2010: WMO/GAW Glossary of QA/QC-Related Terminology, version 1.0 (last update 2016-05-26 by M. Steinbacher)

[2] WMO, 2018: The 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2017), Dübendorf, Dübendorf, Switzerland, 27-31, August 2017, WMO/GAW No.242.

[3] J. Klausen, C, Zellweger, and H.E. Scheel, 2006: The audit questionnaire for system and performance audits of atmospheric trace gas measurement at WMO/GAW sites, Version 1.3-20061214

[4] WMO, 2018: The Calibration Methods of GC-μECD for Atmospheric SF_6 Measurements, WMO/GAW No.239.

APPENDIX A. WCC-SF_6 analysis results for traveling standards refer to WMO/GAW report No.239.

Table A-1. The analysis result of Cylinder # D376030

2018.8.20	CB11261	D056078	CB10844	CB11261
1	11513.9	11529.7	12068.2	11620.3
2	11514.4	11537.9	12070.2	11648.1
3	11534.7	11518.9	12070.2	11641.3
4	11522.9	11522.7		11654.5
5	11534.2			
Response	11524.0	11527.3	12069.5	11641.1
Standard deviation	10.17	8.36	1.15	14.85
Relative S.D. (%)	0.09	0.07	0.01	0.13
f-drift	-	1.0034	1.0068	-
Corrected peak area	-	11488.4	11988.4	-
certified mole fraction (pmol/mol)	8.59	-	8.94	8.59
cylinder uncertainty	0.01	-	0.01	0.01
drift (%)	-	-	-	1.02
Sample mole fraction	-	**8.563**	-	-
Sample uncertainty	-	**0.014**	-	-

2018.8.20	CB11261	D056078	CB10844	CB11261
1	11620.3	11630.9	12115.5	11700.2
2	11648.1	11631.4	12133.6	11698.3
3	11641.3	11607	12135.8	11703
4	11654.5	11621.7	12132.4	11717.6
5		11651	12151.6	11685.3
Response	11641.1	11628.4	12133.8	11700.9
Standard deviation	14.85	16.04	12.82	11.55
Relative S.D. (%)	0.13	0.14	0.11	0.10
f-drift	-	1.0017	1.0034	-
Corrected peak area	-	11608.5	12092.3	-
certified mole fraction (pmol/mol)	8.59	-	8.94	8.59
cylinder uncertainty	0.01	-	0.01	0.01
drift (%)	-	-	-	0.51
Sample mole fraction	-	**8.565**	-	-
Sample uncertainty	-	**0.020**	-	-

Table A-2. The analysis result of Cylinder # D056072

2018.9.4	CB10844	D056072	CB10909	CB10844
1	12260.7	12906.6	13305	12215.5
2	12227.1	12930.4	13326.8	12251.6
3	12229.6	12930	13318.9	12249.5
4	12249.9	12921.3	13307.9	12225.2
5	12243.4		13326.8	12216.5
Response	12242.1	12922.1	13317.1	12231.7
Standard deviation	14.05	11.14	10.28	17.67
Relative S.D. (%)	0.11	0.09	0.08	0.14
f-drift	-	0.9997	0.9994	-
Corrected peak area	-	12925.8	13324.7	-
certified mole fraction (pmol/mol)	8.94	-	9.76	8.94
cylinder uncertainty	0.01	-	0.02	0.01
drift (%)	-	-	-	-0.09
Sample mole fraction	**-**	**9.458**	-	-
Sample uncertainty	**-**	**0.024**	-	-

2018.9.4	CB10844	D056072	CB10909	CB10844
1	12215.5	12914.1	13308.3	12232
2	12251.6	12874.3	13295.6	12228.8
3	12249.5	12887.6	13283.5	12239.8
4	12225.2	12899.3	13288.1	12206.4
5	12216.5	12910.7	13300.1	12224.9
Response	12231.7	12897.2	13295.1	12226.4
Standard deviation	17.67	16.50	9.79	12.44
Relative S.D. (%)	0.14	0.13	0.07	0.10
f-drift	-	0.9999	0.9997	-
Corrected peak area	-	12899.1	13298.9	-
certified mole fraction (pmol/mol)	8.94	-	9.76	8.94
cylinder uncertainty	0.01	-	0.02	0.01
drift (%)	-	-	-	-0.09
Sample mole fraction	**-**	**9.453**	-	-
Sample uncertainty	**-**	**0.027**	-	-

Table A-3. The analysis result of Cylinder # D376143

2018.9.12	CB10889	D376143	FB03450	CB10889
1	13900	14303.7	16057.5	13913.8
2	13951	14268.8	16105	13886.9
3	13935.5	14297.4	16078.9	13963.2
4	13935.5	14295	16074.2	13932.8
5				13921.9
Response	13930.5	14291.2	16078.9	13923.7
Standard deviation	21.61	15.39	19.67	27.83
Relative S.D. (%)	0.16	0.11	0.12	0.20
f-drift	-	0.9998	0.9997	-
Corrected peak area	-	14293.5	16084.1	-
certified mole fraction (pmol/mol)	10.38	-	12.06	10.38
cylinder uncertainty	0.02	-	0.02	0.02
drift (%)	-	-	-	-0.05
Sample mole fraction	**-**	**10.663**	-	-
Sample uncertainty	**-**	**0.029**	-	-

2018.9.12	CB10889	D376143	FB03450	CB10889
1	13994.3	14278.7	16024.1	13931.6
2	13938.4	14318.5	16022.6	13856.7
3	13938.4	14318.5	16027.1	13946.1
4	13980.3	14327.3	16023.1	13941.4
5	13978.8	14280.5		13932.9
Response	13966.0	14304.7	16024.2	13921.7
Standard deviation	25.95	23.20	2.02	36.85
Relative S.D. (%)	0.19	0.16	0.01	0.26
f-drift	-	0.9989	0.9979	-
Corrected peak area	-	14319.8	16058.2	-
certified mole fraction (pmol/mol)	10.38	-	12.06	10.38
cylinder uncertainty	0.02	-	0.02	0.02
drift (%)	-	-	-	-0.32
Sample mole fraction	**-**	**10.664**	-	-
Sample uncertainty	**-**	**0.035**	-	-

Table A-4. The analysis result of Cylinder # D376143

2018.9.20	CB10844	D376117	CB10909	CB10844
1	14474	15948	16688.9	14495.8
2	14507.6	15944.8	16688.4	14483.6
3	14506.6	15945.4	16665.1	14508.7
4	14474	15947	16688.9	14495.8
5		15948		
Response	14496.1	15946.3	16680.8	14496.0
Standard deviation	19.12	1.47	13.60	12.55
Relative S.D. (%)	0.13	0.01	0.08	0.09
f-drift	-	1.0000	1.0000	-
Corrected peak area	-	15946.3	16680.8	-
certified mole fraction (pmol/mol)	10.38	-	12.06	10.38
cylinder uncertainty	0.01	-	0.02	0.01
drift (%)	-	-	-	0.00
Sample mole fraction	**-**	**11.495**	-	-
Sample uncertainty	**-**	**0.033**	-	-

2018.9.20	CB10844	D376117	CB10909	CB10844
1	14495.8	15929.1	16651.4	14380.2
2	14473.2	15925.3	16629.7	14333.3
3	14483.6	15933.6	16613.6	14298.1
4	14508.7	15948.8	16599.3	
5		15948		
Response	14490.3	15934.2	16623.5	14337.2
Standard deviation	15.34	10.31	22.36	41.19
Relative S.D. (%)	0.11	0.06	0.13	0.29
f-drift	-	0.9965	0.9930	-
Corrected peak area	-	15990.5	16741.4	-
certified mole fraction (pmol/mol)	10.38	-	12.06	10.38
cylinder uncertainty	0.01	-	0.02	0.01
drift (%)	-	-	-	-1.06
Sample mole fraction	**-**	**11.500**	-	-
Sample uncertainty	**-**	**0.034**	-	-

Table A-5. Final result

	D056078			D056072		
	SF_6 ppt	Uncer.	RDS(%)	SF_6 ppt	Uncer.	RDS(%)
Set1	8.563	0.014	0.165	9.458	0.024	0.249
Set2	8.565	0.020	0.230	9.453	0.027	0.287
Mean	**8.564**	**0.020**		**9.455**	**0.027**	
	D376143			**D376130**		
	SF_6 ppt	Uncer.	RDS(%)	SF_6 ppt	Uncer.	RDS(%)
Set1	10.663	0.029	0.276	11.495	0.033	0.290
Set2	10.664	0.035	0.327	11.500	0.034	0.292
Mean	**10.664**	**0.035**		**11.497**	**0.034**	

Here total uncertainty was decided by quadrature sum of greatest uncertainty and standard deviations of mean value in a set.

APPENDIX B. The inter-comparison experiment result between WCC-SF_6 and CCL (Central Calibration Laboratory).

Table B-1. The comparison result between CCL and WCC in 2019

	CCL-SF_6 (NOAA)		WCC-SF_6 (KMA/NIMS)		WCC-CCL
	SF_6 (ppt)	Stdev (ppt)	SF_6 (ppt)	Unc. (ppt)	Diff. (ppt)
D376143	10.680	0.013	10.664	0.035	**-0.016**
D056072	9.499	0.011	9.455	0.027	**-0.044**

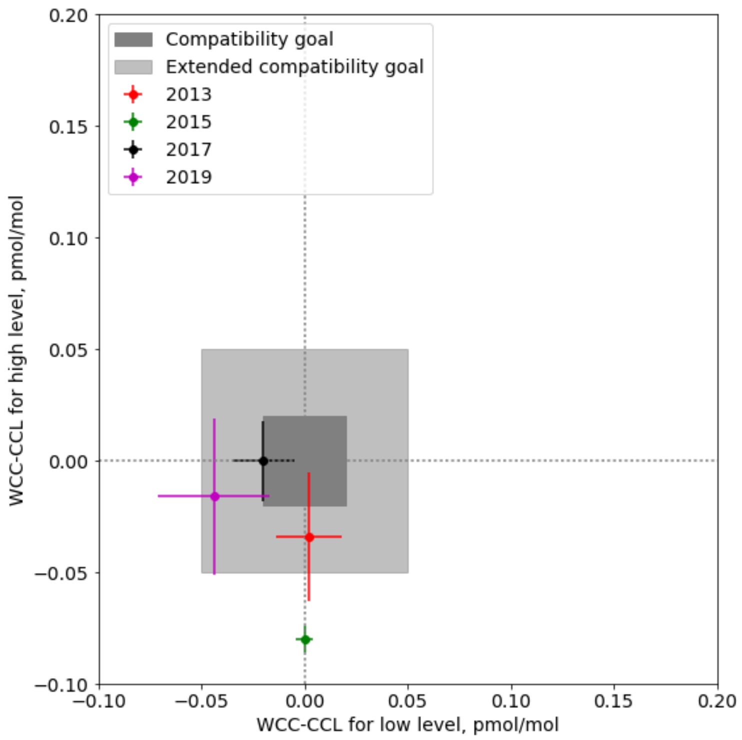


Figure B-1. The youden plot of differences between WCC and CCL from 2013 to 2019.