

Supporting information

Gravimetric standard gas mixtures for global monitoring of atmospheric SF₆

Jeong Sik Lim^{*,†‡}, Jinbok Lee[†], Dongmin Moon[†], Jin Seog Kim^{†‡}, Jeongsoon Lee^{*,†‡}

[†] Center for Gas Analysis, Korea Research Institute of Standard and Science (KRISS),
Gajeong-ro 267, Yuseong-gu, Daejeon 34113, Republic of Korea

[‡] Science of Measurement, Korea University of Science and Technology (UST)
Gajeong-ro 217, Yuseong-gu, Daejeon 34113, Republic of Korea

Bradley D. Hall

Global Monitoring Division, National Oceanic and Atmospheric Administration,
325 Broadway, Boulder, CO 80305

ST1. Gas analyzers

Purity assessments were performed according to ISO/CD 19229.^[21] Each gaseous species was quantitatively and qualitatively analyzed by gas chromatography (GC). A gas chromatograph (6890N, Agilent, USA) was coupled to an atomic emission detector (AED, G2350A, Agilent, USA) for the detection of carbon dioxide, total hydrocarbons, halocompounds, N₂, SO₂, and the sulfur-containing compounds SF₄ and S₂F₁₀, which are typical byproducts of the SF₆ synthetic process. A pulsed discharge ionization detector (PDD, Valco 2D, USA) was used to detect trace amounts of permanent gases such as H₂, O₂, Ar, CH₄, and CO₂. For these system, capillary columns are used. To perform measurements of SF₆ in pmol/mol level, micro electron capture detector (μ ECD, Agilent, USA) with P-5 carrier gas (5% CH₄ in Ar, Deokyang Energen Co., Korea) was used. An Activated Alumina F1 (AA-F1, 80/100 mesh, 6 m \times 1/8 inch) or Porapak Q (PP-Q, 80/100 mesh, 6 m \times 1/8 inch) columns separated O₂ and SF₆. A reduction of the dead volume along the sample injection gas line was accomplished by removing the liner from the inlet of the GC- μ ECD and using gauge-less regulators. This process might be necessary for flushing the gas line and eventually calming the instrument into a low-drift condition within a short period of time. Carrier gas was passed through an auxiliary electronic pressure controller to maintain the stability of the gas flows. A dew point meter with a chilled mirror (DP-30, MBW Calibration, Switzerland) was used to measure the water vapor concentration. All the instruments employed were calibrated against KRISS traceable standard gas mixtures. A mass flow controller (MFC, 5850E, Brooks, USA), which restricts the tolerance of the flow rate as gas samples are introduced, was adapted along the sample injection lines in order to keep the injected amounts of sample gases constant. In the event that the compositions of matrices of the standard and testing gases were different, the potential bias in the loading amount controlled by the MFC was compensated by a calibrated mass flow meter. A column that produced a symmetric peak shape was selected in order to facilitate peak integration, and the resolution of the resulting chromatograms was sufficiently optimized to eliminate any interference effect. For conducting verification tests of the attempted gravimetry process, a thermal conductivity detector (TCD, Agilent, USA) and a micro-electron capture detector (μ ECD, Agilent, USA) were used with the gas chromatograph. For trace level analysis, a flow restrictor attached at the vent of the sample loop provided a pressurized injection of sample, enhancing the detection response and improving the signal to noise ratio, leading to better analytical precision compared to a bare sample loop. A Fourier transform infrared spectrometer (FTIR, IG-2000, Otsuka, Japan) was also used in the continuous flow mode. In all cases, the analyzer responses were determined by integrating the area under the SF₆ peak on the chromatograms or spectra. Therefore, instrumental parameters affecting peak shape, oven temperature, carrier gas flow rate (for GC), and gas cell temperature (for FTIR) were carefully controlled to yield the best possible analytical precision.

ST2. Preconcentrator for LOD enhancement of GC- μ ECD

The preconcentration system contained an adsorption trap with Carboxen 1000, a coolant compressor, an electric heater, a 6-port valve, and the associated controllers. A total of three valves in the analytical system controlled the gas stream route, as presented in Figure S1. The cryogenic adsorption trap was packed with about 5 g of the Carboxen 1000 (40–60 mesh, Supelco, USA) in a 1/8 inch OD stainless steel tube, and both ends of

the tube were filled with glass fiber wool. The adsorbent was activated by heating at 250 °C under a constant flow of He for 2 h before use. Ultra-pure He (99.9999%, Deokyang Energen Co., Korea) was used to purge the gas plumbing and the cold trap. The coolant compressor provided a consistent cryogenic state around -80 °C. At this temperature, most of the matrix elements, including N₂, O₂, and Ar, passed through the adsorption trap. Analytes were introduced to the GC- μ ECD coupled with a preconcentrator at identical gas flow rates as controlled by the MFC, which was set at 0.1 L/min. During the desorption step, the trapped gases were released at 200 °C by ramping the temperature at a rate of 15 °C/s. In order to focus the analyte stream, the desorption step was performed in a closed trap. The GC analyte injection was automatically triggered by the signal generated by the preconcentration system after 10 s of releasing the analytes.

ST3. Automatic weighing system

A comparator balance (Mettler-Toledo XP26003L, Switzerland) with a 15 kg maximum capacity and a 1 mg minimum readability was used for weighing the target gases. A position-controlled turntable and customized weighing pan were attached to the comparator balance for tight control of the loading position. Cylinders were automatically and sequentially loaded onto the exact same spot on the weighing pan, as monitored by position sensors; this careful automation led to an extremely low weighing uncertainty. The automatic weighing system was enclosed in a transparent chamber to block air turbulence, which can cause less precise measurements. Though the weighing procedure was performed under well-controlled laboratory conditions maintained by a central HVAC system, the slow variation of ambient pressure can lead to a buoyancy fluctuation, causing drift in the comparator balance. By using a tare cylinder, this instrumental drift could be effectively corrected by the following procedure. A tare cylinder and the target cylinder, which would be filled with the gas mixtures, were sequentially measured to give the mass difference, Δm_e . The mass difference between the tare cylinder and the gas-filled target cylinders were then measured to give Δm_f . Consequently, the mass of the filled gas was equal to $\Delta m_f - \Delta m_e$. In this way, the measurement drift due to the buoyancy variation caused by the surroundings was properly compensated. The mass of the gases being weighed, up to 1 kg, could be measured with a total gravimetric uncertainty of ~3–4 mg (2σ), considering the instrumental precision, the loading point of the cylinders, and various experimental factors including cylinder handling. The uncertainty budget of the gravimetry attempted in this study is tabulated in Table S1 of the Supporting Information. Even though the buoyancy drift was corrected, the highest uncertainty contribution originated from the buoyancy effect of the cylinders and calibration weight.

ST4. NOAA primary standard

NOAA primary standards were prepared by static dilution. An aliquot of 99.99% SF₆ was diluted with synthetic zero-grade air to create level-1 primary standards (μ mol/mol). Subsequent dilutions to nmol/mol and pmol/mol were performed also using zero-grade synthetic air as the dilution gas. Equation (S1) was used to calculate the mole fraction of SF₆ in the first step.

$$X_{SF_6} = \frac{Pf \frac{m_1}{MW_{SF_6}}}{Pf \frac{m_1}{MW_{SF_6}} + \frac{m_2}{MW_{air}}} \quad (S1)$$

where P is the mole fraction (or purity) of the SF₆ source material, f is the transfer efficiency, m₁ is the mass of the SF₆ aliquot, m₂ is the mass of dilution gas (air), and MW_{SF₆} and MW_{air} are molecular weights. The molecular weight of air was determined by measuring the oxygen fraction of the dilution gas using a Beckman E2 paramagnetic O₂ analyzer, relative to NIST SRM 2569a (20.863 +/- 0.021 % O₂ in N₂, k=2). The uncertainty in MW_{air} was determined using the NIST Metrology software for “R” (Guthrie et al., 2012). The Metrology software was also used to calculate the uncertainty for each primary standard and the uncertainty in the response function. Similar results are obtained using the NIST Uncertainty Machine (<https://uncertainty.nist.gov/>).

In the next step, we take an aliquot from a level-1 primary and dilute with zero-grade synthetic air (S2).

$$X_{SF_6} = \frac{M_{SF_6}}{M_{SF_6} + M_2 + M_3 + \dots} \quad (S2)$$

where M_i is the number of moles species *i*, determined from masses added, mole fractions, and molecular weights as in (1). In the third step (level-3) we use an aliquot from a level-2 primary, but also add N₂O from a ppm-level standard and pure CO₂ to better mimic natural air. The uncertainties associated with N₂O and CO₂ contribute very little to the SF₆ uncertainty. The CO₂ was analyzed by ECD and found to contain SF₆ at less than detectable amounts, and we since we add less than one gram of CO₂, we ignore this contribution in the SF₆ uncertainty budget.

The X2014 scale was defined based analysis of 17 primary standards by GC-ECD. We used a 2nd order polynomial fit to the ECD response, relative to a reference gas (natural air) at 8.29 pmol/mol. Table S8 show the prepared mole fractions, standard uncertainties, and mole fractions assigned based on the 2nd order polynomial. Because the scale is defined by the polynomial and assigned values, we use the regression to calculate the scale uncertainty. The curve fit coefficients were determined using weighted orthogonal distance regression (Igor Pro, Wavemetrics). Weight factors were determined from standard uncertainties listed in Table S8 and repeatability of the analysis. The fit coefficients are shown in Table S9, and correlation coefficients are shown in Table S10.

From the parameters in Tables S9 and S10, we estimate a standard uncertainty of 0.018 pmol/mol at 9 pmol/mol. We then add two additional components. Because the NOAA scale is transferred through analysis, we include the analytical reproducibility associated with the scale transfer, which was determined by repeat analysis of

many cylinders over 6 years (2010-2016). We estimate the reproducibility to be 0.02 pmol/mol at the 95% confidence level at 9 pmol/mol. However, the reproducibility is not constant for all mole fractions. It increases to ~0.03 pmol/mol at mole fractions outside the ambient range (factor of two or three relative to reference gas). We also consider the fact that SF₆ in the dilution gas, which is lower than our detection limit, cannot be treated as independent since some primary standards were prepared from the same source of dilution gas. We therefore include an additional 0.04/sqrt(3) pmol/mol uncertainty over the entire range.

Our final uncertainty estimate at nominal 9 pmol/mol = $\sqrt{0.018^2 + 0.010^2 + 0.023^2}$ = 0.0309 pmol/mol (k=1), or 0.062 pmol/mol (k=2). Expanded uncertainty as a function of mole fraction (2-20 pmol/mol) is shown in Figure S5.

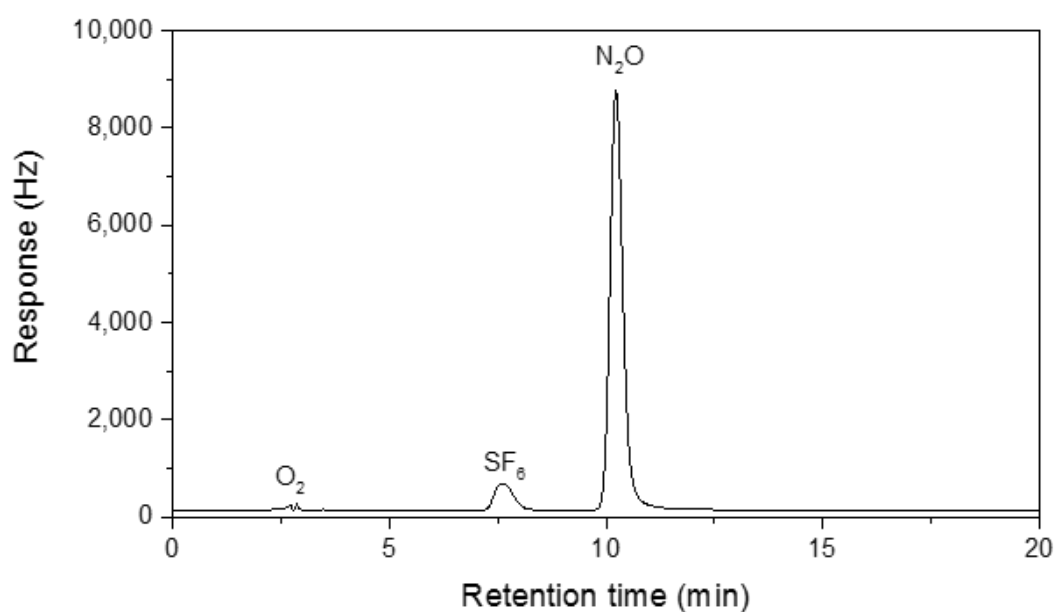
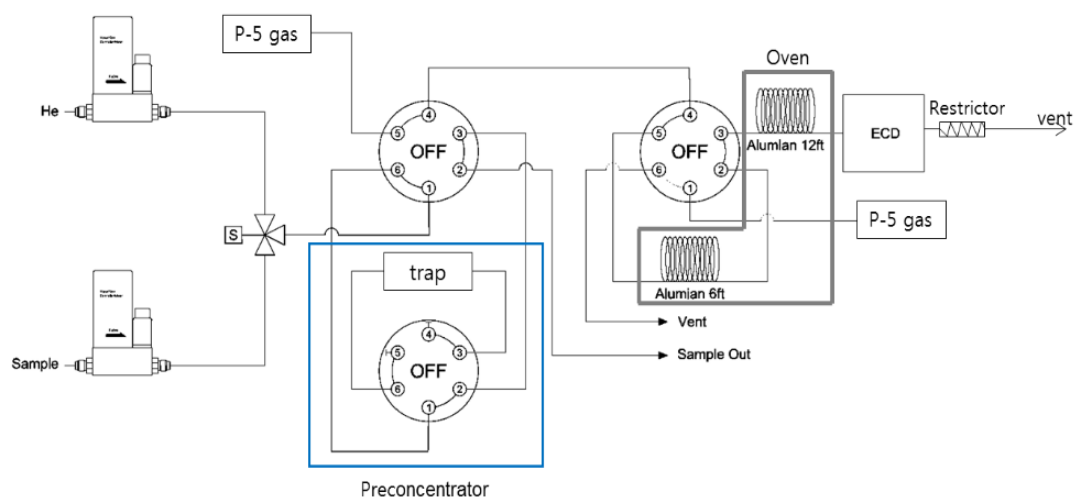


Figure S1. (Upper) Schematic diagram of GC-μECD coupled with preconcentrator. Only gas plumbing, including adsorption trap, valves, separation column and restrictors, is shown. (Lower) Chromatogram of dried air taken with a Carboxen 1000 (100 mg) cooled at $-50\text{ }^{\circ}\text{C}$ and a separation column filled with activated alumina F1 80/100 (18 ft \times 1/8 inch) maintained at $60\text{ }^{\circ}\text{C}$. Carrier gas is P5 (5% CH₂ in Ar), which constantly flows by EPC at 85 psi. He (99.999%) is used for flushing the adsorbent trap between sampling.

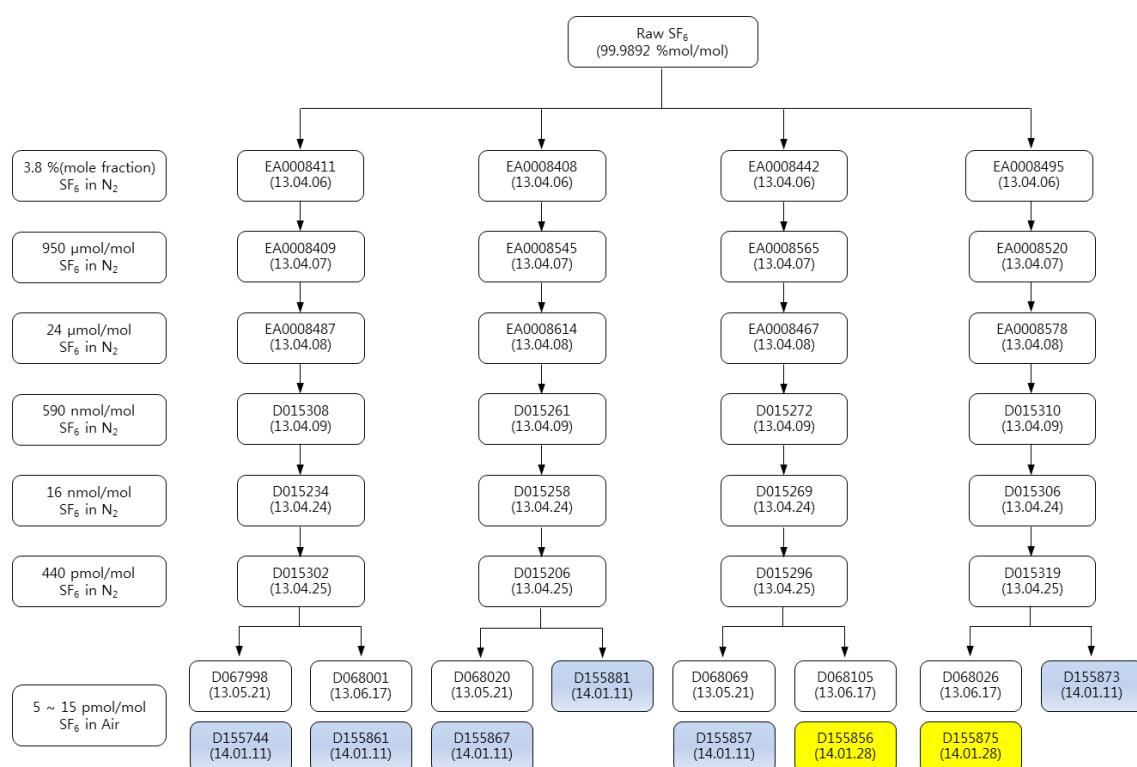
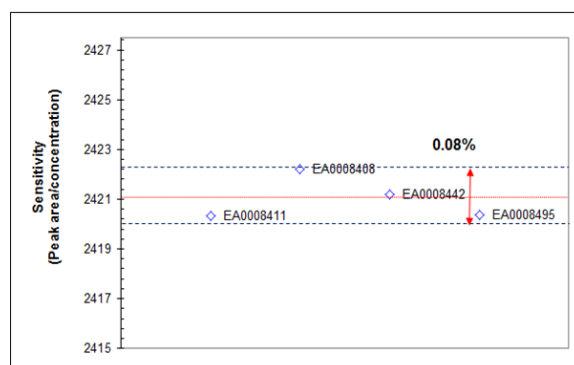
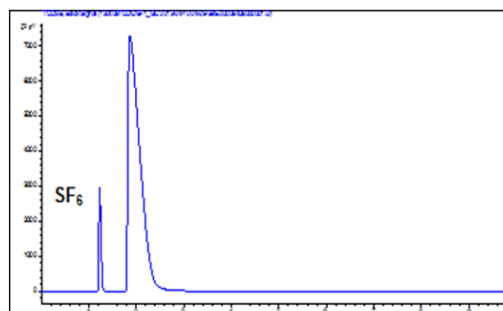


Figure S2. Gravimetric dilution hierarchy of suites of SF₆/air standard gas mixtures. The nominal mole fraction of SF₆ and matrix component at a respective step is given in the left-most boxes. Manufacturing dates are given in the parentheses below the cylinder IDs. In the final dilution step, the color code denotes families grouped by manufacturing dates.

Figure S3. Verification test results and analytical conditions for 1st–6th preparation steps. Analytical precisions are no more than 0.1% for each step.

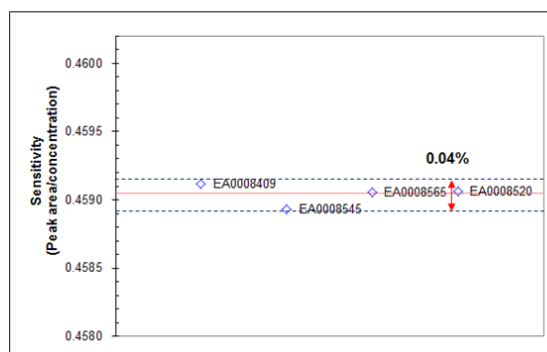
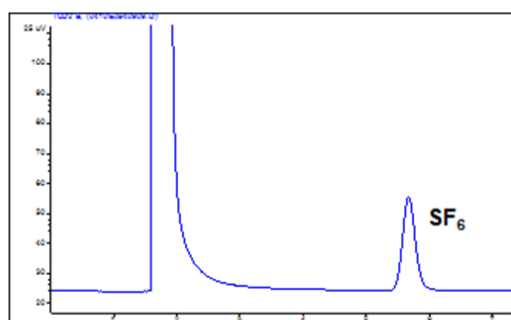
<1st step>

	Condition
Detector	TCD
Detector temp.	260 °C
Reference flow	55 mL/min
Oven temp.	120 °C
Column	Molesieve 5A 80/100 18ft(6m)*1/8 inch SUS
Sample loop	1 mL
Carrier flow	He, 30psi
Sample flow	100 mL/min



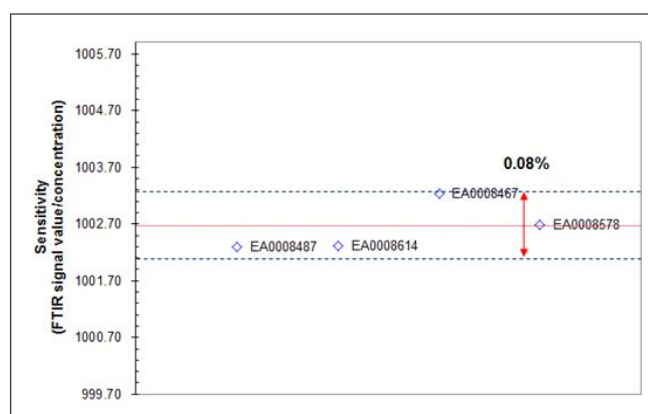
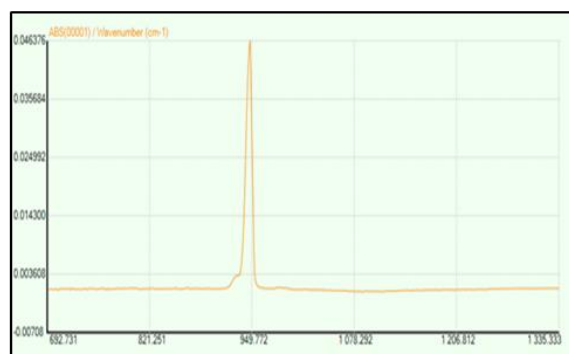
<2nd step>

	Condition
Detector	TCD
Detector temp.	250 °C
Reference flow	45 mL/min
Oven temp.	75 °C
Column	PP-Q 80/100 20ft* 1/8 inch SUS
Sample loop	1 mL
Carrier flow	He, 50psi
Sample flow	100 mL/min



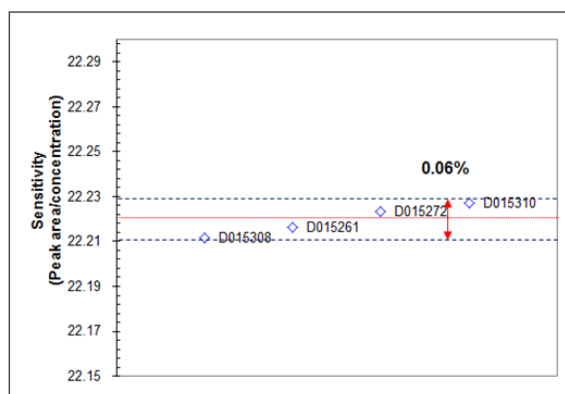
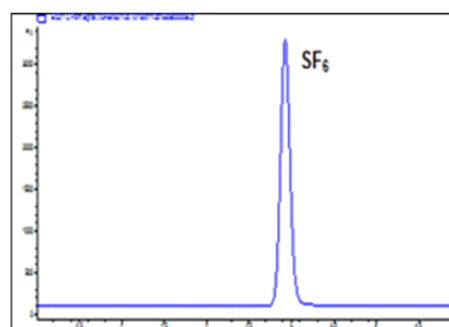
<3rd step>

	Condition
Detector	FTIR
Heater temp.	50.4 °C
Pressure	101.4 kPa
Cell temp.	42.1 °C
Sample flow	800 mL/min
Cell length	0.097 m
Scan	128



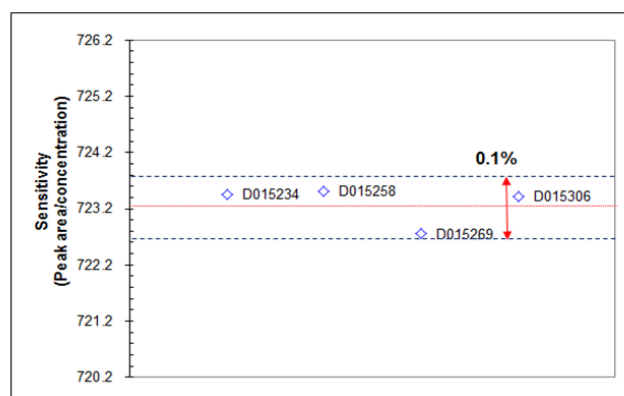
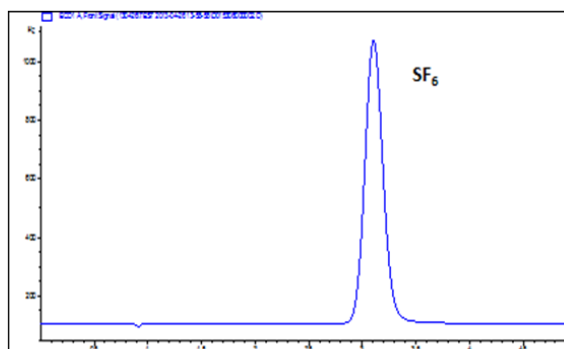
<4th step>

	Condition
Detector	GC-μECD
Detector temp.	375 °C
Make up gas	20 mL/min
Column	PP-Q 80/100 13 ft* 1/8 inch SUS
Oven temp.	80 °C
Carrier flow	P5, 29 psi
Sample loop	5 μL
Sample flow	100 mL/min



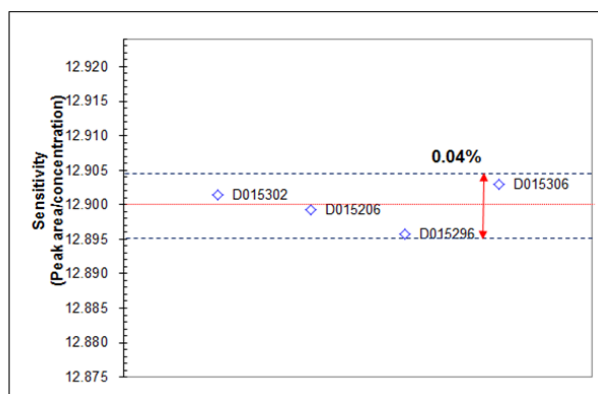
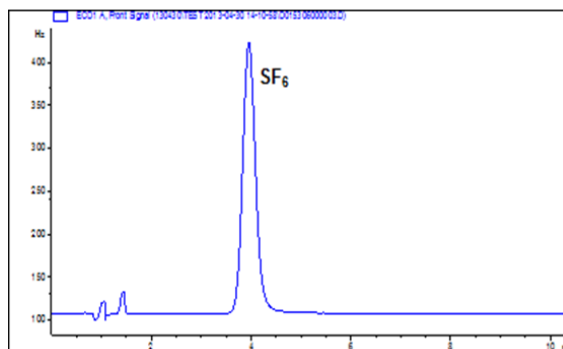
<5th step>

	Condition
Detector	μECD
Detector temp.	350 °C
Reference flow	20 mL/min
Oven temp.	80 °C
Column	PP-Q 80/100 13ft* 1/8 inch SUS
Sample loop	0.25 mL
Carrier flow	P-5, 50psi
Sample flow	100 mL/min



<6th step>

	Condition
Detector	μECD
Detector temp.	350 °C
Reference flow	20 mL/min
Oven temp.	65 °C
Column	PP-Q 80/100 13ft* 1/8 inch SUS
Sample loop	5 mL
Carrier flow	P-5, 50psi
Sample flow	150 mL/min



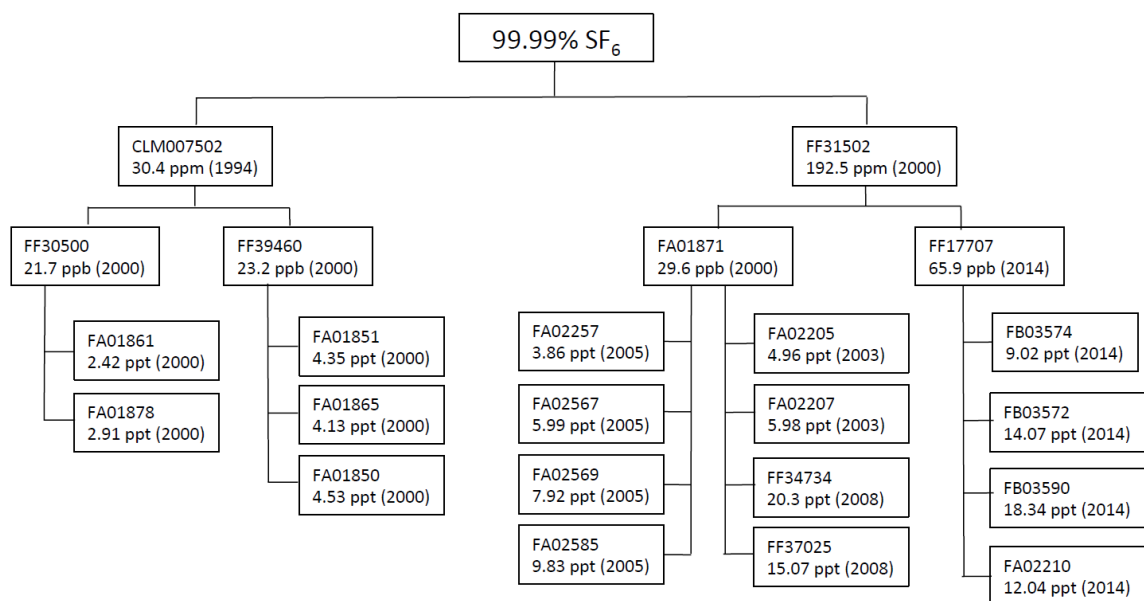


Figure S4. Hierarchy of NOAA primary standards (ppm = $\mu\text{mol/mol}$, ppb = nmol/mol , ppt = pmol/mol).

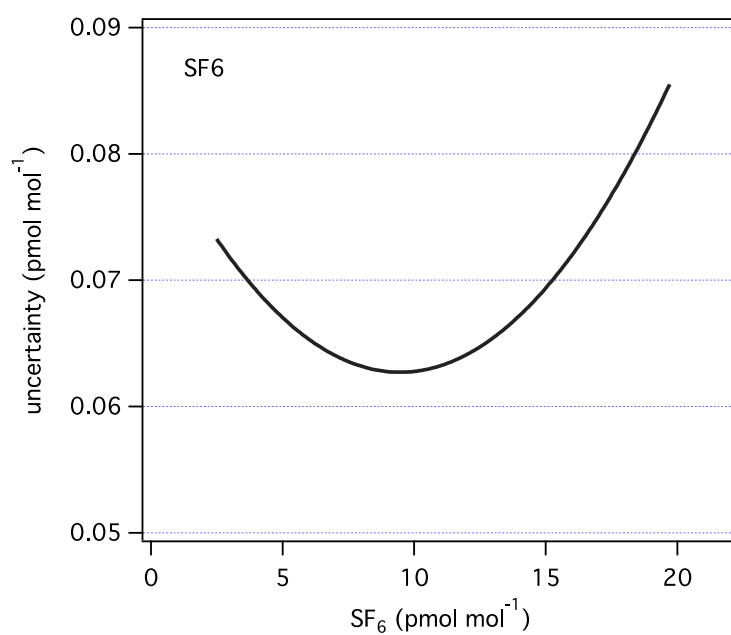


Figure S5. Expanded uncertainty for transfer of the NOAA X2014 scale, estimated as a function of mole fraction.

Table S1. Impurity assessment of SF₆ raw gas. Amount fraction of impurities and associated uncertainty are tabulated along with dedicated analyzers.

Component	Measured conc. (μmol/mol)	Detector	Distribution	Amount fraction (μmol/mol)	Standard uncertainty (μmol/mol)
H ₂	<0.02	GC-PDD	rectangular	0.01	0.006
O ₂ +Ar	0.56	GC-PDD	normal	0.56	0.056
N ₂	55.19	GC-AED	normal	55.19	5.52
CH ₄	1.94	GC-PDD	normal	1.94	0.194
CO	<0.03	GC-PDD	rectangular	0.02	0.009
CO ₂	2.47	GC-AED	normal	2.47	0.25
THC	<1.00	GC-AED	rectangular	0.50	0.289
H ₂ O	13	Dew point meter	normal	13	1.3
CF ₄	1.94	GC-AED	normal	1.94	0.194
C ₂ F ₆	31.98	GC-AED	normal	31.98	3.198
C ₃ F ₈	<1.00	GC-AED	rectangular	0.50	0.29
SO ₂	<0.005	GC-AED	rectangular	0.003	0.001
S compounds	<0.005	GC-AED	rectangular	0.03	0.001
Impurities				108.11	6.533
Purity of raw SF ₆ (% mol/mol)				99.9892	0.0013 (<i>k</i> =2)

Table S2. Uncertainty budget for the gravimetry. This table is valid only if the best performance was carried out. In case significant human error occurs during the weighing or handling of the gas cylinders, those errors are detected in verification measurements to be treated as outliers.

Uncertainty related to the balance & weights	Value (mg)	Distribution	Standard uncertainty (mg)
1. Resolution of balance	1	Rectangular	0.3
2. Accuracy of balance linearity	1	Rectangular	0.6
3. Incorrect zero point	1	Rectangular	0.3
4. Drifts (thermal and time effects)	1	Rectangular	0.3
5. Instability due to draught	Negligible		
6. Loading location of cylinder on the weighing pan	Negligible		
7. Uncertainty of the weights for calibration	0.05	Rectangular	0.03
8. Buoyancy effect on the calibration weight used	1.68	Rectangular	1.0
Sub total			1.3
Uncertainty related to the gas cylinder	Value (mg)	Distribution	Standard uncertainty (mg)
1. Loss or gain of metal sludge from cylinder surface and threads of valves	0.5	Rectangular	0.3
2. Loss or gain of dirt sitting on cylinder and valves	0.1	Rectangular	0.06
3. Adsorption or desorption effects on the external cylinder surface	0.1	Rectangular	0.06
4. Buoyancy of the cylinder			
4.1. Cylinder temperature differs from surrounding air due to e.g. gas fill	0.6	Rectangular	0.4
4.2 Variation of cylinder volume during gas fill	1.1	Rectangular	0.6
4.3 Change of density of surrounding air due to changes in temperature, air, pressure, humidity and composition	Negligible		
Sub total			0.8
Uncertainty related to the gas fill	Value (mg)	Distribution	Standard uncertainty (mg)
1. Residual gas in the evacuated cylinder	0.06	Rectangular	0.03
2. Gas leak during transfer			
2.1 Leakage of air into the cylinder after evacuation	1	Rectangular	0.3
2.2 Leakage of gas from cylinder into transport line	1	Rectangular	0.3
Sub total			0.4
Total			1.7

Table S3. Uncertainty budget of the mole fraction of SF₆ in the gravimetrically prepared standard gas mixture (D155875).

Quantity		Value	Standard Uncertainty	unit	Dist.	Sensitivity coefficient	Uncertainty Contribution* (pmol/mol)		Fractional contribution* (%)
Molecular mass	SF ₆	S	32.065	0.0025	g/mol	normal	0.062	1.50e-04	0.6
		F	18.9984032	0.00000025	g/mol	normal	0.37	9.20e-08	
	N ₂		28.0134	0.0002	g/mol	normal	0.5	5.00e-05	0
	O ₂		31.9988	0.0003	g/mol	normal	0.12	1.70e-05	0
	Ar		39.948	0.0005	g/mol	normal	0.0021	1.10e-06	0
Purity**	SF ₆ raw gas		0.99989189	0.00000699	mol/mol	normal	9.5e-05	3.3e-10	0
	N ₂ raw gas		0.9999995	0.0000303	mol/mol	normal	7.1	2.1e-04	0
	SF ₆ in N ₂		1.0	0.58	fmol/mol	rect.	7.8e+11	4.50e-04	5.4
	SF ₆ in Ar		1.0	0.58	fmol/mol	rect.	9.4e+09	5.4e-06	0
	SF ₆ in O ₂		1.0	0.58	fmol/mol	rect.	2.1e+11	1.2e-04	0.4
1 st step (dilution)1 0.1 13.1	δW**		0	0.00174	g	rect.	0.42	7.40e-05	0.1
	Added mass of SF ₆		139.64367	0.00178	g	normal	0.053	1.80e-05	
	Added mass of N ₂		680.13133	0.00178	g	normal	0.011	3.70e-06	
2 nd step (dilution)	δW		0	0.00174	g	rect.	0.42	7.20e-04	14.4
	Added mass of SF ₆ /N ₂		20.41667	0.00178	g	normal	0.44	1.50e-04	
	Added mass of N ₂		695.14867	0.00181	g	normal	0.013	4.20e-06	
3 rd step (dilution)	δW		0	0.00174	g	rect.	0.47	8.30e-04	18.6
	Added mass of SF ₆ /N ₂		18.02333	0.00178	g	normal	0.5	1.70e-04	
	Added mass of N ₂		691.68900	0.00181	g	normal	0.013	4.20e-06	
4 th step (dilution)	δW		0	0.00174	g	rect.	0.49	8.50e-04	19.8
	Added mass of SF ₆ /N ₂		17.49167	0.00178	g	normal	0	0	
	Added mass of N ₂		680.97433	0.00178	g	normal	0.51	1.70e-04	
5 th step (dilution)	δW		0	0.00174	g	rect.	0.45	7.80e-04	17.1
	Added mass of SF ₆ /N ₂		19.06967	0.00181	g	normal	0.47	1.60e-04	
	Added mass of N ₂		688.19767	0.00178	g	normal	0.46	1.50e-04	
6 th step (dilution)	δW		0	0.00174	g	rect.	0.42	7.30e-04	13.9
	Added mass of SF ₆ /N ₂		20.36800	0.00174	g	normal	0	0	
	Added mass of N ₂		720.03367	0.00178	g	normal	0.012	4.10e-06	
7 th step (mixing)	δW		0	0.00174	g	rect.	0.34	5.90e-04	9.6
	Added mass of SF ₆ /N ₂		24.56233	0.00178	g	normal	0	0	
	Added mass of N ₂		916.18967	0.00204	g	normal	0.0075	7.50e-06	
	Added mass of O ₂		283.26133	0.00178	g	normal	0.00093	3.10e-07	
	Added mass of Ar		16.12367	0.00178	g	normal	0.36	1.20e-04	

* Uncertainty contribution to the total uncertainty of the amount fraction of SF₆ in the final step, which is less than 1.0e-06 or 0.01%, is denoted as 0.

** Pre-evaluated gravimetric preparation uncertainty. Detailed budget is tabulated in Table S1 (Supporting information)

Table S4. Computed gravimetric fractions of SF₆ and the associated relative standard uncertainty in the intermediate steps.

<First step>

Cylinder No.	Mole fraction (cmol/mol)	Expanded uncertainty (cmol/mol)	Rel U ($k=2$) (%)
EA0008411	3.8309	0.00027	0.0071
EA0008408	3.7679	0.00027	0.0071
EA0008442	3.8016	0.00028	0.0074
EA0008495	3.7888	0.00027	0.0071

<Second step>

Cylinder No.	Mole fraction (μ mol/mol)	Expanded uncertainty (μ mol/mol)	Rel U ($k=2$) (%)
EA0008409	967.78	0.180	0.019
EA0008545	907.27	0.190	0.020
EA0008565	945.75	0.180	0.019
EA0008520	931.41	0.170	0.019

<Third step>

Cylinder No.	Mole fraction (μ mol/mol)	Expanded uncertainty (μ mol/mol)	Rel U ($k=2$) (%)
EA0008487	24.446	0.007	0.027
EA0008614	23.797	0.007	0.028
EA0008467	22.863	0.007	0.029
EA0008578	22.955	0.007	0.028

<Fourth step>

Cylinder No.	Mole fraction (nmol/mol)	Expanded uncertainty (nmol/mol)	Rel U ($k=2$) (%)
D015308	599.03	0.200	0.034
D015261	580.92	0.200	0.035
D015272	589.42	0.200	0.034
D015310	595.88	0.200	0.034

<Fifth step>

Cylinder No.	Mole fraction (nmol/mol)	Expanded uncertainty (nmol/mol)	Rel U ($k=2$) (%)
D015234	15.978	0.006	0.039
D015258	15.997	0.006	0.038
D015269	15.574	0.006	0.038
D015306	15.663	0.006	0.038

<Sixth step>

Cylinder No.	Mole fraction (pmol/mol)	Expanded uncertainty (pmol/mol)	Rel U ($k=2$) (%)
D015302	440.05	0.210	0.047
D015206	439.81	0.180	0.041
D015296	441.71	0.180	0.041
D015306	440.07	0.180	0.041

Table S5. Computed gravimetric mole fraction of SF₆ and associated standard uncertainty in the 7th step.

Cylinder ID	Mole fraction of SF ₆ (pmol/mol)	Standard uncertainty (<i>k</i> = 2, pmol/mol)	Relative standard uncertainty (<i>k</i> = 2, %)
D067998	5.511	0.0029	0.053
D068069	8.174	0.0036	0.045
D068020	11.949	0.0050	0.042
D068001	15.039	0.0070	0.046
D068105	8.154	0.0037	0.045
D068026	9.020	0.0040	0.044
D155744	5.476	0.0030	0.055
D155867	7.008	0.0032	0.046
D155857	8.167	0.0037	0.045
D155873	9.219	0.0040	0.0444
D155861	10.327	0.0051	0.049
D155881	11.841	0.0051	0.043
D155856	7.900	0.0036	0.045
D155875	9.001	0.0039	0.044

Table S6. Computed gravimetric fractions of O₂, N₂ and Ar and the associated standard uncertainty in the 7th step.

Cylinder ID	N ₂		O ₂		Ar	
	Mole fraction (cmol/mol)	Relative standard uncertainty ($k=2$, %)	Mole fraction (cmol/mol)	Relative standard uncertainty ($k=2$, %)	Mole fraction (cmol/mol)	Relative standard uncertainty ($k=2$, %)
D067998	78.1511	5.2e-3	20.8960	5.5e-3	0.95270	0.023
D068069	78.2665	5.2e-3	20.8005	5.6e-3	0.93277	0.023
D068020	78.3297	5.2e-3	20.7381	5.5e-3	0.93195	0.022
D068001	78.1934	5.3e-3	20.8981	5.5e-3	0.90826	0.023
D068105	78.2502	5.2e-3	20.8135	5.5e-3	0.93607	0.025
D068026	78.3634	5.2e-3	20.7208	5.5e-3	0.91558	0.024
D155744	78.0581	5.3e-3	21.0540	5.9e-3	0.88764	0.026
D155867	78.2425	5.2e-3	20.8194	5.5e-3	0.93791	0.022
D155857	78.3495	5.2e-3	20.7132	5.5e-3	0.93708	0.022
D155873	78.2665	5.2e-3	20.7783	5.5e-3	0.95497	0.022
D155861	78.1956	5.3e-3	20.8860	5.5e-3	0.91820	0.022
D155881	78.2311	5.3e-3	20.8408	5.5e-3	0.92786	0.023
D155856	78.2597	5.2e-3	20.8118	5.5e-3	0.92824	0.023
D155875	78.3932	5.2e-3	20.6644	5.5e-3	0.94219	0.022

Table S7. Variables associated with serial dilution of SF₆ to nominal 9 pmol/mol. These data correspond to primary standards FF31502 (192.5 pmol/mol), FF17707 (65.9 nmol/mol), and FB03574 (9.02 pmol/mol) shown in Figure 5. The right-most column shows the fractional contribution (%) to uncertainty for each step. Fractional contributions for some components are not shown as they are combined into other terms. The transfer efficiency, f, is ignored for level-2 and level-3 dilutions. Note that the level-3 dilution shown here was performed in 2014, and larger uncertainties were associated with dilutions made in prior years (see Table S8).

Quantity		Value	Standard uncertain ty	unit	Dist.	unc. (%)	Fractional Contribution to SF ₆ uncertainty(%)
Level 1							
MW _{SF6}		146.056	0.002	g/mol	Normal		1.4
	S	32.066	0.002	g/mol	Normal		
	F	18.9984	0.0001	g/mol	Normal		
MW _{air}		28.8464	0.0170	g/mol	Normal		60.2
amount	O ₂	20.902	0.059	%	Normal		
amount	N ₂	79.098	0.059	%	Normal		
molar mass	O ₂	15.9994	0.0001	g/mol	Normal		
molar mass	N ₂	28.0134	0.0001	g/mol	Normal		
f		0.999989	0.000007		Normal		0.7
P		0.9999	0.000058		Rect.		5.9
m ₁ (SF ₆)		0.6863	0.0002	g	Normal		29.8
m ₂ (dilution air)		703.990	0.014	g	Normal		2.0
X_{SF6}		192.478	0.128	μmol/mol		0.067	
Level 2							
P		192.478	0.128	μmol/mol	Normal		64.2
m ₁ (Level-1 aliquot)		0.20298	0.00007	g	Normal		32.5
m ₂ (dilution air)		591.980	0.017	g	Normal		3.3
MW _{m1_air}		28.8464	0.0170	g/mol	Normal		
MW _{m2_air}		28.8518	0.0170	g/mol	Normal		
X_{SF6}		65.936	0.046	nmol/mol	Normal	0.070	
Level 3							
P		65.936	0.046	nmol/mol	Normal		14.4
m ₁ (Level-2 aliquot)		0.10070	0.00006	g	Normal		8.1
MW _{m1_air}		28.8518	0.0170	g/mol	Normal		
m ₂ (dilution air)		735.6920	0.017	g	Normal		14.7
MW _{m2_air}		28.8549	0.0170	g/mol	Normal		
m ₃ (CO ₂)		0.4510	0.0002	g	Normal		<i>Negligible</i>
MW _{m3}		44.0096	0.0002	g/mol	Normal		<i>Negligible</i>
m ₄ (N ₂ O)		3.848E-4	2.2E-07	g	Normal		<i>Negligible</i>
MW _{m4}		44.013	0.001	g/mol	Normal		<i>Negligible</i>
X _{SF6_in_dilution_air}		0.0	0.023	pmol/mol	Rect.		62.8
X_{SF6}		9.019	0.025	pmol/mol	Normal	0.277	

Table S8. NOAA X2014 standards at pmol/mol level. Note that uncertainties have generally improved with time.

Cylinder	Year prepared	Prepared (pmol/mol)	Standard Unc. (pmol/mol)	Assigned (pmol/mol)	Residual (pmol/mol)
FA01861	2000	2.42	0.034	2.42	0.002
FA01878	2000	2.91	0.034	2.91	0.003
FA02557	2005	3.86	0.034	3.84	-0.017
FA01865	2000	4.13	0.035	4.14	0.014
FA01851	2000	4.32	0.051	4.35	0.028
FA01850	2000	4.53	0.035	4.52	-0.005
FA02205	2003	4.96	0.035	4.94	-0.018
FA02207	2003	5.98	0.021	6.00	0.021
FA02567	2005	5.99	0.036	6.00	0.008
FA02569	2005	7.92	0.024	7.91	-0.008
FB03574	2014	9.02	0.025	9.02	-0.002
FA02585	2005	9.83	0.039	9.81	-0.015
FA02210	2014	12.04	0.029	12.05	0.005
FB03572	2014	14.07	0.033	14.07	0.005
FF37025	2008	15.07	0.035	15.05	-0.019
FB03590	2014	18.34	0.040	18.35	0.006
FF34734	2008	20.32	0.045	20.31	-0.009

Table S9. Coefficients from the 2nd order polynomial fit used to define the SF₆ scale and assign mole fractions to the primary standards (Figure 5). These parameters correspond to the equation: $\text{response} = aX^2 + bX + c$, where X is the mole fraction of SF₆, and the reference gas has a response of 1.0.

Coefficient	Value	Std. uncertainty
a	-3.4251E-04	3.02E-05
b	1.2356E-01	6.45E-04
c	-7.2106-04	2.76E-03

Table S10. Correlation coefficients used in the uncertainty estimate.

	a	b	c
a	1	-0.9786	0.8671
b		1	-0.9357
c			1