


Analysis of Sulfur Hexafluoride in Air

GMD Technical Procedure

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1. Purpose

This document provides the technical procedures for the analysis of sulfur hexafluoride (SF₆) in air by gas chromatography with electron capture detection. Sulfur hexafluoride amount of substance is expressed as dry air mole fraction, and is traceable to the SI unit amount of substance fraction.

2. Scope

NOAA/ESRL/GMD provides compressed gas standards (reference materials) to the WMO/GAW community. Natural air or modified natural air standards (tertiary standards) are analyzed for SF₆. Sulfur hexafluoride dry air mole fractions are determined by gas chromatography with electron capture detection, relative to the WMO SF₆ calibration scale. The WMO SF₆ mole fraction scale is derived from gravimetrically-prepared primary standards (see TP_XXXX.doc). The procedures described here only pertain to SF₆ analysis for which a certificate of analysis is issued.

3. References

Hall, B.D., G.S. Dutton, and J.W. Elkins (2007), The NOAA nitrous oxide standard scale for atmospheric observations, *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006JD007954.

Hall, B.D., G.S. Dutton, D.J. Mondeel, J. D. Nance, M. Rigby, J.H. Butler¹, F.L. Moore, D.F. Hurst, and J.W. Elkins (2011), Improving measurements of SF₆ for the study of atmospheric transport and emissions, *Atmos. Meas. Tech. Discuss.*, 4, 4131-4163.

JCGM (2008), International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200:2008.

Salameh, P.K., Scripps Institution of Oceanography, Unix-based Integrator and Chromatographic Database, personal communication, 1997.

4. Terms and Definitions

analysis system: Includes the gas chromatograph, hardware, and computer used to analyze SF₆ in compressed gas cylinders (synonymous with measuring system).

gas standard: A cylinder of compressed gas with mole fractions assigned by metrological methods or by comparison to higher-level standards, used to characterize the response of an instrument for calibration or quality control purposes. For the purposes of this TP, primary, secondary, and tertiary standards are gas standards.

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mole fraction: The ratio of the number of moles of analyte to the total number of moles. Dry air mole fraction is the ratio of the number of moles of analyte to the total number of moles in dry air. Within the scope of this TP, all samples are analyzed for dry air mole fraction.

primary standard: A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention.

reference cylinder: Cylinder of dry air designated for the calibration of other standards for quantities of the same kind. The instrument response curve is often determined from instrument response relative to the reference cylinder. The reference cylinder is also used to track instrument drift on short time scales.

regulator: A device used to reduce the pressure in a gas cylinder (input) to a lower pressure (output). High-purity and Ultra-high purity regulators are used.

response curve: A function that relates the instrument response to amount of substance (mole fraction).

secondary standard: A standard whose value is determined through analysis relative to primary standards, for a quantity of the same kind. These standards are used to calibrate the instrument response. Use of secondary standards for routine calibration prolongs the life of primary standards. For SF₆, values for secondary standards may also be assigned by comparison to other secondary standards, with verification performed by comparison to primaries.

target tank: A tertiary standard used for routine monitoring of system performance. The system should be capable of reproducing the assigned value of the target tank (within expected uncertainties).

tertiary standard: A standard whose value is determined through analysis relative to secondary standards, for a quantity of the same kind.

WMO/GAW: World Meteorological Organization, Global Atmosphere Watch.

5. Procedures

5.1 Gas Handling

Cylinders to be analyzed are stored in a common location and moved to the SF₆ analysis room when needed. Prior to analysis, a regulator is attached. Several regulators models are used. For

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SF₆, regulator purity is generally not an issue although high purity or ultra-high purity are preferred to preserve the integrity of other trace gases that might be compromised with sub-standard regulators. Upon connecting the regulator, the residual gas in the regulator is purged (flushed) with air from the cylinder. It is left to the analyst to determine the amount of flushing and condition time required, as it depends on the history of the regulator and the mole fraction of the gas being analyzed. The cylinder to be analyzed is connected to one of the analysis ports on the analysis system. The flow rate should be set to ~100 mL min⁻¹. The flow rate of the reference cylinder should also be set to ~100 mL min⁻¹.

A small amount of drying agent, Mg(ClO₄)₂, is typically used in the sample line. Gas from both the reference cylinder and sample cylinder are passed through the drying agent. The drying agent should be inspected after analysis of a series of moist air samples, and replaced as necessary. The drying agent will be exhausted after about 20 moist samples (80%-90% relative humidity).

5.2 Analysis System

The sulfur hexafluoride analysis system is described in Hall et al. (2007) and Hall et al. (2011). Briefly, gas samples are loaded into a fixed-volume, stainless steel sample loop by flushing the loop, and then injected onto a series of packed columns using a multi-port valve. N₂O and SF₆ are separated from other compounds and detected in the electron capture detector. To improve SF₆ results, we moved from a 2-column system to a 3-column system in 2006 (Hall et al., 2011).

The cylinder to be analyzed is compared to a reference cylinder in an alternating, A-B-A-B-A..., manner. The reference cylinder consists of natural air at continental background mole fraction SF₆. A computer program controls the stream selection valve, the gas sample valve, and stores the data from the detector (via the electrometer). The operating conditions should not be changed without just cause. The SF₆ results are sensitive to ECD temperature, flow rate, and quality of the carrier gas. The performance of the system should be verified following major changes.

Each unknown should be analyzed against the reference cylinder on at least two occasions (3 is preferred). Each analysis episode should consist of at least 6 injections. The analyst should compare the results from the two independent runs. If the results disagree by more than the typical reproducibility (see section 6.2) a third run should be performed.

5.3 Quality Control

It is critical that assignments made using the analytical system are reproducible. For a sample mole fraction that does not change with time, the system must be capable of reproducing the assigned value (within uncertainties) over the long term.

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The experienced analyst can easily determine when the system is performing normally. Indicators of performance include, but are not limited to, the SF₆ response of the reference cylinder, day-to-day variability of the baseline, repeatability of 6-10 repeat injections, peak shape, baseline noise, and response curve shape, residuals, and stability. Typically, the response curve is determined every 1-2 months by comparing the reference cylinder to five secondary standards. Experience has shown that it is not necessary to analyze secondary standards more often than this. However, it is up to the technical lead to determine if this frequency is sufficient to define the response curve within the expected uncertainties. In addition, one or more target tanks are analyzed every few weeks. Target tanks are a key indicator of system performance (assuming long-term changes in mole fraction due to drift are known). Additionally, cylinders with known SF₆ (previously analyzed on the system) can also be used to assess performance.

6.0 Calculations

6.1 Mole Fraction

The amount of SF₆ is determined by comparing the peak height (or peak area) of the unknown sample to that of the reference cylinder. Peak height and peak area are determined using custom-built integration software (gcwerks.com; Salameh, 1997).

The ratio of peak height or peak area between the unknown and the reference cylinder is the key variable used to calculate mole fraction. A response curve $R = f(C)$, is determined from analysis of the secondary standards, where C is dry air mole fraction and R is the peak area or peak height ratio. The functional form is quadratic:

$$R = a_2C^2 + a_1C + a_0 \quad (1)$$

Equation (1) is solved for C with R determined from analysis. The choice of peak area or peak height depends on peak shape, repeatability, and integration parameters. Peak height is generally preferred since the SF₆ peak is symmetric and provides for better repeatability.. In either case, it is important that the method be consistent between analysis of secondary standards and unknowns. Any bias between using peak area or peak height should be noted.

The coefficients for the response function are determined using orthogonal distance regression, taking uncertainties (one standard deviation) of both independent and dependant variables into account. The mole fraction of an unknown is determined from the response curve (1) and the peak height ratio, R , determined for the unknown.

The current WMO SF₆ scale, named X2014, was developed in 2014 and transferred to a set of secondary standards that year. The previous scale (X2006) was developed based on a linear response function. We then learned that a quadratic function was more appropriate, especially

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when the SF₆ mole fraction in the unknown was more than about 20% larger than that of the reference gas. A scale update from X2006 to X2014 was implemented in September 2014.

6.2 Uncertainties

Two estimates of uncertainty are reported for each sample. The first is the expanded uncertainty associated with the value assignment (see TP_primary_gravimetry.docx). The second quantity reported is the long-term reproducibility of the system based on repeated analysis of multiple cylinders (95%ile) (see 10.3). The objective is to report an uncertainty that can be used to assess possible drift in cylinders over time scales of typical use, and to assess the role of reference materials on inter-laboratory compatibility. Cylinders distributed to WMO/GAW laboratories are often returned to GMD 3-5 years after initial calibration. The expanded uncertainty of the WMO/GAW calibration scale, based on uncertainties associated with gravimetric standards and scale transfer, is not useful for assessing possible drift or inter-laboratory compatibility among laboratories on a common scale. For the purposes of SF₆ analysis within the WMO/GAW community, reproducibility is the key quantity.

Current estimates of expanded uncertainty and reproducibility (~95% confidence level), for SF₆ in the ambient mole fractions range (~9 pmol mol⁻¹), are 0.07 pmol mol⁻¹ and 0.03 pmol mol⁻¹, respectively.

7.0 Data Collection and Storage

Data are stored in both raw format (raw chromatograms) and in several higher processed forms (integrated peak areas and heights and response ratios) to facilitate efficient data processing and quality control. Data are stored on two computer systems: the analysis system computer and the data processing computer. Both the processing computer and the analysis system computer are backed up regularly.

Mole fractions assigned to secondary standards are stored in a MySQL database, and retrieved by the processing program. For final processing, data stored as peak height and peak area ratios are stored in a single master file, which can be re-processed easily. Updates to the response curve can be handled with ease. In the unlikely event that raw chromatograms require re-integration, this can be done on a case-by-case basis.

Final sample mole fraction assignments are stored on the processing computer (backed up daily) and uploaded to a web server through which assigned values can be accessed by users according to cylinder serial number.

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8.0 Safety

It is NOAA policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized cylinders should be secured (except when they are being weighed). Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high noise environment.

9.0 Documentation

Notes pertaining to cylinder analysis are recorded in a notebook dedicated to the analysis system. For each analysis, the cylinder number, date, and time of analysis should be recorded, along with any variables likely to affect the result. It is left to the analyst to determine which, if any, additional data should be recorded.

Significant notes relating to the performance and maintenance of the analytical system should be recorded using ELOG (an electronic record system).

10.0 Appendix

10.1 Equipment

The following equipment is critical to the functions described in this TP.

Item	Manufacturer	Model Number
Gas Chromatograph	Agilent Technologies	6890
Computer	Dell	
Electron Capture Detector	Agilent Technologies	G1533A
Valves	Valco	EC12WE, ECSD10MWE
Packed Columns	Alltech (custom length)	porapak Q, molecular sieve 5A
Temperature Controller	Omega	CN76000

10.2 Reproducibility

Reproducibility is estimated from repeated analysis tertiary standards. For example, three cylinders have been analyzed numerous times from 2005-2011 under similar measurement conditions, but relative to different reference cylinders and two different sets of secondary standards. Nearly all data are within 0.03 ppt of the assigned value.

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From analysis of 149 measurement pairs between April 2010 and September 2014, the 95TH percentile of absolute SF₆ differences is 0.025 ppt. Thus, we estimate the SF₆ reproducibility as 0.03 ppt.

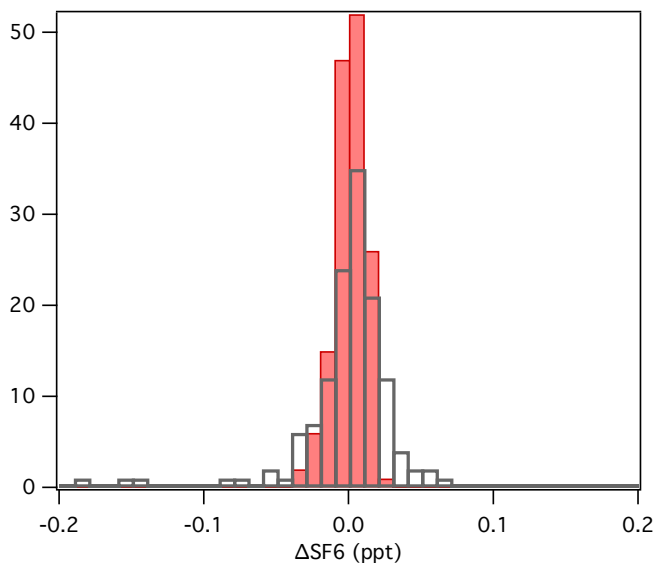
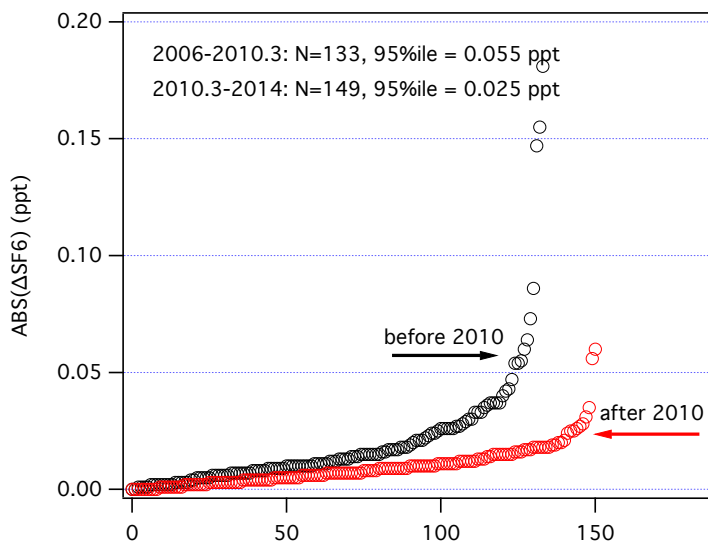


Figure A1: Histogram plot of differences between initial and subsequent SF₆ measurements (occurring several months to 8 years apart) for the periods 2006-2010.3 (gray), and 2010.3-2014 (red).



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Figure A2: Distribution of absolute differences between initial and subsequent SF₆ measurements (occurring several months to 8 years apart) for the periods 2006-2010.3 (gray), and 2010.3-2014 (red).

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