Preparation of Carbon Monoxide in Synthetic Air at Ambient Level by Gravimetric Method and High Accuracy Determination by Gas Chromatography

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***Abstract*—The atmospheric lifetime of CO varies from weeks to months depending on OH radical concentrations. CO itself does not directly contribute to the greenhouse effect, but the reaction of OH radical with CO controls the concentration distribution and variation in space and time of the other greenhouse gases such as CO_2, CH_4, O_3 etc. And then it will impact on regional environment and global climate. Ambient CO ranges from 50 nmol/mol to 300 nmol/mol at marine boundary, from 100 nmol/mol to 500 nmol/mol at city area. The World Meteorological Organization (WMO) requires exact analysis of CO at ambient level as 2 % uncertainty. In this paper CO in synthetic air with the concentration level of 350 nmol/mol was prepared by gravimetric method and standard uncertainty was less than 0.3%. By using gas chromatography with FID/Methanator the RSD of the peak area of CO was less than 0.2% through the optimization of gas chromatographic conditions. Our lab on behalf of China participated in the CCQM-K84 international comparison of CO and achieved good agreement with other national labs.**

Keywords-preparation; CO; high accuracy; uncertainty; international comparison

I. INTRODUCTION

In recent years, the greenhouse effect and global warming has become one of the most important environmental issues in the world. According to experts, the earth's surface temperature went up to (0.74~ 0.18)℃ in the past 100 years, and it will continue to go up from 1.5 to 5.8℃ in 1990 to 2100. Global warming will lead to a series of environmental problems, such as sea level rise, low altitude regions flooded, pests and diseases increase, crop loss; abnormal climate and ocean storm increase.

Major sources of CO are industry, transportation, and biomass burning. CO itself does not directly contribute to the greenhouse effect, but the reaction of OH radical with CO controls the concentration distribution and variation in space and time of the other greenhouse gases such as CO_2, CH_4, O3 etc.[1-2] The atmospheric lifetime of CO varies from weeks to months depending on OH radical concentrations and ambient CO ranges from 50 nmol/mol to 300 nmol/mol at marine boundary, from 100 nmol/mol to 500 nmol/mol at city area. In order to measure precisely CO in atmosphere, National Oceanic & Atmospheric Administration/ Earth System Research Laboratory- global monitoring division (NOAA/ESRL-GMD) is the designated Calibration Center Laboratory (CCL) for CO in the Global Atmosphere Watch (GAW) program. In addition, The World Meteorological Organization (WMO) requires exact analysis of CO at ambient level as 2 % uncertainty. For these reasons, it's necessary for the measurement results to be accurate and consistent among the assigned values for standards.

In the present study we prepared CO in synthetic air with the concentration level of 350 nmol/mol by gravimetric method and the uncertainty of CO was less than 0.33%. By using gas chromatography with FID/Methanator the RSD of the peak area of CO was less than 0.2% through the optimization of gas chromatographic conditions. By preparation of high accuracy primary standard and optimized GC conditions, the expand uncertainty for measurement of trace CO may be controlled less than 0.8% (k=2) that meet the WMO's requirement for measurement of ambient CO. Furthermore our lab on behalf of China participated in the CCQM-K84 international comparison of CO and achieved good results. The comparison results will provide evidence of the international measurement equivalence of the laboratory, which enables the laboratory to provide measurement traceability for CO monitoring in China.

II. MATERIALS AND METHODS

A. Pure Gas

High purity gases for preparation of Carbon monoxide in Synthetic air include high purity nitrogen, high purity oxygen, high purity argon and high purity monoxide carbon.

B. Cylinder

4L and 6L aluminum cylinders were produced by Fushun Jineng Technology Company and Luxfer limited company.

C. Balance

Mettler Toledo, XP10003S comparator, Capacity, 10100g, readability, 1mg

D. Instrument

GC with pulsed discharged helium ionization detector(PDHID) for analysis of the purity of N_2, O_2 and CO, Agilent, 7890N.

GC with flame ionization detector(FID)/methanator for analysis of CO in Synthetic air, Agilent 7890.

E. GC conditions for CO

CO was analyzed by GC-FID/methanator with a column of molesieve 5A 80/100(9ft*1/8inch*2.0mm).

GC conditions:
Oven temp: 110ºC isotherm 4min
Detector temp: 285ºC
Carrier gas: N_2
Carrier gas flow: 75 psi
Combustible gas: H_2
Combustible gas flow: 65mL/min
Auxiliary gas: Air,
Auxiliary gas flow: 650mL/min
Sample loop: 5mL
Sample Flow: 400 mL/min

III. PREPARATION OF PRIMARY STANDARD MIXTURE

A. Purity Analysis

Firstly N_2 (nominal purity>99.999%, CO<0.1μmol/mol), O_2(nominal purity>99.999%, CO<0.05μmol/mol), Ar(nominal purity>99.999%, CO<0.1μmol/mol) and CO(nominal purity>99.999%) were analyzed by GC-PDHID and other analyzers. And Table I to Table IV show that results of the purity analysis. Table V shows the result of purity analysis of N_2 after purified by high pressure purifier (Nupure, made in Canada, E0600-CA, CO<1nmol/mol).

B. Preparation frame of CO in Synthetic Air

According to ISO6142[3] CO in synthetic air were prepared by gravimetric method and similar preparation procedure of gas mixture has been reported [4-5]. Pure CO was diluted by 4 steps and the frame in Figure I shows that the weighing data of gravimetric dilution with CO amount fraction.

TABLE I. PURITY TABLE FOR N_2

Component	Mole fraction μmol/mol	Distribution	Uncertainty μmol/mol
H_2	0.05	Rectangular	0.029
Ar	78	Normal	3.9
O_2	0.8	Normal	0.08
CO	0.03	Normal	0.006
CO_2	0.01	Rectangular	0.006
CH_4	0.005	Rectangular	0.003
H_2O	1	Rectangular	0.6
N_2	999920.08	-	3.95

C. Evaluation of Uncertainty

Evaluation of sources of uncertainty for gravimetric method and calculations of uncertainty separately references ISO6142 and the reported paper [6]. Table VI shows that the gravimetric value and expand uncertainty of primary standards.

TABLE II. PURITY TABLE FOR O_2

Cylinder No.	Gravimetric Value μmol/mol	Expand Uncertainty(k=2) (μmol/mol)
CAL017806	0.3631	0.0017
CAL017758	0.3721	0.0017

TABLE III. PURITY TABLE FOR AR

Component	Mole fraction μmol/mol	Distribution	Uncertainty μmol/mol
H_2	0.05	Rectangular	0.029
Ar	10	Rectangular	5.8
N_2	4.9	Normal	0.49
CO	0.01	Normal	0.003
CO_2	0.01	Rectangular	0.006
CH_4	0.005	Rectangular	0.003
H_2O	1	Rectangular	0.6
O_2	999984.03	-	5.86

TABLE IV. PURITY TABLE FOR CO

Component	Mole fraction μmol/mol	Distribution	Uncertainty μmol/mol
H_2	0.05	Rectangular	0.029
O_2	0.9	Normal	0.09
N_2	0.8	Normal	0.08
CO	0.0005	Rectangular	0.0003
CO_2	0.01	Rectangular	0.006
CH_4	0.005	Rectangular	0.003
H_2O	1	Rectangular	0.6
Ar	999997.23	-	0.61

TABLE V. PURITY TABLE FOR N2 AFTER PURIFICATION

Component	Mole fraction μmol/mol	Distribution	Uncertainty μmol/mol
H_2	0.05	Rectangular	0.029
O_2	0.3	Normal	0.03
N_2	7.4	Normal	0.74
Ar	0.6	Normal	0.06
CO_2	0.01	Rectangular	0.006
CH_4	0.005	Rectangular	0.003
H_2O	3	Rectangular	1.7
CO	999988.64	-	1.86

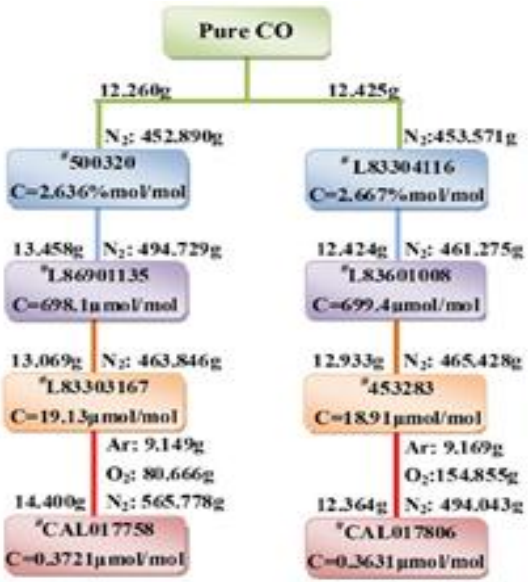

FIGURE I. THE FRAME OF PREPARATION OF CO IN SYNTHETIC AIR

TABLE VI. GRAVIMETRIC VALUE AND EXPAND UNCERTAINTY OF PRIMARY STANDARDS

Component	Mole fraction μmol/mol	Distribution	Uncertainty μmol/mol
H_2	0.005	Rectangular	0.003
Ar	78	Normal	3.9
O_2	0.1	Rectangular	0.06
CO	0.0005	Rectangular	0.0003
CO_2	0.005	Rectangular	0.003
CH_4	0.005	Rectangular	0.003
H_2O	0.1	Rectangular	0.06
N_2	999921.78	-	3.90

IV. RESULTS AND DISCUSSION

A. Analysis Method

Usually CO in lab with low concentration (ppm level) is analyzed by GC-FID/Methanator with packed column of TDX or by CO analyzer based on optical principle such as non-dispersion infrared(NDIR). But for ambient CO at 350 nmol/mol, the uncertainty of common method is more than 5% which cannot meet the requirement of WMO(2% uncertainty). In order to meet the requirement of WMO, the instruments with high sensitive need be used such as GC-PDHID or CO Cavity Ring Down Spectrometer(CRDS). CO CRDS is used widely by environmental protection departments and monitoring spots of WMO, because it is continuously and stably monitoring the CO in the air. CO CRDS is very sensitive for CO, but it is not regular instrument because of high price and specifity. Furthermore, isotope effect possibly affects the measurement accuracy. In fact, GC-FID/Methanator can also be used to measure trace CO by optimizing the GC conditions.

Firstly, the column molseive 5A instead of the column of TDX was selected because the retention time of CO is longer to avoid the effect of signal fluctuation due to sample injection. Secondly, the sensitive of CO in the GC can be enhanced by increase of sample load. Thorough increase of the volume of sample loop and flow of sample can realize increase of sample load. Finally, the flow of H_2 and Air need be increased otherwise the sample will put out the flame of FID when it reach the detector. The RSD of the peak area of CO was less than 0.2% by using the optimization conditions listed in I. E.

B. Purification of N_2

Table I and table II shows that trace amount of CO was found in N_2 and O_2. For N_2 and O_2, the standard uncertainty of CO contributed from the impurity is about 1.37% and 0.17% separately. The purity of N_2 cannot meet the WMO requirement that uncertainty of analysis of CO at ambient level is less than 2 %. So high purity N_2 is needed to assure that the uncertainty meet the requirement. The high pressure N_2 purifier was used to remove CO in N_2. Table IV shows that the concentration of CO in N_2 was less than 1nmol/mol after purification and standard uncertainty of CO contributed from the impurity in N_2 decreases to 0.14%.

C. Consistence of Primary Standards

To avoid possible mistake in the procedure of preparation, two primary standards were prepared from the pure CO separately and the detail is showed in Figure II. The consistence of two primary standards was checked by the analysis method discussed above. When CO was analyzed, 'A-B-A-B-A' type calibration was used. That means one primary standard(reference) and the other primary standard(sample) were measured in the order of Reference – Sample – Reference – Sample – Reference. The gas flow at the sample loop of GC was controlled by mass flow controller at almost same value during one analysis sequence. Single point calibration was used to calculate the concentration of CO. The equation [7] below can be used to evaluate the consistence. The result in Table VII shows that the absolute value of RD is much less than the value of double u_c that explains the consistence of two primary standards is very good.

TABLE VII. EVALUATION OF CONSISTENCE OF TWO PRIMARY STANDARDS

Cylinder No.	C_{grav}	$^*C_{cal}$	$\lvert RD \rvert$	u_{grav}	u_{ver}	$2u_c$
	μmol/mol					
[1]CAL017806	0.3631	0.3636	0.14%	0.24%	0.20%	0.62%
[2]CAL017806		0.3629	0.06%			

*- C_{cal} is required by using CAL017758 as the reference.

$$RD = \frac{C_{cal} - C_{grav}}{C_{grav}} \times 100\% \quad (1)$$

$$u_c = \sqrt{u_{grav}^2 + u_{ver}^2} \quad (2)$$

$$\lvert RD \rvert < 2u_c \quad (3)$$

Here, u means relative standard uncertainty.

RD—Relative deviation between calibration value and gravimetric value of primary standard,

C_{cal} —Calibration value of primary standard, mol/mol,
C_{grav} —Gravimetric value of primary standard, mol/mol,
u_{grav} —Uncertainty of gravimetric method,
u_{ver} —Uncertainty of analysis method,
u_c—Combination relative uncertainty of gravimetric method and analysis method.

D. Quantitative Measurement of Trace CO with High Accuracy

By preparation of high accuracy primary standard and optimized GC conditions, the expand uncertainty for measurement of trace CO may be controlled less than 0.8%(k=2). In order to verify reliability of this method our lab participated in the CCQM-K84 comparison.

CCQM-K84 comparison's purpose is to compare the measurement capability of CO at ambient level of 350 nmol/mol. And besides, this key comparison is expected to contribute the establishment of traceability to single scale of CO between National Metrology Institutes(NMIs) by improving the data quality in the network and harmonizing the results from different national stations. Consequently, this key comparison will support the measurement capability of CO at ambient level with the uncertainty within NOAA/ESRL-GMD calibration scale. Korea Research Institute of Standards and Science(KRISS) as the leading laboratory was responsible for this key comparison which total 8 National Metrology Institutes and 3 Lab participated in. We calibrated the sample prepared by KRISS with our primary standard (CAL017806)

in different days. The result is given in Figure II. The result shows the relative deviation between the calibrated concentration and average concentration of CO in K84 comparison sample varied less than 0.3% in different days. The measurement uncertainty of CO was calculated by below equation:.

$$u(c_{COM}) = \sqrt{u^2(c_{PRM}) + u^2(A_{COM}) + u^2(A_{PRM}) + u^2(f_{inter})} \quad (4)$$

Here, u means relative standard uncertainty.

$u(c_{COM})$—Measurement uncertainty of concentration of CO in the comparison sample,

$u(A_{COM})$—Uncertainty of signal reading of the comparison sample from peak area on GC,

$u(A_{PRM})$—Uncertainty of signal reading of the primary standard from peak area on GC,

For the $u(A_{COM})$ and $u(A_{PRM})$, the relative standard uncertainty could be calculated from the relative standard deviation (RSD) of the signal reading,

$u(c_{PRM})$—Uncertainty of concentration of primary standard,

$u(f_{inter})$—Uncertainty of reproducibility in different days. The relative standard uncertainty was calculated from the relative standard deviation (RSD) of repeating test in different days.

The relative expand uncertainty of CO in comparison sample is less than 0.8% in Table VIII. And Figure III shows the comparison result and data in the red circle was from our lab. The result show that our measurement data agrees with the leading lab and most of NIMs and validity of our analysis method.

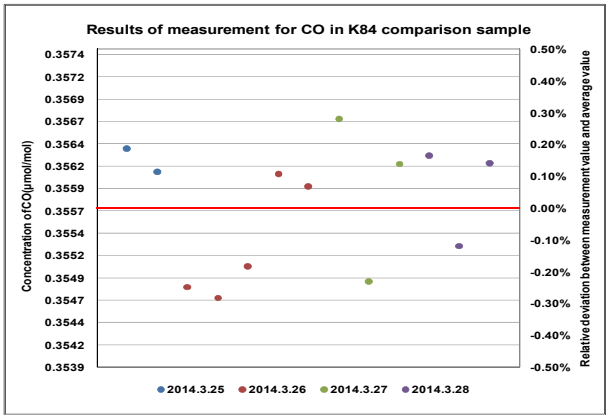

FIGURE II. RESULTS OF MEASUREMENT FOR CO IN K84 COMPARISON SAMPLE IN DIFFERENT DAYS

TABLE VIII. MEASUREMENT UNCERTAINTY OF CO IN COMPARISON SAMPLE

Source of uncertainty	Relative standard uncertainty	Relative expanded uncertainty*
$u(C_{PRM})$	0.24%	0.8%
$u(A_{COM})$	0.18%	
$u(A_{PRM})$	0.18%	
$u(f_{inter})$	0.19%	

*The coverage factor k=2(95% confidence level)

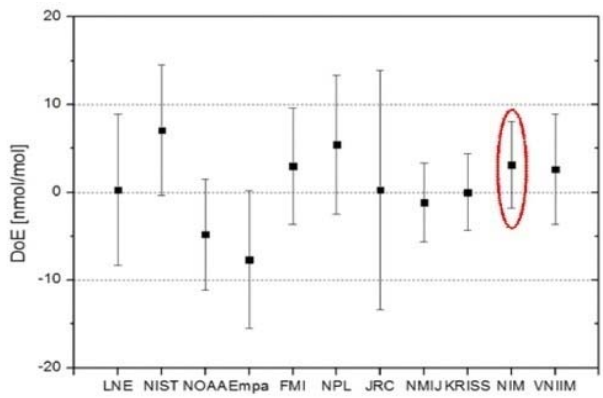

FIGURE III. RESULT OF CCQM-K84 COMPARISON (DATA IN RED CIRCLE IS FROM OUR LAB)

V. CONCLUSIONS

CO in synthetic air with the concentration level of 350 nmol/mol was prepared by gravimetric method and the standard uncertainty was less than 0.3%. By using gas chromatography with FID/Methanator the RSD of the peak area of CO was less than 0.2% through the optimization of gas chromatographic conditions. By preparation of high accuracy primary standard and optimized GC conditions, the expand uncertainty for measurement of trace CO may be controlled less than 0.8% (k=2) that meet the WMO's requirement for measurement of ambient CO.

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