



Short communication

Impurity analyses of high-purity carbon monoxide gas using micro gas chromatography for development as a certified reference material

Nobuhiro Matsumoto*, Takuro Watanabe, Kenji Kato

National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan

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ABSTRACT

High-purity carbon monoxide (CO) gas as a certified reference material (CRM) was analyzed using a micro gas chromatograph (micro-GC) with a micro thermal conductivity detector. The main reason to select the micro-GC was its compact size to provide a safe experimental environment. Thus, both the CO gas cylinder and the micro-GC were placed inside a draft shield with a limited small space. Peaks of several impurities were found in chromatograms of the micro-GC. The main impurities in the CO gas were helium, hydrogen, oxygen, nitrogen and carbon dioxide. It was found that helium was the impurity of the highest concentration. High-accuracy calibration gas mixtures were used to construct calibration lines for the micro-GC. The mixtures were precisely prepared by the gravimetric blending method. Calibration lines had enough linearity and accuracy for quantitative analyses of the impurities. The values of detection limit of the impurities were 0.7–4 $\mu\text{mol/mol}$. The purity of the high-purity CO gas was around 99.996%, which was the value estimated from the sum of the concentrations of the impurities.

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1. Introduction

Various gas analyzers such as gas chromatographs (GC) and non-dispersive infrared gas analyzers are widely used for quantitative analyses of carbon monoxide (CO) in automobile exhaust gas, stack gas and atmospheric air [1]. Calibration gas mixtures traceable to the International System of Units (SI) are helpful for reliable analyses using these gas analyzers. In Japan, various traceable reference gas mixtures filled in high-pressure gas cylinders have been supplied to end users under the Japanese Calibration Service System (JCSS) [2], which is a metrological traceability system in Japan. Major components of the mixtures are nitrogen (N_2) or synthetic air. One of the minor components is CO. In the preparation of the JCSS primary gas mixtures, a gravimetric blending method [3] is adopted. The gravimetric concentration of a mixture prepared by this method is expressed as a function of the mass filled in the gas cylinder, the molar mass, and the purity of each component gas. The National Metrology Institute of Japan (NMIJ), one of the National Metrology Institutes (NMIs), has signed a Mutual Recognition Arrangement (CIPM MRA) for national measurement standards [4] and is required to supply high-purity gas CRMs with a certified value of purity, to link the JCSS primary reference gas mixture and the SI, rigorously. Purity of these CRMs has been determined by “the subtraction method”, which is described in ISO Guide 35 [5]

and ISO 6142 [3]. The purity, x_{pure} , equals 1 mol/mol subtracted by the sum of mole fractions of each analyzed impurity, x_i . In the case of CO, the high-purity gas CRM with a purity of more than 99.99% was requested for the preparation of JCSS primary gas mixtures of CO in N_2 (CO/N_2). If both the high-purity CO gas with a purity of more than 99.99% and high-purity N_2 gas with a purity of more than 99.9999% are used for the preparation of CO/N_2 , the sum of impurities in the mixture should be lower than 0.001%.

CO is a colorless and odorless toxic gas. For safety reasons, care must be taken in the impurity analyses of high-purity CO gas [6,7]. In this study, a compact micro-GC will be placed inside a limited space in a draft shield to prevent any accidents due to unexpected gas leaks from the connectors between the CO cylinder and the gas analyzer and others. In addition to the advantage of its small body size, fast analysis by the micro-GC saves on the amount of sample gas use. The detection limits and uncertainties of analytical concentrations for the impurities by micro-GC will be evaluated for this purpose. Detailed analytical methods and results are reported herein.

2. Experimental

2.1. High-purity CO gas cylinder for CRM

Semiconductor grade high-purity CO gas in a 9.5 l aluminum-alloy cylinder was purchased from Japan Fine Products (Oyama, Japan). The manufacturer's purity was more than 99.995%. This grade was the highest purity available among specifications

* Corresponding author. Tel.: +81 29 861 2255; fax: +81 29 861 6854.
E-mail address: nobu-matsumoto@aist.go.jp (N. Matsumoto).

described in Japanese gas manufacturers' catalogs. The filling pressure was 9.8 MPa at 35 °C.

2.2. Analyzed impurities

A micro-GC with a micro thermal conductivity detector (Agilent, CA, USA, model 3000A) was used for quantitative analyses of impurities such as helium (He), hydrogen (H₂), O₂, N₂ and CO₂ in the high-purity CO gas. For water (H₂O) analysis, a moisture analyzer using a quartz-crystal oscillator sample cell (AMETEK, PA, USA, model 5800) was used. These impurities were selected on the basis of information on starting materials during the manufacturing process of the CO gas and by atmospheric constitutions.

2.3. Configuration of micro-GC and gas handling operation

The micro-GC was placed inside a compact draft shield with an effective working space of 820 mm width, 600 mm depth, 850 mm maximum height and 660 mm minimum height (AS ONE Corporation, Osaka, Japan, model CD-900SE-I). A high-purity He gas cylinder with a purity of 99.9999% (Japan Air gases, Tokyo, Japan) or high-purity argon (Ar) gas cylinder with a purity of 99.9999% (Japan Fine Products) as carrier gas was connected to the micro-GC. The gas flow channel from the sample gas cylinder to the injection port of the micro-GC consisted of a SUS tube, a pressure regulator (Nissan TANAKA, Saitama, Japan, model TORR1300), a plug valve (Swagelok, OH, USA, model SS-4P4T), a union tee (Swagelok) and a float-type flowmeter (KOFLOC, Kyoto, Japan, model RK1150). The sample gas cylinder was a high-purity CO gas cylinder or calibration gas mixtures. The software, Certy Networked Data System for Chemical QA/QC (Agilent Technology), was installed onto a personal computer for control and data processing of the micro-GC.

In the gas handling operation of the sample cylinder, the pressure regulator was first evacuated with a small dry pump. After evacuation, the plug valve of the regulator was connected to the gas flow channel. To eliminate the air inside the pressure regulator, it was flushed repeatedly 10 times by alternatively opening and closing the valve attached to the sample cylinder. After flushing, the secondary pressure of the regulator was adjusted such that the gas flow rate at the float-type flowmeter was approximately 80 ml/min. Part of the sample gas around the union tee flowed into the 1/16 inch tube and passed through a sample loop inside the micro-GC.

2.4. Calibration method of micro-GC

Calibration of the micro-GC was performed according to ISO 6143 [8]. A Deming's least squared method was used for regression analyses to construct calibration lines. For analyses of N₂, O₂ and CO₂, calibration gas mixtures diluted with He were prepared by the gravimetric blending method. For He and H₂, calibration gas mixtures diluted with N₂ were also prepared by the same method. Three calibration gas mixtures with different concentrations for each component were individually prepared. Three-point calibration line for each component was constructed using data set of gravimetric concentrations of the mixtures and responses recorded on the software for the micro-GC.

These mixtures were filled in 9.5 l aluminum alloy high-pressure gas cylinders (Luxfur, Australia) with a weight of 10 kg. A home-made automatic balance was used for mass measurements of targeted gases filled into the cylinders [9–11]. This equipment included an electronic mass comparator with a maximum capacity of 15 kg and a minimum readability of 1 mg (Mettler-Toledo, Greifensee, Switzerland). The mass of gas filled in the cylinder was typically 1 g to 1 kg and was measured with a small uncertainty of 3–4 mg [11]. As an example of the good accuracy of the calibration

gas mixture prepared with this equipment, a CO₂ in N₂ mixture with the gravimetric concentration of 6.20441 cmol/mol had an expanded uncertainty of 0.00028 cmol/mol with the confidence level of 95% [11].

In the case of calibration gas mixtures for water (H₂O), the gravimetric blending method was not adopted, because molecules of H₂O were much easier to adsorb on an internal wall of the high-pressure aluminum alloy gas cylinder, than molecules of inert gas species. Concentrations of H₂O calibration gas mixtures diluted with N₂ in high pressure gas cylinders were determined with a dew-point meter (Michell Instruments, Cambridgeshire, UK, models S4000 Precision Dewpointmeter and S4000 Cooled Mirror Sensor).

3. Results and discussion

Fig. 1 shows chromatograms for the high-purity CO gas under the analytical conditions in Table 1. Separations between He and H₂ peaks, between O₂ and N₂ peaks, and between CO and CO₂ peaks were found. In Fig. 1(a) and (b), the CO peak was eliminated by setting appropriate values for back-flush time, analytical time and post-run time as in Table 1. The height of the He peak was much larger than that of the H₂ peak even though the concentration of He was not described in the specification of the gas manufacturer's catalog. The existence of He in the high-purity CO gas at concentration more than the atmospheric concentration of He was confirmed using a helium leak detector with a 90° magnetic field detection mass spectrometer (ALVAC, Kanagawa, Japan, model HERIOT 710). For this measurement, a small amount of gas in the high-purity CO gas cylinder was filled in a small container and then the gas from the container flowed to the probe of the leak detector.

Since He and H₂ peaks in Fig. 1(a) have similar retention times and overlap slightly, the height of each peak was recorded as the response, y , and used for measurement of the analytical concentration of the impurity. In the case of He, relative standard deviations of peak heights were 0.8–2.5%. Three He calibration gas mixtures diluted with N₂ with the gravimetric concentration of 66.66 μmol/mol (the standard uncertainty [12] was 0.26 μmol/mol), 38.58 μmol/mol (0.15 μmol/mol) and 8.18 μmol/mol (0.13 μmol/mol) were used for making a calibration line for the response, y , versus the concentration, x . Regression analysis for a calibration line, $y = a + bx$, was carried out by Deming's least squared method. The results of parameters a and b were 1.25 and 4.128, respectively. The expanded uncertainties of a and b were $U(a) = 1.4$, $U(b) = 0.054$, and $u(a \text{ and } b) = -0.0153$, where $U(a)$ and $U(b)$ were expanded uncertainties with the coverage factor of 2, and the $u(a \text{ and } b)$ was the covariance between a and b . The value of goodness-of-fit, Γ , for this calibration line was 1.12. A value of Γ less than 2 indicates that linearity of the regression line is good. From the value of the He peak height for the high purity CO gas and the parameters of the calibration line, the analytical concentration, x_{anal} , was calculated to be 25.11 μmol/mol with a standard uncertainty of 0.21 μmol/mol. The x_{anal} is much higher than the detection limit L_x of 0.93 μmol/mol for He concentration. The existence of He in the CO gas was due to its use for purifying the CO gas during the manufacturing process. The value of L_x was calculated by the following equation [13]:

$$L_x = \frac{L_y - a}{b}$$

$$L_y = a + 2 \cdot t(\varphi, \alpha) \cdot s$$

where L_y is detection limit of the response, φ is degree of freedom, α is probability of an error of the first kind [14], and $t(\varphi, \alpha)$ is t -value of Student's t distribution. The s is the standard deviation of response when the calibration gas mixture is injected n times and the He

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