

Certification of a Multicomponent Reference Material from Natural Gas Mixture by Gravimetry and Dual GC-FID/TCD System

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Abstract

Natural gas (NG) is one of the most important sources of energy for industrial and domestic consumption in the present era because it is cheap and free from sulfur impurities. Therefore, accurate and precise measurement of its composition is of fundamental importance for trade reasons. To improve the quality of NG gas measurements, certified reference materials (CRMs) should be used for calibration of measuring equipment in order to ensure the traceability of the measurement results to the SI units. For the traceability purpose, a multicomponent natural gas mixture was prepared gravimetrically as a reference material according to ISO 6142 from pure helium, hydrogen, n-pentane, i-pentane, n-butane, i-butane, propane, ethane, hexane, methane and nitrogen. The preparation was done in two dilution steps in 5 L aluminum cylinders. The calculated mole fractions and associated uncertainties of natural gas components were verified by a dual GC-FID/TCD system in accordance with ISO 6143 calibrated by a series of primary gas mixtures (CRMs) produced by an NMI. The results obtained by gravimetry and by GC measurements have been checked for compatibility as required by ISO 6142 and were found in very good agreement. Details of the preparation and calculation of the mole fractions and uncertainties of all gas components are explained in this article.

Keywords

Pure Gases, Gravimetry, Reference Material, Stability, GC Verification, Uncertainty

1. Introduction

The processed natural gas consists of methane (main constituent), ethane, pro-

pane and hydrocarbons of heavier molecular masses as well as other gases such as nitrogen, helium, and water vapor [1]. Natural gas is one of the most important alternative energy sources to oil because it is a highly efficient fuel, has very little environmental polluting emissions, cheap and safe. This importance as an international trading cheap commodity to consumers has made the accuracy of the determination of the natural gas components very important [2]. The pricing of natural gas depends on the heating value, which is determined from calorimetry measurements or is calculated based on the concentration of each component using GC [3]-[8]. The GC can be equipped with a thermal conductivity detector or a flame ionization detector [9] [10]. While the TCD is used in measuring the concentrations of nitrogen, carbon monoxide, and hydrocarbons with low molecular masses, the FID is used in measuring the mole fraction of hydrocarbons with higher molecular masses, whose quantities quickly vanish as the number of carbon atoms increases [11]. Budiman *et al.* [12] have developed a method for comparison between GC-TCD and GC-FID for the analysis of propane. They came to a conclusion that the sensitivity of the GC-FID is 66 times higher than that of the GC-TCD and the GC-FID method exhibited a wider linear range (0.161%mol/mol - 2.18%mol/mol) than the GC-TCD method (0.242%mol/mol - 2.18%mol/mol). Analysis of natural gas can also be carried out by other techniques such as NIR. Barbosa *et al.* [13] have developed a new NIR detection system using a cheap handheld NIR spectrometer and a tungsten lamp coupled to a lab-made NIR flow cell for the successful automatic quantification of methane, ethane, and propane in natural gas and biogas samples. They concluded that, once the NIR detection system has been previously calibrated via an automatic or batch process, it can be used to monitor light hydrocarbons or other gases inline (as in pipelines). However, confidence in the GC and other analytical methods of natural gas must be ensured by method validation. An example of method validation of propane component has been reported by Zuas and Budiman [14]. They have investigated the precision and accuracy of the GC-TCD method for the measurement of C₃H₈ with CO₂ and CO as pollutant models at different flow rate of helium (He) as carrier gas ranging from 17.50 to 36.25 mL/min. They concluded that, since carrier gas acts as a transporter of components of the mixture in the form of vapor or gas through the column, setting of the flow rate of carrier gas should in proper level achieve a precision and accuracy of the GC-TCD method. The response of the measuring GC instruments is calibrated using a suit of reference gases with certified values (CRMs) for each component [15]. A CRM is defined as a reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures [16]. The certified reference materials from calibration gas mixtures are prepared by transferring parent gases (pure gases or gravimetrically prepared mixtures of known composition) quantitatively by gravimetry from supply cylinders to the cylinder in which the calibration gas mixture will be

contained [17]. The amount of gaseous component added from the parent gas is determined by weighing after each successive addition. The composition of a gas mixture prepared gravimetrically is to be verified by separate determination of the mole fraction of every specified analyte. Gas chromatography is among the well-established analytical techniques for gas mixtures verification [18]. An example on the use of GC-TCD in CO and CO₂ gas mixture verification has been reported by Shehata and co-authors [19] [20]. The possible interferences of other components on the measurement of the analyte under consideration should be considered by the user and taken into account. In the present article, the aim was to prepare and certify a natural gas mixture composed of helium, hydrogen, nitrogen, methane, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane and n-hexane. The gravimetric preparation of the gas mixture was carried out in accordance with ISO 6142 and its analytical verification was carried out by the dual GC-FID/TCD system based on ISO 6143. The method of analysis was simplified by using a single column with an FID detector for each component of the gas mixture under study. The mole fraction calculated from the gravimetric preparation and its associated uncertainty for each gas component was found compatible with that determined by GC. Details of the gas mixture preparation and certification are explained in this article.

2. Materials and Methods

2.1. The Pure Gases

The pure gases of n-pentane (99.50%), i-pentane (99.50%), n-butane (99.50%), i-butane (99.50%), propane (99.50%), ethane (99.50%), methane (99.99%), n-hexane (99%), helium (99.999%), hydrogen (99.999%) and nitrogen (99.99%) were purchased from Linde Gas, Germany. These pure gases contain impurities from argon, carbon monoxide, carbon dioxide, total hydro carbons (C_xH_y), water, sulphur dioxide and hydrogen.

2.2. Gravimetric Preparation of the NG Mixture

According to ISO 6142, a two-step dilution approach was used to prepare the target natural gas mixture since small uncertainties and low concentrations of the impurities components were required [17]. In this preparation, a primary standard mixture, PSM A was prepared by dilution from pure helium and hydrogen. This mixture together with the pure gases mentioned above was used for the preparation of 5 primary standard mixtures, PSM (1 - 5) by second dilution. The 5 PSMs were then used in the gravimetric preparation of the candidate reference material (PSM RM) according to the preparation scheme shown in **Figure 1**. This Reference material gas mixture contains 11 gas components, which are i-pentane, n-pentane, n-hexane, methane, n-butane, i-butane, propane, ethane, helium, hydrogen and nitrogen.

The weighing of gas components was carried out using an automatic weighing system (Mittler Toledo, TUBITAK UME, Türkiye) of capacity 10,100 g and

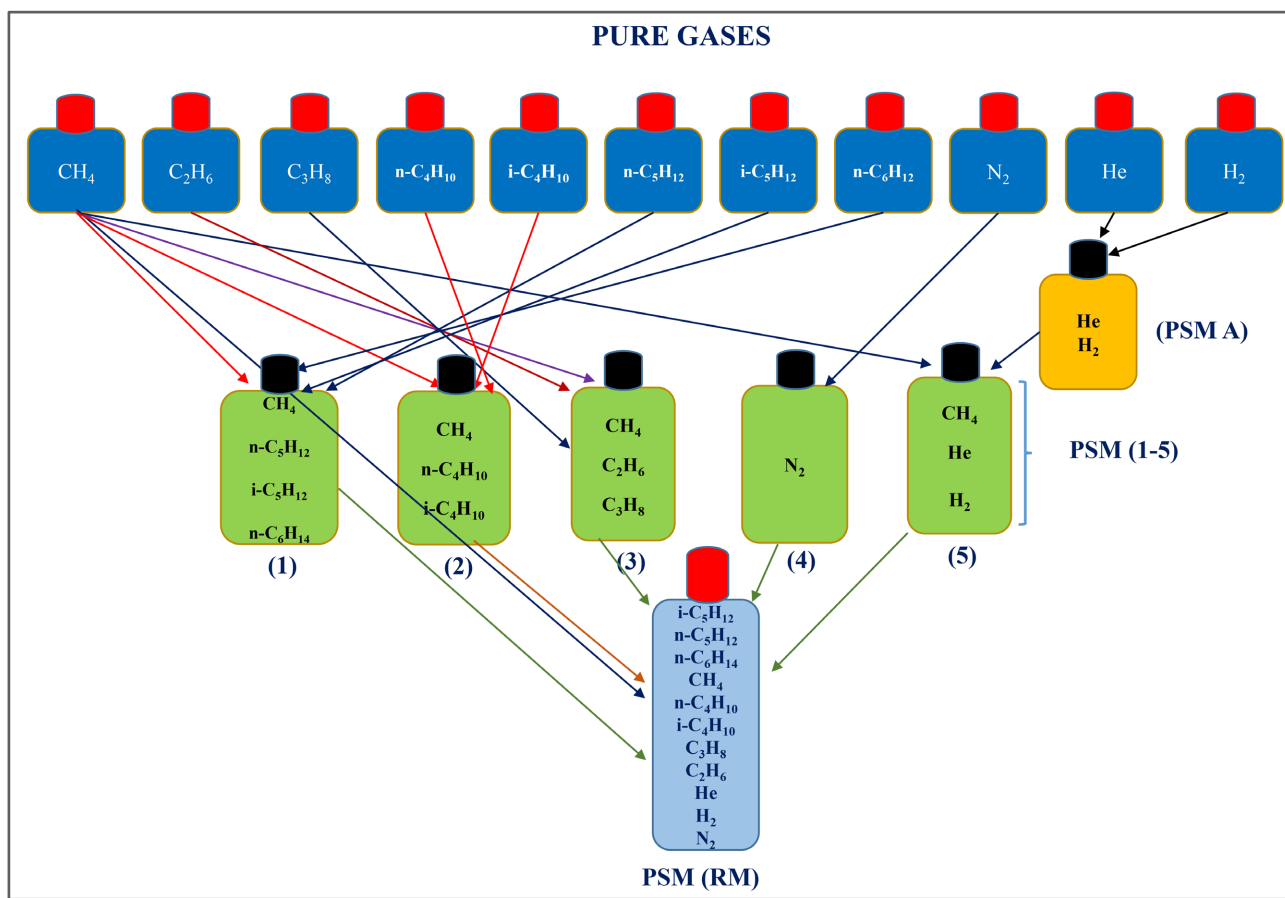


Figure 1. The gravimetric preparation of the reference material gas mixture PSM (RM).

readability of 0.001 g. The mass of each gas component (g) in every gas mixture was calculated based on the target mole fraction using Equation (1) [19].

$$m_i = \frac{x_i \times p_f \times V_{cyl} \times M_i}{R \times T \times Z_f} \quad (1)$$

where

m_i —mass of each gas component in the mixture (g)

x_i —intended mole fraction of each gas component (mol/mol)

p_f —filling pressure of the mixture (Pa)

V_{cyl} —volume of the cylinder (m³)

M_i —the molar mass of each gas component (g/mol)

R —the universal gas constant (8.314 J/mol·K)

T —the filling temperature (K)

Z_f —the compression factor of the mixture at T and P_f

2.2.1. Injection of the Liquid Gas Components in PSM 1

Iso-pentane, n-pentane and n-hexane were liquid injected into the cylinder of the PSM 1 in collaboration with staff at TUBITAK UME, Türkiye and the filled cylinder was shipped to SASO/NMCC, KSA. Before filling, the cylinder was vacuum cleaned at a pressure between 10^{-7} and 10^{-8} mbar. Then, a heating cable

was wrapped around the filling line in order to prevent condensation of the delivered gas components. Three temperature sensors were placed in 3 different locations between the heating apparatus and the injection port for temperature follow-up. The heating cable, the filling line and the liquid injection apparatus were covered with aluminum foil and then heating was made up to 45°C. The syringe to be used for injection of the liquid gases was weighed empty and then weighed with the gas component to be injected. The amount of the component withdrawn from the cylinder was determined as the difference between the two weighing results. The needle of syringe was fully immersed into the liquid injection apparatus and it was ensured that the gas component in the syringe was filled into the line. Then, methane gas was allowed to flow in order to push the injected gas component into the cylinder and then, empty syringe was weighed. Weighing of the empty syringe (S) was carried out 5 times and that of the reference syringe (R) was carried out 4 times in the sequence SRSRSRSRS. This weighing process was repeated for injection of the liquefied i-pentane, n-pentane and n-hexane. A schematic representation of the injection system is shown in **Figure 2**.



Figure 2. Injection system of liquefied i-pentane, n-pentane and n-hexane natural gas components.

2.2.2. Preparation of the PSM A and the PSM (2 - 5)

The cylinder to be filled with each of the PSM A and the four PSM (2 - 5) was cleaned by vacuum until the pressure reaches a value between 10^{-7} and 10^{-8} mbar, then connected to the filling station. The filling line was purged first with nitrogen 3 times and then with the gas components to be filled once before filling. The calculated mass (g) of each gas component was delivered into the PSM cylinder as described elsewhere [19].

2.2.3. Preparation of the Candidate Reference Material PSM RM

The candidate PSM RM was prepared from the five PSMs 1 - 5 and methane as balance gas. The mass (g) of each PSM and methane was calculated by the weighing system based on the target mole fraction (mol/mol), volume of the cylinder (V) and the pressure (bar) inside it. Calculations were done in accordance with the universal gas law, $PV = nRT$, where n is the number of moles, R is the universal gas constant and T is the thermodynamic temperature. The calculated masses and the filling pressures of each PSM and pure methane are shown in **Table 1**.

Table 1. Gas component, mass and pressure of each PSM to be filled in the PSM RM cylinder.

Primary mixture	Gas component	Mass (g)	Filling pressure (bar)
PSM 1	CH ₄	41.725	11
	i-C ₅ H ₁₂		
	n-C ₅ H ₁₂		
	n-C ₆ H ₁₄		
PSM 2	CH ₄	42.609	11
	n-C ₄ H ₁₀		
	i-C ₄ H ₁₀		
PSM 3	CH ₄	36.386	9.2
	C ₂ H ₆		
	C ₃ H ₈		
PSM 4	N ₂	16.292	2.2
PSM 5	CH ₄	12.444	4.5
	He		
	H ₂		
Pure Methane	CH ₄	62.8	17

The cylinder to be filled with the PSM RM was vacuum cleaned to a pressure between 10^{-7} and 10^{-8} mbar, and connected to the filling station. The filling line was purged first with nitrogen 3 times and with PMS to be filled once before filling. The calculated mass (g) of each PSM and methane was delivered into the PSM RM cylinder as described elsewhere [19].

2.3. The GC Measurements of the PSM RM Gas Components

The mole fractions of the components of the PSM RM gas mixture were determined on an Agilent Technologies 7890B GC dual system equipped with front FID, back TCD and auxiliary TCD. The chromatographic separation of the 8 hydrocarbons in the mixture was achieved on HP-AL/S capillary column (27 m × 0.320 mm i.d. × 8.0 μm) and their detection was made by FID. Meanwhile, the

chromatographic separation of hydrogen, nitrogen and helium was achieved by five packed columns which are: 2 ft.1/8n.2 mm ultimet NG063776, 3 ft.1/8n.2 mm ultimet NG064393, 4 ft.1/8n.2 mm ultimet NG064565, 8 ft.1/8n.2 mm ultimet NG063777 and 8 ft.1/8n.2 mm ultimet NG063776. Detection of these three gases was made by the back and auxiliary TCD. The inlet temperature was 250 °C and temperatures of FID and TCD detectors were 250 °C and 280 °C respectively. The oven temperature program for the GC dual system was: 60 °C (1 min), 20 °C/min, 80 °C (0 min), 30 °C/min 190 °C (1.333 min). The carrier gas was helium and the flow rate was 30 mL/min at 40 psi for both GC-FID and GC-TCD. Meanwhile, helium was used as gas reference and gas make up for GC-TCD at flow rate 45 mL/min and 2 mL/min respectively. On the other hand, the flow rates of H₂, air and N₂ were 40, 350 and 2 mL/min respectively for GC-FID. The software used to run the computer for monitoring the gas signals was Pro-Chem-Release: 2.7.9a. The natural gas sample was introduced into the GC system through a mass flow controller (MFC) manufactured by *SRA_{instruments}*, France to ensure consistent sample flow of 40 mL/min. The FID and TCD were calibrated by 5 concentrations (mol/mol) of a certified reference material (CRM) for each measured gas component. The number of injections was 10 for each CRM and 10 for each gas component of the prepared candidate PSM RM.

3. Results and Discussion

3.1. The Mole Fractions of the Gravimetrically Prepared PSM A, PSM 1 - 5 and the Candidate PSM RM

The mole fraction of each gas component in the prepared PSM A, PSM 1 - 5 and the PSM RM gas mixtures was calculated based on the added masses of gases. The calculations were performed based on equation 2 laid down in ISO 6142 using the software XLGENLINEv1_1.xls developed and validated by the National Physical Laboratory, NPL-UK

$$x_i = \frac{\sum_{A=1}^p \left(\frac{x_{i,A} \cdot m_A}{\sum_{i=1}^n x_{i,A} \cdot M_i} \right)}{\sum_{A=1}^p \left(\frac{m_A}{\sum_{i=1}^n x_{i,A} \cdot M_i} \right)} \quad (2)$$

where

x_i : the mole fraction of the component i in the final mixture, $i = 1, \dots, n$

P : the total number of the parent gases

n : the total number of the components in the final mixture

m_A : the mass of the CO or N₂ determined by weighing, $A = 1, \dots, P$

M_i : the molar mass of the component i , $i = 1, \dots, n$

$x_{i,A}$: the mole fraction of the component i , $i = 1, \dots, n$, in parent gas A , $A = 1, \dots, P$

The purity results obtained by the automatic weighing system for the PSM A and the PSM (1 - 5) are given in **Tables 2-7**.

Table 2. Composition, mole fraction and uncertainty (mol/mol) of PSM A.

PSM A			
Component	Symbol	Mole fraction	Uncertainty
Carbon monoxide	CO	2.500×10^{-7}	0.012×10^{-5}
Carbon dioxide	CO ₂	2.500×10^{-7}	0.012×10^{-5}
Total hydrocarbon	C _x H _y	2.500×10^{-7}	0.012×10^{-5}
Helium	He	19.020×10^{-2}	0.010×10^{-3}
Hydrogen	H ₂	80.976×10^{-2}	0.010×10^{-3}
Water	H ₂ O	1.000×10^{-6}	0.048×10^{-5}
Nitrogen	N ₂	2.310×10^{-6}	0.012×10^{-4}
Oxygen	O ₂	1.000×10^{-6}	0.048×10^{-5}

Table 3. Composition, mole fraction and uncertainty (mol/mol) of PSM 1.

PSM 1			
Component	Symbol	Mole fraction	Uncertainty
Argon	Ar	3.889×10^{-5}	0.022×10^{-3}
Methane	CH ₄	98.505×10^{-2}	0.250×10^{-4}
n-pentane	n-C ₅ H ₁₂	5.056×10^{-3}	0.014×10^{-3}
i-pentane	i-C ₅ H ₁₂	5.046×10^{-3}	0.014×10^{-3}
n-hexane	n-C ₆ H ₁₄	4.805×10^{-3}	0.013×10^{-3}

Table 4. Composition, mole fraction and uncertainty (mol/mol) of PSM 2.

PSM 2			
Component	Symbol	Mole fraction	Uncertainty
Argon	Ar	9.513×10^{-5}	0.039×10^{-3}
Methane	CH ₄	97.986×10^{-2}	0.472×10^{-4}
n-butane	C ₄ H ₁₀	9.999×10^{-3}	0.019×10^{-3}
i-butane	C ₄ H ₁₀	1.002×10^{-2}	0.019×10^{-3}
Total hydrocarbon	C _x H _y	1.483×10^{-5}	0.060×10^{-4}
Hydrogen	H ₂	2.450×10^{-7}	0.014×10^{-5}
Water	H ₂ O	3.950×10^{-6}	0.023×10^{-4}
Nitrogen	N ₂	1.255×10^{-5}	0.071×10^{-4}
Oxygen	O ₂	3.204×10^{-7}	0.015×10^{-5}
Sulfur dioxide	SO ₂	1.006×10^{-8}	0.041×10^{-7}

Table 5. Composition, mole fraction and uncertainty (mol/mol) of PSM 3.

PSM 3			
Component	Symbol	Mole fraction	Uncertainty
Argon	Ar	4.171×10^{-4}	0.018×10^{-2}
Methane	CH ₄	91.654×10^{-2}	0.267×10^{-3}
Ethane	C ₂ H ₆	5.946×10^{-2}	0.021×10^{-2}
Propane	C ₃ H ₈	2.355×10^{-2}	0.061×10^{-3}
Total hydrocarbon	C _x H _y	9.166×10^{-6}	0.053×10^{-4}
Hydrogen	H ₂	2.291×10^{-6}	0.013×10^{-4}
Water	H ₂ O	3.666×10^{-6}	0.021×10^{-4}
Nitrogen	N ₂	1.146×10^{-5}	0.066×10^{-4}
Oxygen	O ₂	2.291×10^{-6}	0.013×10^{-4}

Table 6. Composition, mole fraction and uncertainty (mol/mol) of PSM 4.

PSM 4			
Component	Symbol	Mole fraction	Uncertainty
Carbon monoxide	CO	1.876×10^{-7}	0.011×10^{-5}
Carbon dioxide	CO ₂	24.978×10^{-2}	0.535×10^{-5}
Total hydrocarbon	C _x H _y	1.876×10^{-7}	0.011×10^{-5}
Water	H ₂ O	1.324×10^{-5}	0.072×10^{-4}
Nitrogen	N ₂	75.020×10^{-2}	0.786×10^{-5}
Oxygen	O ₂	8.120×10^{-6}	0.038×10^{-4}

Table 7. Composition, mole fraction and uncertainty (mol/mol) of PSM 5.

PSM 5			
Component	Symbol	Mole fraction	Uncertainty
Methane	CH ₄	69.621×10^{-2}	0.018×10^{-3}
Carbon monoxide	CO	0.076×10^{-6}	0.037×10^{-6}
Carbon dioxide	CO ₂	0.076×10^{-6}	0.037×10^{-6}
Total hydrocarbon	C _x H _y	0.070×10^{-4}	0.040×10^{-4}
Helium	He	0.578×10^{-3}	0.409×10^{-5}
Hydrogen	H ₂	0.246×10^{-2}	0.014×10^{-3}
Water	H ₂ O	0.031×10^{-4}	0.016×10^{-4}
Nitrogen	N ₂	0.094×10^{-4}	0.050×10^{-4}
Oxygen	O ₂	0.020×10^{-4}	0.010×10^{-4}

Meanwhile, the purity results of the pure methane gas provided by Linda company is given in **Table 8**. The tables show the mole fractions and the associated uncertainties of the gas components and impurities in each mixture. In addition, the purity results of the target PSM RM are given in **Table 9** which shows the mole fractions and uncertainties of the gas mixture components: methane, ethane, propane, n-butane, i-butane, n-pentane, i-pentane, n-hexane, helium, hydrogen and nitrogen.

Table 8. Composition, mole fraction of methane (%) and impurities (ppmV).

Pure Methane				
Component	Symbol	Mass fraction	Concentration	Units
Methane	CH ₄	≥99.99	≥99.99	%
Hydrogen	H ₂	<10	≤05	ppmV
Oxygen	O ₂	<10	≤05	ppmV
Nitrogen	N ₂	<35	≤25	ppmV
Other hydrocarbon	C _x H _y	≤25	≤20	ppmV
Moisture		≤10	≤8	ppmV

Table 9. The purity table of the PSM RM showing the mole fraction (x_i) and *uncertainty* $u(x_i)$.

Gas component	Symbol	x_i (mol/mol)	$u(x_i)$ (mol/mol)	$u(x_i)$, %
Argon	Ar	9.583×10^{-5}	0.032×10^{-3}	33.18
Methane	CH ₄	91.321×10^{-2}	0.469×10^{-4}	0.01
Carbon monoxide	CO	1.396×10^{-8}	0.053×10^{-7}	38.32
Carbon dioxide	CO ₂	1.015×10^{-2}	0.014×10^{-4}	0.01
Ethane	C ₂ H ₆	9.840×10^{-3}	0.033×10^{-3}	0.33
Propane	C ₃ H ₈	3.897×10^{-3}	0.097×10^{-4}	0.25
n-butane	C ₄ H ₁₀	2.013×10^{-3}	0.037×10^{-4}	0.18
i-butane	C ₄ H ₁₀	2.017×10^{-3}	0.037×10^{-4}	0.18
n-pentane	C ₅ H ₁₂	9.935×10^{-4}	0.028×10^{-4}	0.28
i-pentane	C ₅ H ₁₂	9.915×10^{-4}	0.027×10^{-4}	0.27
Total hydrocarbon	C _x H _y	8.223×10^{-6}	0.024×10^{-4}	28.79
Helium	He	4.824×10^{-3}	0.074×10^{-5}	0.02
Hydrogen	H ₂	2.054×10^{-2}	0.030×10^{-4}	0.01
Water	H ₂ O	3.448×10^{-6}	0.098×10^{-5}	28.35
Nitrogen	N ₂	3.048×10^{-2}	0.051×10^{-4}	0.02
Oxygen	O ₂	1.022×10^{-6}	0.029×10^{-5}	27.90
Sulfur dioxide	SO ₂	2.025×10^{-9}	0.083×10^{-8}	40.83
n-hexane	C ₆ H ₁₄	9.441×10^{-4}	0.024×10^{-4}	0.26

From **Tables 2-7**, it can be realized that the gas components in the PSM A and each of the PSM (1 - 5) are the same components delivered in the cylinders during the preparation as shown in **Figure 1**, which indicates that the gas mixtures were properly prepared.

On the other hand, the Ar, CO, CO₂, C_xH_y, H₂O and O₂ impurities exist in the composition of the PSM RM shown in **Table 9** are related to the compositions of PSM A and PSM (1 - 5). For Ar impurity, it can be noticed that it has been delivered to the PSM RM from PSM 1, 2 and 3, while the CO and CO₂ impurities came from PSM A, PSM 4 and PSM 5. The total hydrocarbons, C_xH_y impurity came from PSM A, PSM 2, PSM 3, PSM 4, PSM 5 and pure methane. In addition, the H₂O and O₂ impurities came from PSM A, PSM 2, PSM 3, PSM 4, PSM 5 and methane. Moreover, the tables show that the summation (Σ) of mole fractions (x_i) for each PSM equals unity. This confirms that the composition of each prepared PSM is in agreement with the requirement of ISO 6142. The mole fraction of each gas component can be calculated as $x_j = 1 - [\Sigma x_j + \Sigma x_i]$, where x_j and x_i represent the mole fraction of each of the other gas components and the mole fraction of each of the existing impurity in the gas mixture respectively.

3.2. The Uncertainty Associated with the Gravimetric Mole Fractions

The uncertainty associated with the mole fraction calculated from the gravimetric preparation can be estimated from three sources as pointed out in ISO 6142. These are: 1) uncertainty in the weighing of the parent gases, 2) uncertainty in the purity of the parent gases and 3) uncertainty in molar masses. The model of calculations specified by ISO 6142 is that, the targeted component quantities x_i have been expressed as functions of input quantities z_1, z_2, z_3 , *i.e.* $x_i = f(z_1, z_2, z_3)$. The combined standard uncertainties $u_c(x_i)$ are given by equation 3 where p is the number of uncertainty inputs, df/dz_i is the sensitivity coefficient and $u(z_i)$ is the uncertainty of the individual input quantity.

$$u_c = \sqrt{\sum_{i=1}^p \left(\frac{\partial f_i}{\partial z_i} \right)^2 \cdot u(z_i)} \quad (3)$$

A detailed description of the uncertainty calculation using this approach was explained elsewhere [20]. In the present work uncertainty calculations were carried out according to this approach using the software XLGENLINEv1_1.xls developed by the NPL, UK and the results obtained were reported in **Tables 2-4** and **Table 6** for gas components in the mixtures: PSM A, PSM 1, PSM 2, PSM 3, PSM 4, PSM 5 and the candidate PSM RM respectively. With regard to the 11 gas components of the candidate PSM RM shown in **Table 9**, it can be noticed that the uncertainty values ranged from 0.01% - 0.33%, which is small enough giving rise to the good quality of the preparation of these mixtures.

3.3. The GC-FID and GC-TCD Measurements of the Mole Fractions

The mole fractions of the gravimetrically prepared reference material PSM RM have been verified by the dual GC-FID/TCD system in accordance with ISO

6143. **Figure 3** shows the GC-FID calibration graphs for n-pentane, i-pentane, i-butane and n-butane, while **Figure 4** shows GC-FID for ethane, propane, methane and n-hexane. On the other hand, **Figure 5** shows the GC-TCD calibration graphs for nitrogen, helium and hydrogen. From these curves, it is clear that the R^2 of each calibration line is almost 1, which indicates an excellent linear response of both the GC-FID and GC-TCD.

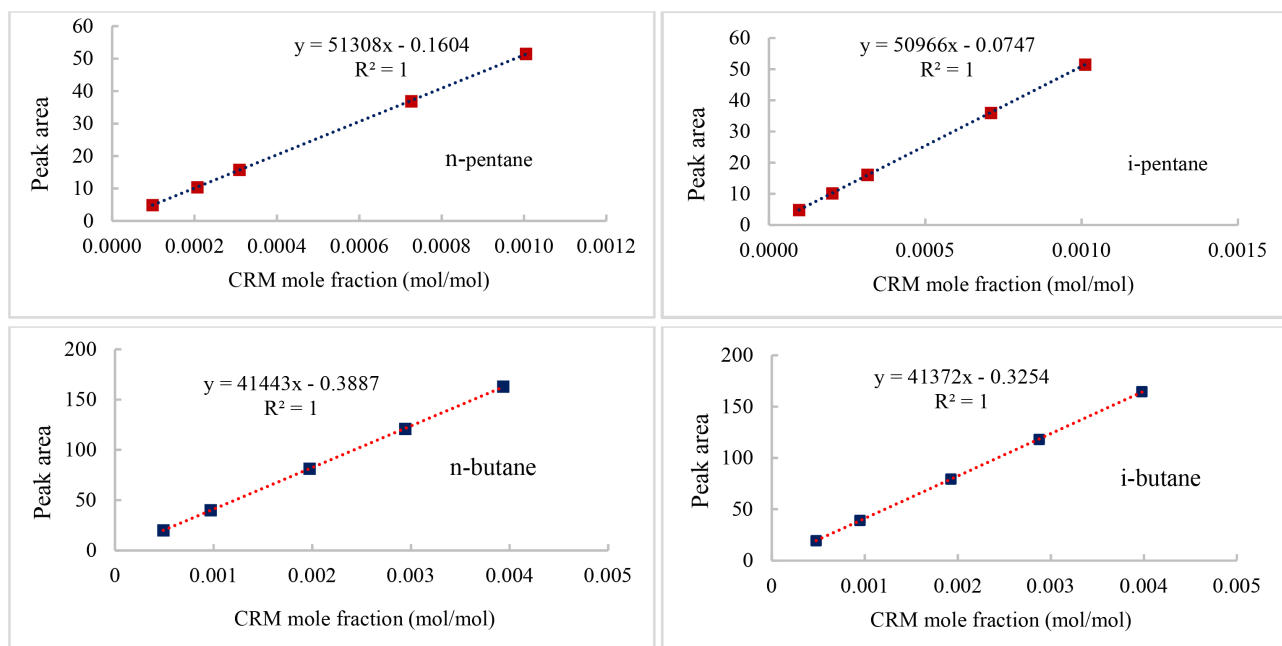


Figure 3. Calibration graphs of GC-FID by CRMs of n-pentane, i-pentane, n-butane and i-butane natural gas components.

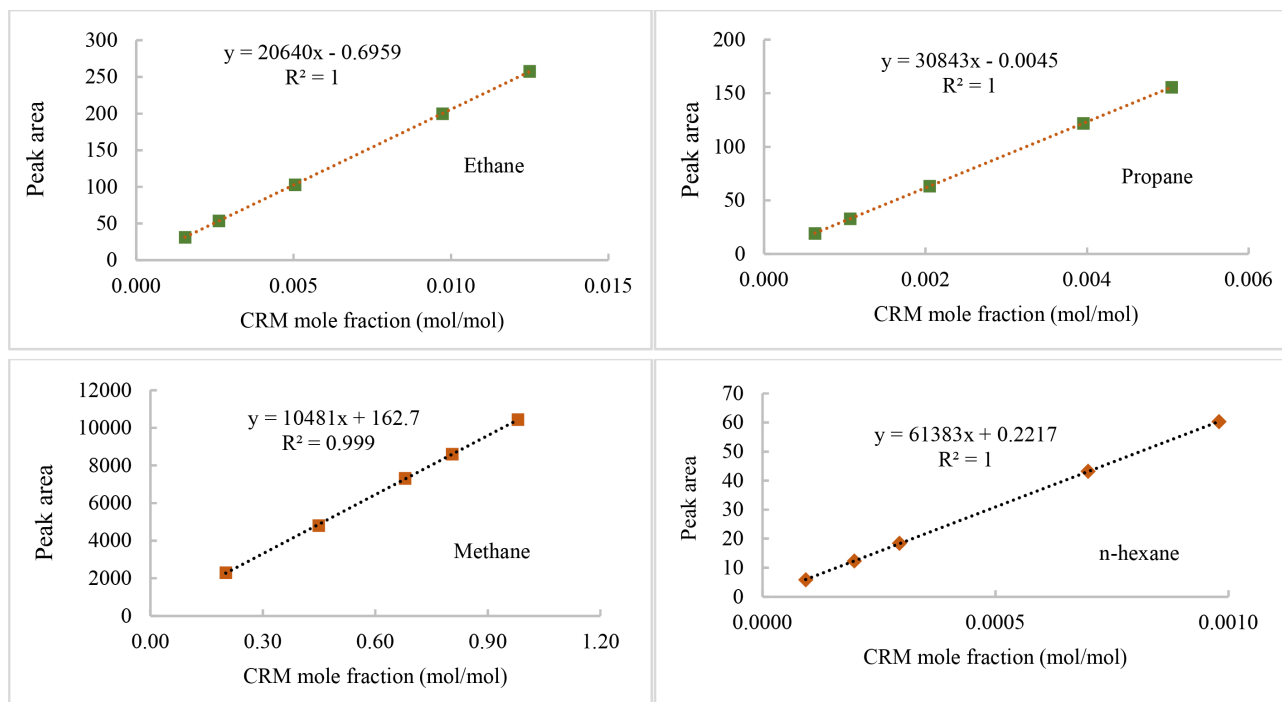


Figure 4. Calibration graphs of GC-FID by CRMs of ethane, propane, methane and n-hexane components.

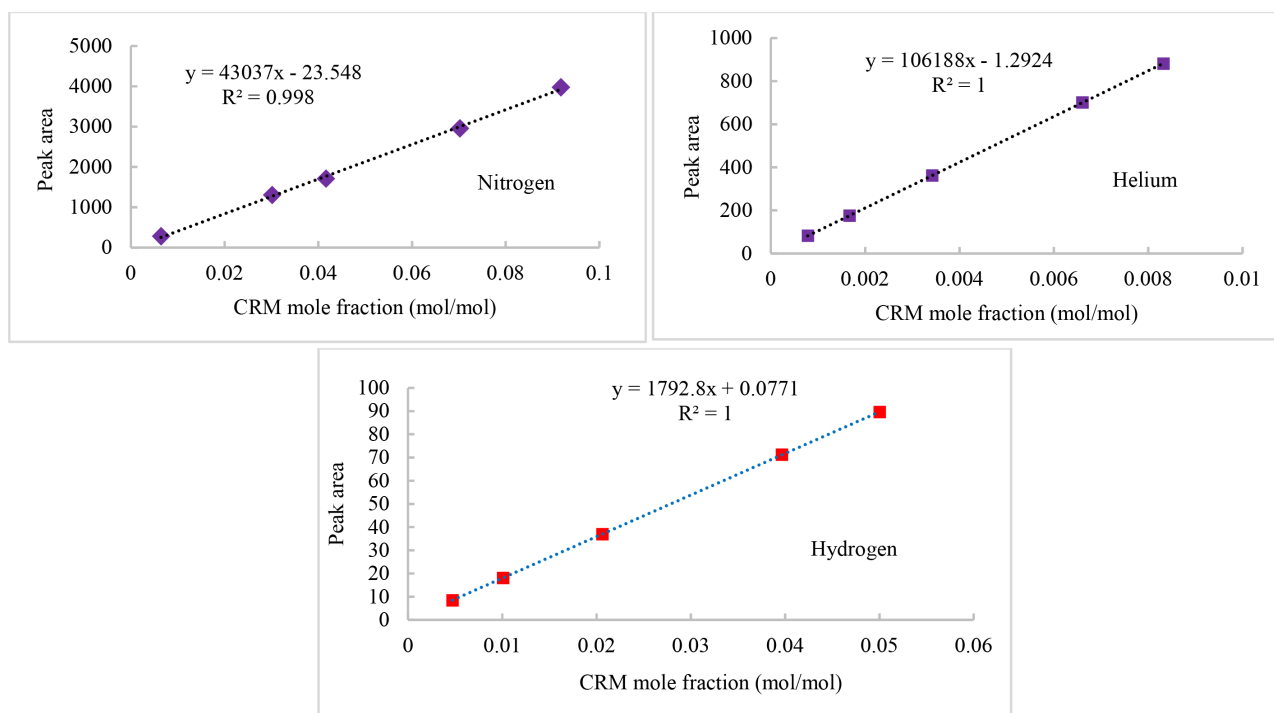


Figure 5. Calibration graphs of GC-TCD by CRMs of nitrogen, helium and hydrogen components.

This linearity provides a good basis for the accuracy of the mole fractions to be measured.

A sample of the PSM RM was injected 10 times into the calibrated GC-FID/TCD dual system and the resulting chromatogram is shown in **Figure 6**.

From this chromatogram, it can be noticed that each gas component is represented by a well separated peak and no other interfering peaks can be observed near the retention time of any of them. The eight hydrocarbons detected by FID: n-hexane, methane, ethane, propane, i-butane, n-butane, i-pentane and n-pentane with blue peaks were retained at 0.834 min, 1.180 min, 1.356 min, 2.039 min, 3.293 min, 3.438 min, 4.708 min and 4.824 min respectively. It can also be noticed that methane was further detected by the back TCD and showed good separation of hydrocarbons can be interpreted on the basis that the FID

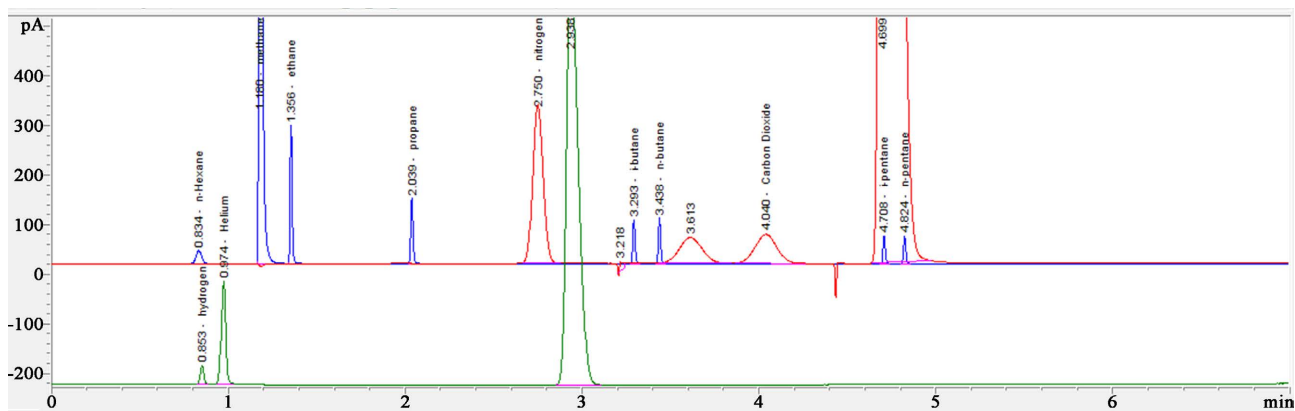


Figure 6. Typical GC-FID/TCD chromatogram of the PSM RM natural gas components.

an intense peak (red) at 4.699 min, but it has been quantified by the FID. This shows an excellent response to the hydrocarbon compounds that burn in a flame resulting from air and hydrogen [12] [21] [22]. In the meanwhile, nitrogen was detected (red peak) by the back TCD and retained at 2.750 min, but hydrogen and helium have been detected by the auxiliary TCD and showed peaks (green) at 0.835 min and 0.974 min respectively. There is also a green peak detected by the auxiliary TCD at 3 min but is it not known to which gas can it be assigned. Looking to the retention times of all gas components in the chromatogram, it can be seen that the total run time is about 5 minutes, which means that the method of analysis is rapid and economic.

The average peak area of 10 measurements by GC-FID and GC-TCD and the corresponding mole fractions (x_i) were calculated by the linear calibration function as: $x_i = y - b/a$. The uncertainty of the measurement results were also calculated and reported in **Table 10**.

Table 10. The average peak area, mole fraction (x_i) and uncertainty $u(x_i)$ of each gas component.

<i>Gas component</i>	<i>Peak area</i>	x_i (mol/mol)	$u(x_i)$ (mol/mol)
GC-FID			
n-C ₅ H ₁₂	50.60527	9.894×10^{-4}	0.018×10^{-4}
i-C ₅ H ₁₂	50.38118	8.999×10^{-4}	0.022×10^{-4}
n-C ₄ H ₁₀	83.22765	2.018×10^{-3}	0.024×10^{-4}
i-C ₄ H ₁₀	83.50855	2.026×10^{-3}	0.031×10^{-4}
C ₃ H ₈	120.64097	3.911×10^{-3}	0.048×10^{-4}
C ₂ H ₆	201.74042	9.808×10^{-3}	0.018×10^{-3}
CH ₄	9720.87373	91.200×10^{-2}	0.190×10^{-2}
n-C ₆ H ₁₄	58.50793	9.468×10^{-4}	0.011×10^{-4}
GC-TCD			
He	363.08978	3.407×10^{-3}	0.047×10^{-4}
H ₂	52.11940	2.054×10^{-2}	0.29×10^{-1}
N ₂	1287.90354	3.047×10^{-2}	0.042×10^{-3}

Looking to these mole fraction values, it can be noticed that they are very close to the values produced by the gravimetric preparations reported in **Table 9**, which indicates a good preparation of the gas mixture.

3.4. The Uncertainty of the Mole Fractions Measured by GC

The uncertainty of the mole fraction measurements by GC was calculated in accordance with the requirements of ISO 6143, which specifies three sources of uncertainty. These are: 1) the uncertainty associated with the mole fraction of the CRM, 2) peak area of the CRM and 3) peak area of the gas sample. Uncer-

tainty of source 1 was calculated using Equation (4), whereas uncertainties of sources 2 and 3 were calculated using Equation (5) [18].

$$u_{CRM} = \frac{U_{CRM}}{2} \quad (4)$$

$$u(y_i) = \frac{1}{\sqrt{90}} \sqrt{\sum_{j=1}^{10} (y_{ij} - y_i)^2} \quad (5)$$

The combined standard uncertainty, $u_c(x_i)$ was calculated according to ISO 6143 approach as in Equation (6) using the XLGENLINEv1_1.xls software and the calculated results were recorded in **Table 10**.

$$u_c(x_i) = \sqrt{\left(\frac{\partial x}{\partial A_{Un}} \cdot u_{A/Un}\right)^2 + \left(\frac{\partial x}{\partial b} \cdot u_b\right)^2 + \left(\frac{\partial x}{\partial a} \cdot u_a\right)^2 + \left(\frac{\partial x}{\partial x_{CRM}} \cdot u_{CRM}\right)^2} \quad (6)$$

3.5. The Compatibility of the Gravimetric and the GC Mole Fractions

The compatibility of the mole fraction (x_{grav}) and uncertainty (u_{grav}) resulting from the gravimetric preparation with the mole fraction (x_{anal}) and uncertainty (u_{anal}) resulting from the GC measurements was examined using the compatibility criterion in Equation (7) [17]. The results are shown in **Table 11** and it can be seen that the term $|x_{grav} - x_{anal}|$ is smaller than the term $2 \times \text{SQRT}(u_{grav})^2 + (u_{anal})^2$. This means that the criterion is fulfilled for all gas components indicating that the natural gas mixture preparation is valid.

$$|x_{grav} - x_{anal}| \leq 2\sqrt{(u_{grav})^2 + (u_{anal})^2} \quad (7)$$

Table 11. The mole fractions (mol/mol) and uncertainties measured by gravimetry (x_{grav}) and by GC (x_{anal}).

Gas component	x_{grav}	x_{anal}	$x_{grav} - x_{anal}$	$u_{x_{grav}}$	$u_{x_{anal}}$	$2\sqrt{(u_{grav})^2 + (u_{anal})^2}$
He	0.003401	0.003407	0.00000600	0.00000074	0.0000047	0.0000095
H ₂	0.020535	0.020535	0.00000000	0.000003	0.000031	0.000062
n-C ₅ H ₁₂	0.000994	0.0009894	0.000004600	0.0000028	0.0000018	0.0000067
i-C ₅ H ₁₂	0.000992	0.00099	0.000002000	0.0000027	0.0000022	0.0000070
n-C ₄ H ₁₀	0.002013	0.002018	0.000005000	0.0000037	0.0000024	0.0000088
i-C ₄ H ₁₀	0.002017	0.002026	0.000009000	0.0000037	0.0000031	0.0000097
C ₃ H ₈	0.003897	0.003911	0.00001400	0.00001	0.0000048	0.000022
C ₂ H ₆	0.00984	0.009908	0.00006800	0.000033	0.000018	0.000075
CH ₄	0.913207	0.91567	0.002463	0.000047	0.0019	0.0038
N ₂	0.030483	0.03054	0.00005700	0.0000051	0.000042	0.000085
n-C ₆ H ₁₄	0.0009441	0.0009468	0.000002700	0.0000024	0.0000011	0.0000053

3.6. Stability of the Natural Gas Mixture

The stability of the mole fraction of each of the eight hydrocarbon gas components

was measured by GC-FID and stability of hydrogen, helium and nitrogen components was measured by GC-TCD over a period of 4 years. **Figure 7** shows the stability results of n-pentane, i-pentane, n-butane and i-butane. **Figure 8** shows the stability results of propane, ethane, methane and n-hexane. Meanwhile, **Figure 9** shows the stability results of nitrogen, helium and hydrogen. In these figures, the solid lines represent the certified values and the dashed lines represent the certified uncertainty limits. Looking to these figures, it can clearly be noticed that the measured values of mole fractions along the four years fall within the limits of certified uncertainty, which indicates a good stability of the PSM RM gas mixture.

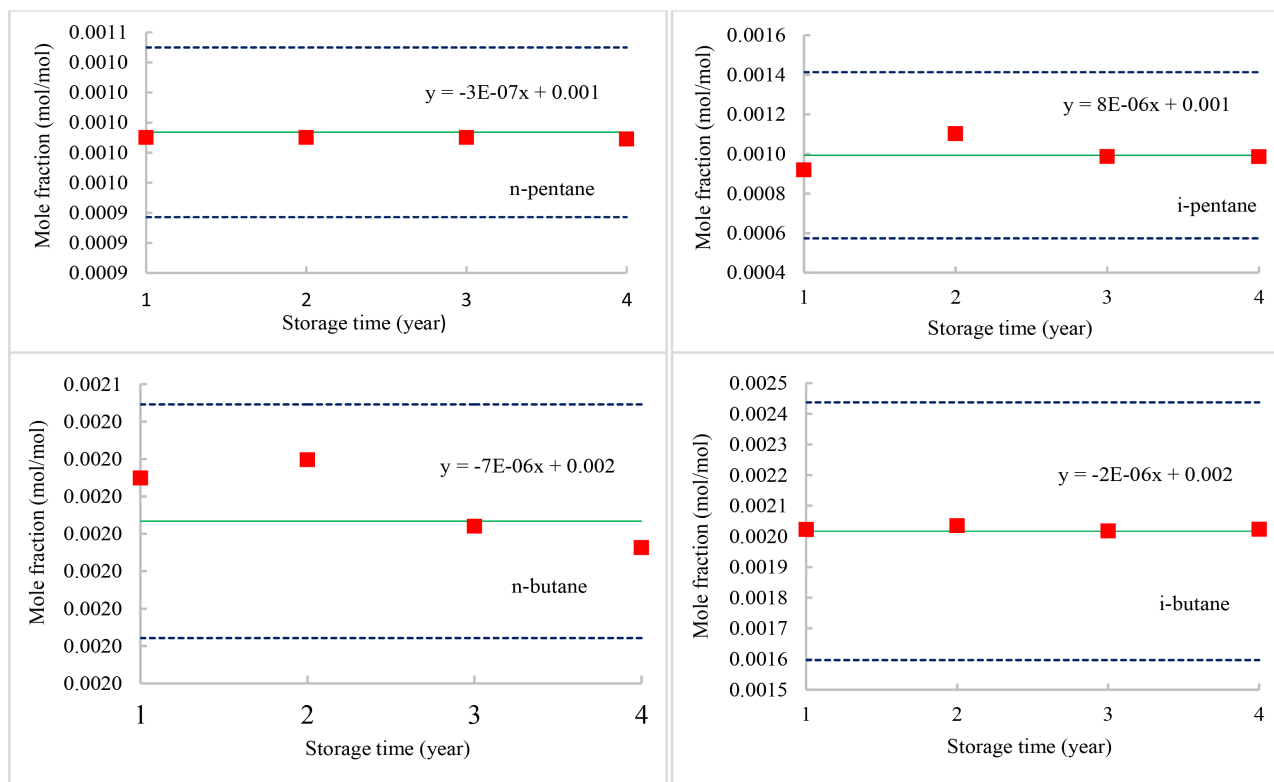


Figure 7. Mole fractions of n-pentane, i-pentane, n-butane and i-butane within the certified uncertainty limits measured by GC-FID along 4 years.

Moreover, these stability results were assessed by linear regression analysis according to ISO Guide 35 in order to detect any trend that might be in the results [23]. The regression line can be defined by Equation (8) in which y_i is the response, b_0 the intercept, b_1 the slope, x_i the standard mole fraction and ε_i is the error in the model.

$$y_i = b_1x + b_0 + \varepsilon_i \quad (8)$$

The slope of regression (b_1) and its standard error $s(b_1)$ were calculated using Equations (9) and (10) respectively and the standard deviation of the residuals (S) was calculated using Equation (11) [23].

$$b_1 = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^n (x_i - \bar{x})^2} \quad (9)$$

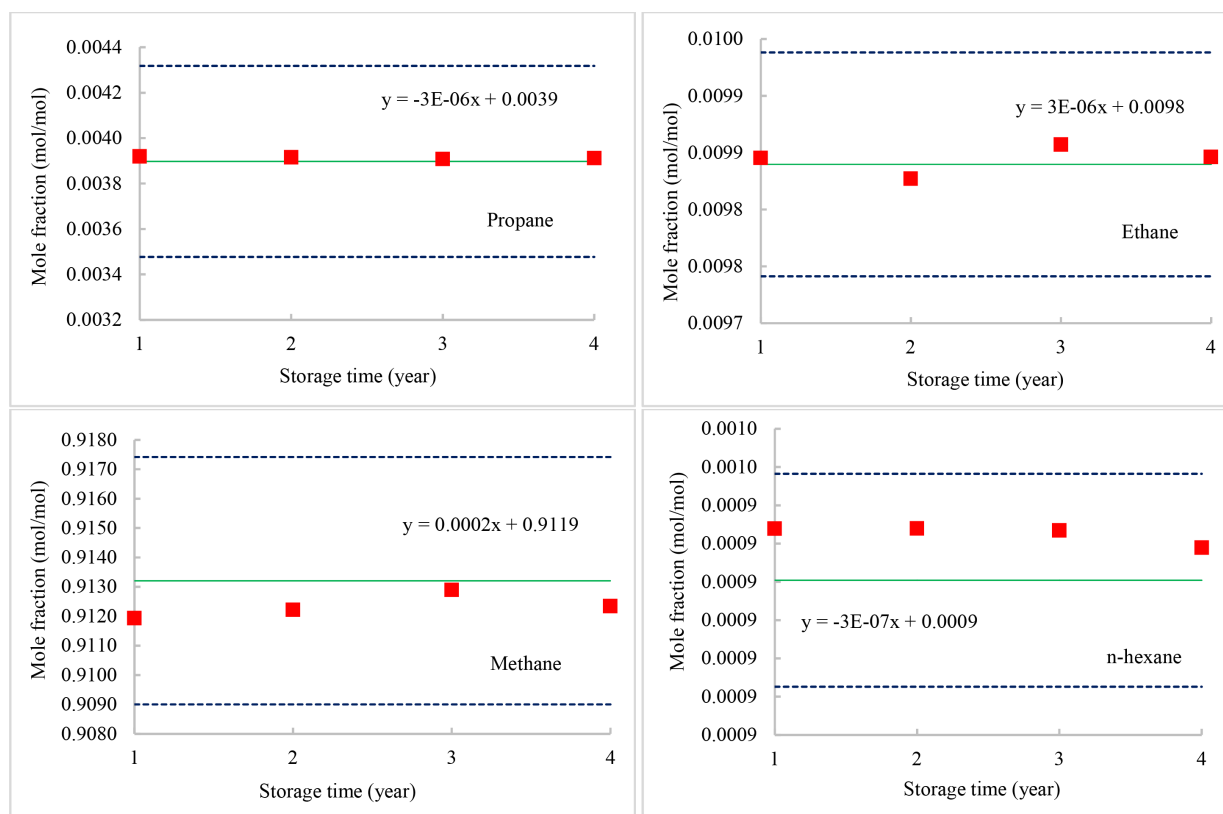


Figure 8. Mole fractions of propane, ethane, methane and n-hexane within the certified uncertainty limits measured by GC-FID along 4 years.

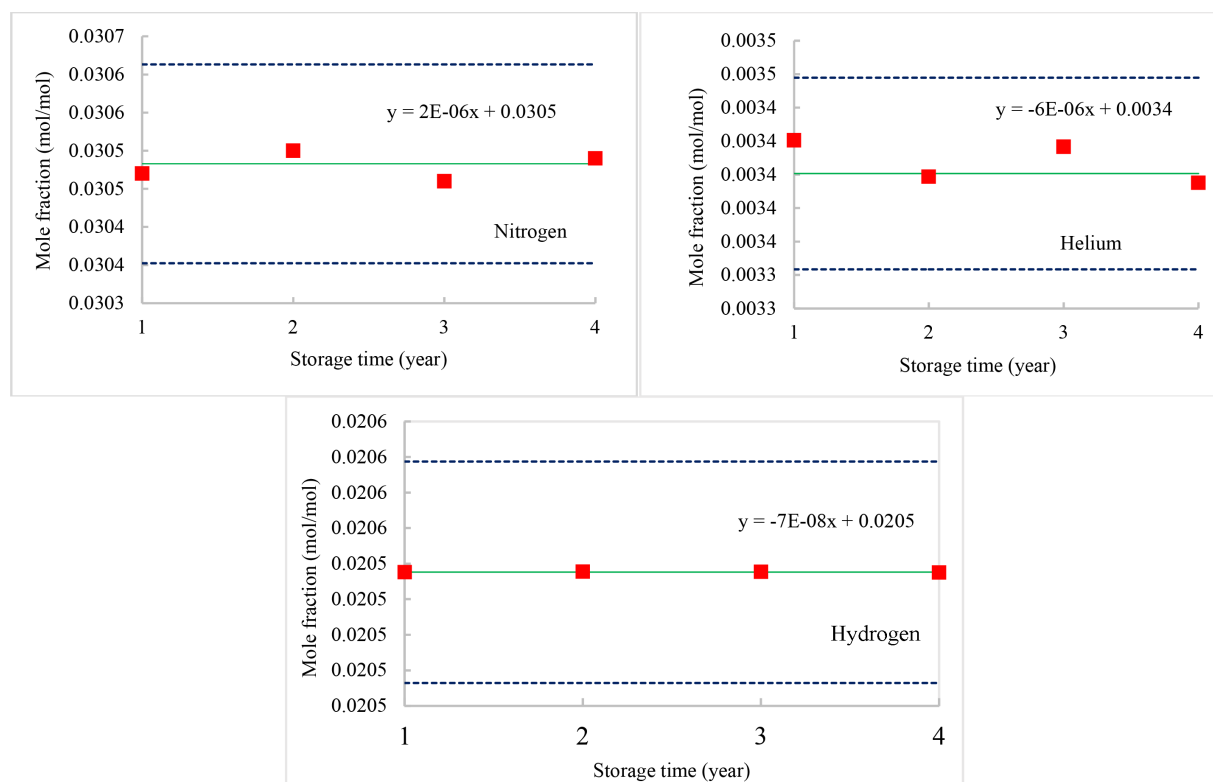


Figure 9. Mole fractions of nitrogen, helium and hydrogen within the certified uncertainty limits measured by GC-TCD along 4 years.

$$S(b_1) = \sqrt{\frac{S^2}{\sum_{i=1}^n (x_i - \bar{x})^2}} \quad (10)$$

$$S = \sqrt{\frac{\sum_{i=1}^N (x_i - b_0 - b_1 x_i)^2}{N - 2}} \quad (11)$$

The t-statistic was calculated as $b_1/s(b_1)$ and compared with the t-tabulated obtained from the two-sided t-table at 95% confidence interval using degrees of freedom $df=3$. **Table 12** shows the calculated values and one can notice that the t-statistic $b_1/s(b_1)$ is smaller than t-tabulated for all gas components, which means that all slopes of regression do not significantly deviate from zero. Consequently, it can be clearly concluded that the stability monitoring results do not suffer any trend, which in turn confirms stability of the PSM RM natural gas mixture during the validity period.

Table 12. The linear regression analysis results for the stability of the gas components in PSM RM.

Component	Slope (b_1)	$s(b_1)$	df	$t_{0.95, n-2}$	$b_1/s(b_1)$	p-value	Result
He	6×10^{-06}	5.567×10^{-06}	3	3.182	1.078	0.404	No trend
n-pentane	3×10^{-07}	1.720×10^{-07}	3	3.182	1.744	0.221	No trend
i-pentane	8×10^{-06}	4.134×10^{-05}	3	3.182	0.193	0.859	No trend
n-butane	7×10^{-06}	2.973×10^{-06}	3	3.182	2.354	0.132	No trend
i-butane	6×10^{-06}	4.134×10^{-05}	3	3.182	0.145	0.859	No trend
Propane	3×10^{-06}	4.134×10^{-05}	3	3.182	0.072	0.859	No trend
Ethane	3×10^{-06}	6.407×10^{-06}	3	3.182	0.468	0.659	No trend
Methane	2×10^{-04}	1.750×10^{-04}	3	3.182	1.143	0.392	No trend
Nitrogen	3×10^{-07}	9.899×10^{-06}	3	3.182	0.030	0.858	No trend
n-hexane	3×10^{-07}	1.518×10^{-07}	3	3.182	1.977	0.181	No trend
Hydrogen	8×10^{-08}	1.425×10^{-07}	3	3.182	0.561	0.458	No trend

3.7. Uncertainty of the Mole Fraction Stability

The uncertainty resulting from the stability monitoring was calculated using Equation (12) and the results were recorded in **Table 13** [23] [24] [25].

$$u_{stab} = Slope \times t_{Cert} \quad (12)$$

These values will be part of the certified uncertainty associated with the certified mole fractions.

3.8. Certified Values and Uncertainty (mol/mol)

The certified value of each gas component shown in **Table 13** reported in 4 significant figures was taken as the mole fraction calculated from the gravimetric

Table 13. The certified values and certified uncertainty, UCRM (mol/mol).

Component	Symbol	Certified value (mol/mol)	$u_{gravimetry}$	$u_{analytical}$	$u_{stability}$	U_{CRM}
Methane	CH ₄	91.321×10^{-02}	4.69×10^{-05}	1.91×10^{-03}	8.80×10^{-04}	4.20×10^{-03}
Ethane	C ₂ H ₆	9.84×10^{-03}	3.30×10^{-05}	1.80×10^{-05}	3.20×10^{-05}	9.90×10^{-05}
Propane	C ₃ H ₈	3.90×10^{-03}	9.70×10^{-06}	4.80×10^{-06}	2.10×10^{-04}	4.20×10^{-04}
n-butane	C ₄ H ₁₀	2.01×10^{-03}	3.70×10^{-06}	2.40×10^{-06}	1.50×10^{-05}	3.10×10^{-05}
i-butane	C ₄ H ₁₀	2.02×10^{-03}	3.70×10^{-06}	3.10×10^{-06}	2.10×10^{-04}	4.20×10^{-04}
n-pentane	C ₅ H ₁₂	9.94×10^{-04}	2.80×10^{-06}	1.80×10^{-06}	2.80×10^{-05}	5.60×10^{-05}
i-pentane	C ₅ H ₁₂	9.92×10^{-04}	2.70×10^{-06}	2.20×10^{-06}	2.10×10^{-04}	4.20×10^{-04}
Helium	He	3.40×10^{-03}	3.70×10^{-06}	4.70×10^{-06}	2.80×10^{-05}	5.70×10^{-05}
Hydrogen	H ₂	2.05×10^{-02}	3.00×10^{-06}	3.10×10^{-05}	7.10×10^{-07}	6.20×10^{-05}
Nitrogen	N ₂	3.05×10^{-02}	5.10×10^{-06}	4.20×10^{-05}	5.00×10^{-05}	1.30×10^{-04}
n-hexane	C ₆ H ₁₄	9.44×10^{-04}	2.40×10^{-06}	1.10×10^{-06}	8.00×10^{-07}	5.60×10^{-06}

preparation of the PSM RM with traceability to the SI unit mass expressed as mol/mol. The certified uncertainty, U_{CRM} was calculated from three contributions using Equation (13) [23] [26]. The results obtained were reported also in **Table 13** as mol/mol in two significant figures.

$$U_{CRM} = 2\sqrt{(u_{grav})^2 + (u_{anal})^2 + (u_{stab})^2} \quad (13)$$

where,

u_{grav} —uncertainty of the gravimetric mole fractions

u_{anal} —uncertainty of the mole fractions determined by GC

u_{stab} —uncertainty due to the stability of the mole fractions

4. Conclusion

A primary standard mixture of natural gas composed of 8 hydrocarbons together with hydrogen, helium and nitrogen was gravimetrically prepared in accordance with the requirements of ISO 6142. The calculated mole fractions were verified by the dual GC-FID/TCD system in accordance with ISO 6143. The measured mole fractions and uncertainties were found in very good compatibility with those obtained by gravimetry, indicating a good quality of the gas mixture preparation. The stability of the primary standard natural gas mixture was tested along 4 years and the mole fractions were found stable within the certified uncertainty limits. The uncertainty due to the instability was calculated and used with the uncertainty of the gravimetry and GC measurements to calculate the certified uncertainty in accordance with ISO Guide 35. The produced natural gas CRM is very important for gas analytical laboratories in calibration and quality control purposes.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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