Development of CO_2 in N_2 Primary Gas Mixtures as Certified Reference Materials for Supporting the Climate Change Monitoring Measurements

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Abstract: Carbon dioxide (CO_2) is an important heat-trapping gas, which leads to a rise in the earth's temperature causing climate changes with adverse effects. This climate change created the need for national and international programs to monitor the levels of carbon dioxide emissions into the atmosphere. The CO_2 monitoring programs should be supported with traceability of the measurement results to the SI units to provide confidence in the monitoring results based on which, the right decisions for environmental treatment could be made. In this research paper, a primary CO_2 in nitrogen gas mixture of concentration 199.42 mmol/mol has been gravimetrically prepared from pure CO_2 and N_2 in a 5L aluminum gas cylinder based on ISO 6142. From this mixture, five diluted gas mixture of mole fractions 9.998, 24.916, 49.828, 74.664 and 99.825 mmol/mol were prepared. The prepared gas mixtures were analyzed by GC-TCD according to ISO 6143 to verify their mol fractions and the obtained results were in good agreement with those obtained by the gravimetric preparations. These reference materials are very useful for the periodical calibration of CO_2 monitors operated within the climate change monitoring programs and those used for car exhaust measurements. A multipoint calibration of two CO_2 monitors using the prepared CO_2 CRMs has been performed as an application and the monitors showed very good linear response with reasonable uncertainty.

Keywords: Gas Mixture, Mole Fraction, GC-TCD, Uncertainty, CRM, Calibration, CO_2 Monitors

1. Introduction

The greenhouse effect occurs in the lower atmosphere (the troposphere) where life exists and weather occurs. In the absence of the greenhouse effect, the average temperature on the Earth's surface is estimated at -19°C instead of the current average of 14°C [1]. The greenhouse effect is produced by greenhouse gases (GHGs), which are natural and anthropogenic gaseous components in the atmosphere that absorb and emit radiation in the thermal infrared range and their effects are found in the troposphere [2]. The most abundant greenhouse gas is CO_2 [3] with varying percentage

daily, seasonally and annually and is responsible for 20% of heat absorption [4, 5]. Natural sources of carbon dioxide include organic decomposition, ocean release and respiration while anthropogenic sources include activities like cement manufacturing, deforestation, and burning of fossil fuels like coal, oil, natural gas, etc. It has been published that 24% of direct carbon dioxide emissions come from agriculture, forestry and other land uses and 21% come from industry [2]. In the past two centuries, atmospheric carbon dioxide concentrations have risen dramatically from about 270

µmol/mol in 1750 to concentrations above 385µmol/mol [6, 2] and about 50% of cumulative human carbon dioxide emissions between 1750 and 2010 occurred Since the seventies [2]. There is a fear that the temperature rise resulting from high concentrations of carbon dioxide as well as the positive feedback of water will increase 3-5°C over the average surface temperature of the Earth in the year 2100 if the emissions problem is not taken seriously [2]. More than 100 countries have adopted a global warming limit of 2°C or less (relative to pre-industrial levels) as a guiding principle for mitigation efforts to reduce the risks, impacts and damages of climate change [7, 8]. Cancun pledges on global warming have identified responsibilities for carbon dioxide emissions in developed and developing countries, and it has become imperative for each country to reduce its annual emissions [9]. This is in addition to what is stated in the United Nations Framework Convention on Climate (UNFCCC), which requires each country to take its responsibilities to reduce the CO$_2$ emissions [10]. Therefore, monitoring of CO$_2$ levels in air is of fundamental importance for clean environment in each country and consequently for better climate. However, effective monitoring programs depend on accurate and reliable CO$_2$ measurement results which can be produced if reference materials are used [11]. They provide a very good technical tool for testing laboratories around the world to produce accurate and comparable measurement results. Reference materials are of diverse uses in the calibration of measuring instruments, method validation, assigning values to materials and analytical quality control [12, 13]. They are of critical importance in establishing comparability and accuracy of analytical results between different locations and over the time. A reference material is defined as: a material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process [14]. The CO$_2$ in nitrogen gas mixtures are important certified reference materials used for the calibration of CO$_2$ analyzers in order to achieve traceability of measurement results to the SI units [14]. They are prepared gravimetrically in accordance with ISO 6142 and the prepared concentrations are verified according to ISO 6143 using a reliable analytical technique such as GC-TCD [15]. In this paper, we report the gravimetric preparation of a primary gas mixture of CO$_2$ in N$_2$ of concentration 199.2 mmol/mol by one dilution of pure CO$_2$ and N$_2$ gases. From this primary mixture, calculated masses of CO$_2$ were taken with calculated masses of pure N$_2$ gas to prepare five primary gas mixtures of concentrations: 9.99781, 24.91618, 49.82818, 74.66373 and

99.82487 mmol/mol [16]. These prepared concentrations were verified by measurement using a GC-TCD and the agreement of the two results was tested by applying the criterion laid down in ISO 6143 [17]. The five prepared gas mixtures were applied in a multi-point calibration of two CO$_2$ gas monitors using a validated and accredited laboratory procedure. Uncertainty of the calibration measurement results was estimated according to ISO GUM [18]. The calibration was of very good linearity and the calibration uncertainty was small indicating the suitability of the produced gas mixtures for the CO$_2$ monitors calibration purposes.

2. Materials and Methods

2.1. The Pure Gases

The pure CO$_2$ (99.8%) and N$_2$ (99.9999%) gases were delivered by LINDE-SIGAS, Germany and the 5L aluminum cylinders in which the gas mixtures were filled-in were supplied by Air Liquide, the Netherlands.

2.2. The Automatic Weighing Process

The main primary gas mixture (MA) and the five diluted gas mixtures (M1-M5) were prepared according to ISO 6142:2001 by gravimetric mixing method. The nominal compositions were determined by the ideal gas equation, $PV = nRT$ based on the target mole fractions, then corrected by a compression factor according to equation (1) [14].

$$m_i = \frac{x_i \; x \; p_F \; x \; V_{cyl} \; x \; M_i}{R \; x \; T \; x \; Z_f} \qquad (1)$$

where,

m_i- mass of CO$_2$ or N$_2$ in the mixture, g;

x_i- intended mole fraction of CO$_2$ or N$_2$, mol/mol;

p_f - filling pressure of the mixture, Pa;

V_{cyl} - volume of the cylinder, m^3;

M_i - the molar mass of CO$_2$ (44.01g/mol) and of N$_2$ (28.012 g/mol);

R - the gas constant (8,314 51 J/mol. K);

T - the filling temperature, K;

Z_f - the compression factor of the mixture at T and P_F;

The weighed masses of CO$_2$ and N$_2$ of the all prepared gas mixtures, MA and M1-M5 together with the corresponding concentrations are shown in Table 1.

Table 1. The weighing results of CO$_2$ and N$_2$ of the primary CO$_2$ gas mixtures.

Gas mixture	Mole fractions (mmol/mol)	Mass of CO$_2$ (g)	Mass of N$_2$ (g)
MA	199.20	181.535	462.421
M1	9.998	31.762	541.530
M2	24.916	23.599	585.9553
M3	49.828	46.573	563.628
M4	74.664	58.475	459.702
M5	99.825	91.967	527.490

2.3. The Gas Filling Process

Previously cleaned and evacuated 5L aluminum cylinders were used for filling the gas mixtures in and each gas component was added through a filling station in which the tubes and valves were flushed with nitrogen and carbon dioxide and made free of oil. In each mixture, the mass of each component was determined using a mass comparator balance and the mixture was prepared by gravimetric addition of each component. Details of the filling process, homogenization and weighing of the gas cylinders are described elsewhere [19]. A scheme of the filled cylinders is shown in Figure 1.
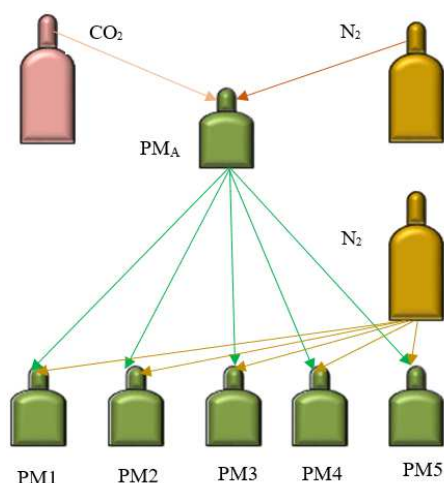

Figure 1. Scheme of the prepared CO_2 in N_2 gas mixtures.

2.4. The Gas Chromatography-TCD Conditions

The gas chromatography machine used for the measurement of CO_2 gas is an Agilent Technologies 7890B GC system with thermal conductivity detector, TCD. The chromatographic separation was carried out using an HP-plot (19091 P-S12 HP-AL/S) column (25 m x 320 mm x 8.0 um). The injector temperature was set at 250°C and that of the detector at 280°C. The GC oven program was started at 60°C (for 1 min) then increased to 80°C at 20°C/min and to 200°C at 30°C/min. This temperature was hold for 1.33 min and the total run time was 7 min. The carrier gas was helium at a flow rate of 2 mL/min and the flow of the reference was 5 mL/min.

2.5. The CO_2 Monitors to Be Calibrated by the Developed CO_2 Gas Mixtures

Two exhaust gas monitors were brought for calibration by the produced CO_2 gas mixtures. The first is BS EN50379-3, KANE, UK and the second is Testo 350, TESTO, Germany.

3. Results and Discussion

3.1. Traceability of the Measurement Results

The traceability of the mole fraction measurement results of the gas components in the prepared gas mixtures has been established to the SI units through purity, the masses of CO_2 and N_2 weighed by a calibrated automatic weighing system and the IUPAC definition of the molecular weight of the gas components.

3.2. The Mole Fractions of the Pure CO_2 and N_2 Gases

The pure CO_2 gas cylinder was accompanied by a certificate from the supplier showing the purity of CO_2 as 99.8% with impurities of O_2 and H_2O in the limits: <50 ppm and <100 ppm respectively. Also the certificate of pure N_2 from the supplier indicated the purity of N_2 as 99.999% with impurities of CO, CO_2, THC (CH_4), O_2 and H_2O in the limits: <0.5 ppm, <0.5 ppm, <0.5 ppm <5 ppm and <2 ppm respectively. For calculation of the mole fraction of each impurity in ppm, a low limit was set as zero and the upper limit was taken as indicated in the supplier certificate, then both limits were summed and divided by 2 [11]. The calculated mole fraction was divided by 1000000 to express it in mol/mol as shown in Tables 2 and 3. The mole fraction of the pure CO_2 and the pure N_2 was then calculated using equation (2) in which n is the number of impurities.

$$Mole\ fractionon\ of\ pure\ CO_2\ or\ N_2 = 1 - \sum_{i=1}^{n} mole\ fraction\ of\ impurities \qquad (2)$$

3.3. The Mole Fractions of the Prepared Gas Mixtures (M_A and M_1-M_5)

The mole fraction of the CO_2 gas component delivered in the prepared gas mixtures M_A and M_1-M_5 were calculated using equation (3), meanwhile the mole fraction of N_2 was calculated by equation (4).

$$x_{CO_2} = \frac{\dfrac{x_{CO_2 A} \cdot m_{CO_2}}{x_{CO_2 A} \cdot M_{CO_2}}}{\dfrac{m_{N_2}}{x_{N_2} \cdot M_{N_2}} + \dfrac{m_{CO_2}}{x_{CO_2 A} \cdot M_{CO_2}}} \qquad (3)$$

where,

x_{CO_2}- is the mol fraction of CO_2 gas in the final mixture;
x_{CO2A}-is the mol fraction of the parent CO_2 gas;
m_{CO2}-is the mass of CO_2 determined by weighing;
M_{CO2} - is the molar mass of CO_2;
x_{N2}- is the mole fraction of N_2 gas;
m_{N2} - is the mass of N_2 determined by weighing;
M_{N2} - is the molar mass of N_2.

$$x_{N_2} = \frac{\dfrac{x_{N_2} \cdot m_{N_2}}{x_{N_2} \cdot M_{N_2}}}{\dfrac{m_{N_2}}{x_{N_2} \cdot M_{N_2}} + \dfrac{m_{CO_2}}{x_{CO_2A} \cdot M_{CO_2}}} \quad (4)$$

In case of the first step filling in which the mixture MA has been produced, the mole fraction of the parent gas, x_{CO2A} was used in the calculations. But in case of the second step filling in which the mixtures M1-M5 have been prepared, the mole fraction of the mixture MA was used. The calculated mole fractions of the prepared gas mixtures are shown in Table 3.

Table 2. *The mole fraction of CO_2 and N_2 in the gravimetrically prepared CO_2 gas mixtures.*

Primary gas mixture	Gas component	mole fraction (mmol/mol)
MA	CO_2	199.200
	N_2	800.063
M1	CO_2	9.998
	N_2	989.997
M2	CO_2	24.916
	N_2	974.910
M3	CO_2	49.838
	N_2	950.025
M4	CO_2	74.664
	N_2	925.090
M5	CO_2	99.825
	N_2	900.100

Table 3. *Uncertainties of the impurities contained in the pure CO_2 and N_2 gases.*

Impurity component	Manufacturer specification	Low limit	Upper limit	Assigned mole fraction (ppm)	Mole fraction (mol/mol)	$u(x_i)$ (mol/mol)
Impurities of CO_2						
O_2	< 50 ppm	0	50	25	2.50E-05	1.443E-05
H_2O	< 100 ppm	0	100	50	5.00E-05	2.887E-05
Impurities of N_2						
CO	<0.5 ppm	0	0.5	0.25	2.50E-07	1.443E-07
CO_2	<0.5 ppm	0	0.5	0.25	2.50E-07	1.443E-07
THC (CH_4)	<0.5 ppm	0	0.5	0.25	2.50E-07	1.443E-07
O_2	<5 ppm	0	5	2.5	2.50E-06	1.443E-06
H_2O	<2 ppm	0	2	1	1.00E-06	5.773E-07

3.4. Uncertainty in the Mole Fractions Measured Gravimetrically

The mathematical measurement model used for calculation of the mole fractions of gas components in the gas mixture prepared by gravimetric method is given in equation (3). From this equation, the sources of uncertainty can be identified in three categories, which are: 1) purity of parent CO_2 and N_2, 2) weighing of the parent gases CO_2 and N_2, and 3) molar mass of CO_2 and N_2 [17]. Details of calculation of each of the uncertainty contributions are explained below.

3.5. Uncertainty in the Purity of CO_2 and N_2 Parent Gases

Table 3 shows the impurity components contained in the pure CO_2 and N_2 parent gases and their manufacturer specifications from which the assigned mole fractions (ppm) of these impurities were calculated as mentioned above. The assigned mole fractions were divided by 1000000 to get them in mol/mol and the resulting values were divided by $\sqrt{3}$ to obtain the standard uncertainties, $u(x_i)$ listed in the table. The combined standard uncertainty of the impurities in CO_2 was calculated using equation (5) and that of impurities in N_2 was calculated using equation (6).

$$u_{CO_2} = \sqrt{\left(c_1 \cdot u_{O_2}\right)^2 + \left(c_2 \cdot u_{H_2O}\right)^2} \quad (5)$$

$$u_{N_2} = \sqrt{(c_1 \cdot u_{CO})^2 + (c_2 \cdot u_{CO_2})^2 + \left(c_3 \cdot u_{CH_4}\right)^2 + \left(c_4 \cdot u_{O_2}\right)^2 + \left(c_5 \cdot u_{H_2O}\right)^2} \quad (6)$$

In equations (5) and (6), c_1, c_2, c_3, c_4 and c_5 are the sensitivity coefficients and each of them equals 1 since they are expressed in the same unit (mol/mol) which the impurity of CO_2 and N_2 are expressed in. The calculated uncertainty values were 3.23E-05 and 5.77E-07 mol/mol for CO_2 and N_2 respectively.

3.6. Uncertainty in Weighing of the Parent CO_2 and N_2 Gases

The uncertainty of the weighing process is estimated from four contributions, which are: balance (u_m), calibration certificate of the balance (u_{Cal}), buoyancy effects (u_B) and the residual gas (u_R) [16]. Each of these contributions is discussed as below.

3.6.1. Balance (u_m)

The uncertainty has been determined by repeated weighing of a cylinder that was filled with gas mixture and it includes resolution of the balance, drift, incorrect zero point and the positioning of the gas cylinder on the ban. The cylinder of each gas mixture has been weighed three times under statical control thus producing three weighing sets of data (N=3). For each data set, the standard deviation was calculated and the pooled estimate of standard deviation was calculated using equation (7),

$$S_p = \sqrt{\frac{(n_1-1)\,s_1 + (n_2-1)\,s_2 + (n_3-1)\,s_3}{(n_1-1) + (n_2-1) + (n_3-1)}} \qquad (7)$$

where

S_p- pooled standard deviation;

s- standard deviation of each weighing data set;

$n-1$- degree of freedom of each weighing data set (8-1).

The standard uncertainty (u_m) was calculated by equation (8) in which N is the number of data sets which equals 3.

$$u_m = \frac{S_p}{\sqrt{N}} \qquad (8)$$

3.6.2. Calibration Certificate

The calibration certificate of the balance contains an uncertainty function shown in equation (9), from which the standard uncertainty resulting from the balance calibration can in case of weighing each gas mixture cylinder be calculated where R is the mass of the filled gas cylinder.

$$u = 2.939 \times 10^{-7} \times R \qquad (9)$$

3.6.3. Buoyancy Effects (u_B)

As a result of the change of temperature, relative humidity and atmospheric pressure during the weighing process of the gas mixture cylinders, the air density inside the room of the automatic weighing system changes [11]. This change causes a slight mass difference between the sample and the reference cylinders due to the difference in their volumes (4.99, 5L) giving rise to what is known as air buoyancy effect [16]. The temperature, relative humidity and the air pressure were recorded during the weighing of each gas cylinder and were used to calculate the air density by equation (10).

$$\rho_a = \frac{0.34848\,p - 0.009\,(rh)\,x\exp(0.061\,t)}{273.15 + t} \qquad (10)$$

where,

ρ_a - the air density (kg/m^3);

p - the air pressure (Pa);

t - the temperature (°C);

rh - the relative humidity (% RH).

From the calculated values of (ρ_a), it was found that the largest air density difference ($\Delta\rho$) equals 0.005 kg/m^3. This difference was multiplied by the difference in cylinders' volume (V_S-V_R) as in equation (11) to give the uncertainty due to the air buoyancy, u_B [20]. A rectangular distribution was assumed for the calculated value and therefore, it was divided by √3 to obtain the standard uncertainty as 0.00003 mg.

$$u_B = \Delta\rho_a\,(V_S - V_R) \qquad (11)$$

3.6.4. Residual Gas (u_R)

Each gas cylinder was purged with nitrogen to get rid of any contaminant gas residue and evacuated at 10^{-7} mbar before filling. As pointed out in ISO 6142, it is assumed that the residual nitrogen pressure after evacuation is 0.1 bar [11]. The mass of this remaining nitrogen gas residue is considered as an uncertainty and was calculated using equation (12),

$$m = \frac{PVM}{RT} \qquad (12)$$

where

m- mass of nitrogen residue (mg);

P- residual nitrogen gas (0.1 bar);

V- volume of the gas cylinder (4.99 L);

R- universal gas constant (8.31451 J/mol. K);

M- molar mass of nitrogen (28.00614 g/mol);

T- thermodynamic temperature (K).

The residual mass was found 5.7 mg and the standard uncertainty was calculated as u_R = 5.7/√3 = 3.3 mg.

3.6.5. The Combined Standard Uncertainty of Weighing

The combined standard uncertainty in weighing the CO_2 and N_2 masses can be calculated from equations (13) and (14) respectively, in which c_1, c_2 and c_3 are the sensitivity coefficients that was considered equal 1 since the uncertainties are expressed in mass unit (mg).

$$u_c\,m_{CO_2} = \sqrt{(c_1 \cdot u_{\text{Balance}})^2 + (c_2 \cdot u_{\text{Calb Cert}})^2 + (c_3 \cdot u_{Buoyancy})^2 + (c_4 \cdot u_{Residual\ gas})^2} \qquad (13)$$

$$u_c\,m_{N_2} = \sqrt{(c_1 \cdot u_{\text{Balance}})^2 + (c_2 \cdot u_{\text{Calb Cert}})^2 + (c_3 \cdot u_{Buoyancy})^2 + (c_4 \cdot u_{Residual\ gas})^2} \qquad (14)$$

3.7. Uncertainty of the Molar Mass of CO_2 and N_2

The atomic weights of C, O and N and their uncertainties issued by IUPAC are shown in Table 4 [21].

Uncertainty of the molar mass of CO_2 (u_{MCO2}) was calculated using equation (15) in which c_1 and c_2 are the sensitivity coefficients which are considered equal 1 since the uncertainties are expressed in the same unit, g/mol. Uncertainty of the molar mass of N_2 was calculated according to equation (16) in which the factor 2 represents the two nitrogen atoms.

Table 4. *IUPAC atomic weights of C, O and N elements and their uncertainties.*

Element	Atomic weight	Uncertainty	Standard uncertainty
C	12.0107	0.00080	0.00046
O	15.9994	0.00030	0.00017
N	14.00307	0.00017	0.00010

$$u_{M_{CO_2}} = \sqrt{\left(c_1 . u_C\right)^2 + 2\left(c_2 . u_O\right)^2} \tag{15}$$

$$u_{M_{N_2}} = \sqrt{2\left(u_N\right)^2} \tag{16}$$

3.8. The Combined Standard Uncertainty, u_c

The combined standard uncertainty in the mole fraction of each gas mixture, has been calculated according to equation (17), which combines all the previously discussed uncertainty sources.

$$u_c = \sqrt{\left(\frac{\partial x_{CO_2}}{\partial x_{CO_2A}} . u_{x_{CO_2A}}\right)^2 + \left(\frac{\partial x_{CO_2}}{\partial m_{CO_2}} . u_{m_{CO_2}}\right)^2 + \left(\frac{\partial x_{CO_2}}{\partial M_{CO_2}} . u_{M_{CO_2}}\right)^2 + \left(\frac{\partial x_{CO_2}}{\partial x_{N_2}} . u_{x_{N_2}}\right)^2 + \left(\frac{\partial x_{CO_2}}{\partial m_{N_2}} . u_{m_{N_2}}\right)^2 + \left(\frac{\partial x_{CO_2}}{\partial M_{N_2}} . u_{M_{N_2}}\right)^2} \tag{17}$$

In this equation, the sensitivity coefficients: $\delta x_{CO2}/\delta x_{CO2A}$, $\delta x_{CO2}/\delta m_{CO2}$, $\delta x_{CO2}/\delta M_{CO2}$, $\delta x_{CO2}/\delta x_{N2}$, $\delta x_{CO2}/\delta m_{N2}$ and $\delta x_{CO2}/\delta M_{N2}$ were obtained by differentiation of equation (3) and their values for the all mixtures are given in Table 5. These values were multiplied by the corresponding standard uncertainties to obtain the uncertainty contribution (c_i, u_{xi}). A typical example of the uncertainty budget is given in Table 6 for the CO_2 gas mixture MA and the combined standard uncertainties for the all mixtures are given in Table 7.

Table 5. *Values of sensitivity coefficients resulting from differentiaon of equation (3).*

Sensitivity coefficient, c_i	Gas mixture					
	MA	M1	M2	M3	M4	M5
$\delta x_{CO2}/\delta x_{CO2A}$	4.01E-02	2.90E-03	8.71E-03	2.71E-02	6.02E-02	9.50E-02
$\delta x_{CO2}/\delta m_{CO2}$	8.80E-04	7.64E-04	7.14E-04	6.16E-04	6.31E-04	4.62E-04
$\delta x_{CO2}/\delta M_{CO2}$	-5.71E-03	-2.31E-04	-3.83E-04	-6.52E-04	-8.38E-04	-9.65E-04
$\delta x_{CO2}/\delta x_{N2}$	1.60E-01	1.27E-02	2.11E-02	3.58E-02	4.61E-02	5.31E-02
$\delta x_{CO2}/\delta m_{N2}$	-3.46E-04	-2.26E-04	-2.88E-05	-5.09E-05	-8.02E-05	-8.05E-05
$\delta x_{CO2}/\delta M_{N2}$	-3.46E-04	-2.26E-04	-2.88E-05	-5.09E-05	-8.02E-05	-8.05E-05

Table 6. *Uncertainty budget for the mole fraction for the CO_2 gas mixture MA.*

Quantity	Estimate x_i	Standard uncertaint $u(x_i)$	Unit	Probability distribution	Sensitivity coefficient c_i	Uncertainty contribution (c_i. u_{xi})
Mole fraction (purity) of CO_2	0.1992	0.000032	mol/mol	Rectangular	0.04008182	1.29E-06
Mass of CO_2	181.5350	0.003327	g	Normal	0.00088028	2.93E-06
Molar mass of CO_2	44.01	0.000523	g/mol	Rectangular	-0.00570598	-2.98E-06
Mole fraction (purity) of N_2	0.800063	0.000001	mol/mol	Rectangular	0.15980398	9.23E-08
Mass of N_2	462.421	0.003327	g	Normal	-0.00034558	-1.15E-06
Molar mass of N_2	28.00614	0.000139	g/mol	Rectangular	0.00570598	7.92E-07
Combined standard uncertainty, u_c			mol/mol		4.59E-06	

Table 7. *The combined standard uncertainty of the gas mixtures (mol/mol).*

Gas mixture	MA	M1	M2	M3	M4	M5
The combined standard uncertainty (mol/mol)	4.59E-06	2.68E-06	2.42E-06	2.28E-06	2.92E-06	3.49E-06

3.9. GC-TCD Measurements of the Mole Fractions of the Gas Mixtures

In accordance with the requirements of ISO 6143, a validated (GC-TCD) method was selected to verify the mole fraction of the gravimetrically prepared gas mixtures. Six certified reference materials (CRMs) of concentrations: 0.005, 0.01, 0.04984, 0.07474, 0.09987 and 0.1999 mol/mol were used for the GC calibration to provide metrological traceability of the measurement results to SI units. The calibration and sample cylinders were connected to the GC in the sequence: R-S-R-S-R-S-R-R, where R represents the reference and S represents the sample to be measured. The reason for that particular sequence was to ensure the quality of calibration data and stability of the GC system response. Each CRM was injected 10 times and the sample was

injected 10 times under intermediate precision conditions. A typical chromatogram that includes a peak for CO_2 at RT 4.012 min and a peak for N_2 at 2.609 min is shown in Figure 2 and the calibration function of the GC-TCD was plotted between the CRMs mole fractions and the corresponding peak areas as shown in Figure 3. The equation of this function from which the mole fraction (x) can be calculated is: y = 51036x – 35.257.

The obtained peak area (PA) results of all the prepared gas mixtures, average, standard deviation, (SD) and the RSD %

were recorded in Table 8. By examining these results, it has been found that the relative standard deviation (RSD %) values were very small, which means that the results are of very good precision. This confirms the appropriateness of the GC-TCD method for these CO_2 measurements. Using the calibration function: $y = 51036x - 35.257$ in which y is the measured peak area, the mole fractions (x) of the prepared gas mixtures (M1-M5) and M_A were calculated as: 0.00999, 0.02500, 0.04987, 0.07481, 0.09981 and 0.19958 mol/mol respectively.
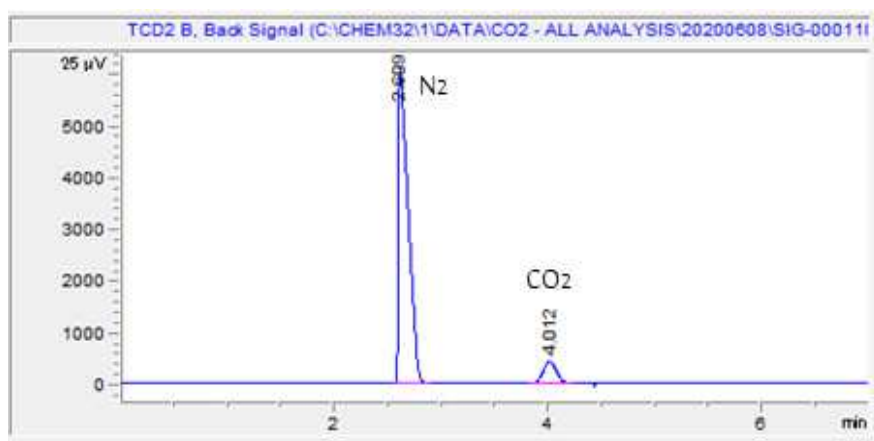

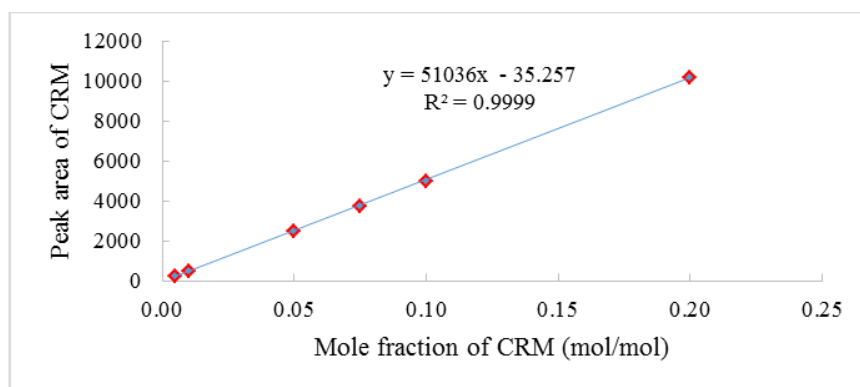**Figure 2.** *GC-TCD Chromatogram showing CO_2 and N_2 peaks.*

Figure 3. *Calibration line of GC-TCD.*

Table 8. *Peak areas of the CO_2 in the prepared gas mixtures.*

Gas mixture	MA	M1	M2	M3	M4	M5
	10150.640	474.287	1240.832	2510.897	3780.633	5058.961
	10150.640	474.444	1240.549	2510.719	3782.522	5058.408
	10150.445	474.498	1239.585	2510.766	3783.128	5058.646
	10150.793	474.559	1240.826	2510.635	3783.641	5058.578
Peak area	10150.501	474.719	1240.955	2510.415	3782.52	5058.778
	10150.185	474.592	1240.212	2510.045	3781.013	5058.452
	10150.984	474.68	1240.355	2510.26	3782.319	5058.368
	10150.553	474.923	1240.499	2509.174	3786.961	5058.601
	10150.940	474.799	1240.078	2509.311	3783.641	5058.112
	10150.692	474.82	1240.585	2509.11	3782.52	5058.368
Average	10150.637	474.6321	1240.448	2510.133	3782.8898	5058.527
SD	0.2371863	0.1935174	0.411633	0.693227	1.7355796	0.239483
RSD%	0.0023367	0.0407721	0.033184	0.027617	0.0458797	0.004734
Mole fraction (mol/mol)	0.199583	0.00999	0.02500	0.04987	0.07481	0.09981

3.10. Uncertainty of the GC-TCD Measurement Results

Uncertainty in the measurement results of the mole fraction of carbon dioxide obtained by GC-TCD can be calculated from a number of sources referred to in ISO 6143, namely, peak area (PA) of the measured CO$_2$ (Repeatability), the mole fraction of CRM and the peak area (PA) of CRM. Uncertainty of the mole fraction of CO$_2$ determined by gravimetry has been added to these sources. All these sources are explained in the fishbone structure in Figure 4.
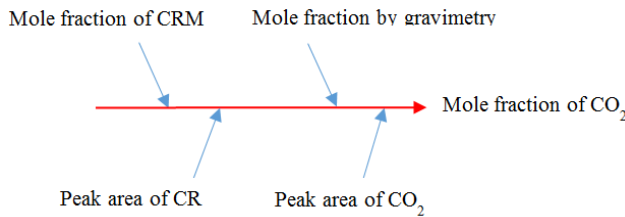

Figure 4. Fishbone structure showing the uncertainty sources.

The uncertainty resulting from the measurement of the peak area of the CO$_2$ reference material and the prepared CO$_2$ gas mixtures was calculated using equation (18). Then the uncertainty average of the 6 CRMs was divided by the peak area average to represent the uncertainty contribution of the peak area of CRMs.

$$u(y_i) = \frac{1}{\sqrt{90}} \sqrt{ \sum_{j=1}^{10} (y_{ij} - y_i)^2 } \qquad (18)$$

where,

$u(y_i)$- standard uncertainty of the measured peak area (PA);
y_{ij}- the individual peak area result;
y_i-average of the 10 peak area measurements.

The uncertainty of the mole fraction of the CRMs used for calibration was calculated by dividing the expanded uncertainty contained in the material certificate by 2 and then the uncertainty average of the 6 CRMs was divided by the mole fraction average to represent the uncertainty contribution of the CRMs. Meanwhile uncertainty of the mole fraction measured by gravimetry was calculated as explained above. The combined standard uncertainty was calculated using equation (19).

$$u_c = x_{CO_2} \sqrt{ \left(\frac{u_{CRM}}{x_{CRM}} \right)^2 + \left(\frac{u_{PA\ CRM}}{PA_{CRM}} \right)^2 + \left(\frac{u_{PA\ (rept)}}{PA_{CO_2}} \right)^2 + \left(\frac{u_{x\ gravimetry}}{x_{gravimetry}} \right)^2 } \qquad (19)$$

where,

x_{CO2}- mole fraction measured by GC-TCD;
x_{CRM}- mole fraction of the CRM;
PA_{CRM}- peak area of the CRM;
PA_{CO2} - peak area of the CO$_2$ in the gas mixtures;

$x_{gravimetry}$- mole fraction determined by gravimetry.

The expanded uncertainty was calculated by multiplying the combined standard uncertainty by 2 to provide a confidence level of 95%. The obtained uncertainty results for all the CO$_2$ mixtures are given in Table 9.

Table 9. Uncertainty sources and values of the GC-TCD mole fraction measurements.

Source of uncertainty	Gas mixture					
	MA	M1	M2	M3	M4	M5
u ratio of the mole fraction of CRM	0.0012					
u ratio of the peak area of CRM	0.0003					
$u_{peak\ area}$/peak area of CO$_2$	0.000001	0.000054	0.000019	0.000016	0.000024	0.000020
$u_{x\ gravimetry}$/gravimetry	0.000023	0.000268	0.000097	0.000046	0.000039	0.000035
Combined standard uncertainty, u_c	0.00001	0.00003	0.00006	0.00009	0.00012	0.00025
k	2	2	2	2	2	2
Expanded uncertainty (mol/mol)	0.00003	0.00007	0.00013	0.00019	0.00025	0.00049
Mole fraction (mol/mol)	0.199583	0.00999	0.02500	0.04987	0.07481	0.09981
U_{exp} (%)	±0.24	±0.25	±0.24	±0.24	±0.24	±0.24

3.11. Evaluation of Compatibility of the Measurement Results Obtained by Gravimetry and by GC-TCD

The compatibility between the results obtained by gravimetry and by GC-TCD is a prerequisite for acceptance of the gas mixtures certification. To test this compatibility, the mole fractions and their associated uncertainties given in Tables 2 and 8 has been tested by the criterion in equation (20) which is specified by ISO 6142 and ISO 6143. It has been found that the mole fractions calculated by gravimetry (Table 2) are compatible with those calculated by GC-TCD

(Table 8) indicating correctness of the CO$_2$ in N$_2$ gas mixtures preparations [17].

$$\left| x_{grav} - x_{anal} \right| \leq 2 \sqrt{ u(x_{grav})^2 + u(x_{anal})^2 } \qquad (20)$$

3.12. Evaluation of Long Term Stability of the Prepared CO$_2$ in N$_2$ Gas Mixtures

ISO 6142 requires that checks be carried out for the stability of the prepared CO$_2$ gas mixtures to make sure that the stability of their mole fractions have not affected

by storage conditions or any inappropriate handling factors. Therefore, the mole fraction of each mixture was measured once a year along four years during the storage at room temperature. The measurements were carried out using a calibrated GC-TCD, and the calibration function was used to calculate the results of the measured mole fractions. Figure 5 shows the results of this stability study for each CO_2 gas mixture in which the mole fraction was

set against the number of years. The solid line shows the certified mole fraction that is given in the certificate of each gas mixture CRM and the dashed lines show the associated expanded uncertainty limits. In these figures it can be seen that the measurement results along the 4 years fall within the uncertainty limits, which clearly indicates the stability of the mole fractions of the prepared CO_2 in N_2 gas mixtures.
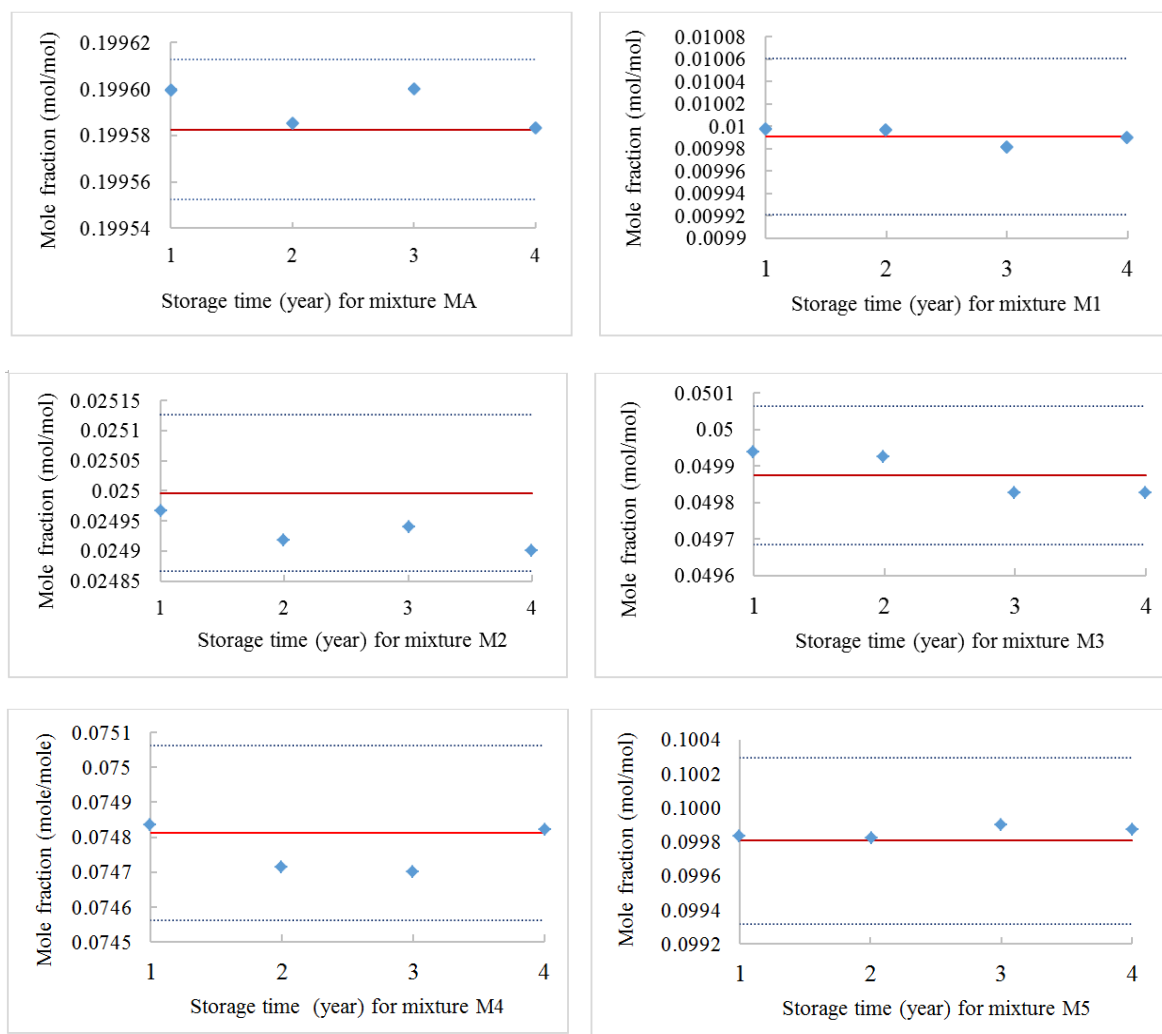

Figure 5. The stability of the CO_2 gas mixtures (MA, M1-M5) along 4 years.

3.13. Calibration Results and Their Uncertainty of Two CO_2 Monitors Using the Prepared CO_2 Gas Mixtures CRMs

After production of the five CO_2 in N_2 gas mixtures (M1-M5) and calculating the certified value and the associated uncertainty for each mixture, they were used in a multi-point calibration of two CO_2 monitors in order to evaluate the performance of these CRMs for the purpose which they were developed for. The calibration was carried out using an accredited laboratory procedure that takes into consideration the recommendations of the manufacturer and covered the

range (9-100 mmol/mol). The two monitors showed a very good response to the prepared CO_2 in N_2 CRMs which can be noticed from the calibration curves A and B given in Figure 6. The calibration function of the curve A is: $y = 0.9559x - 0.4212$ with R^2 equals 1, meanwhile the calibration function of the curve B is: $y = 1.0076x + 0.0018$ with R^2 equals 0.9993. Values of R^2 indicate a very good linearity of both curves. In addition, values of the intercepts are small enough giving rise to a tendency of both calibration lines to approach the point zero, which means that the calibration is of very good quality.
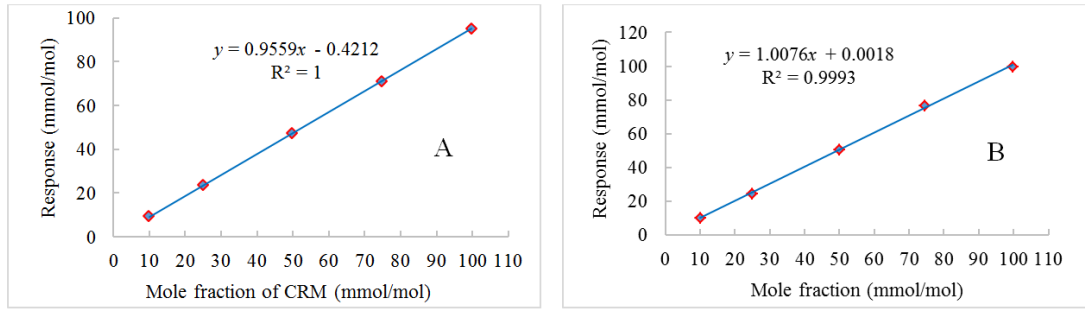
Figure 6. *Calibration curves of two CO_2 monitors (A and B) using the produced CRMs (M1-M5).*

The uncertainty was calculated for each calibration point according to the requirements of ISO GUM. The sources of uncertainty were identified from the mathematical model in equation (21).

Peak area = slope * mole fraction of CRM + int ercept (21)

From this equation, the explicit sources of uncertainty are the mole fraction of CRM, slope, and intercept of the calibration line, while implicit sources are the resolution, accuracy of the CO_2 monitor under calibration in addition to the repeatability of measurements. All these sources can be seen in the fishbone structure in Figure 7.
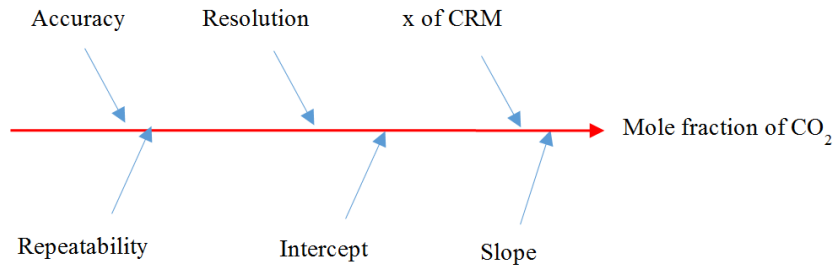

Figure 7. *Fishbone structure showing uncertainty sources of CO_2 monitor calibration.*

The contribution of each source was calculated using an ISO GUM based accredited procedure. The combined standard uncertainty, u_c was calculated using equation (13) in which, uncertainty contributions of the resolution and accuracy of the monitor under calibrations and uncertainty of the repeatability of measurements have been added to the uncertainty contribution of the CRM in order to fit the measurement model in equation (22),

$$u_c = \sqrt{\left(\frac{\partial f}{\partial x_{CRM}} \cdot u_{x\,CRM}\right)^2 + \left(\frac{\partial f}{\partial a} \cdot u_a\right)^2 + \left(\frac{\partial f}{\partial b} \cdot u_b\right)^2} \quad (22)$$

where
$\delta f/\delta x, \delta f/\delta a, \delta f/\delta b$: sensitivity coefficients;
u_a: uncertainty of slope;
u_b: uncertainty o intercept.

The expanded uncertainty was calculated by multiplying the combined standard uncertainty, u_c by a coverage factor $k = 2$ as in equation (23) to provide confidence level of approximately 95%. The results obtained for monitor A are shown in Table 10 and for monitor B are shown in Table 11. Looking to these results, it can be seen the percent uncertainty is small enough indicating a good quality of the calibration of the two CO_2 gas monitors.

$$U_{exp} = u_c \, x \, k \quad (23)$$

Table 10. *Uncertainty results at each calibration point for CO_2 monitor A.*

Uncertainty source	Calibration points				
	C_1	C_2	C_3	C_4	C_5
Mole fraction of CRM	9.99	25	49.87	74.81	99.81
u_c (mmol/mol)	0.03	0.08	0.14	0.21	0.29
U_{exp} (mmol/mol)	0.07	0.15	0.29	0.43	0.57
U_{exp} %	0.68	0.60	0.58	0.57	0.57

Table 11. *Uncertainty results at each calibration point for CO_2 monitor B.*

Uncertainty source	Calibration points				
	C_1	C_2	C_3	C_4	C_5
Mole fraction of CRM	9.99	25	49.87	74.81	99.81
uc (mmol/mol)	0.13	0.32	0.64	0.97	1.28
U_{exp} (mmol/mol)	0.26	0.64	1.28	1.93	2.56
U_{exp} %	2.62	2.57	2.57	2.58	2.57

4. Conclusion

In order to support the quality of CO_2 emission measurements, five mixtures of carbon dioxide in nitrogen were prepared gravimetrically in accordance with ISO 6142 and the mole fractions and their associated uncertainty were calculated according. The mole fractions were verified in accordance with ISO 6143 by analysis using GC-TCD calibrated by CRMs produced by an NMI signatory to the CIPM MRA. The results obtained by the two methods were tested for compatibility as required by the two standards and the results were found to be in good agreement. Thus the mole fractions of the five materials were certified as: 9.99±0.024 (24%), 25.00±0.063 (25%), 49.87±0.120 (24%), 74.81±0.180 (24%) and 99.81±0.240 (24%) mmol/mol. These five CRMs were used in multipoint calibration of two CO_2 monitors and the calibration was of excellent linearity confirming the possibility of using the prepared CRMs for the climate change monitoring programs.

Conflict of Interest

All the authors do not have any possible conflicts of interest.

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