

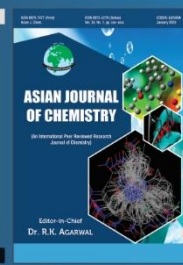


Asian Journal of Chemistry;

Vol. 38, No. 10 (2026), 2559-2566

ASIAN JOURNAL OF CHEMISTRY

<https://doi.org/10.14233/ajchem.2026.35537>



Preparation and Certification of Propane in Nitrogen as Reference Material for Ensuring Traceability of Hydrocarbon Emission Measurements

ABDULLAH S. ALOWAYSI[✉], ABDULRAHMAN R. ALASKAR[✉] and ADEL B. SHEHATA^{*,✉}

Department of Chemistry, National Measurement and Calibration Center, Saudi Standards, Metrology and Quality Organization (SASO), Riyadh 11471, Kingdom of Saudi Arabia

*Corresponding author: E-mail: adelshhata63@yahoo.com

Received: 30 December 2025

Accepted: 28 August 2026

Published online: 9 October 2026

AJC-22486

Propane in nitrogen (C_3H_8/N_2) gas mixtures are widely used as calibration standards for hydrocarbon measurements in environmental monitoring, energy production and industrial process control. Five C_3H_8/N_2 gas mixtures, covering the range of 804.8148-12053.8148 $\mu\text{mol/mol}$, were gravimetrically prepared according to ISO 6142 using a two-step dilution approach with high-purity propane and nitrogen. The prepared mixtures were validated by gas chromatography with flame ionization detection (GC-FID) in accordance with ISO 6143. The GC-FID results showed good agreement with the gravimetric values, confirming the validity of the preparation method. The certified values determined by gravimetry were established for 4 mixtures (B, C, D, E) as 12053.81 ± 97.49 , 9013.23 ± 78.11 , 5998.011 ± 57.72 and 2987.29 ± 66.91 $\mu\text{mol/mol}$, respectively. The mole fraction of the mixture F, 804.81 ± 35.97 $\mu\text{mol/mol}$ was considered an information value since it was associated with large uncertainty of 7.016%. The performance of the produced certified reference materials (CRMs) was checked by using them to calibrate the GC-FID, then measure a CRM sample of 8010 $\mu\text{mol/mol}$ as an unknown. The precision (%RSD) and accuracy of the measured results were found to be 0.12% and 99.75%, respectively. These results confirm that the prepared C_3H_8/N_2 mixtures meet the criteria for certified reference materials and are suitable as calibrants for hydrocarbon emission measurement instruments in industrial gas analysis and environmental monitoring.

Keywords: Propane, Nitrogen, Gravimetry, Hydrocarbon emission, GC-FID, Certified value, Uncertainty.

INTRODUCTION

Propane (C_3H_8) is an important hydrocarbon widely used in the energy and industrial sectors. It also serves as a calibration standard for instruments used in hydrocarbon emission measurements. Accurate measurement of propane is therefore essential to ensure that the propane standards meet the application purposes [1,2]. The United States Environmental Protection Agency (EPA) and automobile manufacturers require the use of certified reference materials (CRMs) of propane for the calibration of total hydrocarbon analyzers (THAs) in order to meet federal emission standards [2]. Since natural gas pricing depends on its heating value, which is calculated from the concentration of its components, the accuracy of propane determination directly influences both economic and regulatory aspects [3]. Several methods are available for propane measurement in gaseous mixtures.

Gas chromatography (GC) is the most widely used, typically coupled with flame ionization detection (FID) or thermal

conductivity detection (TCD) [4,5]. While GC/FID offers higher sensitivity, GC/TCD can be applied at higher concentrations. Budiman *et al.* [6], showed that GC-FID has 66 times higher sensitivity than GC-TCD, with a wider linear range of (0.161-2.18 %) mol/mol for GC-FID versus 0.242-2.18 % mol/mol for GC-TCD [6]. Alternative approaches have been proposed such as the handheld near infrared (NIR) system developed by Barbosa *et al.* [7], which automatically quantifies methane, ethane and propane in natural gas and biogas samples. In addition, Zuas & Budiman [8] validated propane measurements using GC-TCD in the presence of CO_2 and CO , highlighting the importance of carrier gas flow optimization for accuracy and precision.

The total hydrocarbons analyzer (THA/FID), which measures the total concentration of hydrocarbons (THC) in a gas stream, without separating them by chromatography is widely used in automotive applications, but their response is strongly affected by oxygen in the gas stream [9,10]. Previous studies have also addressed the effect of the matrix gas on propane

This is an open access journal, and articles are distributed under the terms of the Attribution 4.0 International (CC BY 4.0) License. This license lets others distribute, remix, tweak, and build upon your work, even commercially, as long as they credit the author for the original creation. You must give appropriate credit, provide a link to the license, and indicate if changes were made.

measurements. Work carried out at NIST compared propane in nitrogen with propane in air, revealing a measurable difference of about 0.63% in concentration due to the influence of oxygen on the FID response [11]. This highlights the need to use standards prepared in the same matrix as the unknown samples to ensure accurate and reliable results [12].

To secure measurement traceability, GC systems are calibrated against CRMs, which are defined as reference materials accompanied by documentation with specified property values, uncertainties and traceability [13,14]. Such CRMs are commonly prepared gravimetrically by transferring parent gases into cylinders and their composition is verified by analytical techniques such as GC [15,16]. The primary gas mixtures are also used in key comparisons to determine the degree of equivalence between the national metrology institutes [17-19]. The aim of the present work is to prepare and certify a series of reference materials from C₃H₈/N₂ gas mixtures for the use in calibration of hydrocarbon analyzers used in periodic vehicle check. The gravimetric preparation of the gas mixtures has been carried out in accordance with ISO 6142 and the verification was carried out by GC-FID in accordance with ISO 6143 in the context of certification based on the requirements of ISO 17034 [20].

EXPERIMENTAL

High purity gases were used throughout the experiments. Propane (99.5%) and nitrogen (99.9994%) were supplied by Linde, the Netherlands, while 5 L aluminum alloy cylinders for preparing the mixtures were obtained from Air Liquide, the Netherlands. Cylinder evacuation and the gas filling were carried out using an evacuation pump and gas filling apparatus manufactured by Pfeiffer Vacuum, Germany. The filling apparatus has electro polished stainless-steel flow lines, which can bear pressures up to 200 bar and connected to a turbo-molecular pump, allowing evacuation of the entire system to 1×10^{-6} mbar. For gravimetric preparation of mixtures, an automatic weighing system manufactured by Mettler Toledo was used. The system compares the mass of sample cylinders with that of a reference cylinder and is run by a software enables precise gas mixture preparation in compliance with ISO 6142 requirements. The C₃H₈ in N₂ gas mixture characterization was conducted using an Agilent Technologies 7890B gas chromatograph equipped with a flame ionization detector (FID). The four CRMs used for calibration were provided by TUBITAK UME, Türkiye. Their mole fractions were, 702.50 ± 17.50 , 3008.00 ± 75 , 8010 ± 20 and 14750 ± 35 $\mu\text{mol/mol}$. Prior to analysis, the GC-FID instrument was stabilized for 4 h. Samples and reference materials (CRMs) were injected in the sequence R-S-S-R-S-R-S-S-R ensuring that each set of samples was bracketed by CRM injections to minimize potential drift or bias. The chromatographic separation was achieved on an HP-AL/S capillary column (27 m $\times$ 0.320 mm i.d. $\times$ 8.0 μm). The injector and detector temperatures were maintained at 250 °C. The carrier gas (helium) flow was set at 30 mL/min and the reference gas flow at 40 mL/min. The total GC run time was 7 min.

Mass of propane and nitrogen: Mixture A and the target C₃H₈/N₂ reference materials (B, C, D, E and F) were of

molar concentrations viz. 39601.9, 12053.8, 9013.2, 5998, 2987.3 and 804.8 $\mu\text{mol/mol}$, respectively to cover the calibration range required for hydrocarbon monitor used for periodic vehicle inspection. In order to prepare these gas mixtures in 5 L aluminum cylinders, the required masses (g) of propane and nitrogen were determined using eqn. 1 [15,21]:

$$m_i = \frac{x_i \cdot p_F \cdot V_{\text{cyl}} \cdot M_i}{R \cdot T \cdot Z_f} \quad (1)$$

where m_i = mass of C₃H₈ or N₂ in the mixture (g); x_i = intended mole fraction of C₃H₈ or N₂ ($\mu\text{mol/mol}$); p_F = filling pressure of the mixture (bar); V_{cyl} = volume of the cylinder (m^3); M_i = the molar mass of C₃H₈ (44.097 g/mol) and of N₂ (28.012 g/mol); R = the gas constant (8.314 51 J/mol K), T = filling temperature (K); Z_f = compression factor of the mixture at T and p_F .

The masses of C₃H₈ and N₂ of the prepared gas mixtures, A and (B, C, D, E, F) together with the corresponding mole fractions are shown in Table-1.

TABLE-1
CALCULATED MASSES OF C₃H₈ AND N₂ REQUIRED
FOR GAS MIXTURE PREPARATION (A–F)

Mixture	Gas component	Mole fraction ($\mu\text{mol/mol}$)	Mass (g)	Filling p (bar)
A	C ₃ H ₈ /N ₂	39601.9	36.17	4.00
			554.65	96.00
B	C ₃ H ₈ /N ₂	12053.8	4.26	0.48
			221.050	39.52
C	C ₃ H ₈ /N ₂	9013.2	2.82	0.36
			196.030	39.64
D	C ₃ H ₈ /N ₂	5998.0	34.95	0.24
			191.45	39.76
E	C ₃ H ₈ /N ₂	2987.3	17.97	0.12
			215.36	39.45
F	C ₃ H ₈ /N ₂	804.8	5.14	0.030
			242.49	39.70

Gas filling and homogenization: Each cylinder was initially evacuated using a high-vacuum system to remove any residual gaseous impurities from the inner walls. The evacuation process was maintained for 24 h, during which the pressure was continuously monitored until it reached approximately 1.5×10^{-7} mbar. Upon evacuation completion, the cylinder was disconnected from the vacuum line. After allowing sufficient time for temperature stabilization, the cylinder was weighed on the automated balance described above against a reference cylinder of identical type and mass. Prior to filling, the gas filling system was carefully inspected to ensure it is free from any leak. This was achieved by pressurizing the system and applying a leak detection liquid to all joints, where the absence of bubbles confirmed the absence of leaks. The filling strategy was designed in a two-step dilution process. In the first step, mixture A (39600) $\mu\text{mol/mol}$ was prepared using the pure nitrogen and pure propane (C₃H₈). Following the same procedure, mixtures B (12054 $\mu\text{mol/mol}$) and C (9013 $\mu\text{mol/mol}$) were prepared. In the second step, mixture A was further used as a source of propane to obtain the diluted mixtures D, E and F with mole fractions of 5998,

2987 and 805 $\mu\text{mol/mol}$, respectively. For the preparation of mixture A, propane was introduced first due to its lower filling pressure compared with nitrogen. The filling lines were purged with propane to eliminate any residual gases. The cylinder designated for mixture A was connected to the filling manifold and placed on a high precision balance to monitor the added mass. Propane was allowed to flow slowly until the target mass was reached. The propane cylinder was then disconnected and replaced with the nitrogen cylinder, which was opened for nitrogen to flow until the required mass was obtained. The filled cylinder was sealed and disconnected from the system. mixtures B and C were prepared using the same procedure. For the preparation of mixtures D, E and F, the filling lines were purged with propane and nitrogen in the same sequence as for mixture A. Propane was sourced from mixture A, while nitrogen was supplied directly from the pure cylinder. Fig. 1 illustrates the complete filling process. Each prepared C₃H₈/N₂ mixture was then homogenized by continuous rotation using a mixing machine for 8 h [22,23].

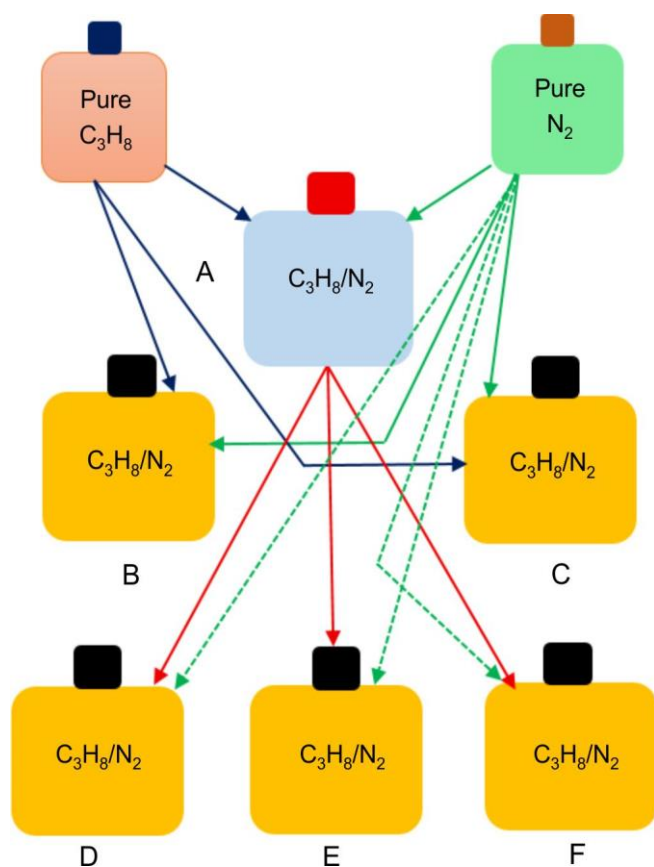


Fig. 1. Schematic workflow for Filling C₃H₈/N₂ RM gas mixtures

RESULTS AND DISCUSSION

Mole fractions of pure C₃H₈ and N₂ gases: The certificate accompanying the pure C₃H₈ cylinder stated a purity level of 99.5% with other impurity gases at approximately 5000 ppm. Likewise, the certificate for the pure N₂ cylinder confirmed a purity of 99.9995% with trace impurities reported as total hydrocarbons (expressed as CH₄) < 2.5 ppm,

H₂O < 1 ppm and O₂ < 2.5 ppm. To estimate the mole fraction of each impurity in ppm, a range was defined by setting the lower bound at zero and the upper bound at the limit specified by the supplier. The mean of these two values was taken as the best estimate and these impurity estimates were summed as $\Sigma x_{\text{impurities}}$ [15]. The mole fractions of the parent C₃H₈ and N₂ were then determined using eqn. 2 where n denotes the number of considered impurities and are given in Table-2.

$$x_{\text{pure C}_3\text{H}_8 \text{ or N}_2} = 1 - \sum_{k=0}^n x_{\text{impurities}} \quad (2)$$

Parent gas	Component	Symbol	Mole fraction (μmol/mol)	u_c (μmol/mol)
N ₂	Total hydrocarbon	C _x H _y	2.5000	1.44
	Water	H ₂ O	1.0000	0.58
	Nitrogen	N ₂	999994	2.12
	Oxygen	O ₂	2.5000	1.44
	Total		1000000	
C ₃ H ₈	Argon	Ar	5000	2886.75
	Propane	C ₃ H ₈	995000	2886.75
	Total		1000000	

Mole fractions of C₃H₈ in the prepared gas mixtures (B, C, D, E, F): For the prepared gas mixtures B, C, D, E and F, the mole fraction of the C₃H₈ component was calculated using eqn. 3 [15]:

$$x_{\text{C}_3\text{H}_8} = \frac{\frac{x_{\text{C}_3\text{H}_{8A}} \cdot m_{\text{C}_3\text{H}_8}}{x_{\text{C}_3\text{H}_{8A}} \cdot M_{\text{C}_3\text{H}_8}}}{\frac{m_{\text{C}_3\text{H}_8}}{x_{\text{C}_3\text{H}_8} \cdot M_{\text{C}_3\text{H}_8}} + \frac{m_{\text{N}_2}}{x_{\text{N}_2} \cdot M_{\text{N}_2}}} \quad (3)$$

where $x_{\text{C}_3\text{H}_8}$ = mol fraction of C₃H₈ in prepared gas mixture, $x_{\text{C}_3\text{H}_{8A}}$ = mol fraction of parent C₃H₈ gas, $m_{\text{C}_3\text{H}_8}$ = mass of C₃H₈ determined by weighing; $M_{\text{C}_3\text{H}_8}$ = molar mass of C₃H₈; x_{N_2} = mole fraction of N₂ gas; m_{N_2} = mass of N₂ determined by weighing; M_{N_2} = molar mass of N₂.

The calculated mole fractions of C₃H₈ and its impurities, along with their corresponding uncertainties, were reported for each of the five gas mixtures (B, C, D, E and F) in the purity (Table-3). From these data, the mole fractions of C₃H₈ were determined to be 12053.81, 9013.23, 5998.011, 2987.29 and 804.81 $\mu\text{mol/mol}$ for mixtures B, C, D, E and F, respectively. These values show a consistent and systematic mole fraction decrease across the five mixtures, in direct agreement with the expected changes in composition when varying the masses of propane and nitrogen during preparation. The consistent decrease and relatively low associated uncertainties demonstrate the proper application of the gravimetric method, with effective control of the weighing procedures and parent-gas purity. The close agreement between the calculated mole fractions and targeted nominal values further confirms the accuracy and reliability of the gravimetric preparation approach.

TABLE-3
THE PURITY TABLE OF THE C₃H₈/N₂ GAS MIXTURE
B, C, D, E AND F PREPARED BY GRAVIMETRY

Component	Mole fraction (μmol/mol)	u _c (μmol/mol)
Mixture B		
Argon	60.5719	34.81
Propane	12053.8148	31.30
Total hydrocarbon	2.4697	1.43
Water	0.9879	0.57
Nitrogen	987879.6860	46.77
Oxygen	2.4697	1.43
Total	1000000	
Mixture C		
Argon	45.2926	26.033
Propane	9013.2292	23.47
Total hydrocarbon	2.4774	1.43
Water	0.9909	0.57
Nitrogen	990935.5326	35.11
Oxygen	2.4774	1.43
Total	1000000	
Mixture D		
Argon	30.1408	17.32
Propane	5998.01059	14.35
Total hydrocarbon	2.4849	1.24
Water	0.9940	0.50
Nitrogen	993965.8848	23.40
Oxygen	2.4849	1.24
Total	1000000	
Mixture E		
Argon	15.01150	8.63
Propane	2987.2890	7.12
Total hydrocarbon	2.4925	1.34
Water	0.9970	0.54
Nitrogen	996991.7175	11.82
Oxygen	2.4925	1.34
Total	1000000	
Mixture F		
Argon	4.04430	2.32
Propane	804.8148	1.92
Total hydrocarbon	2.4980	1.41
Water	0.9992	0.57
Nitrogen	999185.1458	3.77
Oxygen	2.4980	1.414
Total	1000000	

Uncertainty in the gravimetric mole fractions: Uncertainty in gravimetric mole fraction measurements arises from several key sources as outlined in ISO 6142 [15]. First, the purity of the C₃H₈ and N₂ parent gases contributes to uncertainty because impurities in these gases affect the mole fraction values. The standard uncertainty of Argon (u_{Ar}) impurity in C₃H₈ was calculated by eqn. 4 and the uncertainty of impurities in N₂ (u_{CO₂}, u_{H₂O}, u_{O₂} and u_{CH₄}) was determined using eqn. 5.

$$u_{C_3H_8} = \sqrt{(c_1 \cdot u_{Ar})^2} \quad (4)$$

$$u_{N_2} = \sqrt{(c_1 \cdot u_{CO_2})^2 + (c_1 \cdot u_{H_2O})^2 + (c_1 \cdot u_{CH_4})^2 + (c_1 \cdot u_{O_2})^2} \quad (5)$$

Second, weighing of the parent gases introduces multiple contributions. Balance performance factors such as repeatability, drift, resolution, zero-point error and positioning contributed to the standard uncertainty by calculating the pooled standard deviation, S_p by eqn. 6 and dividing it by $\sqrt{n}$ using eqn. 7, where n is the number of measurements.

$$S_p = \sqrt{\frac{(n_1 - 1)s_1 + (n_2 - 1)s_2 + (n_3 - 1)s_3}{(n_1 - 1) + (n_2 - 1) + (n_3 - 1)}} \quad (6)$$

$$u_m = \frac{S_p}{\sqrt{n}} \quad (7)$$

Uncertainty contributions arise from the balance calibration certificate. The uncertainty function was applied according to eqn. 8, where R represents the cylinder mass, and the calibration factor of 4.415×10^{-8} was taken from the calibration certificate of the automatic balance.

$$u = 4.415 \times 10^{-8} \times R \quad (8)$$

The buoyancy effects, caused by changes in air density (ρ_a) changes during weighing, were accounted for by calculating air density from environmental parameters, pressure (p), relative humidity (rh) and temperature (t) using eqn. 9. Then, the associated uncertainty, u_B was determined using eqn. 10 in which V_S is the volume of sample cylinder and V_R is the volume of reference cylinder.

$$\rho_a = \frac{0.34848(p) - 0.009(rh) \times \exp(0.061t)}{273.15 + t} \quad (9)$$

$$u_B = \Delta \rho_a (V_S - V_R) \quad (10)$$

Another uncertainty contribution arises from residual gas remaining in the cylinder after evacuation. The residual N₂ mass was estimated by arranging the universal gas law (PV = nRT), which becomes eqn. 11.

$$m = \frac{PVM}{RT} \quad (11)$$

where m = mass of residual N₂; p = pressure inside the cylinder, V = volume of the cylinder; M = molecular weight of N₂; R = the universal gas constant; T = temperature (K).

The combined standard uncertainty of weighing C₃H₈ and N₂ was then calculated using eqns. 12 and 13, respectively.

$$u_c m_{C_3H_8} = \sqrt{(c_1 \cdot u_{balance})^2 + (c_2 \cdot u_{cal cert})^2 + (c_3 \cdot u_{buoyancy})^2 + (c_4 \cdot u_{residual gas})^2} \quad (12)$$

$$u_c m_{N_2} = \sqrt{(c_1 \cdot u_{balance})^2 + (c_2 \cdot u_{cal cert})^2 + (c_3 \cdot u_{buoyancy})^2 + (c_4 \cdot u_{residual gas})^2} \quad (13)$$

Third, the molar masses of C₃H₈ and N₂ contribute to uncertainty due to the atomic weight uncertainties of C, H and N based on IUPAC values. The uncertainty, u_{MC₃H₈}, was expressed by eqn. 14 in which 3 and 8 are the numbers of carbon and hydrogen atoms in propane and the uncertainty, u_{MN₂} was calculated by eqn. 15 in which 2 is the number of nitrogen atoms.

$$uM_{C_3H_8} = \sqrt{3(c_1 \cdot u_C)^2 + 8(c_2 \cdot u_H)^2} \quad (14)$$

$$uM_{N_2} = \sqrt{2(c_1 \cdot u_N)^2} \quad (15)$$

Finally, the combined standard uncertainty, u_c was obtained by propagating all contributions, parent gas purity, weighing and molar masses using eqn. 16 [15,23].

$$u_c = \sqrt{\left(\frac{\delta x_{C_3H_8}}{\delta x_{C_3H_8} A} \cdot u_{x_{C_3H_8} A}\right)^2 + \left(\frac{\delta x_{C_3H_8}}{\delta m_{C_3H_8} A} \cdot u_{m_{C_3H_8} A}\right)^2 + \left(\frac{\delta x_{C_3H_8}}{\delta M_{C_3H_8}} \cdot u_{M_{C_3H_8}}\right)^2} + \sqrt{\left(\frac{\delta x_{C_3H_8}}{\delta x_{N_2}} \cdot u_{x_{N_2}}\right)^2 + \left(\frac{\delta x_{C_3H_8}}{\delta m_{N_2}} \cdot u_{m_{N_2}}\right)^2 + \left(\frac{\delta x_{C_3H_8}}{\delta M_{N_2}} \cdot u_{M_{N_2}}\right)^2} \quad (16)$$

The sensitivity coefficients $\delta x_i / \delta y_i$ in eqn. 16 were derived by differentiating eqn. 3, which represents the measurement model. These coefficients are used to transform the different sources of uncertainty expressed in various units, such as % purity of the parent gas, the mass of gas used in preparing the mixture (g) and the molar masses of C and O atoms (g/mol) into the mole fraction unit $\mu\text{mol/mol}$. Uncertainty calculations were carried out using the software developed by NPL_XLGENLINE, which is widely applied in gas analysis. The resulting combined standard uncertainties, u_c for mixtures B, C, D, E and F were found to be: 31.30, 23.47, 14.35, 7.12 and 1.92 $\mu\text{mol/mol}$, respectively.

Verification of the C₃H₈ gravimetric mole fractions by GC-FID: In compliance with ISO 6143, the mole fractions of the gravimetrically prepared gas mixtures were verified using a validated GC-FID method. Calibration of the instrument was performed using the 4 CRMs, thereby establishing metrological traceability of the measurement results to the SI units. The CRMs and sample cylinders were introduced to the GC analysis in the sequence: R-S-S-R-S-R-S-S-R (R = reference, S = sample). This sequence was designed to assure that no trend would affect the measurement results. Each reference mixture was injected ten times and the test sample was also injected 10 times. A representative chromatogram (Fig. 2) displays a well resolved C₃H₈ peak at a retention time of 1.989 min and an N₂ peak at 2.655 min.

A calibration curve of the GC-FID was established by correlating the mole fractions of the propane CRMs with their corresponding mean peak areas ($\bar{x}$), yielding the linear equation: $y = 0.0305x - 0.2315$. The peak areas of the tested gas mixtures (B, C, D, E and F), were measured and the mean

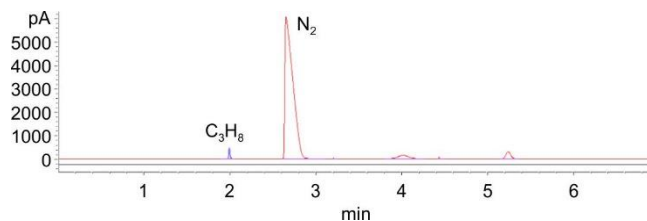


Fig. 2. GC-FID chromatogram for C₃H₈ in N₂ mixture

The peak area of the four C₃H₈/N₂ CRMs measured by GC-FID are reported in Table-4 together with the average, $\bar{x}$ and standard deviation, SD.

TABLE-4 GC-FID DETERMINED PEAK AREAS OF THE C ₃ H ₈ /N ₂ CRMS				
	CRM mole fraction ($\mu\text{mol/mol}$)			
	14750	8010	3008	702.5
Peak area	447.347	244.351	91.863	21.085
	451.599	244.133	91.478	21.095
	452.176	242.910	91.247	21.152
	449.275	244.279	91.667	21.152
	448.052	244.035	91.910	21.193
	450.174	243.022	91.543	21.130
	446.327	242.844	91.490	21.172
	449.280	244.173	91.318	21.171
	449.283	244.620	91.475	21.186
	450.003	242.571	91.595	21.296
$\bar{x}$	449.3516	243.6938	91.5586	21.1632
SD	1.795	0.762	0.212	0.059

values ($\bar{x}$), standard deviations (SD) and relative standard deviations (RSD%) were calculated and reported in Table-5. The consistently low RSD% values highlight the excellent repeatability of the analytical results, thereby demonstrating the reliability of the GC-FID technique for C₃H₈ quantification. Then, the mole fraction (x) of each gas mixture was derived using the calibration function ($y = 0.0305x - 0.2315$). The calculated mole fractions were found to be 12081.4164, 9007.5246, 5987.04260, 2970.5993 and 805.9508 $\mu\text{mol/mol}$ for mixtures B, C, D, E and F, respectively.

TABLE-5 PEAK AREAS AND MOLE FRACTIONS OF GAS MIXTURES (B–F) MEASURED BY GC-FID					
	Gas mixture				
	B	C	D	E	F
Peak area	367.587	275.216	182.284	90.407	24.203
	368.501	275.572	182.910	90.24	24.464
	368.769	274.589	182.924	90.669	24.397
	368.607	273.047	182.703	90.429	24.407
	368.626	274.484	183.152	90.283	24.253
	366.932	273.112	183.271	90.489	24.284
	369.116	273.968	181.693	89.905	24.277
	368.138	275.168	181.959	90.423	24.421
	368.181	274.719	181.106	90.501	24.365
	368.061	275.105	181.731	89.856	24.429
$\bar{x}$	368.252	274.498	182.373	90.372	24.35
SD	0.63	0.87	0.73	0.21	0.089
RSD %	0.17	0.32	0.40	0.24	0.36
Mole fraction ($\mu\text{mol/mol}$)	12081.42	9007.52	5987.043	2970.60	805.95

Uncertainty of the GC-FID measurement results: The uncertainty associated with the measured propane mole fraction by GC-FID arises from three contributions as required by ISO 6143. These are: the mole fraction of the CRM, the peak area of the CRM and the peak area of the propane sample. These contributions define the measurement uncertainty by accounting for the accuracy of the calibration standard and the precision of the instrumental response. The uncertainty associated with the peak area of the CRM and propane sample was calculated according to eqn. 17, as specified in ISO 6143 [16].

$$u(y_i) = \frac{1}{\sqrt{90}} \sqrt{\sum_{j=1}^{10} (y_{ij} - y_i)^2} \quad (17)$$

where $u(y_i)$ = standard uncertainty of the measured peak area (A); y_{ij} = individual peak area value; y_i = average of the 10 peak area measurements.

The mean value of the peak area uncertainties for the 4 CRMs was calculated and divided by the mean peak area, A_1 of the four CRMs to give (u_{A1}/A_1) . Also, the mean value of the 4 CRM mole fraction uncertainty u_x was calculated and divided by the mean mole fraction, x_{CRM} of the four CRMs to give (u_x/x_{CRM}) . In addition, the uncertainty of the peak area u_{A2} of the C_3H_8 in each gas mixture was divided by the average peak area A_2 to give (u_{A2}/A_2) . The combined standard uncertainty, u_c of the measured mole fraction, $x_{C_3H_8}$ was then calculated using eqn. 18:

$$u_c(x_{C_3H_8}) = x_{C_3H_8} \sqrt{\left(\frac{u_x}{x_{CRM}}\right)^2 + \left(\frac{u_{A1}}{A_1}\right)^2 + \left(\frac{u_{A2}}{A_2}\right)^2} \quad (18)$$

where $x_{C_3H_8}$ = mole fraction measured by GC-FID; x_{CRM} = average mole fraction of the CRM; A_1 = average peak area of the CRM; A_2 = peak area of C_3H_8 in each gas mixture (B–F).

The calculated uncertainty values of the mole fractions verified by the GC-FID are shown in Table-6 as 32.90, 25.69, 17.68, 8.40 and 2.34 $\mu\text{mol/mol}$, for the gas mixtures, B, C, D, E and F, respectively.

Compatibility of the mole fractions obtained by gravimetry and by GC-FID: ISO 6142 requires verification of compatibility of the mole fraction of a calibration mixture prepared gravimetrically with the mole fraction measured using GC-FID [15]. This helps to identify any significant errors during the preparation process. The ISO standard specifies the compatibility criterion shown in eqn. 19:

$$|x_{\text{grav}} - x_{\text{anal}}| \leq 2\sqrt{u(x_{\text{grav}})^2 + u(x_{\text{anal}})^2} \quad (19)$$

Upon examining the results presented in Table-7, it is evident that all values of the absolute difference, $|x_{\text{grav}} - x_{\text{anal}}|$ are lower than the term, $2\sqrt{u(x_{\text{grav}})^2 + u(x_{\text{anal}})^2}$. This finding demonstrates the compatibility of the two methods, thereby confirming the validity of the gas mixture preparation.

Long-term stability: Long-term stability describes the behaviour of a reference material during storage under conditions specified by the producer or user. The long-term stability of the C_3H_8/N_2 mixtures was previously investigated and the mixtures remained stable over a four-year period [1]. The study yielded an average uncertainty of 17.73 $\mu\text{mol/mol}$, which was included as a component of the certified uncertainty (U_{CRM}) associated with the certified mole fractions of the C_3H_8/N_2 gas mixtures (B–F) [24].

Certified uncertainty: Using the approach in ISO 33405 concerning the certified uncertainty, the U_{CRM} associated with the reference value of C_3H_8 in N_2 was calculated using eqn. 20 [24]:

$$U_{CRM} = 2\sqrt{(u_{\text{grav}})^2 + (u_{\text{anal}})^2 + (u_{\text{its}})^2} \quad (20)$$

TABLE-6
UNCERTAINTY VALUES OF MOLE FRACTIONS DETERMINED BY GC-FID

Uncertainty sources	Gas mixtures				
	B	C	D	E	F
Average $u_{\text{Peak area CRM}}$			0.22		
Average peak area CRM			201.442		
Average $u_{\text{Mole fraction CRM}}$			16.063		
Average mole fraction CRM			6617.63		
$u_{\text{Peak area sample}}$	0.20	0.28	0.23	0.084	0.028
Average peak area sample	368.252	274.498	182.373	90.372	24.350
Mole fraction GC ($\mu\text{mol/mol}$)	12081.42	9007.52	5987.043	2970.60	805.95
u_c ($\mu\text{mol/mol}$)	32.90	25.69	17.68	8.40	2.34

Note: each of the uncertainty of the peak area CRM and of the mole fraction CRM was taken as an average of the uncertainties of the mixtures B, C, D, E and F.

TABLE-7
COMPARISON OF MOLE FRACTIONS ($\mu\text{mol/mol}$) DETERMINED BY GRAVIMETRIC AND GC-FID METHODS

Mixture	x_{grav}	x_{anal}	$ x_{\text{grav}} - x_{\text{anal}} $	u_{grav}	u_{anal}	$2\sqrt{u(x_{\text{grav}})^2 + u(x_{\text{anal}})^2}$
B	12053.82	12081.42	27.6010	31.30	32.90	90.82
C	9013.23	9007.52	5.7046	23.47	25.69	69.59
D	5998.011	5987.043	10.9680	14.35	17.68	45.54
E	2987.29	2970.60	16.6897	7.12	8.40	22.013
F	804.81	805.95	1.1360	1.92	2.34	6.053

where u_{grav} = uncertainty of the gravimetric mole fraction; u_{anal} = uncertainty of the GC-FID measured mole fraction; u_{lis} = uncertainty of the long-term stability.

The uncertainty values of the u_{grav} , u_{anal} and u_{lis} for the C₃H₈/N₂ the CRM gas mixtures (B–F) are reported in Table-8.

Mixture	u_{grav}	u_{anal}	u_{lis}	U_{CRM}	$U_{\text{CRM}} (\%)$
B	31.30	32.90	17.73	97.49	0.81
C	23.47	25.69	17.73	78.10	0.87
D	14.35	17.68	17.73	57.72	0.96
E	27.10	8.40	17.73	66.91	2.25
F	1.92	2.34	17.73	35.97	4.46

The certified uncertainty (U_{CRM}) was calculated using eqn. 21 and yielded values of 97.49, 78.11, 57.72, 66.91 and 35.97 $\mu\text{mol/mol}$ for mixtures B, C, D, E and F, respectively. The reported data show that the relative uncertainty of the certified reference values at higher concentration levels (B–D) was below 1%, indicating good control of the measurement system within this range. At 2970.60 $\mu\text{mol/mol}$ (mixture D), the relative uncertainty increased to 2.25%, which remains comparable to the uncertainties reported by TÜBİTAK UME, Türkiye, for the GC-FID calibration used in this study. For mixture F (805.95 $\mu\text{mol/mol}$), the relative uncertainty increased to 4.46%. This higher uncertainty arises from the application of the long-term stability uncertainty of 17.73 $\mu\text{mol/mol}$ uniformly across all concentration levels as a conservative approach, in the absence of concentration-specific stability data. Thus, the value of $805.95 \pm 4.46 \mu\text{mol/mol}$ was reported as an information value.

NIST has prepared and analytically verified gravimetric propane mixtures with expanded relative uncertainties typically ranging from 0.3-0.5%, depending on the concentration level and balance-gas matrix [25,26]. The uncertainties obtained in our study were below 1% for mixtures B, C and E, while the 2.25% uncertainty for mixture D was comparable to the TÜBİTAK UME values. These results support the suitability of the prepared C₃H₈/N₂ CRMs as reliable calibration standards.

Performance evaluation of C₃H₈/N₂ mixtures (B–F) as calibrants: The CRM gas mixtures (B–F) were used to calibrate the GC-FID measurement system and ensure accurate and reliable measurements. The average peak areas obtained for these mixtures are shown in Table-6 and were plotted against their corresponding mole fractions.

The calibration plot demonstrated an excellent linear relationship between the CRM mole fractions and the corresponding peak areas, expressed by the calibration function: $y = 0.0306x - 0.7095$ with a coefficient of determination, $R^2 = 1$. The slope of the calibration line (0.0306) represents the sensitivity of the GC-FID response, corresponding to the change in peak area per unit change in mole fraction. The intercept (-0.7095) is close to zero, which indicate negligible baseline effects and systematic bias at low concentrations. The calibration curve exhibited excellent linearity ($R^2 = 1$) and thus support the reliable quantification of C₃H₈/N₂.

The performance of mixtures B–F was further assessed by analyzing a C₃H₈/N₂ CRM with a certified mole fraction of 8010 $\mu\text{mol/mol}$ as an unknown sample. Ten peak area measurements were recorded (Table-9) and the corresponding mole fraction was calculated using the calibration function, $y = 0.0306x - 0.7095$. The measured mole fraction was 7990.36 $\mu\text{mol/mol}$, with a standard deviation of 9.47 $\mu\text{mol/mol}$. Method precision, expressed as %RSD, was 0.12%, while the accuracy calculated using eqn. 21 was 99.75% [27].

$$\text{Accuracy } (\%) = \frac{\bar{x}}{x_{\text{CRM}}} \times 100 \quad (21)$$

y (area)	a (slope)	b (intercept)	x ($\mu\text{mol/mol}$)
243.841	0.0306	-0.7095	7991.85
244.150	0.0306	-0.7095	8001.94
243.574	0.0306	-0.7095	7983.12
243.919	0.0306	-0.7095	7994.39
243.779	0.0306	-0.7095	7989.82
243.922	0.0306	-0.7095	7994.49
243.764	0.0306	-0.7095	7989.33
243.379	0.0306	-0.7095	7976.75
243.383	0.0306	-0.7095	7976.88
244.245	0.0306	-0.7095	8005.049
$\bar{x}$			7990.36
SD			9.47
RSD (%): 0.12; Accuracy (%): 99.75			

The %RSD value of 0.12% indicates excellent repeatability, with minimal variation among replicate measurements. The accuracy of 99.75% reflects the close agreement between the measured mole fraction and the certified value of 8010 $\mu\text{mol/mol}$, supporting the suitability of mixtures B–F as calibration standards. The results confirm that the prepared C₃H₈/N₂ calibrants provide precise and accurate analytical measurements.

The quality of the prepared C₃H₈/N₂ reference materials as calibrants was further assessed using the E_n value, calculated according to eqn. 22:

$$E_n = \frac{x_{\text{Un}} - x_{\text{CRM}}}{\sqrt{(U_{\text{Un}})^2 + (U_{\text{CRM}})^2}} \quad (22)$$

where x_{Un} = mole fraction of the analyzed CRM as unknown; x_{CRM} = mole fraction of the CRM (8010 $\mu\text{mol/mol}$); U_{Un} = expanded uncertainty in the unknown result (20 $\mu\text{mol/mol}$); U_{CRM} = expanded uncertainty in the CRM mole fraction.

To apply this equation, the combined standard uncertainty (u_c) was first calculated using eqn. 18. The expanded uncertainty (U_{Un}) was then obtained by applying a coverage factor of $k = 2$, resulting in a value of 43.33 $\mu\text{mol/mol}$. Using these uncertainty values, the E_n number was calculated and found to be -0.41. Since the absolute value of E_n is less than 1, this demonstrates satisfactory agreement between the measured concentration, 9770.36 $\mu\text{mol/mol}$ and the certified value of the reference material, 8010 $\mu\text{mol/mol}$ [28]. This level of agreement confirms that the measurement method is accurate and fit for its intended purpose.

Conclusion

Five C₃H₈/N₂ gas mixtures (B, C, D, E and F) covering the mole fraction range 804.81-12053.81 µmol/mol were successfully prepared by gravimetric method in accordance with ISO 6142. The mole fractions were verified by GC-FID in accordance with ISO 6143. The mole fraction values obtained by gravimetry were in good agreement with those obtained by GC-FID, supporting the validity of the preparation approach. The certified mole fraction values were established as 12053.81 ± 97.49, 9013.23 ± 78.11, 5998.011 ± 57.72 and 2987.29 ± 66.91 µmol/mol. For mixture F, the value of 804.81 ± 35.97 µmol/mol was reported as an information value due to its relatively high uncertainty of 4.46%. The low uncertainties associated with the other mixtures support their reliability and metrological traceability. Calibration of the GC-FID using the five prepared C₃H₈/N₂ CRMs yielded a precision of 0.12% RSD and an accuracy of 99.75%. The calculated E_n value of -0.41 indicates close agreement between the measured value of 7990.36 µmol/mol and the certified value of the reference material. These results establish the suitability of the prepared C₃H₈/N₂ CRMs as calibration standards for accurate and traceable hydrocarbon measurements in industrial gas analysis and environmental monitoring.

ACKNOWLEDGEMENTS

The authors acknowledge the Center for Studies and Research at SASO for their financial support and continuous follow up throughout this study, which greatly contributed to its successful completion and publication.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language and no data, results or scientific conclusions were generated by AI. All analyses, interpretations and conclusions are the authors' own. The authors reviewed and edited the content and take full responsibility for the published work.

REFERENCES

1. B.D. Skrbic and M.J. Zlatkovic, *Chromatographia*, **17**, 44 (1983); <https://doi.org/10.1007/BF02265109>
2. A.B. Shehata, A.R. AlAskar, N.H. AlYami and A.S. AlOwaysi, *Green Sustain. Chem.*, **13**, 269 (2023); <https://doi.org/10.4236/gsc.2023.134015>
3. E.C. de Oliveira, *Metrol. Meas. Syst.*, **19**, 405 (2012); <https://doi.org/10.2478/v10178-012-0035-6>
4. ISO, ISO 6974-3:2001, Natural Gas Determination of Composition with Defined Uncertainty by Gas Chromatography, Part 3: Determination of Hydrogen, Helium, Oxygen, Nitrogen, Carbon Dioxide and Hydrocarbons up to C-8 using Two Packed Columns (2001); <https://www.iso.org/standard/25854.html>
5. T.J. Lechner-Fish, Enhanced Performance of an Integrated Gas Chromatograph for On-Line Natural Gas Analysis, 4th International Symposium on Fluid Flow Measurement, Denver, 27-30 June (1999); <https://es.studenta.com/content/111273256/14-02-gas-cromatographs-cesar-delgado>
6. H. Budiman, Nuryatini and O. Zuas, *Procedia Chem.*, **16**, 465 (2015); <https://doi.org/10.1016/j.proche.2015.12.080>
7. M.F. Barbosa, J.R.B. Santos, A.N. Silva, S.F.C. Soares and M.C.U. Araujo, *Microchem. J.*, **170**, 106752 (2021); <https://doi.org/10.1016/j.microc.2021.106752>
8. O. Zuas and H. Budiman, *Hem. Ind.*, **70**, 451 (2016); <https://doi.org/10.2298/HEMIND150315051Z>
9. G.C. Rhoderick, *J. Chromatogr. A*, **1017**, 131 (2003); <https://doi.org/10.1016/j.chroma.2003.08.002>
10. C.J. Cowper, *J. Chromatogr. A*, **56**, 1 (1995); [https://doi.org/10.1016/S0301-4770\(08\)61280-4](https://doi.org/10.1016/S0301-4770(08)61280-4)
11. G.C. Rhoderick, *J. Chromatogr. A*, **1187**, 226 (2008); <https://doi.org/10.1016/j.chroma.2008.01.087>
12. A.S. Brown, M.J.T. Milton, C.J. Cowper, G.D. Squire, W. Bremser and R.W. Branch, *J. Chromatogr. A*, **1040**, 215 (2004); <https://doi.org/10.1016/j.chroma.2004.04.007>
13. J.S. Barrabin, B.C. Garrido, G.A. Machado, W. Wollinger, R.F.M. Freitas, A.C.S. Feliciano and M.N.S. De la Cruz, *Accredit. Qual. Assur.*, **20**, 483 (2015); <https://doi.org/10.1007/s00769-015-1168-6>
14. JCGM, International Vocabulary of Metrology, Basic and General Concepts and Associated Terms (VIM), JCGM 200:2012, BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML, edn 3 (2012); https://www.bipm.org/documents/20126/2071204/JCGM_200_2012.pdf
15. ISO, ISO 6142-1:2015, Gas Analysis: Preparation of Calibration Gas Mixtures-Part 1: Gravimetric Method for Class I Mixtures (2015); <https://www.iso.org/standard/59631.html>
16. ISO, ISO 6143:2025, Gas Analysis: Comparison Methods for Determining and Checking the Composition of Calibration Gas Mixtures (2025); <https://www.iso.org/standard/85579.html>
17. ISO, ISO 19229:2019, Gas Analysis-Purity Analysis and the Treatment of Purity Data, edn 1 (2019); <https://www.iso.org/standard/72010.html>
18. A. Alink, *Metrologia*, **37**, 35 (2000); <https://doi.org/10.1088/0026-1394/37/1/5>
19. A.M.H. van der Veen and M.G. Cox, *Metrologia*, **40**, 18 (2003); <https://doi.org/10.1088/0026-1394/40/2/303>
20. ISO, ISO 17034:2016, General Requirements for the Competence of Reference Material Producers (2016); <https://www.iso.org/standard/29357.html>
21. A.B. Shehata, A.R. AlAskar, N.H. AlYami and A.S. AlOwaysi, *Acta IMEKO*, **14**, 1 (2025); <https://doi.org/10.21014/actaimeko.v14i1.1945>
22. A.B. Shehata, N.H. AlYami, A.S. AlOwaysi and A.R. Alaskar, *J. Chem. Metrol.*, **15**, 11 (2021); <https://doi.org/10.25135/jcm.58.21.04.2055>
23. A.B. Shehata, A.R. AlAskar, N.H. AlYami and A.S. AlOwaysi, *Sci. J. Chem.*, **10**, 133 (2022).
24. ISO, ISO 33405:2024, Reference Materials, Approaches for Characterization and Assessment of Homogeneity and Stability (2024); <https://www.iso.org/standard/84226.html>
25. NIST, Certificate of Analysis: Standard Reference Material 2644a, Propane in Nitrogen (2022); <https://tsapps.nist.gov/srmext/certificates/2644a.pdf>
26. NIST, Certificate of Analysis: Standard Reference Material 1665b, Propane in Air (2024); <https://tsapps.nist.gov/srmext/certificates/1665b.pdf>
27. Eurachem, The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics, edn 3 (2025); <https://www.eurachem.org/index.php/publications/guides/mv>
28. ISO 13528 Statistical Methods for Use in Proficiency Testing by interlaboratory comparison (2022); <https://www.iso.org/standard/78879.html>