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TRACEABLE IN-HOUSE PREPARATION OF RM CO_2/N_2 GAS MIXTURE USING GRAVIMETRIC STANDARDIZED METHOD

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Abstract:

The necessity for national and international programs to monitor the levels of carbon dioxide emissions in the atmosphere has arisen as a result of the recent large greenhouse gas emissions that cause a rise in the Earth's temperature and climate changes with severe impacts. In order to give confidence in the monitoring results and enable the proper decisions to be made regarding the supply of environmental treatment and air quality through the limiting and monitoring of emission, it is required to maintain the traceability of the measurement data to SI units. Gas measurements laboratory at SASO-NMCC uses the gravimetric method to prepare reference gas mixtures of CO_2 in N_2 as primary standard mixtures (PSMs) cylinders based on universal gas law. The produced PSMs used as working standards to transfer the traceability from CRMs to customers' artefacts. The used method fully complies with ISO 6142. Description of the steps of the production process and its method verification as well as equipment used and associated uncertainty are presented in this work. In accordance with the requirements of ISO 6143, a validated gas chromatography thermal conductivity detector (GC-TCD) method was selected to verify the mole fraction of the gravimetrically prepared gas mixtures. Reproducibility of the produced concentrations is demonstrated through mid-term and long-term evaluations. Eight certified reference materials (CRMs) of different concentrations were used for the GC calibration to provide metrological traceability of the measurement results to SI units. Associated uncertainty budget, with brief description of different components and error sources, is presented.

Keywords: Reference Materials (RMs), Primary Standard Mixtures (PSMs), CRMs, CO_2, GC-TCD, ISO 6142 & 6143.

1. Introduction

According to the Global Monitoring Laboratory's annual report, the average amount of carbon dioxide in the atmosphere around the world reached a new high record in 2022 of 417.06 ppm. The increase in atmospheric carbon dioxide between 2021 and 2022 was 2.13 ppm, marking the 11th year in a row where the increase was greater than 2 ppm. The annual average carbon dioxide in 2022 at Mauna Loa Observatory in Hawaii, where the carbon dioxide record began in 1958, was 418.56 ppm [1-2].

The primary cause of the rise in carbon dioxide concentrations is the use of fossil fuels by humans as a source of energy. We are adding carbon to the atmosphere in only a few hundred years that plants removed from the atmosphere through photosynthesis over many millions of years in the form of fossil fuels like coal and oil. According to the Global Carbon Budget 2022, annual emissions from burning fossil fuels have climbed steadily since the middle of the 20th century, from roughly 11 billion tons in the 1960s to a projected 36.6 billion tons in 2022 [2].

Applications for atmospheric monitoring demand a high level of uniformity in CO_2 calibration standards. Currently, the standard uncertainties of primary gas standards, produced using a gravimetric preparation process offering traceability to the SI, are too high to be employed in measurements where minute temporal and spatial variations are significant. Due to an anticipated increase in demand based on the proliferation of atmospheric greenhouse gas (GHG) measurements globally, an international task group has been established under the Metre Convention, led by NIST, to develop a system to more efficiently disseminate accurate and consistent GHG standards [3].

In order to establish a NIST CO_2 Scale, the Gas Sensing Metrology Group is creating a new set of CO_2/Air Primary Standard Mixtures (PSMs) with

nominal concentrations ranging from 374 µmol/mol to 999 µmol/mol. The NIST CO_2 Scale will include a group of eight working standards with nominal CO_2 concentrations ranging from 385 µmol/mol to 895 µmol/mol. Additionally, CH_4, N_2O, Ar, and O_2 values will be assigned. Using the CIPM MRA process, this scale will be compared internationally, and a relationship to a standard scale, such as the WMO-Scale, will be developed for the interpretation of integrated datasets.

Seawater CO_2 measurements are crucial to attempts to monitor ocean carbon because human activities are affecting the chemistry of the ocean's carbon content. The demand for these reference resources is projected to rise as more nations step up their ocean monitoring efforts and novel technologies, including ocean carbon dioxide removal, are developed. In order to ensure SI traceability, the Gas Sensing Metrology Group is collaborating with the Inorganic Chemical Metrology Group to create the capacity to offer services for the analysis of total dissolved inorganic carbon utilizing CO_2/Air primary standard mixtures (PSMs) [3].

In this work, we show a preparation scheme of reference gas mixtures of CO_2 in N_2 as CRM cylinders using the gravimetric method in accordance with the universal gas law. The procedure being employed complies with ISO 6142 [4]. In this work, the equipment employed and the associated uncertainty, together with a description of the production process's steps and method verification, are described. To confirm the mole fraction of the gravimetrically generated gas mixtures, a validated gas chromatography thermal conductivity detector (GC-TCD) method was chosen in compliance with ISO 6143 standard [5-7, 8-13].

2. Equipment and method

A. Materials

Gas mixtures reference materials are produced from pure gases whose molecules are spread between inert nitrogen gas molecules or pure air molecules as a medium that helps stabilize the concentration of the prepared gas. It is preferable to produce the CRMs in two stages, the first includes the production of a mixture of high concentration that should have metrological traceability, then from this mixture diluted lower concentrations with traceability acquired. This scheme of production is simplified in Figure 1 a and b.

The gravimetric dilution of primary gas mixtures uses the certified reference gas mixtures (CRMs), the pure CO_2 (99.8%) and N_2 (99.9999%) gases, provided by LINDE-SIGAS, Germany as the parent gas. 5L Aluminum cylinders in which the gas mixtures were filled-in were supplied by Air Liquide, the Netherlands.

B. EQUIPMENT

Equipment comprises the evacuation system, filling system, weighing system, balance, homogenizer system, and Gas Chromatography system (GC-TCD) for verification analysis. List of the used equipment is shown in table 1.

C. SCHEME

Preparation method of the primary gas mixtures was done according to “ISO 6142-1: Gas analysis – preparation of calibration gas mixtures” [4]. Steps of the method, as per the standard, can be summarized as follows: 1- Calculate masses and uncertainties, 2- preparation composition including filling sequence, 3- perform purity analysis, 4- prepare mixture and determine masses, 5- determine molar masses, calculate mixture composition and uncertainty, 6- homogenize mixture, 7- perform verification, and 8- if verification result is positive, then report the results of concentrations and associated uncertainties (certificate).

Table 1: List of the used equipment

Name	Manufacturer	Model
VACUUM PUMP SYSTEM	PFEIFFER	HICUBE 300 CLASSIC
WEIGHING SYSTEM	METTLER TOLEDO + IDEAL MAKINE (TUBITAKUME)	XPE10003SC + RTK-10
BALANCE	METTLER TOLEDO	MS16001L01
ROLLING BENCH	HKTM (TUBITAKUME)	AGM6 80 A
GAS CHROMATOGRAPHY (GC)	AGILENT	7890B

Carbon dioxide gas with a concentration of (0.02900 ± 0.000001) mol/mol and nitrogen in balance is produced. The method used for the preparation process, as shown in Figure 1, is broken down into a number of steps, beginning with completely emptying the cylinder. To do this, the cylinder is connected to a vacuum device for a period of 12 hours, during which time all impurities were removed. When the cylinder is completely empty, the pressure indicator changes

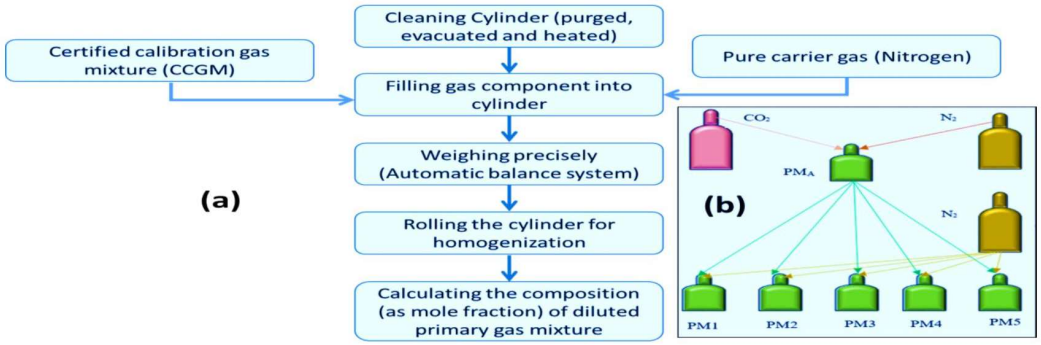

Figure 1: Scheme for the gravimetric dilution of the primary gas mixture: (a) detailed steps (flow-chart), (b) for visualization

to 1×10^{-7}, signifying that the preparation process is complete.

The Evacuation System (PFEIFFER, model: HiCUBE) is used to evacuate the sample cylinder and to purge used and new cylinder (see Figure 2). The Evacuation System is built up with a pumping station with maximum four cylinder-connections by changing the existing valve locations; See Figure 2.

Following discharge, the procedure of calculating the quantity based on the prepared target concentration using the weighing equipment commences. By contrasting the sample cylinder with the reference cylinder, the device is intended to automatically weigh the gas cylinder (Figure 3).

The ideal gas law PV=nRTz is the foundation of the system. The maximum weight and volume permitted for a cylinder are also shown in Figure 3, where the permitted weight varies from (1 mg to 10 100 g) and the size of its cylinder is (5 L).

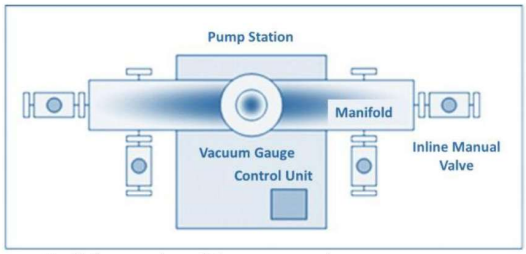

Figure 2: Schematic of the evacuation system.

Figure 3: Photograph of the weighing system.

Then, we start the filling process using a filling system after finishing the weighing procedure based on the ideal gas law, which gives us the necessary weight to achieve the desired concentrations. The primary gas mixtures are obtained by filling amounts of pure gas or gas mixtures using the gas filling mechanism. According to ISO Standard 6142-2001(E), "Gas

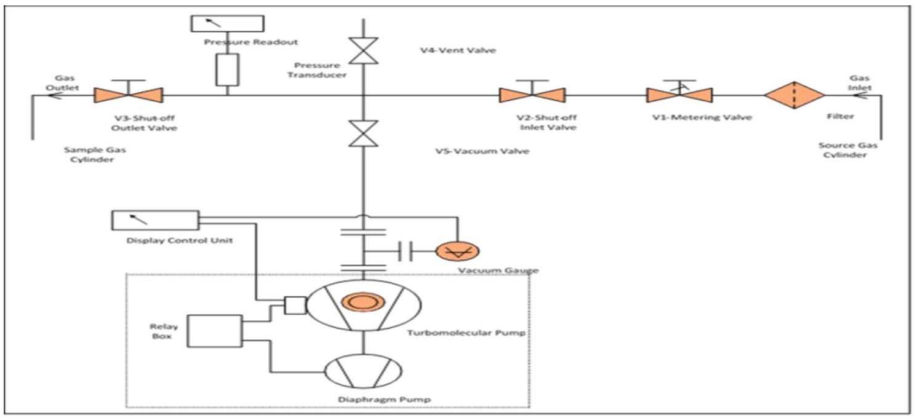

Figure 4: Schematic of gas filling system.

analysis - Preparation of calibration gas mixtures - Gravimetric method," the system is able to fill the 5L-cylinders. All gas flow lines are made of stainless steel that has been electro-polished and can resist 200 bar of pressure. All lines from pure gases down to sample cylinders can be evacuated by the system to a vacuum of approximately 1×10^{-6} mbar. Figure (4) shows the filling system schematic diagram.

Following the determination of the quantity and filling as well as the gas concentrations, the mixing stage is next to increase the homogeneity between the gases, which is a requirement of the reference material when utilizing a mixing device. Figure 5 depicts the cylinder homogenization system, which consists of three rollers on which the cylinder is put and a control panel that regulates the rollers' rotational speeds and directions. The motor turns the roller in the system's center, and the rollers on the system's edge sides move independently of one another. The technology allows for the simultaneous mixing of one or two cylinders. The center roller's rotational direction, duration, and speed can be changed via the control panel.

Figure 5: Photograph of the homogenizer.

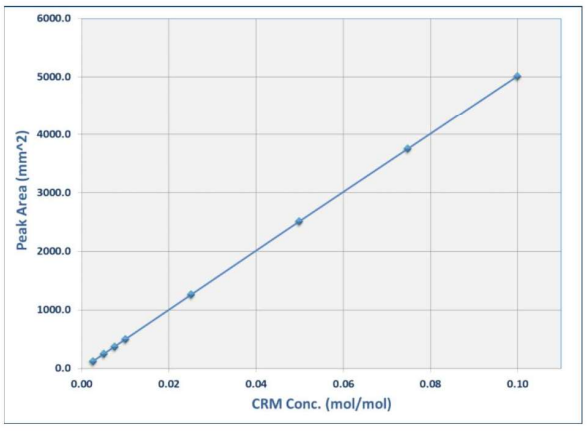

Figure 6: Calibration Curve: The relationship between the response of the device (GC) and the values of the reference materials concentrations.

3. VERIFICATION OF GAS MIXTURE COMPOSITION USING GC-TCD

The primary gas mixtures of CO_2 in N_2 propagated gravimetrically according to ISO 6142 have been verified by GC–TCD in accordance with ISO 6143. For producing and certification of eight primary mixtures, we use CRMs for verification process with concentration range (0.0100 – 0.100000) (mol/mol). So that the concentration of the unknown sample was in the middle of that range each calibration concentration was injected 10 times and the unknown was injected 10 times the average was calculated and the calibration curve was obtained by plotting the concentration (x) against the peak area (y) (see table 2). The concluded calibration curve is shown in Figure 6.

4. UNCERTAINTY ANALYSIS

The uncertainty estimation of the measurement of CO_2 concentration was carried out using the bottom-up approach based on EURACHEM/CITAC Guide CG4 [14].

The potential sources of uncertainty and how they might affect the value of the measurand are identified and preliminary analyzed; full analysis with fish bone diagram and full uncertainty budget is beyond the scope of this paper and it is part of future work for another publication. It is clear that the mass of CO_2 in the N_2 balance in the CRM, the mass of the N_2 balance gas contributed, the molecular weight of the gas components, and the uncertainty from the CRM itself are the main uncertainty sources for the preparation of PSMs by gravimetric dilution.

In addition, there are many factors affecting the GC analysis, which can be summarized in many categories as follows [15]:

A. Result of analysis: carrier gas flow rate, column temperature, sample size, and split ratio.
B. Peak area: carrier gas flow rate, baseline drift, noise, and peak resolution, among others.
C. Peak height: column temperature, detector temperature, integrator settings, and repeatability of sample injection, among others.
D. Split injection: injector liner, injector temperature, split ratio, among others.
E. TCD: detector temperature, wire temperature, carrier gas flow rate.

-The combined standard uncertainty, u_c

Taking into account the previously mentioned factors (errors), which can be categorized into type

A and Type B uncertainty, as per [16]. Since the standard uncertainties are of different units, the combined standard uncertainty, u_c is calculated as ratios and the resulting ratio is multiplied by the sample gas concentration, C_0, as shown in equation 1, to assign a unit to the calculated uncertainty.

$$u_c = C_0 \sqrt{(\frac{u_{CRM}}{C_{CRM}})^2 + (\frac{u_{PACRM}}{PA_{CRM}})^2 + (\frac{u_{PAsample}}{PA_{sample}})^2} \quad (1)$$

The expanded uncertainty at 95% confidence level (k=2) of eight PSMs was calculated in the range of 0.01 to 0.10 relative to the mole fraction of final gas mixtures from the estimation of uncertainty for the gravimetric dilution of calibration gas mixtures (CO_2 in N_2 Balance). The preliminary uncertainty budget is shown in table 3. The detailed estimation of different uncertainty components with error analysis and treatment is a topic of another on-going work.

Table 2: Verification of gas mixture composition using GC

Code	Concentration	Uncertainties associated with x-values	y-values	Uncertainties associated with y-values
CRM	0.010000	0.000004	504.000000	0.206000
CRM	0.010000	0.000002	504.000000	0.419000
CRM	0.020000	0.000002	1010.000000	1.020000
CRM	0.025000	0.000002	1260.000000	0.362000
PSM	**0.029000**	**0.000001**	**1470.615700**	**0.251250**
CRM	0.050000	0.000008	2520.000000	1.290000
CRM	0.050000	0.001104	2520.000000	1.490000
CRM	0.075000	0.000069	3780.000000	1.200000
CRM	0.100000	0.001698	5050.000000	1.660000

Table 3: Uncertainty budget (preliminary)

Cylinder	Source	X	u(X)	Unit	u(X)/X
PSM266406	**CRM**	0.010000	0.000004	mol/mol	0.000040
		0.010000	0.000002		0.000020
		0.020000	0.000002		0.000010
		0.025000	0.000002		0.000008
		0.050000	0.000008		0.000016
		0.050000	0.001104		0.002208
		0.075000	0.000069		0.000092
		0.100000	0.001698		0.001698
		u_c(CRM)			**0.00287**
		y	u(y)		u(y)/y
	Peak Area (R)	504.000000	0.206000	mm^2	0.000409
		504.000000	0.419000		0.000831
		1010.000000	1.020000		0.001010
		1260.000000	0.362000		0.000287
		2520.000000	1.290000		0.000512
		2520.000000	1.490000		0.000591
		3780.000000	1.200000		0.000317
		5050.000000	1.660000		0.000329
		u_c(PA (R))			**0.00166767**
	Peak Area (S)	1470.6157	0.2513	mm^2	**0.000170881**
C_0 (mol/mol)		**2.90E-02**			
u_c		**3.25E-03**			
C_0 x u_c		**9.43E-05**		**mol/mol**	
U_{Exp}		**1.89E-04**		**mol/mol**	
U_{Exp} %		**0.65**		**%**	

4. RESULTS AND DISCUSSION

In this work, we prepared eight PSMs with different concentrations, using the CRM (certified gas mixture) using the scheme described in section 2. The concentration range of the prepared PSMs is 0.010000 to 0.100000 mol/mol. The verification process using GC-TCD had been done as shown in table 2. The summary of the prepared concentrations and the associated uncertainties are

shown in table 4. The produced reference PGMs are used for the calibration of the customers' artefacts with maintaining the traceability of the relevant calibration activities.

Table 4. Summary of the prepared PSMs concentrations and associated uncertainties

PSM Code	Concentration mol/mol	Expanded uncertainty (%)
PSM-1	0.010000	0.000014
PSM-2	0.022000	0.000013
PSM-3	0.025000	0.000023
PSM-4	0.029000	0.000001
PSM-5	0.050100	0.000019
PSM-6	0.049000	0.001109
PSM-7	0.074900	0.000073
PSM-8	0.100000	0.001798

5. CONCLUSION AND ON-GOING WORK

Preparation scheme of primary standard mixtures of CO_2 in N_2 is presented. The prepared eight PSMs with different concentrations are used as working standards in the lab to transfer the traceability from the parent CRMs to the customers DUTs. The detailed description of the used processes; cleaning and evacuating the cylinders, automatic weighing, gas filling, mixing and homogenization processes as well as the used equipment are shown. Different sources of uncertainty, such as weighing, gas cylinder, component gas, certified calibration gas mixture, purity of N_2 balance, and molar mass of gas component, affected the uncertainty of the fraction mole of final gas mixtures, are studied, and preliminary uncertainty budget has been shown in this work. The full uncertainty analysis is beyond the scope of this paper, and under on-going preparation for another subsequent publication.

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