# Report on the system and performance audit of Sulfur Hexafluoride

# Global GAW station Zugspitze- Schneefernerhaus (ZSF) Germany November 2017

Submitted to the World Meteorological Organization by


Haeyoung Lee, Sang-Ok Han, and Sang-Boom Ryoo

World Calibration Centre for $SF_6$
Environmental Meteorological Research Division
National Institute of Meteorological Sciences
Korea Meteorological Administration
Republic of Korea


WCC-$SF_6$ Report 2018-2

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**WCC-$SF_6$ Report 2018-2**
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# Contents

# 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 Zugspitze-Schneefernerhaus (ZSF) in Germany were conducted from 20 to 24 November, 2017.

WCC-SF6 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 five different level cylinders.

This report includes the results from system and performance audits and will be distributed to the ZSF station, the German GAW country contact, and the WMO/GAW secretariat. The report also will be posted on the WMO GAW webpage.

## 1.2 System audit of the observatory

The Zugspitze-Schneefernerhaus GAW station is well operated and supported by Umweltbundesamt (UBA) with great facilities for atmospheric monitoring and research. It is located on the southern slope of Zugspitze together with the meteorological observatory Hohenpeissenberg (40 km north) on the platform established as Global GAW station Zugspitze/Hohenpeissenberg. At the station, the consortium of 10 organizations monitors various atmospheric species and holds regular meetings between scientists and between heads of each organization to share scientific knowledge in a supportive environment.

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.

Due to its location on the highest mountain of the German Alps (47.42° N, 10.98°E, 2656 m a.s.l.), its instrumentation systems, and facilities, the station is well suited for monitoring activities under 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.

## 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 follow the WMO/GAW requirement.

The gas chromatographic system with three detectors was suited for six species of greenhouse gases, including $SF_6$, simultaneously. Few analytical conditions should be modified to separate $N_2O$ and $SF_6$ better. However, through the inter-comparison experiment, it was confirmed that this system is good at the target level of atmospheric $SF_6$.

The linearity test with laboratory standards which is traceable to WMO-X2014 scale showed non-linearity characteristics. In this case, two-point calibrations (bracketing) is necessary for continuous measurement.

The inter-comparison experiment with traveling standard gases was performed as part of the audit. This result was quite similar to the previous SICE 2016-2017. This is the reason that the laboratory standard at ZSF does not cover the range below 8 ppt, that the uncertainty increases, and that the values were behind the compatibility goal in that range.

## 1.4 Recommendations

- GAWSIS information about staff and the $SF_6$ monitoring system should be updated.
- It is suggested that $SF_6$ values are determined by two-point working standards since the detector shows a non-linear characteristic.
- The analytical condition needs to be adjusted to separate $N_2O$ and $SF_6$. ZSF has a plan to exchange its $N_2O$ instrument from GC-ECD to ICOS so that there is a possibility it can set the new analysis condition of only targeting $SF_6$.

## 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-$SF_6$ Sang-Ok Han

Director of the division Sang-Boom Ryoo

## 2. Introduction

The Korea Meteorological Administration (KMA) has played a role as the 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 Zugspitze-Schneefernerhaus GAW global station is one of the important background stations within the GAW network as it is ideal for continuously monitoring the physical and chemical properties in the atmosphere. According to the record, audits were conducted by WCC-KIT ($N_2O$) in 2005 and WCC-Empa (WCC for $O_3$, CO, $CH_4$ and $CO_2$) in 2011. Also, it attended many inter-comparison experiments such as the Round Robin hosted by the WMO/GAW CCL (Central Calibration Laboratory), the WMO/GAW WCC (World Calibration Centre), and the Cucumber intercomparison programme in Europe. This station also runs GAWTEC (GAW Technical and Education Course), which is deeply involved in the GAW Program.

In agreement with Umweltbundesamt (UBA), WCC-$SF_6$ conducted the first system and performance audit of $SF_6$ at the Zugspitze-Schneefernerhaus GAW station from 20 to 24 November, 2017.

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 5 traveling standards (TS) of the WCC-

$SF_6$. The linearity test was also confirmed with lab standard gases which are tertiary NOAA-X2014 scale.

Finally, WCC-$SF_6$ appreciates all Zugspitze-Schneefernerhaus staff and the Umweltbundesamt for their cooperation in WCC-$SF_6$ activities.

## 3. System and performance audit for sulfur hexafluoride

### 3.1 Description of the site environment

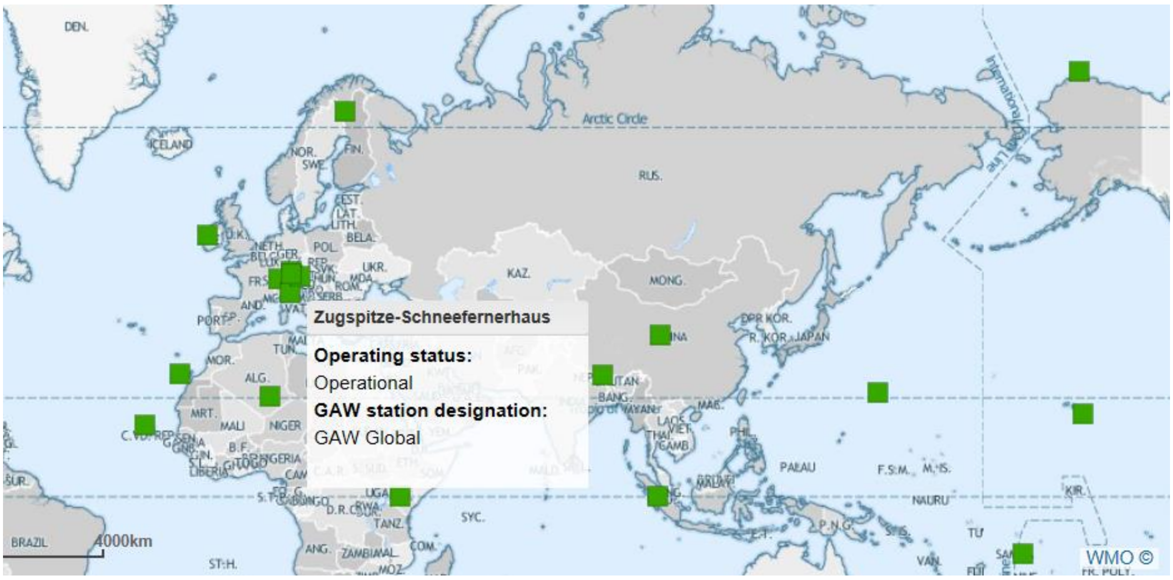



Figure 1. ZFS Global GAW stations (source: GAWSIS, https://gawsis.meteoswiss.ch).

The northern hemisphere GAW Global Station Zugspitze-Schneefernerhaus (ZSF, 47.42°N, 10.98° E) is located on the southern slope of Zugspitze, which is the highest mountain of the German Alps (3962 m a.s.l), 90 km southwest of Munich, on the Austrian border near the town of Garmisch-Partenkirchen. The time zone is UTC +1. More detailed information can be obtained from GAWSIS (https://gawsis.meteoswiss.ch)

A previous study described the geography and environment at ZSF*[4]* . Due to its location, the southern flank of the mountain is covered with Germany's largest glacier, the Schneeferner, which is surrounded by a mountain arc that shields it from winds coming from the north, west, and south. The Schneeferner is unshielded towards the south-west where melt water streams run down the mountain. UFS is situated on the north side of the glacier, at a height of about 2650 m. The mountain ridge to the west of the glacier is known as the Schneefernerkopf. Over a length of about 200 m, erosion has decreased the height of the ridge significantly, and the lowest point is about 175 m lower than the Schneefernkopf summit[5]. This part is known as the 'wind hole', because it directs the wind from the west over the glacier snf over UFS like a funnel.

The weather at Zugspitze is mainly influenced by the westerlies and synoptic-scale systems that lead to heavy precipitation on the northwest side of the Zugspitze massif. In addition to this, with about 60 days per year, the weather is dominated by foehn winds, which push against the massif from the south, resulting in relatively high temperatures during winter. The average temperature at the peak of Zugspitze during the standard reference period (1961-1990) was -4.8℃, while the lowest and the highest were -35.6 and 17.9 ℃, respectively [6], and the average precipitation was 2003 mm per year [7].


Figure 2. Views of the ZSF building (left) and the consortium of 10 organizations (right)

## 3.2 Description of the observatory

The Schneefernerhaus is operated by the Bavarian State Ministry of the Environment and 10 leading German research institutes have come together at this station with its spacious and advanced facilities. It provides roomy laboratories, a presentation and seminar room, and a guest house. It is kept clean and in good shape and all gas cylinders are clean and safe. ZSF is the ideal platform for continuous atmospheric research as well as measurement campaigns. Also, GAWTEC is held here regularly and the station is popular and famous among GAW communities.

Umweltbundesamt monitors greenhouse gases, reactive gases, and halogen species in cooperation with Colorado Univ., and aerosols in cooperation with the Tropos Institute (Table 1) and the WMO/GAW Programme.

## 3.3 Staff/operator

Three people are involved in ZSF station monitoring activities, including the station manager. They work at the station four days a week and monitor all instruments and species remotely one day a week. They also have a tele-conference once a week with head office to report their activities and invite relevant experts to share their scientific knowledge.

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 was well trained and has expertise.

Table 1. Staff responsible for the trace gas measurements at the ZSF station

| Name/duty | Responsibility |
|---|---|
| Ludwig Ries/ Station manager | Station managing/data QA/QC |
| Cedric Couret | $CO_2$, $CH_4$ by CRDS |

| | |
|---|---|
| /Station Engineer | $N_2O$, CO by ICOS<br>$CH_4$, CO, $N_2O$, $SF_6$, $H_2$ by<br>A GC with different detectors |
| Cooperation with Colorado Univ.<br>*The data authority belongs to UBA* | VOC, HFC, PFC by GC-MS |
| Ludwig Ries and Ralf Sohmer | Aerosols |

Staff who are involved in the audit from 20 to 24, Nov are listed below.

| | | |
|---|---|---|
| WCC-$SF_6$ | Haeyoung Lee | Research scientist (Auditor) |
| ZUF station | Ludwig Ries<br>Cedric Couret | Station manager<br>Station Engineer |

## 3.4 Monitoring set-up and procedure

### 3.4.1 Air inlet system

The location of the air intake with rain cap is on the 2.5 m tower above the roof deck on the 5th floor of the station (Figure 3 (Left)). The temperature of the cap is kept 1 to 3 ℃ higher than ambient levels with a sensor which can read the temperature outside. Also, it is heated 6 ℃ higher than outdoors to avoid condensation inside of the inlet line. The intake line consists of borosilicate glass in a stainless steel tube and is connected to a horizontal glass tube of 3 m length mounted under the ceiling of the laboratory (Figure 3 (Right)).

Total flow of the glass tube is 500 L $min^{-1}$ by way of a turbine type and the air is drawn from the glass tube through 1/4" and 1/8" stainless steel tubes via a cooling trap (glass vessel at – 80 °C) by a pump (KNF 220 mL min$^{-1}$). The glass vessel of the cooling trap is changed twice a week, which is documented in a log book. During summer, with higher atmospheric humidity, the vessel is changed up to three times per week (Figure 4).

Figure 3. The 2.5 m intake on the roof deck (left) and the glass tube linked to the inlet inside of the laboratory (right)


Figure 4. The thermoregulator TC100 E (left) and the cooling trap (right)

### 3.4.2 Gas chromatography system

**The GC-μECD (Agilent 6890)**: There has been no big change in the monitoring system since 2000, which is when the system was first set up, with the exception of changing from ECD to μECD in 2013. The model of gas chromatography is Agilent 6890 with three channels of FID (Flame Ionization Detector) for $CH_4$ and $CO_2$, of ECD for $SF_6$ and $N_2O$, and of HgO for CO and $H_2$.

Figure 5. The valve system (left) and the connections to GC (right)

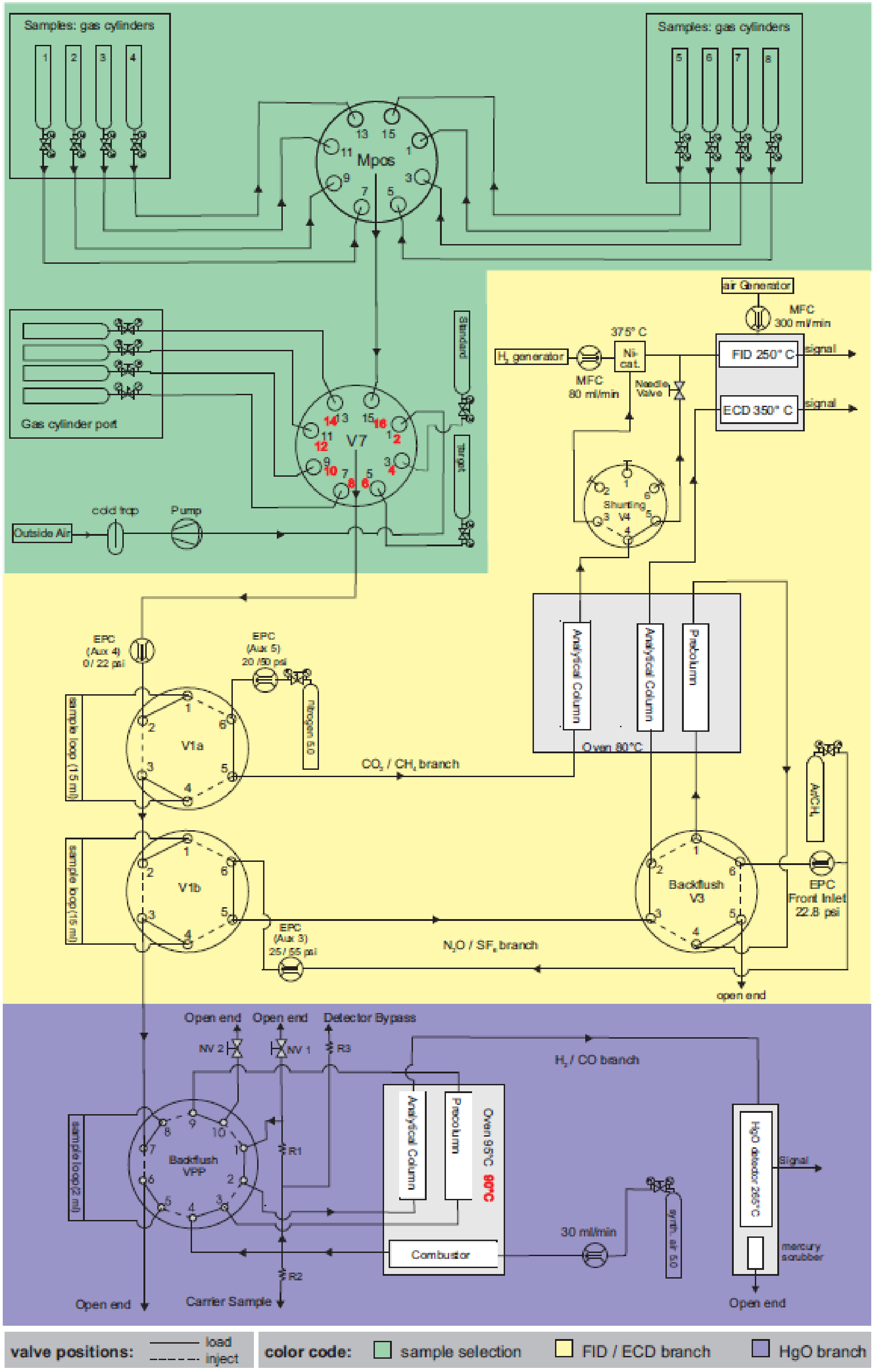



Figure 6. Schematic setup of the combined GC system. The color code represents the different sections of, FID/ECD branch, and HgO branch respectively. When two numbers are given, the red ones refer to Zugspitze, the black ones to Schauinsland. (Müller, 2009)

**The stream selection valve**: After the dehumidification system, the sample air moves through 1/8″ tubing of stainless steel to the inlet of a stream selection valve, vici (8 ports with 16 positions) with micro-electrical actuator. The pressure equilibration prior to sample injection is achieved by switching the SSV to plugged position.

**The injection valve**: The two injection valves are vici with 6 ports with sample loop 15 mL. The back-flush method is applied for $N_2O$ and $SF_6$ with main column (Heysep 80/100 mesh, 6 feet (3/16″), 80°C) and pre-column (Heysep 80/100 mesh, 4 feet (3/16″), 80°C).

**The carrier gas**: Ar/CH4 (95% / 5%) is used as a carrier gas with the trap for removing oxygen and moisture between the pressure regulator at the cylinder and GC.

Here we see the current analytical condition (Table 2).This entire system is well documented in the references (Müller., 2009).

Table 2. Analytical condition at ZSF

| **Analytical Condition** | |
|---|---|
| Detector | μECD (from 2013) |
| Detector temperature | 350℃ |
| Column | Pre: Heyesep 80/100 mesh, 4 feet (3/16″)<br>Main: Heysep 80/100 mesh, 6 feet (3/16″) |
| Loop size | 15 mL |
| Makeup Flow | No makeup gas |
| Sample Flow | 170 mL/min |
| Carrier gas, pressure | P-5 gas, 65 psi → 22 psi |
| Oven temperature | 80 ℃ |

The general chromatogram is shown in Figure 7. The sequence of peaks in the chromatogram after the passage of the oxygen signal is $N_2O$ around 3.6 min and $SF_6$ around 4.3 min. The column of Heysep is very similar to Porapak-Q and the $SF_6$ peak shape is broadened while the $N_2O$ peak is Gaussian with this column. ZSF also showed similar peak shapes of $N_2O$ and $SF_6$ since it was analyzed through Heysep. In this regard, the peaks of $N_2O$ and $SF_6$ overlapped slightly.

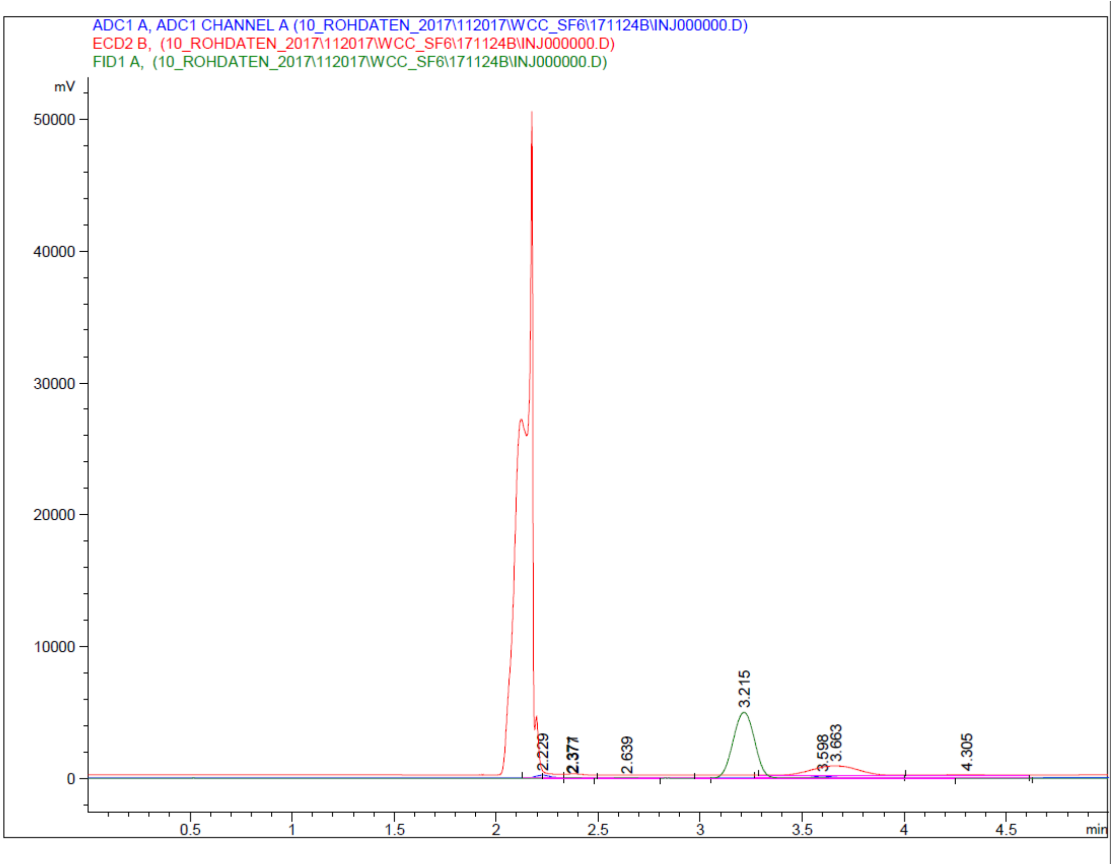



Figure 7. Example of a chromatogram obtained with the FID (green peaks) and ECD (red peaks) channel of the GC system

### 3.4.3 Recommendation

- The air inlet and dehumidification system are adequate for the measurement of $SF_6$.
- The GC system with its peripheral devices is sophisticated and is well suited for high-quality $N_2O$ and $SF_6$ measurements.

- To separate both $N_2O$ and $SF_6$ peaks, more delicate adjustments are necessary in analysis conditions such as flow rate. However, in the given situation, this might be difficult since three detectors are combined in one GC system. In the future, ZSF will monitor $N_2O$ with ICOS and only $SF_6$ with GC-ECD so that there is a possibility to adjust the analysis condition.

## 3.5 Calibration and maintenance

### 3.5.1 General

The station has been operated by three staff under the UBA (Umweltbundesamt) and they work at the station 4 days a week to maintain the whole system. One day, the entire system can be monitored remotely.

### 3.5.2 Sampling and calibration

**A leak check:** The gas leakages between every connector have been checked in 2014 and the system is leak free. The cylinders connections are checked daily basis and the instruments are also checked when unusual signals are monitored.

**Sequence of analyses and calibration method:** The sequence of the working standard (W) and ambient air (A) is: A-A-W-A-A-W-A-A-W... over 22.5 hours with 5 mins interval between injection and then W-T (Target Tank)-A-W-T-A-W-T-A... over another 3 hours with 5 mins interval between injection and then the first sequence is run again. The ambient $SF_6$ are corrected by a working standard of around 8.88 ppt now.

**Linearity, repeatability and reproducibility of measurement:** These were tested with 6 laboratory cylinders regularly every two months and implemented during the audit period with 5 cylinders (CA05769, CA05775, ND56763, ND56764, ND56757).

The repeatability was reported as the standard deviation with 29 to 37 duplicates for each cylinder and those values were from 0.06 to 0.1 ppt during the audit period. Reproducibility was expressed by the standard deviations from Nov. 2016 to Nov. 2017 and those were between 0.01 to

0.02 ppt (Table 3).

Table 3. The repeatability and reproducibility assessment. Repeatability represents the standard deviations of 29 to 37 duplicates during the audit period. Reproducibility represents the standard deviations over the last one year (from Nov. 2016 to Nov. 2017). The unit is ppt.

| Cylinder | Repeatability (ppt, N = 29) | Reproducibility (ppt, N = 8) |
|---|---|---|
| CA05769 : 10.78 ± 0.02 ppt | 0.10 | 0.02 |
| ND65763 : 9.78 ± 0.01 ppt | 0.09 | 0.02 (N=6) |
| ND56757 : 9.20 ± 0.02 ppt | 0.07 | 0.02 |
| CA05775 : 8.84 ± 0.01 ppt | 0.06 (N=37) | 0.01 (N=7) |
| ND56763 : 8.10 ± 0.01 ppt | 0.07 (N=31) | 0.01 |

The linearity test of the detector (μECD) is recommended with 3-point standard gases that are well separated from each other at least [2]. Since the response curve has non-linear characteristics on μECD normally, this test is very important for the calibration. ZSF conducts this test every two months with 6 cylinders, which is adequate for the test.

While conducting the linearity test during the audit period, the analysis sequence was the same as the ambient air; in place of ambient air, laboratory standard gases listed in table 3 were sampled.

For the linearity test, each cylinder was assigned a working standard (8.8 ppt this time) first, and then the calibration curve was applied again to correct the value. The difference between two types of regression curve, linear fit and second order fit, was compared and is shown in Table 4 and Figure 7.

When the linearity fit was applied, the residuals between laboratory standard (CCL) and corrected measurement value were between -0.03 to 0.04 ppt, while those values were -0.01 to 0.01 ppt for the second order fit.

Table 4. The differences in mole fractions between the linear and second order fits. ZSF analysis results come from the corrected value with working standard. S.D. (standard deviation) represents the repeatability of 29 to 37 duplicates. CCL represents the laboratory standards, certified reference materials from WMO/GAW Central Calibration Lab. Units are ppt.

| Cylinder | ZSF analysis | S.D. | CCL | CCL uncertainty | Differences from linear fit | Differences from second order fit |
|---|---|---|---|---|---|---|
| CA05769 | 10.70 | 0.10 | 10.78 | 0.02 | -0.02 | 0.00 |
| ND56763 | 9.71 | 0.09 | 9.78 | 0.01 | 0.01 | -0.01 |
| ND56757 | 9.18 | 0.07 | 9.24 | 0.01 | 0.04 | 0.01 |
| CA05775 | 8.83 | 0.06 | 8.84 | 0.01 | 0.00 | -0.01 |
| ND56764 | 8.11 | 0.07 | 8.06 | 0.01 | -0.03 | 0.00 |

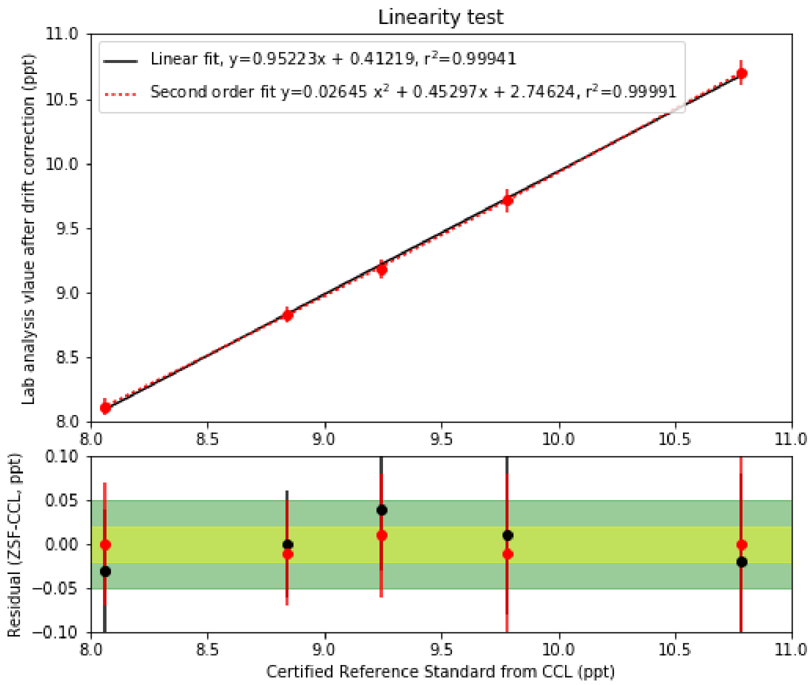



Figure 8. (Top) A comparison of two regression curves. (Bottom) Black dots indicate the residuals when linearity fit was applied to each cylinder. Red dots represent the residual when the second order polynomial fit was applied. Yellow indicates the compatibility goal ± 0.02 ppt, and the extended goal is for the green area.

According to the previous experiment [8], the coefficient of determination ($r^2$) can be used as the basis to assess linearity and if $r^2$ is improved with secondary polynomial indicating the value greater than 0.9999 (four decimal point) from the linear fit, the detector response would be non-linear.

This result suggested the regression curve from μECD in ZSF is more suitable to the second order fit rather than to the linear one. In this case, two-point calibration is suggested.

It was also confirmed that the differences between laboratory standard and measurement value in a lab decreased when the secondary polynomial curve was applied.

### 3.5.3 Maintenance

The one working standard is used for data correction and laboratory standards are used to disclose where the problems come from through the linearity test and reproducibility.

Excessive baseline noise or peak shape degradation usually results from the carrier gas that the purifier or carrier gas was exchanged.

The staff check the cylinder pressure and detector etc. and record it in the log book.

### 3.5.4 Recommendations

- All systems are well maintained by staff working at the station and through remote monitoring.
- The technician has enough experience and problem-solving skills that the monitoring activity at ZSF is very reliable.
- According to the linearity test, it shows a non-linear characteristic so that two-point calibration is recommended rather than one-point.

## 3.6 Standard

### 3.6.1 Regulators and connections

The pressure regulators are Tescom with two stages and Scott with two stages as well. The tubing from the cylinders to the valve is made out of stainless steel (Figure 10).

Figure 9. The regulator in the laboratory

### 3.6.2 Laboratory standards

Six laboratory standards were prepared and their information is listed in Table 4. They were NOAA tertiary standards with the range nominally from 8 to 11 ppt and converted to the NOAA-X2014 scale according to the webpage of NOAA (www.esrl.noaa.gov/gmd/ccl/refgas.html). For $CO_2$, $CH_4$, and CO, it is highly recommended that they be recalibrated every 3 years for precision. There is no certain period for the $SF_6$ recalibration but it is recommended to recalibrate them for long term stability and precision. Their information is in Table 3.

Since the cylinder with the number CA05606 has low pressure, 27 bar, it was not used. WMO/GAW recommended that when cylinder pressure has decreased to 20 bar, the standards should be replaced. Also, the laboratory cylinders were regularly recalibrated so that ZSF seems to maintain the laboratory standard very well.

Table 4. Laboratory standards for $SF_6$ at the station. Cylinder numbers, mole fractions with standard deviation as reported by the Central Calibration Laboratory. For $SF_6$ , the scale is NOAA-X2014.

| Cylinder S/N (pressure) | $CO_2$ [ppm] | $CH_4$ [ppb] | CO [ppb] | $N_2O$ [ppb] | $SF_6$ [ppt] |
|---|---|---|---|---|---|
| **CA05769 (48 bar)** | 393.80 | 1946.19±0.2 | 391.88±0.4 | 340.38±0.11 | 10.78±0.02 |
| **ND56763 (113 bar)** | 413.45±0.01 | 1962.06±0.29 | 267.63±1.22 | 335.25±0.05 | 9.78±0.01 |
| ***CA05606 (27 bar)*** | *374.24±0.07* | *1847.19±0.3* | *209.66±0.86* | *329±0.04* | *9.63±0.02* |
| **ND56757 (119 bar)** | 399.02±0.01 | 1940.25±0.1 | 154.13±0.06 | 337.11±0.13 | 9.24±0.01 |
| **CA05775 (56 bar)** | 362.40±0.02 | 1813.19±0.23 | 120.58±0.96 | 298.94±0.1 | 8.84±0.01 |
| **ND56764 (120 bar)** | 378.60 | 1834.73±0.21 | 124.18±0.07 | 319.99±0.13 | 8.06±0.02 |

### 3.6.3 Working standards

Working standard was prepared with one cylinder at the station for the routine determination of ambient mole fractions. The cylinder is 40 L type aluminum Luxfer and high pressure with ambient air. The comparison of the working standards with laboratory standards is performed for $N_2O$ quarterly but not for $SF_6$. Working standard was sampled at the Schauinsland GAW station, which is located close to the big city Freiburg im Breisgau. It is certified regularly when the instrument is calibrated.

### 3.6.4 Target gas

Target gas was prepared in one cylinder at the station for the routine determination of instrumental drift. The cylinder is 50 L type aluminum Luxfer and high pressure with ambient air. The target tank was sampled at the Schauinsland GAW station as well. However, it was not certified.

### 3.6.5 Recommendations

- Lab standards and working standards were linked to WMO X2014 scale and well maintained. At least one target tank was recommended and two spanning a range in mole fraction for measured species are preferred according to the GAW guideline. Those are well managed at ZSF.

## 3.7 Data acquisition and processing

### 3.7.1 General

Data acquisition of the gas chromatographic signals and parameters is handled by Chemstation and GC organizer, which was developed by Heidelberg University. It is controlled remotely. The data is synchronized in the local time zone. GC organizer re-corrected the value using a working standard, and data visualization is implemented to check its consistency (Figure 10).

After the drift correction, data were filtered by a logbook, which includes the information such as visitors and snow blower, and flagging. The large variations in the data were also rejected, as were not real data, such as signals due to instrument malfunction. However, there is no outlier for data filtering.

Final data validation is implemented by Dr. Ludwig Ries with his developed software GAWSTAT (www.gawstat.de, Figure 11). This software is very useful not only for the data QA/QC but also to reflect the standard scale updates. It was presented at the GGMT meeting in 2013 [9].

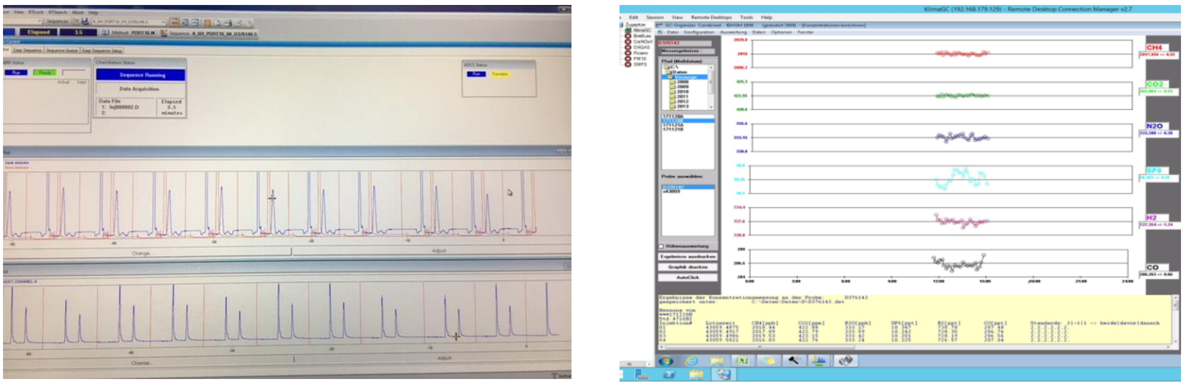


Figure 10. The chemstation (left) and GC organizer (right).


Figure 11. GAWSTAT developed by Ludwig Ries [9].

### 3.7.2 Chromatogram evaluation

Every report of the chromatogram from GC is stored in the drive and includes retention time, peak area, width and height. This information is used for data quality control. Peak integration is performed automatically.

The sequence of peaks was $O_2$, $N_2O$, and $SF_6$, and the tail of the $O_2$ peak does not overlap the tail of $N_2O$ peak. There is a possibility of overlapped $N_2O$ tails, which was described in 3.4.2.

### 3.7.3 Recommendations

- The data expert is involved in data QA/QC with proper software and handles it delicately so that the data from ZSF are very reliable.

## 3.8 Data management and submission

### 3.8.1 General

ZSF is generally following up the WMO/GAW report no. 150 [10]. All the data from ZSF station are delivered to the storage in the lab every minute with metadata and recovered once a week. The raw data are shared and delivered through FTP to UBA and other institutes, which consist of a consortium, within a digital logbook.

The flagging consists of artifact, inter-comparison, calibration, instrumental issue, pollution episode, and shorter or longer episode which cannot be representative of the background level. The data with flagging were checked once a year.

Data back-up is implemented every day, every week, and every month.

The data so far have been submitted to the World Data Centre for Greenhouse Gases.

### 3.8.2 Recommendations

- Data management and submission to the World Data Centre on Greenhouse Gases are well implemented.

## 3.9 Documentation

The WMO GAW Measurement guideline 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 five traveling standards with five pressure regulators to the ZSF station. They arrived at the station before the audit.

Table 5. Cylinder information on the $SF_6$ traveling standards

| | |
|---|---|
| Manufacture | Luxfer Gas cylinders (UK) |
| Cylinder # | D376117, D376125, D376120, D376142, D376140 |
| The level of $SF_6$ | Between 6 and 11 ppt in natural dry air |
| Material | Aluminum 10 L cylinders |

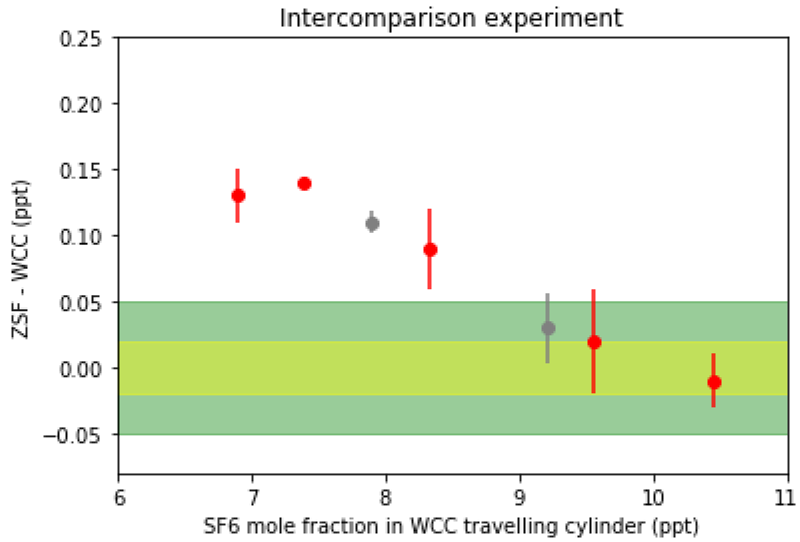
Five traveling standards for this inter-comparison experiment are listed in Table 5. The WCC-$SF_6$ analysis method is described [8]. For WCC-$SF_6$, five traveling standards were calibrated against laboratory standards of WMO-X2014 scale with a two-point analysis method. The standards to certify the traveling standards were selected with a similar level that covers the target range for the calibrations. The analysis results are shown in APPENDIX.

ZSF participated in the first $SF_6$ inter-comparison experiment (SICE) and showed the difference from WCC-$SF_6$ as 0.11 ppt and 0.03 ppt at 7.89 ppt and 9.21 ppt respectively [11] in 2016.

During the audit period, five traveling standards were calibrated 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. The one cylinder was duplicated.

### 3.10.2 Results of the $SF_6$ inter-comparisons

This result is similar to SICE-2016 when the linear fit was applied to each cylinder. From 9 ppt the differences between WCC and ZSF decreased, indicating they were in the compatibility goal. On the other hand, this shows low correlation with time (Figure 13). Two reasons are assumed for these differences. Laboratory standards range from 8 ppt to 11 ppt so that the $SF_6$ mole fractions which are out of the range cannot be assured. Another reason is detector non-linear characteristics described in 3.5.2. Since we applied the secondary polynomial fit to each cylinder, the bias decreased (Figure 14). Even if linear fit is used for the calibration, since observed $SF_6$ is above 9 ppt, the data is plausible. In this case, we would like to recommend that the working standard be higher than now and be at a similar level to that of ambient air, or a two-point calibration is highly recommended.



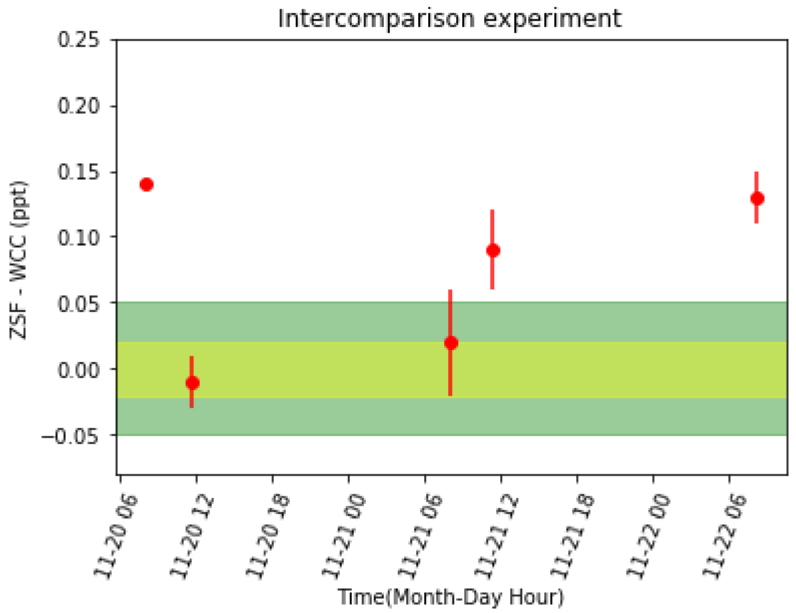




Figure 12. The differences between ZSF and WCC. Two labs used WMO-X2014 scale for the calibrations. The error bars show the standard deviation of individual measurement points. Yellow and green areas correspond to WMO compatibility and extended compatibility goal. (Top) Red dots represent the differences between two labs with respect to the WCC traveling standards, while grey dots indicate the difference in SCIE, 2016. (Bottom) The differences in time dependence.

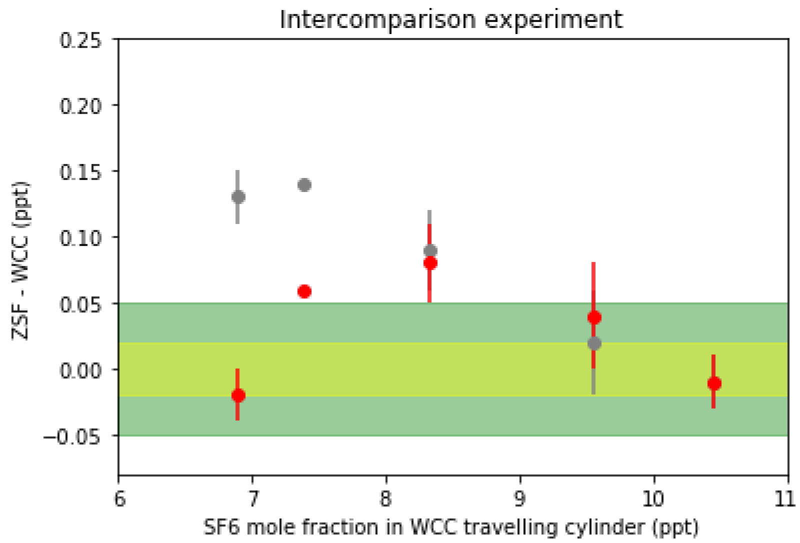



Figure 13. The differences between ZSF and WCC. Two labs used WMO-X2014 scale for the calibrations. The error bars show the standard deviation of individual measurement points. Yellow and green areas correspond to WMO compatibility (± 0.02 ppt) and extended compatibility (± 0.05 ppt) goal. Red dots represent the differences between two labs with respect to the WCC traveling standards when secondary polynomial fit was applied. Grey dots indicate the difference when linear fit was applied. If the analysis sequence was a series of the 5 laboratory standards, the bias would be decreased more than now since analysis conditions are not the same every time.

Table 6. Summary results for the inter-comparison as reported by WCC-$SF_6$ and ZSF. ZSF decided $SF_6$ values with linear regression fit.

| Cyl# | WCC | Uncertainty | ZSF | S.D | ZSF-WCC |
|---|---|---|---|---|---|
| D376120 | 6.896 | 0.01 | 7.02 | 0.02 | 0.13 |
| D376125 | 7.384 | 0.02 | 7.53 | 0 | 0.14 |
| D376140 | 8.333 | 0.02 | 8.42 | 0.03 | 0.09 |
| D376117 | 9.551 | 0.03 | 9.57 | 0.04 | 0.02 |
| D376142 | 10.445 | 0.03 | 10.44 | 0.02 | -0.01 |

# 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)*

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*[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] Risius, S., H.Xu, F. Di Lorenzo, H.Xi, H.Siebert, R.A.Shaw, and E. Bodenschatz, 2016, Schnnefernerhaus as a mountain research station for clouds and turbulence, Atmos. Meas. Tech., 8, 3209-3218*

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*[6] DWD: Wetter und Klima – Deutscher Wetterdienst – Flächenpräsenz, available at: http://www.dwd.de/zugspitze (last access: 15 February 2015), 2000.*

*[7] Siebert, H., Gerashchenko, S., Gylfason, A., Lehmann, K., Collins,L. R., Shaw, R. A., and Warhaft, Z.: Towards understanding the role of turbulence on droplets in clouds: In situ and laboratory measurements, Atmos. Res., 97, 426–437, 2010.*

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

*[9] WMO, 2014: The 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), Beijing, China, 10-13, June 2013, WMO/GAW No.213*

*[10] WMO,2003: Updated Guidelines for Atmospheric Trace Gase*

*Data Management, WMO TD No.1149 and WMO/GAW No.150.*

*[11] WCC-$SF_6$, 2017: The report of the result on $SF_6$ Inter-comparison Experiment, 2016-2017*

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

1. Cylinder # D376120

| 2017.09.19 | CB11249 | D376120 | CB11159 | CB11249 |
|---|---|---|---|---|
| 1 | *13574.9 | 13890.0 | 15806.4 | 13498.4 |
| 2 | 13557.1 | 13899.4 | 15814.6 | 13484.3 |
| 3 | 13539.6 | *13867.2 | 15812.6 | *13469.9 |
| 4 | 13534.9 | 13903.5 | 15800.6 | 13474.5 |
| 5 | 13541.4 | 13890.3 | 15796.7 | 13499.3 |
| Response | 13543.3 | 13895.8 | 15806.2 | 13489.1 |
| Standard deviation | 9.63 | 6.74 | 7.63 | 11.93 |
| Relative S.D. (%) | 0.07 | 0.05 | 0.05 | 0.09 |
| f-drift | - | 1.0013 | 1.0027 | - |
| Corrected peak area | - | 13914.3 | 15848.4 | - |
| certified mole fraction (pmol/mol) | 6.72 | - | 7.83 | 6.72 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | -0.40 |
| **Sample mole fraction** | - | **6.899** | - | - |
| **Sample uncertainty** | - | **0.012** | - | - |

| 2017.09.19 | CB11249 | D376120 | CB11159 | CB11249 |
|---|---|---|---|---|
| 1 | *13470.3 | 13873.0 | *15732.7 | 13442.1 |
| 2 | 13529.9 | 13859.0 | 15707.7 | 13417.7 |
| 3 | 13559.9 | 13857.9 | 15710.2 | 13424.7 |
| 4 | 13555.1 | *13823.5 | 15675.9 | 13434.8 |
| 5 | 13530.2 | *13794.1 | 15672.5 | 13449.7 |
| Response | 13543.8 | 13863.3 | 15691.6 | 13433.8 |
| Standard deviation | 15.97 | 8.42 | 20.14 | 12.89 |
| Relative S.D. (%) | 0.12 | 0.06 | 0.13 | 0.10 |
| f-drift | - | 1.0027 | 1.0054 | - |
| Corrected peak area | - | 13900.9 | 15777.0 | - |
| certified mole fraction (pmol/mol) | 6.72 | - | 7.83 | 6.72 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | -0.81 |
| **Sample mole fraction** | - | **6.898** | - | - |
| **Sample uncertainty** | - | **0.014** | - | - |

| 2017.09.19 | CB11249 | D376120 | CB11159 | CB11249 |
|---|---|---|---|---|
| 1 | 13498.4 | 13833.9 | 15729.4 | *13457.3 |
| 2 | 13484.3 | 13833.4 | 15742.5 | 13431.7 |
| 3 | *13469.9 | 13819.2 | 15740.1 | 13436.6 |
| 4 | 13474.5 | 13811.8 | 15718.4 | 13420.0 |
| 5 | 13499.3 | 13812.2 | 15716.5 | 13431.6 |
| Response | 13489.1 | 13822.1 | 15729.4 | 13430.0 |
| Standard deviation | 11.93 | 10.95 | 11.97 | 7.05 |
| Relative S.D. (%) | 0.09 | 0.08 | 0.08 | 0.05 |
| f-drift | - | 1.0015 | 1.0029 | - |
| Corrected peak area | - | 13842.3 | 15775.5 | - |
| certified mole fraction (pmol/mol) | 6.72 | - | 7.83 | 6.72 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | -0.44 |
| **Sample mole fraction** | - | **6.891** | - | - |
| **Sample uncertainty** | - | **0.013** | - | - |

2. Cylinder # D376125

| 2017.08.28 | CB11249 | D376125 | CB11159 | CB11249 |
|---|---|---|---|---|
| 1 | *13468.7 | *14609.4 | 15336.2 | 13423.4 |
| 2 | 13456.7 | 14589.8 | 15340.0 | 13436.5 |
| 3 | 13437.6 | 14586.7 | 15356.9 | 13445.2 |
| 4 | 13419.2 | 14565.6 | 15345.7 | 13446.2 |
| 5 | 13432.8 | *14532.6 | 15357.0 | 13466.6 |
| Response | 13436.6 | 14580.7 | 15347.2 | 13443.6 |
| Standard deviation | 15.52 | 13.17 | 9.56 | 15.79 |
| Relative S.D. (%) | 0.12 | 0.09 | 0.06 | 0.12 |
| f-drift | - | 0.9998 | 0.9997 | - |
| Corrected peak area | - | 14578.2 | 15341.8 | - |
| certified mole fraction (pmol/mol) | 6.72 | - | 7.83 | 6.72 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | 0.05 |
| **Sample mole fraction** | - | **7.385** | - | - |
| **Sample uncertainty** | - | **0.021** | - | - |

| 2017.09.04 | CB11249 | D376125 | CB11159 | CB11249 |
|---|---|---|---|---|
| 1 | 13993.1 | 15220.4 | 16003.0 | 13970.2 |
| 2 | 13990.8 | 15197.5 | 16019.4 | 13942.8 |
| 3 | 13981.0 | 15190.2 | 15998.4 | 13964.6 |
| 4 | 13991.4 | 15179.4 | 15998.0 | 13945.1 |
| 5 | 13980.3 | 15173.3 | 16007.7 | 13966.3 |
| Response | 13987.3 | 15192.2 | 16005.3 | 13957.8 |
| Standard deviation | 6.15 | 18.36 | 8.81 | 12.83 |
| Relative S.D. (%) | 0.04 | 0.12 | 0.06 | 0.09 |
| f-drift | - | 1.0007 | 1.0014 | - |
| Corrected peak area | - | 15202.9 | 16027.9 | - |
| certified mole fraction (pmol/mol) | 6.72 | - | 7.83 | 6.72 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | -0.21 |
| **Sample mole fraction** | **-** | **7.381** | - | - |
| **Sample uncertainty** | **-** | **0.020** | - | - |

| 2017.08.28 | CB11249 | D376125 | CB11159 | CB11249 |
|---|---|---|---|---|
| 1 | *13534.1 | 14668.3 | 15394.3 | 13498.7 |
| 2 | 13517.7 | 14642.2 | 15391.8 | 13490.2 |
| 3 | 13497.3 | 14643.8 | 15415.5 | 13509.7 |
| 4 | 13495.0 | 14626.4 | 15407.4 | 13508.6 |
| 5 | 13503.1 | 14599.6 | 15416.8 | 13533.1 |
| Response | 13503.3 | 14636.1 | 15405.2 | 13508.1 |
| Standard deviation | 10.20 | 25.30 | 11.66 | 16.10 |
| Relative S.D. (%) | 0.08 | 0.17 | 0.08 | 0.12 |
| f-drift | - | 0.9999 | 0.9998 | - |
| Corrected peak area | - | 14634.3 | 15401.5 | - |
| certified mole fraction (pmol/mol) | 6.72 | - | 7.83 | 6.72 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | 0.04 |
| **Sample mole fraction** | - | **7.381** | - | - |
| **Sample uncertainty** | - | **0.024** | - | - |

3. Cylinder # D376140

| 2017.09.13 | FB04102 | D376140 | FB04105 | FB04102 |
|---|---|---|---|---|
| 1 | 16103.1 | 16557.1 | 16884.0 | 15949.1 |
| 2 | 16145.5 | 16543.7 | 16897.1 | 15985.5 |
| 3 | 16103.0 | *16612.9 | 16905.6 | 15965.7 |
| 4 | 16113.5 | 16542.1 | 16840.1 | 15961.2 |
| 5 | 16137.9 | 16577.4 | *16835.1 | 15980.6 |
| Response | 16120.6 | 16555.1 | 16881.7 | 15968.4 |
| Standard deviation | 19.91 | 16.33 | 29.12 | 14.77 |
| Relative S.D. (%) | 0.12 | 0.10 | 0.17 | 0.09 |
| f-drift | - | 1.0032 | 1.0063 | - |
| Corrected peak area | - | 16607.3 | 16988.6 | - |
| certified mole fraction (pmol/mol) | 8.12 | - | 8.5 | 8.12 |
| cylinder uncertainty | 0.01 | - | 0.01 | 0.01 |
| drift (%) | - | - | - | -0.94 |
| **Sample mole fraction** | **-** | **8.333** | - | - |
| **Sample uncertainty** | **-** | **0.019** | - | - |

| 2017.09.16 | FB04102 | D376140 | FB04105 | FB04102 |
|---|---|---|---|---|
| 1 | 16416.4 | *16906.9 | 17423.9 | 16538.7 |
| 2 | 16416.1 | 16943.6 | 17407.1 | 16534.2 |
| 3 | 16389.4 | 16944.5 | 17393.5 | *16526.1 |
| 4 | 16387.0 | 16992.1 | 17383.3 | 16574.7 |
| 5 | 16383.4 | *17022.8 | *17335.4 | 16588.6 |
| Response | 16398.5 | 16960.1 | 17402.0 | 16559.1 |
| Standard deviation | 16.38 | 27.75 | 17.58 | 26.77 |
| Relative S.D. (%) | 0.10 | 0.16 | 0.10 | 0.16 |
| f-drift | - | 0.9967 | 0.9935 | - |
| Corrected peak area | - | 16904.9 | 17289.1 | - |
| certified mole fraction (pmol/mol) | 8.12 | - | 8.5 | 8.12 |
| cylinder uncertainty | 0.01 | - | 0.01 | 0.01 |
| drift (%) | - | - | - | 0.98 |
| **Sample mole fraction** | **-** | **8.336** | - | - |
| **Sample uncertainty** | **-** | **0.020** | - | - |

| 2017.09.16 | FB04102 | D376140 | FB04105 | FB04102 |
|---|---|---|---|---|
| 1 | 16638.7 | *17141.2 | *17464.2 | 16558.0 |
| 2 | 16661.9 | *17172 | 17424.3 | *16594.3 |
| 3 | 16666.8 | 17093.3 | 17431.6 | 16575.4 |
| 4 | 16670.6 | 17097.3 | *17382.4 | 16566.9 |
| 5 | 16686.4 | 17082.1 | 17430.7 | *16524.6 |
| Response | 16664.9 | 17090.9 | 17428.9 | 16566.8 |
| Standard deviation | 17.28 | 7.88 | 3.98 | 8.70 |
| Relative S.D. (%) | 0.10 | 0.05 | 0.02 | 0.05 |
| f-drift | - | 1.0020 | 1.0039 | - |
| Corrected peak area | - | 17124.5 | 17497.5 | - |
| certified mole fraction (pmol/mol) | 8.12 | - | 8.5 | 8.12 |
| cylinder uncertainty | 0.01 | - | 0.01 | 0.01 |
| drift (%) | - | - | - | -0.59 |
| **Sample mole fraction** | **-** | **8.330** | - | - |
| **Sample uncertainty** | **-** | **0.016** | - | - |

4. Cylinder # D376117

| 2017.08.25 | CB10844 | D376117 | CB10909 | CB10844 |
|---|---|---|---|---|
| 1 | *17597.7 | 18575.6 | 18952.6 | *17562.1 |
| 2 | 17587.4 | *18566.2 | 18932.7 | 17516.3 |
| 3 | 17560.2 | 18607.6 | 18944 | 17527.6 |
| 4 | 17583.5 | 18597.8 | 18928.6 | 17533.6 |
| 5 | 17578.7 | 18608.6 | 18895.4 | 17544.8 |
| Response | 17577.5 | 18597.4 | 18930.7 | 17530.6 |
| Standard deviation | 17.28 | 7.88 | 3.98 | 8.70 |
| Relative S.D. (%) | 14.71 | 16.40 | 10.91 | 8.78 |
| f-drift | - | 1.0009 | 1.0018 | - |
| Corrected peak area | - | 18613.9 | 18964.4 | - |
| certified mole fraction (pmol/mol) | 8.94 | - | 9.76 | 8.94 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | -0.27 |
| **Sample mole fraction** | **-** | **9.553** | - | - |
| **Sample uncertainty** | **-** | **0.025** | - | - |

| 2017.08.25 | CB10844 | D376117 | CB10909 | CB10844 |
|---|---|---|---|---|
| 1 | *17965.4 | 18785.4 | 19137.8 | 17655.8 |
| 2 | *17877.6 | 18798.3 | 19124 | 17692.7 |
| 3 | 17833.9 | 18813.9 | 19098.8 | 17674.8 |
| 4 | 17827 | 18799.4 | 19072.5 | *17627.2 |
| 5 | 17795.7 | 18797.5 | 19051.8 | *17613.8 |
| Response | 17818.9 | 18798.9 | 19097.0 | 17674.4 |
| Standard deviation | 17.28 | 7.88 | 3.98 | 8.70 |
| Relative S.D. (%) | 4.88 | 11.65 | 28.80 | 18.45 |
| f-drift | - | 1.0027 | 1.0054 | - |
| Corrected peak area | - | 18849.8 | 19200.7 | - |
| certified mole fraction (pmol/mol) | 8.94 | - | 9.76 | 8.94 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | -0.81 |
| **Sample mole fraction** | **-** | **9.552** | - | - |
| **Sample uncertainty** | **-** | **0.025** | - | - |

| 2017.08.25 | CB10844 | D376117 | CB10909 | CB10844 |
|---|---|---|---|---|
| 1 | 17655.8 | 18610.6 | 18982 | 17597.7 |
| 2 | *17692.7 | 18644.9 | 18991.8 | 17587.4 |
| 3 | *17674.8 | 18632.2 | 18972.9 | 17560.2 |
| 4 | 17627.2 | 18650.5 | 18985 | 17583.5 |
| 5 | 17613.8 | 18658.9 | 18952.7 | 17578.7 |
| Response | 17632.3 | 18639.4 | 18976.9 | 17581.5 |
| Standard deviation | 17.28 | 7.88 | 3.98 | 8.70 |
| Relative S.D. (%) | 20.22 | 17.71 | 7.84 | 15.84 |
| f-drift | - | 1.0010 | 1.0019 | - |
| Corrected peak area | - | 18657.3 | 19013.4 | - |
| certified mole fraction (pmol/mol) | 8.94 | - | 9.76 | 8.94 |
| cylinder uncertainty | 0.01 | - | 0.02 | 0.01 |
| drift (%) | - | - | - | -0.29 |
| **Sample mole fraction** | **-** | **9.549** | - | - |
| **Sample uncertainty** | **-** | **0.027** | - | - |

5. Cylinder # D376142

| 2017.08.10 | CB10844 | D376117 | CB10909 | CB10844 |
|---|---|---|---|---|
| 1 | 18889.9 | 20312.8 | 23553.8 | *19087.8 |
| 2 | 18879.7 | 20306.8 | 23549.2 | 19044.6 |
| 3 | *18865.8 | 20276.2 | 23586.5 | 19015.5 |
| 4 | 18889.6 | *20264.7 | 23601.2 | 19044.1 |
| 5 | 18894.2 | *20329 | *23630.2 | *19086.7 |
| Response | 18888.4 | 20298.6 | 23572.7 | 19034.7 |
| Standard deviation | 17.28 | 7.88 | 3.98 | 8.70 |
| Relative S.D. (%) | 5.80 | 19.63 | 25.25 | 16.66 |
| f-drift | - | 0.9974 | 0.9949 | - |
| Corrected peak area | - | 20246.3 | 23451.5 | - |
| certified mole fraction (pmol/mol) | 9.76 | - | 12.06 | 9.76 |
| cylinder uncertainty | 0.02 | - | 0.02 | 0.02 |
| drift (%) | - | - | - | 0.77 |
| **Sample mole fraction** | **-** | **10.444** | - | - |
| **Sample uncertainty** | **-** | **0.024** | - | - |

| 2017.08.10 | CB10844 | D376117 | CB10909 | CB10844 |
|---|---|---|---|---|
| 1 | 19551.5 | 20865.8 | 24157.1 | 19344.8 |
| 2 | 19536.0 | 20859.7 | 24084.7 | 19317.6 |
| 3 | 19499.7 | 20880.8 | 24073.8 | 19328.8 |
| 4 | 19490.0 | 20871.3 | 24043.1 | 19297.6 |
| 5 | - | 20856.6 | 24038.5 | 19335.4 |
| Response | 19519.3 | 20866.8 | 24079.4 | 19324.8 |
| Standard deviation | 17.28 | 7.88 | 3.98 | 8.70 |
| Relative S.D. (%) | 29.20 | 8.96 | 48.28 | 19.84 |
| f-drift | - | 1.0033 | 1.0067 | - |
| Corrected peak area | - | 20936.4 | 24240.4 | - |
| certified mole fraction (pmol/mol) | 9.76 | - | 12.06 | 9.76 |
| cylinder uncertainty | 0.02 | - | 0.02 | 0.02 |
| drift (%) | - | - | - | -1.0 |
| **Sample mole fraction** | **-** | **10.450** | - | - |
| **Sample uncertainty** | **-** | **0.028** | - | - |

| 2017.08.10 | CB10844 | D376117 | CB10909 | CB10844 |
|---|---|---|---|---|
| 1 | 19344.8 | 20710.4 | 23862.0 | 19222.1 |
| 2 | 19317.6 | 20674.7 | 23910.9 | 19238.2 |
| 3 | 19328.8 | 20674.7 | 23875.0 | 19203.5 |
| 4 | 19297.6 | 20648.7 | 23842.0 | - |
| 5 | 19335.4 | 20624.7 | 23846.2 | - |
| Response | 19324.8 | 20666.6 | 23867.2 | 19221.3 |
| Standard deviation | 17.28 | 7.88 | 3.98 | 8.70 |
| Relative S.D. (%) | 19.84 | 25.34 | 28.99 | 17.37 |
| f-drift | - | 1.0018 | 1.0036 | - |
| Corrected peak area | - | 20703.6 | 23952.8 | - |
| certified mole fraction (pmol/mol) | 9.76 | - | 12.06 | 9.76 |
| cylinder uncertainty | 0.02 | - | 0.02 | 0.02 |
| drift (%) | - | - | - | -0.54 |
| **Sample mole fraction** | **-** | **10.445** | - | - |
| **Sample uncertainty** | **-** | **0.027** | - | - |

5. Final analysis

| **D376120** | | | **D376125** | | |
|---|---|---|---|---|---|
| Mean | Uncer. | RDS(%) | Mean | Uncer. | RDS(%) |
| 6.899 | 0.012 | 0.175 | 7.389 | 0.022 | 0.291 |
| 6.898 | 0.014 | 0.204 | 7.385 | 0.021 | 0.291 |
| 6.891 | 0.013 | 0.192 | 7.381 | 0.020 | 0.271 |
| | | | 7.381 | 0.024 | 0.321 |
| **6.896** | **0.013** | | **7.384** | **0.024** | |
| **D376140** | | | **D376125** | | |
| Mean | Uncer. | RDS(%) | Mean | Uncer. | RDS(%) |
| 8.333 | 0.019 | 0.229 | 9.553 | 0.025 | 0.259 |
| 8.336 | 0.020 | 0.236 | 9.552 | 0.025 | 0.257 |
| 8.330 | 0.016 | 0.192 | 9.549 | 0.027 | 0.281 |
| **8.333** | **0.020** | | **9.551** | **0.027** | |
| **D376142** | | | | | |
| Mean | Uncer. | RDS(%) | | | |
| 10.444 | 0.024 | 0.233 | | | |
| 10.445 | 0.028 | 0.264 | | | |
| 10.445 | 0.027 | 0.263 | | | |
| **10.445** | **0.028** | | | | |

Here total uncertainty was decided by quadrature sum of greatest uncertainty and standard deviations of mean value in a set. A set was defined as one cylinder analysis.