Comparison of the Sulfur Dioxide Primary Standard Gases of NPL and KRISS

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Comparison of sulfur dioxide primary standard gases of the Korea Research Institute of Standards and Science (KRISS, Korea) and the National Physical Laboratory (NPL, UK) was performed. 100×10^{-6} mol/mol and $1,000 \times 10^{-6}$ mol/mol primary standard gases (designated NPL S115 and S114, respectively) prepared gravimetrically and validated in NPL were used as transfer standards. Transfer standards were analyzed by NDIR sulfur dioxide analyzer and compared with KRISS PSM 112-03-624 and PSM 112-03-625 prepared gravimetrically. Adsorption corrected relative deviations of the primary standard gases were agreed to within 0.1%, and this agreement is within the expanded uncertainties ($k = 2$) of the primary standards at the two laboratories.

Keywords : Sulfur dioxide, Primary standard gas, Gas analysis, Gravimetry.

Introduction

There are many kinds of air pollutants and their effects on human life are different from chemical species. In a urban area, CO, NO, SO_2, and ozone have been monitored as major gaseous pollutants, and SO_2 is one of main air pollutant which are monitored by several institutes.[1,2] SO_2 is a heavy, colorless, nonflammable, soluble gas with a penetrating odor, and a toxic substance that irritates the eyes and respiratory systems. Occurring sources of SO_2 in nature is volcanic gases and some warm springs, and SO_2 usually is prepared industrially by the burning in air or oxygen of sulfur or such compounds of sulfur as iron pyrite or copper pyrite. Large quantities of SO_2 are formed in the combustion of sulfur-containing fuels.[3,4] From the second half of the 20th century, concentration of SO_2 in air was become significant item to control atmospheric pollution.

Pararosaniline method, acidimetric method, conductivity method, flame photometric method, UV fluorescence method, and NDIR method has become used for SO_2 analysis.[5-7] Recently, NDIR analyser was widely used due to its higher sensitivity, lower detection limits, and the simplicity of measurement for gas samples. To accurate analysis, NDIR analyzer must be calibrated before measurement, and one use a certified reference materials (CRMs). Gas CRMs are produced and/or certified by national metrology institute. Korea Research Institute of Standards and Science (KRISS) in Korea. To certify SO_2 gas mixture as a gas CRM, we have developed primary standard materials prepared by gravimetry method. Because each National Metrology Institute (NMI) in the world can produce and certify its gas CRMs, it is possible to have different quality of CRMs. NMIs around the world that produce traceable gas standards prepare primary standards of gas concentration, which they retain in-house as their ultimate reference for gas measurements. These primary standards are generally known as primary standard materials or primary standard gas mixtures (PSMs).

Therefore, to get a consistency and reliability between CRMs, the mutual recognition for national measurement standards and for calibration and measurement certificates was issued by NMIs, and agreed in 1999 (Mutual Recognition Arrangement: MRA).[8] This bilateral comparison is one of the qualifying method to achieve MRA. Here, we report the results on the bilateral comparison with SO_2 PSMs produced by KRISS and NPL, respectively.

Experimental Section

Reagents and Instruments. 6.0 L aluminum cylinder (Luxfur, Australia) with fine-polished interior surface and stainless steel valve (Hamai, Japan) were used to prepare primary standard gases. High purity SO_2 (99.997%, Matheson, USA) and N_2 (99.9999%, Myung Sin General Gas Co., Korea) gases were used as received.

A high precision electronic balance (ID5, Mettler, Switzerland) with readability of 2 mg and capacity of 15 kg was used to weigh the amounts of the introduced gas in a cylinder. Balance was calibrated using OIML class E_2 weights before measurements.

Gas chromatograph (model 540, Trimetric Inc.) with ultrasonic detector (GC-USD) was used to analyze high concentration (about 1×10^{-2} mol/mol) SO_2 gas. Helium (99.999%, Deokyang Gas Corp., Korea) was used as a carrier and reference gas, and the flow rate of each gas was 25 mL/min. In order to inject sample gas precisely, mass flow controller (model 5258, Brooks) and 6-port gas sampling valve with 1.0 mL sample loop were used. In measurements, packed column (1.83 m, 80/100 mesh, 3.2 mm OD, Porapak N, Supelco) was used to separate sulfur dioxide from nitrogen with oven temperature 170 °C.

NDIR sulfur dioxide analyzer (Ultramat 6E, Siemens) in combination with a multimeter (model 2001, Keithley) was used to analyze low concentration (less than $1,000 \times 10^{-6}$ mol/mol) SO_2 gas, and the flow rate of sample gas was set to 1.2 L/min by mass flow controller.

Preparation of Primary Standard Gases. The primary

standard gases for comparison were prepared according to the ISO 6142[9] in KRISS. All cylinders were evacuated to 1×10^{-3} Pa and heated to 60 °C by heating tape to remove water from interior cylinder surface for two days. Weight measurement of the introduced gases was performed in the balance room where temperature and humidity were controlled at 20 ± 1 °C and $50 \pm 10\%$ R.H. Reference cylinder, like a sample cylinder, was used in weight measurements to compensate external variables such as the changes of the temperature, humidity and buoyancy. Reference and sample cylinders were weighed five times in turn. After weighing, the cylinder was rolled to mix the introduced gases to increase a homogeneity.

The history of PSM preparation and consistency test is shown in Figure 1. Four cylinders of SO_2 with the concentration of 1×10^{-2} mol/mol were prepared gravimetrically and analyzed to check their consistency with gravimetric concentration as follows. They were analyzed in series by GC-USD with four times at each cylinder, respectively. To correct instrumental drifts, first cylinder was re-analyzed. After consistency test, one cylinder was used as a mother cylinder to prepare daughter cylinder with low concentration SO_2. Daughter cylinder, 1.000×10^{-6} mol/mol, was prepared by gravimetrically according to ISO 6142 with high purity nitrogen gas, and consistency test was performed as above. Finally, the grand daughter cylinder, 100×10^{-6} mol/mol, was prepared with same process from daughter cylinder.

Adsorption Test. The adsorption of sulfur dioxide on the

interior surface of the aluminum cylinder was determined by equal-division method as following. One of the prepared PSM cylinders was connected to an evacuated cylinder. After evacuation of connecting line, valves of the two cylinder were opened until to reach an equal pressure in both cylinders. If sulfur dioxide was not adsorbed on the interior surface of the cylinder, the concentration of sulfur dioxide in the original and divided cylinders would be same. We applied this method for $1,000 \times 10^{-6}$ mol/mol and 100×10^{-6} mol/mol SO_2 PSMs to quantify the amount of adsorption.

Results and Discussion

Consistency Test of the Prepared Gases. Table 1 shows gravimetric concentration and results of consistency test. Four cylinders of SO_2 1×10^{-2} mol/mol were analyzed by GC-USD, and three cylinders of SO_2 1.000×10^{-6} mol/mol and two cylinders of 100×10^{-6} mol/mol were analyzed by NDIR analyzer. Generally, it is hard to confirm the concentration of primary standard gas prepared by gravimetric method, because there is no other absolute method. This is the reason for making several primary standard gases with similar concentration, and testing their consistency with analysis. In the consistency test, analytical sensitivities, which was the value of an instrumental response divided by gravimetric concentration, were compared each other to check non-intended mistakes of experimental procedures or miscalculation. In Table 1, the relative deviations between the analytical sensitivities of each primary standard gas within same concentration range are less than 0.2% which is smaller than analytical uncertainties except MD 1377 cylinder. The cylinder MD 1377 was mismatched with target concentration and has a larger analytical uncertainty than others. So, this results indicate that there was a mistake in preparation. The gravimetric concentration was adopted as certified value of the primary standard gases. In this study, MD 1368 and MD 2619 cylinders were used as KRISS PSM 112-03-625 and 112-03-624, respectively.
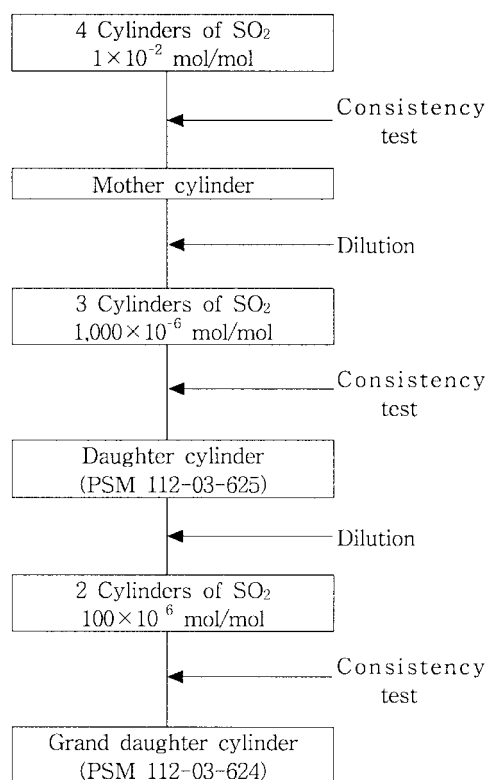

Figure 1. Flow sheet of the procedure preparing sulfur dioxide primary standard gases by gravimetric dilution and the consistency test.

Table 1. Results on the consistency test of primary standards prepared by gravimetry

Cylinder no.	Gravimetric concentration (μmol/mol)	Analytical sensitivity	Remarks
MD 2515	9683 ± 11^a	2085 ± 2.1^b	
MD 2523	9827 ± 6	2086 ± 2.1	
MD 2531	9621 ± 11	2088 ± 4.2	Mother cylinder
MD 2592	9613 ± 11	2086 ± 4.2	
MD 1368	1002.9 ± 1.2	16514 ± 3	Daughter cylinder
MD 1369	998.6 ± 1.2	16524 ± 2	
MD 2594	994.1 ± 1.3	16526 ± 5	
MD 1377	98.06 ± 0.12	996 ± 0.2	
MD 2606	100.02 ± 0.12	1001 ± 0.2	
MD 2619	100.14 ± 0.14	1001 ± 0.3	Grand daughter cylinder

[a]Expanded uncertainty where $k = 2$. [b]Standard deviation where the number of measurement was 4.

Table 2. Uncertainty budget of KRISS PSMs used in bilateral comparison

PSM no. (cylinder no.)	Gravimetric concentration (μmol/mol)	Standard uncertainty (μmol/mol)	Expanded uncertainty (μmol/mol)	Coverage factor	Degree of freedom
112-03-624 (MD 2619)	100.14	0.07	0.14	2	19
112-03-625 (MD 1368)	1002.9	0.6	1.2	2	13

Table 3. Changes of the relative analytical sensitivity of the 100 and $1,000 \times 10^{-6}$ mol/mol level sulfur dioxide gases on the adsorption test and adsorption ratio

	Relative analytical sensitivity[a]	
Original cylinder	100.00	1000.0
Divided cylinder	99.50	999.3
Adsorption ratio(%)	0.50	0.07

[a]Number of measurement was 6.

Table 4. Measurement results of the transfer standards using KRISS PSMs

Measurement no.[a]	NPL S114		NPL S115	
	Concentration (μmol/mol)	RSD (%)	Concentration (μmol/mol)	RSD (%)
1	1002.06	0.03	100.23	0.04
2	1001.98	0.04	100.23	0.03
3	1001.91	0.02	100.27	0.02

[a]Number of sub-measurement was 6.

Uncertainty Budgeting of PSMs.

The uncertainty[10-12] is expressed as an expanded uncertainty. $U = ku_c$. with u_c determined from experimental standard deviations and the coverage factor $k = 2$. Since the concentration values of gaseous PSMs are assumed to be normally distributed with an experimental standard deviation of u_c, the true value for the sulfur dioxide concentration is asserted to lie in the interval defined by the certified value $\pm U$ with a level of confidence of approximately 95%. Table 2 shows the uncertainty budget of SO_2 concentration of PSMs used in the bilateral comparison. These concentration values were calculated by gravimetric data and data sheets of the pure gases. Commercial software (GUM Workbench. Metrodata, Germany) was used to budget uncertainties. The purity data of sulfur dioxide and nitrogen gas was used in calculation. and standard uncertainty related to mass measurement was 8 mg. In this study, expanded uncertainties of the gravimetric preparation of the PSM 112-03-624 and PSM 112-03-625 were 0.14 and 1.2 μmol/mol. and relative expanded uncertainties was 0.14% and 0.12%. respectively.

Adsorption of Sulfur Dioxide on the Al Cylinder. Sulfur dioxide is well known to have adsorption ability to a metal surface and to have reaction with water molecules on the surface of cylinder. Table 3 shows the change of the relative analytical sensitivity between original and divided cylinders prepared by equal-division method. Effect of the adsorption on the concentration will be increase in a low concentration. In this study, the concentration of divided cylinder was compared with that of original cylinder by NDIR analyser for 1.000 and 100 μmol/mol, respectively. To compensate instrumental drift. first sample was re-analyzed. and each sample was measured six times consecutively. From this results. the relative adsorption amount were 0.5% in 100 μmol/mol and 0.07 % in 1,000 μmol/mol.

Comparison with Transfer Standard Gas. After receiving transfer standard cylinders from NPL, cylinders were stood

for one week at analytical laboratory before analysis. NDIR analyser was calibrated by KRISS PSM and high purity nitrogen gas. The sample gases were introduced into NDIR analyzer through mass-flow controller to inject a constant amount of sample gas. Measurements were done six times consecutively for the each samples to observe a repeatability. To compensate instrumental drift. we calibrated analyser with PSM during measurement. To observe a reproducibility, three set of measurements were done in same conditions. Measurement results were shown in Table 4. Relative standard deviations of repeatability and reproducibility was 0.02-0.04% and 0.01-0.02%. respectively.

Figure 2 shows the final results of bilateral comparison with NPL S114 and S115. Gravimetric value of the S114 and S115 received from NPL were 1000.6 ± 1.0 and 99.8 ± 0.5 μmol/mol. respectively. Analytical values of the transfer standards measured using KRISS PSM 112-03-625 and PSM 112-03-624 were 1002.0 ± 1.3 and 100.25 ± 0.14 μmol/mol. respectively. The relative standard deviations of the gravimetric and analytical values for NPL S114 and S115 were 0.14 and 0.45% without adsorption correction, respectively. However, after adsorption correction. two values are agreed within 0.1%.

Because the gravimetric value of NPL and the adsorption corrected value are agreed. we suppose that there was no adsorption of SO_2 in cylinders used by NPL. To minimize an
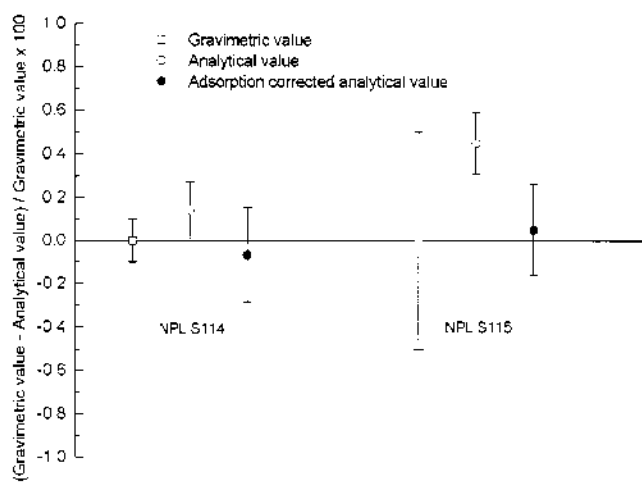

Figure 2. Comparison of the NPL S114 and S115 sulfur dioxide gases with KRISS PSMs. Error bar means the expanded uncertainties values where coverage factor $k = 2$.

Table 5. Results of the bilateral comparison of the NPL S114 and S115 transfer standards with KRISS PSM 112-03-624 and 112-03-625, respectively

Sample	Value	Concentration (μmol/mol)	Extended Uncertainty ($k = 2$)
NPL S114	Gravimetric[a]	1000.6	1.0
	Analytical[b]	1002.0	1.3
	Corrected[c]	1001.3	2.1
NPL S115	Gravimetric	99.8	0.5
	Analytical	100.25	0.14
	Corrected	99.75	0.22

[a]Received values from NPL. [b]Compared values with KRISS PSMs. [c]Adsorption corrected analytical value.

adsorption of reactive gases in cylinder, generally the soaking techniques with higher concentration of SO_2 are used. Possibly, they used this technique for manufacturing SO_2 primary standard gas. In our case, we do not use soaking techniques for manufacturing SO_2 primary standard gas, because we know how to quantify the amount of adsorption.

The expanded uncertainty reported by NPL, 0.1% and 0.5 % as relative uncertainties in Table 5, seems to be estimated by the priori experiences, because the relative uncertainty from gravimetry is usually less than 0.1%. Analytical uncertainties reported by KRISS are included the uncertainty from the gravimetry and measurements. Due to the uncertainty resulted from adsorption test, uncertainty of the adsorption corrected analytical value is about twice than that of the analytical value. However, the uncertainty reported by KRISS is much lower than that reported by NPL in 100 μmol/mol SO_2, because KRISS PSMs are considered the amount of adsorption and the uncertainty of comparison analysis is very low (less than 0.04%, see in Table 4).

In this study, the degree of adsorption on the interior surface of the cylinder could not compare directly, because aluminum cylinder maker and adsorption characteristics of the cylinder used by two institutes were different. However, SO_2 PSMs produced by two institutes are consistent and reliable within their claimed uncertainties.

Conclusion

The transfer standards containing sulfur dioxide, NPL S114 and S115, prepared and validated at NPL were compared with the KRISS PSM 112-03-625 and 112-03-624, respectively. To quantify the amount of adsorption, we applied equal-division method. It was observed that adsorption on the interior surface of the aluminum cylinder of the 100 and 1,000 μmol/mol level sulfur dioxide gas were 0.5 and 0.07 %, respectively. The relative standard deviations between the gravimetric values from NPL and the values measured by KRISS were less than 0.1% in the 100 and 1,000 μmol/mol level sulfur dioxide gases. In conclusion, we confirmed that SO_2 PSMs produced by two institutes were consistent and reliable within their claimed uncertainties.

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