

Development of nitrogen and oxygen certified reference materials in 10 $\mu\text{mol/mol}$ for the purity evaluation

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Abstract: We have developed 10 $\mu\text{mol/mol}$ nitrogen and oxygen certified reference materials (CRMs) in helium, as a SI-traceable gas standard for a quantifying of impurities in pure gases for the first time in Korea. The standard gas mixtures of nitrogen and oxygen were prepared in 5000 $\mu\text{mol/mol}$ and sequentially were diluted to 250 $\mu\text{mol/mol}$ and 10 $\mu\text{mol/mol}$ according to the gravimetric preparation. In each dilution step, two cylinders of CRMs were prepared. The verification of internal consistency among the prepared gas mixtures was performed by using GC-TCD. The amount fractions and those expanded uncertainties ($k=2$) of nitrogen and oxygen in the standard gas mixtures were (10.12 ± 0.08) $\mu\text{mol/mol}$ and (10.18 ± 0.08) $\mu\text{mol/mol}$ for nitrogen, and (9.88 ± 0.06) $\mu\text{mol/mol}$ and (9.94 ± 0.06) $\mu\text{mol/mol}$ for oxygen, respectively. We have conducted a purity assessment of two commercial helium gases using developed CRMs. As the results of the purity assessment, nitrogen and oxygen were detected by (1.66 ± 0.03) $\mu\text{mol/mol}$ and (0.31 ± 0.02) $\mu\text{mol/mol}$, respectively, as the impurities in one of the pure helium.

Key words: gas analysis, purity assessment, gas chromatography, thermal conductivity detector, certified reference material

1. Introduction

The atmosphere of Earth is comprised of nitrogen (~78 %), oxygen (~21 %), argon (~0.9 %), carbon dioxide (~0.03 %), and trace amount of other gases.¹ Therefore, nitrogen (N_2) and oxygen (O_2) are the main sources of contamination in the high-pressurized gas cylinders. The gases contaminated by air can cause various problems in many fields, such as the instruments, the analyses, and the industrial area.²⁻¹¹

Many devices installed in gas chromatography (GC) are susceptible to oxidation at elevated temperature, hence the carrier gases demand a very low oxygen impurity.¹⁰ Furthermore, the air contaminated carrier gases can degrade the analysis results, especially in the trace level analysis. The nitrogen impurity in noble gas can change the ionic composition of the noble gas plasma in gas discharge physics.⁷ Moreover, the gaseous impurities in high-purity nitrogen can negatively affect the manufacturing process in the

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electronics industry such as semiconductors and electronic displays.^{4-6,9,11} The impurities also make a change in the chemical compositions of gases in the cylinder. The oxygen impurity can oxidize a nitric oxide (NO) to nitrogen dioxide (NO_2), which is five to twenty-five times more toxic than the NO.³

To reduce and prevent the adverse effects of gas impurities, the purity assessment should properly be conducted. In the gas analysis field, the GC is the preferred tool for the purity analysis. A thermal conductivity detector (TCD) is used extensively in GC due to its lower cost than the pulsed discharge ionization detector (PDD) and discharge ionization detector (DID), but also the wider sample selectivity than flame ionization detector (FID). Nevertheless, the TCD has not been used for low concentration samples, since the detection limit is relatively poor which is known to be parts per thousand or hundred.¹² Thus, the GC-TCD should be modified to improve the detection limit when it is used for purity analysis.

The quality of analytical procedure and results is evaluated using a certified reference material (CRM). The definition of CRM is a reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a reference material certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.¹³ The CRMs are employed in chemical analysis as the standards to validate the reliability and accuracy of

analytical measurement.¹⁴⁻¹⁶ Due to the important role of CRM in many research fields, the National Metrology Institutes (NMIs) make an effort to develop and produce the CRMs.

In this work, we have first developed 10 $\mu\text{mol/mol}$ N_2 and O_2 CRMs in helium (He) balance gas at Korea Research Institute of Standards and Science (KRISS), the NMI of South Korea. The developed CRMs were prepared based on the gravimetric method,¹⁷ so-called “primary preparation method” to link the CRMs to the SI traceability. Using developed N_2 and O_2 CRMs, we have also performed the purity analysis of commercial high purity He gas by means of GC equipped with TCD. We have modified the GC-TCD system to overcome the poor detection limit of TCD and described details in the Experimental section.

2. Experimental

2.1. Materials

For the CRM preparation, high purity N_2 (99.9999 %), O_2 (99.999 %), and He (99.9999 %) gases were used. Aluminum (Al) cylinders (Luxfer, UK) with an internal volume of 10.1 L and nickel-chrome coated valves (Hamai, Japan) were used for the CRM preparation. All of the Al cylinders were evacuated below 1.0×10^{-2} Pa by using a turbomolecular pump (Varian, USA) and an oil-free rotary pump. During the evacuation, the Al cylinders were heated to 60 °C

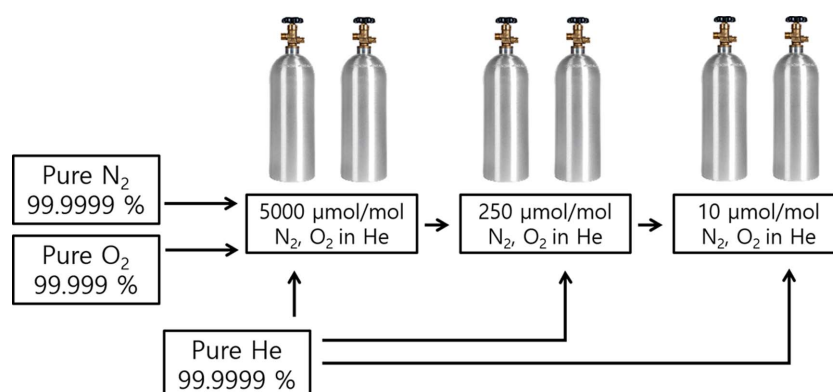


Fig. 1. Schematic diagram of workflow for the CRM preparation and dilution steps. In each dilution step, the gas mixture was gravimetrically prepared.

to remove water and other impurities adsorbed on the inner surface of cylinders. After the first evacuation, Al cylinders were filled with high purity helium about 2 MPa over 24 hours and were re-evacuated to minimize the contamination from the atmosphere.

2.2. CRM preparation by gravimetric method

As shown in *Fig. 1*, the standard gas mixtures of 5000 $\mu\text{mol/mol}$ N_2 and O_2 in He balance were prepared and sequentially were diluted to 250 $\mu\text{mol/mol}$ and 10 $\mu\text{mol/mol}$ according to the gravimetric method.¹⁷ A measuring the masses of gases in the cylinders was carried out using an automatic weighing system, which is composed of three components: (1) a high-precision electronic balance (Mettler-Toledo, XP26003L, Switzerland) which has a maximum load of 26.1 kg and a readability of 1 mg, (2) an automated cylinder exchange system that can measure the weight of 4 cylinders in sequence by rotation, (3) a computer to control the weighing process and automatically record the data.

By subtracting the mass of the gas cylinder before and after gas filling, the amount-of-substance of each component gas that filled into the cylinder was calculated. It is well known that the buoyancy effect should be taken into consideration while mass measurement.^{18,19} According to Matsumoto et al., the buoyancy depends on the volume of the cylinder, but also the air density.¹⁹ The air density can be calculated from many parameters, such as the barometric pressure, temperature, humidity, and CO_2 composition in the atmosphere. These parameters can undergo fluctuation that can cause errors during the mass measurement. To minimize the influence of these fluctuations, the mass of the cylinder was comparatively weighed. An empty Al cylinder, which is nearly identical to the cylinder used for the preparation of CRM, was used as a tare cylinder, and the mass of the tare cylinder was measured while measuring the mass of the sample cylinders to correct the buoyancy effect. The tare cylinder (T) and the sample cylinders (S and S') were alternated in the sequence of S-T-S' in the weighing process.²⁰

2.3. Gas filling with blow-off preparation system

A blow-off type of preparation system²¹ was employed in order to minimize the contamination from the atmosphere. A typical preparation system for the gas mixture contains several valves and pressure gauges that can affect the amount-of-substance fraction of gas mixture due to the residual gases inside those components. On the other hands, the blow-off type preparation system has been eliminated the pressure gauges, thus, it can reduce the amount of the residual gases during the gas filling into the cylinder. Furthermore, terminally placed a ventilation valve that can blow off the residual gases in the gas filling line. In every gas filling into the cylinder, the gas filling lines were purged with target gas and evacuated with a rotary pump at least ten times to prevent the contamination from air or other gases.

2.4. Experimental apparatus and conditions

A schematic diagram of the experimental apparatus for the gas analysis is illustrated in *Fig. 2*. The GC (Agilent, 6890) equipped with the TCD was used for all gas analyses. To achieve a better instrumental sensitivity and a lower detection limit, we have modified our GC system. For general purpose in gas analysis, 250 μL sample loop is typically used,¹⁰ however, we used 10 mL loop to acquire higher sensitivity. The restrictor (0.12 mm inner diameter,

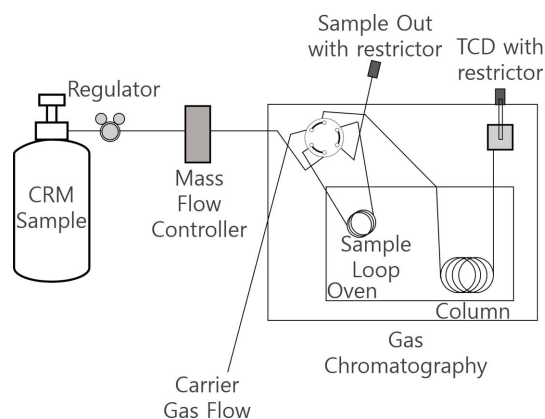


Fig. 2. Schematic diagram of the modified GC-TCD system that lowered the detection limit.

VICI, USA) was also installed at the end of the sample vent line to increase the inner pressure of the sample loop.

Typically, the flow restrictor is installed inside the GC for controlling split ratio²² or dropping the pressure of carrier gas that flows through the column.²³ In contrast, the restrictor in our GC system was used for increasing the pressure inside of the sample loop by restricting the flow of the sample vent line. Moreover, another restrictor was installed at the vent line right after the detector, thus the analysis results could be less influenced by the pressure changes of atmosphere during the analysis. To introduce the reference and sample gases into the GC, the injection part consists of a pressure regulator, a SUS tube, and a mass flow controller (MFC, Brooks 5850E, Japan).

All gas analyses have been performed in the order of A-B-A (Reference-Sample-Reference) to correct the instrumental drift during the analysis. The experimental conditions of the GC system are listed in Table 1.

2.5. Uncertainty evaluation and verification methods

Three sets of 2 mixtures were gravimetrically prepared in this study as shown in Fig. 1. The amount-of-substance fractions of CRMs have been determined by the gravimetric preparation that includes the weighing, atomic weight, and purity analysis. The preparation uncertainty can be expressed as Eq. (1).

$$u_{prep}^2 = u_{grav}^2 + u_{purity}^2 \quad (1)$$

Table 1. The experimental conditions of GC-TCD for analyzing the 10 µmol/mol CRM

Item	Condition
Detector type	TCD
Detector temperature	200 °C
Reference flow rate	40 mL/min
Oven temperature	80 °C
Column type	Molecular Sieve 5 Å, 9 ft × 2
Carrier gas	Helium, 95 psi
Sample flow rate	40 mL/min
Sample loop size	10 mL

where u_{prep} is the uncertainty from the gravimetric preparation, u_{grav} is the uncertainty from gravimetric weighing process and atomic weight, and u_{purity} is the uncertainty from purity analysis. Among the preparation uncertainties, the resolution and the repeatability of the balance, which are parts of u_{grav} , took the largest portion.

Preparation reproducibility has been verified by comparing the amount fractions of the gravimetric preparation and the analytical amount fractions. The analytical amount fractions of sample gas mixture were calculated using the response area, which was measured by using the GC-TCD, and the gravimetrically determined amount fraction of reference gas mixture. We have prepared two gas mixtures for all dilution steps and used one mixture as the reference and used another mixture as the sample. Thus, the analytical amount fraction of the sample can be expressed by the following Eq. (2).

$$x_{spl,i} = \frac{A_{spl,i}}{A_{ref,i}} \times x_{ref,i} \quad (2)$$

where $x_{spl,i}$ and $x_{ref,i}$ are the amount fractions of component i in sample and reference gas mixtures, respectively, $A_{spl,i}$ and $A_{ref,i}$ are the response area of component i in the sample and reference gas mixtures obtained from GC-TCD, respectively. The value of $x_{ref,i}$ is the gravimetric value and it has been considered as a constant value in Eq. (2) to avoid double counting the preparation uncertainty. To verify the internal consistency of prepared gas mixtures, we calculated the normalized sensitivity to reference as the following Eqs. (3) and (4).

$$S_i = A_i/x_i \quad (3)$$

where x_i is the gravimetric value of amount-of-component i fraction.

$$Norm.S_i = S_{spl,i}/S_{ref,i} \quad (4)$$

where $Norm.S_i$ is the normalized sensitivity, $S_{spl,i}$ and $S_{ref,i}$ are the calculated sensitivity of component i in the sample and reference gas mixtures, respectively, using Eqs. (2) and (3).

3. Results and Discussion

3.1. Internal consistency and verification result of the prepared CRMs

The internal consistency of prepared CRMs was verified and the results are depicted in Fig. 3. As shown in Fig. 3, the verification results indicated that the verification values were well agreement with the gravimetric values within their preparation uncertainties. The biggest difference among the all verification results was 0.18 %, resulted from the comparison of O₂ fraction at 250 μmol/mol (Fig. 3(d)). This value is lower than its preparation uncertainty, 0.24 %. The final uncertainties of amount fractions of CRMs ($u(x_{CRM,i})$) can be expressed by Eq. (5).

$$u(x_{CRM,i}) = \sqrt{u(x_{ver,i})^2 + u(x_{prep,i})^2} \quad (5)$$

where $u(x_{ver,i})$ is the verification uncertainty and $u(x_{prep,i})$ is the preparation uncertainty. The verification uncertainty was obtained by sum of the measurement uncertainty and the uncertainty of internal consistency. Therefore, the verification uncertainty can be expressed by Eq. (6).

$$u(x_{ver,i}) = \sqrt{u(x_{anal,i})^2 + u(\Delta x_i)^2} \quad (6)$$

In the Eq. (6), $u(x_{anal,i})$ is the uncertainty of analytical amount fraction of component i , and $u(\Delta x_i)$ is the uncertainty of internal consistency. The uncertainty of internal consistency was calculated by following Eq. (7).

$$u(\Delta x_i) = |1 - Norm, S_i| \times x_{anal,i} \quad (7)$$

where $1 - Norm, S_i$ means a relative difference

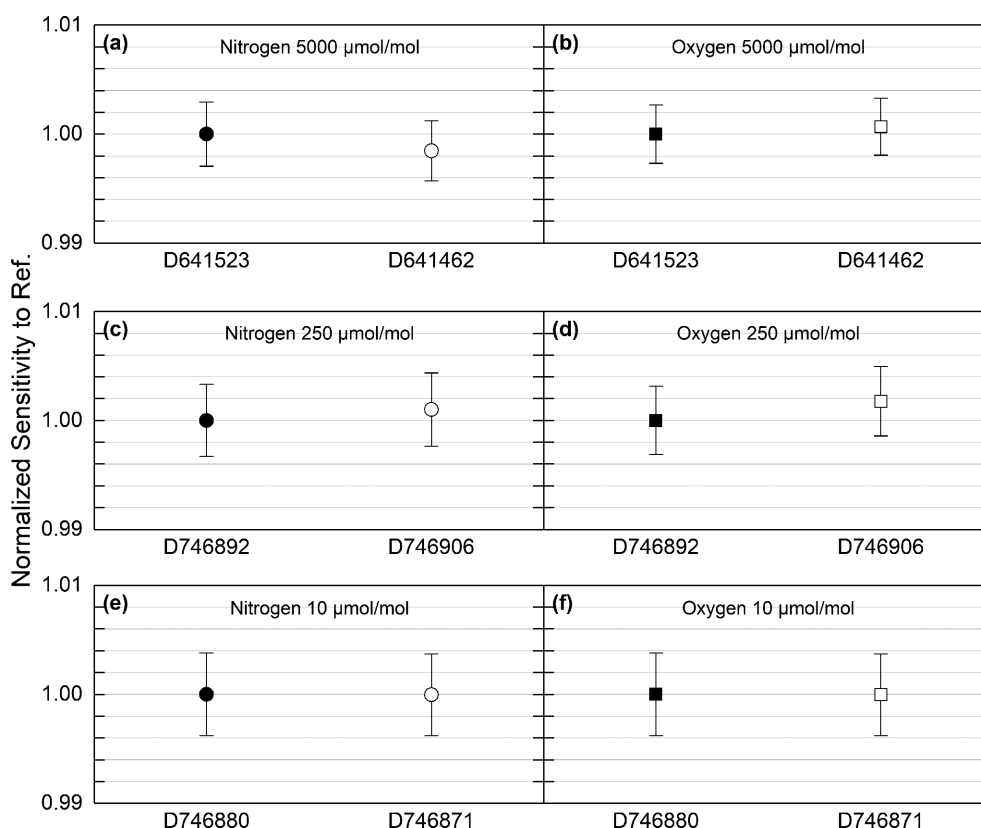


Fig. 3. The verification results for gravimetrically prepared CRMs. The error bars represent their preparation uncertainties ($k = 2$). The black and white symbols represent the normalized sensitivities of reference and sample gas mixtures, respectively. The left side figures (a), (c), and (e) represent the comparison results of N₂ in 5000 μmol/mol, 250 μmol/mol, and 10 μmol/mol, respectively. The right-side figures (b), (d), and (f) represent the comparison results of O₂ in 5000 μmol/mol, 250 μmol/mol, and 10 μmol/mol, respectively.

Table 2. Amount-of-substance fractions and those expanded uncertainties ($k = 2$) of gravimetrically prepared CRMs

Cylinder #	Component	Amount Fraction ($\mu\text{mol/mol}$)
D641462	N_2	5123 ± 22
	O_2	5001 ± 16
D641523	N_2	4922 ± 22
	O_2	5102 ± 16
D746892	N_2	263.1 ± 1.0
	O_2	257.8 ± 1.2
D746906	N_2	259.8 ± 1.0
	O_2	253.6 ± 1.2
D746871	N_2	10.18 ± 0.08
	O_2	9.94 ± 0.06
D746880	N_2	10.12 ± 0.08
	O_2	9.88 ± 0.06

between the preparation value and analytical value. As a result, the final values of amount of N_2 and O_2 fractions in CRMs and those expanded uncertainties ($k = 2$) are listed in Table 2.

3.2. Analysis of the helium gases

The purity analysis of He gases was performed by using the prepared CRMs. The analytical conditions for the purity analysis were identical as listed in Table 1. For the N_2 and O_2 source gases, the purity analysis was not carried out, since their contributions to the final amount fractions were negligible. Nominal amount fractions of N_2 and O_2 were 99.9999 %, 99.999 %, respectively. Even if they had the impurities thousand times more than their nominal values, the impact on the final amount-of-substance fraction would be $0.01 \mu\text{mol/mol}$ which is much lower than the detection limit. The calculated detection limit of our GC-TCD system was $0.2 \mu\text{mol/mol}$. In the He gas, which we used in the dilution process of CRMs, the N_2 and O_2 were not detected by GC-TCD as shown in Fig. 4 (Pure Helium B). On the other hand, $1.66 \mu\text{mol/mol}$ of N_2 and $0.31 \mu\text{mol/mol}$ of O_2 were detected in other He (Pure Helium A in Fig. 4), despite of the nominal purity was 99.9999 %. The chromatograms resulted from the purity assessment of pure He are shown in Fig. 4 and the values of amount of N_2 and O_2 fractions are listed in Table 3,

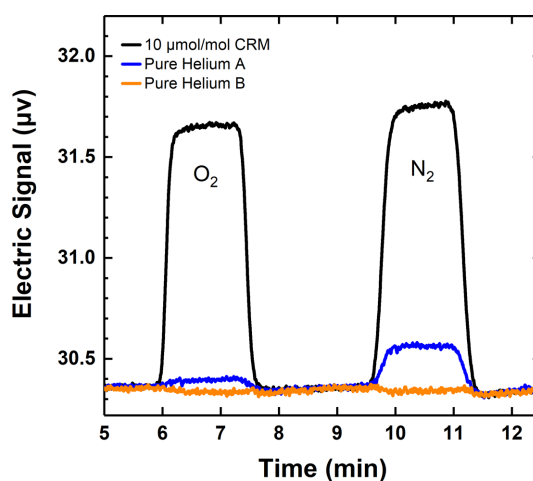


Fig. 4. Chromatograms of two commercial helium resulted from the purity assessment using $10 \mu\text{mol/mol}$ CRM.

Table 3. The amount fractions and those expanded uncertainties ($k = 2$) of N_2 and O_2 impurities in the commercial He gases

	Helium A		Helium B	
	N_2	O_2	N_2	O_2
Amount fraction ($\mu\text{mol/mol}$)	1.66 ± 0.03	0.31 ± 0.02	N/D	N/D

together with those expanded uncertainties ($k = 2$). To evaluate the values of amount fraction and those uncertainties of CRMs, the amount fraction of helium B was set to its nominal value. In addition to it, the amount of impurities fractions in helium B were considered as $1 \mu\text{mol/mol}$, and its standard uncertainty was calculated by using rectangular distribution.

4. Conclusions

To acquire the reliability and the accuracy in the chemical analysis results, using CRM is becoming a necessity nowadays. In gas analysis, nitrogen and oxygen impurities have been dominantly assessed, since they can easily be adulterated into the cylinder. In this study, we first developed $10 \mu\text{mol/mol}$ level of N_2 and O_2 CRMs for purity assessment. The CRMs have been prepared by the gravimetric method and analyzed by GC-TCD. The final amount fractions

and those associated uncertainties are (10.12 ± 0.08) $\mu\text{mol/mol}$ and (10.18 ± 0.08) $\mu\text{mol/mol}$ for nitrogen, and (9.88 ± 0.06) $\mu\text{mol/mol}$ and (9.94 ± 0.06) $\mu\text{mol/mol}$ for oxygen, respectively. Since the TCD is a cheaper instrument and is widely used, this study can extend the opportunity for purity assessment for corporations. The analytic conditions of GC-TCD used in this study can be applied to purity assessment. The evaluated detection limit of TCD for N_2 and O_2 was 0.2 $\mu\text{mol/mol}$. It is sufficient for purity assessment in the industrial area, since the impurity level of pure gases is generally ~ 0.5 $\mu\text{mol/mol}$. Additionally, our result of purity analysis for the 'helium A' indicates that the purity assessment of high purity gases is very important and essential process in many researches and industrial areas.

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