

Article

Chemical and Isotopic Characterization of Industrial Gases: An Integrated and Robust Approach Combining Sampling and Analytical Measurements

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Abstract

In the context of the energy transition and the increasing deployment of low-carbon gases (hydrogen, biomethane), reliable analytical monitoring is required to support integrity assessment and traceability of gas infrastructures under diverse on-site conditions while limiting analytical costs through standardized sampling and a single analytical system. We developed and validated integrated workflows combining sampling and laboratory analysis for chemical and compound-specific isotope analysis (CSIA) of natural gas and associated gaseous effluents in underground storage. An original quantification approach was implemented, linking sampling pressure to the amount of each compound collected in vials, and coupled with $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurements of alkanes ($\text{C}_1\text{--C}_3$), CO_2 and H_2 . Two complementary sampling modes were optimized and compared: conventional high-pressure cylinders and direct collection into vacuum-sealed vials suitable for a broad range of pressures and field conditions. Using reference gas mixtures and operational samples, both approaches showed good reproducibility and isotopic accuracy during laboratory validation and over two years of monitoring. In particular, $\delta^2\text{H}$ determinations for alkanes and H_2 remained robust under low-pressure sampling typical of annular spaces ($\sim 1\text{--}2$ bar), despite gas-composition fluctuations. These validated methodologies provide a flexible basis for routine, standardized monitoring of stored and circulating gases, including emerging low-carbon components.

Keywords: gas monitoring; alkanes; CSIA approach; underground gas storage ‘UGS’; hydrogen



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1. Introduction

Gas infrastructures—encompassing production, transport, distribution, and storage systems for methane, biomethane, hydrogen, and carbon dioxide are a cornerstone of the modern energy transition. They ensure supply flexibility, support large-scale energy storage, and contribute to the decarbonization and resilience of energy networks. Yet, the physical and chemical environments within these infrastructures are dynamic, and the transported or stored gases can be affected by a range of processes, including gas migration

and leakage [1–3], microbial activity [4–6], and geochemical or material interactions with fluids, rocks, and engineered surfaces [7–9]. High-resolution, continuous monitoring is therefore critical to detect subtle anomalies and reaction pathways that may influence gas composition, transport efficiency, or containment integrity. Integrating advanced analytical tools—such as molecular and isotopic fingerprinting—into routine surveillance programs enables the early identification of deviations from baseline conditions. Such data-driven insights not only facilitate timely operational adjustments but also deepen our understanding of gas behavior and reactivity within complex infrastructure systems, ultimately supporting their safe, efficient, and long-term performance.

Gas sampling within monitoring programs requires standardized protocols designed to preserve the integrity of collected samples and avoid fractionation or contamination [10–13]. Common approaches include direct sampling from pipelines, injection, production, or observation wells using pressurized cylinders as described in GPA 2166-22 standard [14], as well as specialized tools capable of capturing fluids under representative pressure and temperature conditions. The choice of sampling frequency and location is guided by system heterogeneity, operational dynamics, and the need to capture representative temporal and spatial variability [15]. Strict quality control during sample collection, storage, and transport is essential to ensure reliable downstream molecular and isotopic analyses [16].

Chemical characterization is typically performed using gas chromatography (GC) to quantify hydrocarbon fractions (C_1 – C_6^+) and non-hydrocarbon gases such as CO_2 , N_2 , and H_2S [11,17]. Stable isotope analyses, commonly achieved through isotope ratio mass spectrometry (IRMS) or cavity ring-down spectroscopy (CRDS), provide valuable tracers for identifying gas origin, migration pathways, and geochemical alterations [18–20]. More advanced techniques, such as compound-specific isotope analysis (CSIA), allow the isotopic composition of individual hydrocarbons (e.g., methane, ethane, propane) to be measured with high precision [9,18,19], enabling detailed interpretation of mixing processes, biodegradation, or thermochemical transformations [2,3,6]. The integration of chemical and isotopic data and tools enhances the capacity to detect subtle changes that may indicate reservoir or operational anomalies.

The analytical methodology developed in this study enables highly precise chemical and isotopic monitoring of industrial gas infrastructures. The sampling system, previously described and used by A. Lecharlier et al. [21] for laboratory applications, has been further optimized here for on-site industrial gas sampling. This latter is applicable to a wide range of field conditions and sampling locations, from high-pressure sources (e.g., gas wellheads) to low-pressure environments (e.g., annulus spaces of well). The procedure ensures full operational safety for users, with no direct contact with the storage matrix during sampling. A second key objective is to guarantee consistent and representative sampling during large-scale field campaigns, which may involve numerous gas wells and sampling points (>10 per day). In addition, reliable long-term monitoring of such structures requires repeated campaigns over several years to achieve a comprehensive understanding of the studied system.

2. Materials and Methods

2.1. Chemicals and Products

A custom-made calibration gas standard was used for quantitative and isotopic analyses of light hydrocarbons. The mixture was gravimetrically prepared and certified by Air Products (France, Paris) to ensure high compositional accuracy and traceability to international reference standards. Its detailed composition, expressed in mol/mol%, is reported in Figure S1. The standard contains methane ($88.765 \pm 0.023\%$), ethane ($3.0066 \pm 0.0075\%$),

propane ($3.0015 \pm 0.0091\%$), and minor components including iso- and n-butane, neopentane, iso- and n-pentane, and n-hexane, as well as hydrogen ($1.972 \pm 0.011\%$), nitrogen ($2.0125 \pm 0.055\%$), and carbon dioxide ($0.9948 \pm 0.0027\%$). This calibration gas was used to verify the linearity, precision, and reproducibility of chromatographic and isotopic measurements. A complete certificate of composition and conformity, provided by the manufacturer, is included in Figure S1.

The carrier gas used for GC–MS analyses was a grade 5.0 gas supplied by Linde (France, Lyon). Two reference gases were used for isotopic ratio calibration: (i) carbon dioxide (CO_2 , grade 4.5, Linde) for carbon isotope ratio ($\delta^{13}\text{C}$) measurements, with a certified $\delta^{13}\text{C}$ value of -3.520% relative to the international VPDB standard, and (ii) hydrogen with a purity $> 99.999\%$ by Air Liquide (France, Paris), characterized by a $\delta^2\text{H}$ value of -161.144% relative to the VSMOW standard.

2.2. Analytical Instruments

Analyses were conducted by gas chromatography–mass spectrometry (GC–MS) and gas chromatography–isotope ratio mass spectrometry (GC–IRMS), with samples introduced through a headspace system (Figure S2). GC–MS analyses were performed on a Thermo Scientific TRACE 1310 GC (Bremen, Germany) coupled to an ISQ QD MS for compound identification and quantification. Compound-specific isotope measurements were obtained using a TRACE 1310 GC connected to an ISOLINK II–IRMS system. Samples were injected with a Headspace HS–TRIPLUS RSH autosampler, and standard-gas reference pulses were delivered via a Thermo Scientific ConFlo IV interface.

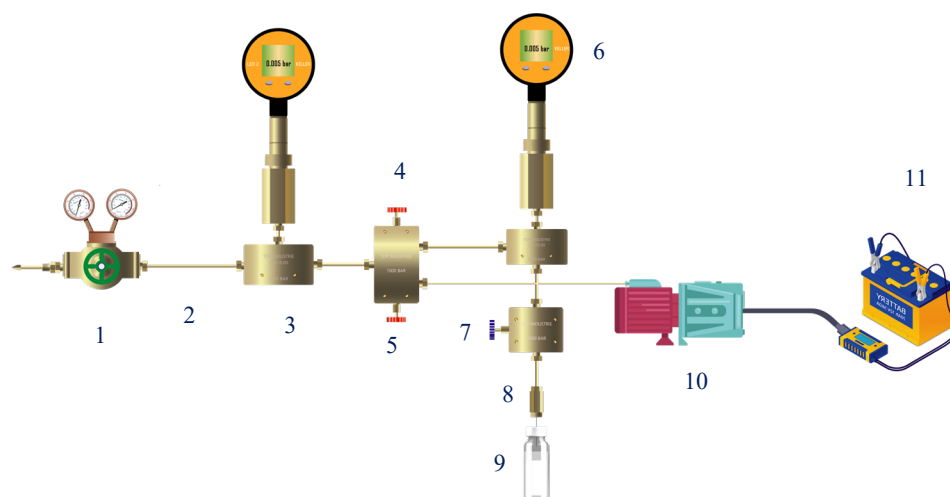
2.3. Sampling Methods

Gas sampling was performed using a pressure-regulated system specifically designed for this purpose. It was developed and optimized for field deployment, while ensuring sampling accuracy and reproducibility equivalent to those achieved under controlled laboratory conditions.

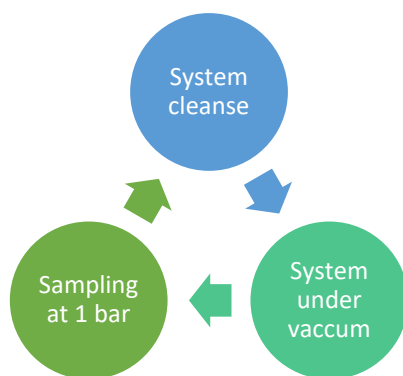
The optimized sampling system can be operated in two modes to accommodate site-specific technical constraints:

- (i) Gas cylinder sampling (high-pressure/high-volume source only): This is the conventional approach, in which gas cylinders are pressurized and filled at the wellhead. The collected gas is subsequently transferred into headspace (HS) vials using the sampling system, which depressurizes the gas to ~ 1 bar and enables filling of evacuated vials while preventing atmospheric contamination.
- (ii) Direct sampling from the gas source: In this configuration, the sampling system is connected directly to the on-site gas source, allowing direct filling of vials regardless of operating conditions (high or low pressure/volume). This is not achievable with the conventional approach. An additional advantage is a substantially reduced sampling cost per well compared with scoot cylinder sampling.

The gas is first sampled in a high-pressure cylinder by connecting it to a high-pressure gas source (typically > 50 bar), such as a gas wellhead (i). When sampling directly into vials, this step is not required (ii). In both methods, the gas is depressurized until a low pressure of 3 bar using the pressure-reducing regulator in the system (Scheme 1) and transferred into Headspace HS vials (20 mL, PTFE) at atmospheric pressure, 1 bar for each sample. Vials should be vacuuming until 0.004 bar right before sampling. The vacuum gas sampling system operates according to three functional steps in Scheme 2. The detailed protocol is given in Data S1, Tables S4 and S5.



Scheme 1. High- and low-pressure gas sampling system 1. pressure-reducing regulator; 2. Capillary; 3. Fitting ‘T’ high pressure; 4. Sampling micrometric hand valve; 5. Vacuum hand valve; 6. digital manometer; 7. sampling/vacuum hand valve; 8. Gastight needle; 9. HS vial; 10. Vacuum pump; 11. Deep cycle battery 140 Ah.



Scheme 2. Sampling process steps.

This system provides an efficient and reliable method for gas sampling from any gas sources, especially those characterized by low pressure, low flow rate, and limited volume such as the annular space of gas storage wells without the need for prior purging or cleaning, owing to its inherent vacuum-maintained configuration. This approach ensures consistent sampling across multiple campaigns over time. It also represents a cost-effective alternative to gas cylinder sampling, which can be more expensive and necessitate specific transport protocols, particularly for highly flammable gases such as hydrogen molecule H_2 . For safety and security reasons, a portion of the system (10 and 11) is systematically installed outside the ATEX-classified zone of the gas well—approximately 10 m from the wellhead—to prevent any potential contact with atmospheric gas within this hazardous area.

This novel method, applied directly using vials (ii), is well suited for large-scale gas sampling campaigns involving multiple gas wells (>10 wells per day). In the present study, it was tested during a single-day campaign involving the collection of 14 gas samples (15 vials per well) and compared to first method (i) largely used in literature.

2.4. GC-MS Quantification Method

Gas Compound separation was achieved using an HP-PLOT Q capillary column, with sample introduction carried out via Headspace ‘HS’ injection. The optimized technical parameters are given in Table 1.

Table 1. HS-GC-MS Experimental Parameters for the Quantitative Analysis of Major Natural Gas Compounds.

Instrument	Parameter	Value/Reference
HeadSpace	Syringe volume	2.5 mL
	Needle length	65 mm
	Sample draw	0.2 mL
	Filling speed	50 mL·min ^{−1}
	Injection speed	50 mL·min ^{−1}
	Injection depth	20 mm
	Penetration Speed	25 mm·s ^{−1}
GC	Inlet temperature	200 °C
	Split ratio	10.0
	Split flow	15 mL·min ^{−1}
	Carrier gas	He
	Gas saver	20 mL/min
	Column	HP Plot Q
	Constant flow in column	1.5 mL/min
	Oven	45 °C (2 min)–10 °C·min ^{−1} –130 °C (2 min)–15 °C·min ^{−1} –200 °C (2 min)–15 °C·min ^{−1} –240 °C (2 min)
MS	MS transfer line	250 °C
	Ion source temp	250 °C
	Ionization mode	Electronic Impact ionization
	Total scan	1–200
	Dwell times	0.2

Quantification is carried out using a custom-certified standard gas (Air Products) with a composition similar to that of natural gas (i). Both the standard and the samples are introduced at atmospheric pressure (1 bar) from 20 mL headspace vials. The mole fraction (%) of each component is calculated using the Equation (1) [11].

$$\% P_i = \frac{A_{i \text{ sample}} \times 100}{A_{i \text{ std}}} \quad (1)$$

$A_{i \text{ sample}}$: Sample peak area of component i

$A_{i \text{ std}}$: Standard peak are of component i

$\% P_i$: Percentage in (% mol/mol)

To ensure reliable comparisons, it is essential that gas standards and field samples are collected, stored, and analyzed under identical conditions. Gas standards must be sampled using the same procedures and methods as those applied to field samples.

The linear regression analysis was conducted using a novel experimental approach designed to assess the system's performance across a range of pressures. Six 20 mL HS vials were filled at controlled pressures of (0.39; 0.52; 0.65; 0.78; 0.91, and 1.00 bar) using a certified gas standard.

The estimation of the measurement repeatability was evaluated by calculating the recovery percentage for each sample to the mean of all samples, using the Equation (2) [22,23].

$$R (\%) = \frac{A_n}{A_m} \times 100 \quad (2)$$

R (%): Recovery percentage

A_n : n sample peak area

A_m : Average peak area

2.5. Isotopic Methods

Isotopic ratio mass spectrometry 'IRMS' analyses were performed using a Thermo Fisher 'ISOLINK II—DELTA V PLUS' GC-IRMS system.

Two main studies were carried out to ensure the accurate determination of isotopic ratios. First, a linearity study was performed using isotopic reference gases CO₂ with a known $\delta^{13}\text{C}$ signature and H₂ with a known $\delta^2\text{H}$ signature referenced to the international standards Vienna Pee Dee belemnite 'V-PDB' and Vienna Standard Mean Ocean Water 'V-SMOW', respectively. Second, a stability assessment was conducted using 10 repeated injections of the reference gas to validate the precision and reliability of the isotopic ratio mass spectrometer.

Alkanes and Carbon Dioxide Isotopic Analyses

• IR $\delta^{13}\text{C}$

Due to the large differences in concentration between methane and the other target compounds (ethane, propane, and carbon dioxide), the analyses were conducted in three separate runs, as illustrated Figure 1 for methane and Figure S3 for ethane 'C₂H₆' and propane 'C₃H₈'. The $\delta^{13}\text{C}$ analytical parameters for each method are detailed (i, ii, iii).

- (i) $\delta^{13}\text{C}$ methane CH₄ experimental parameters for IR determination: Fixed method, Direct injection using Gas-tight syringe, 10 μL split 50:1, gas reference: 6000 mV.
- (ii) $\delta^{13}\text{C}$ Carbene dioxide CO₂ experimental parameters for IR determination: Fixed method, Headspace Injection 'HS', 300 μL , split 50:1, gas reference: 6000 mV.
- (iii) $\delta^{13}\text{C}$ ethane C₂H₆ and propane C₃H₈ experimental parameters for IR determination: Fixed method, Headspace Injection 'HS', 100 μL , split 50:1, gas reference: 6000 mV.

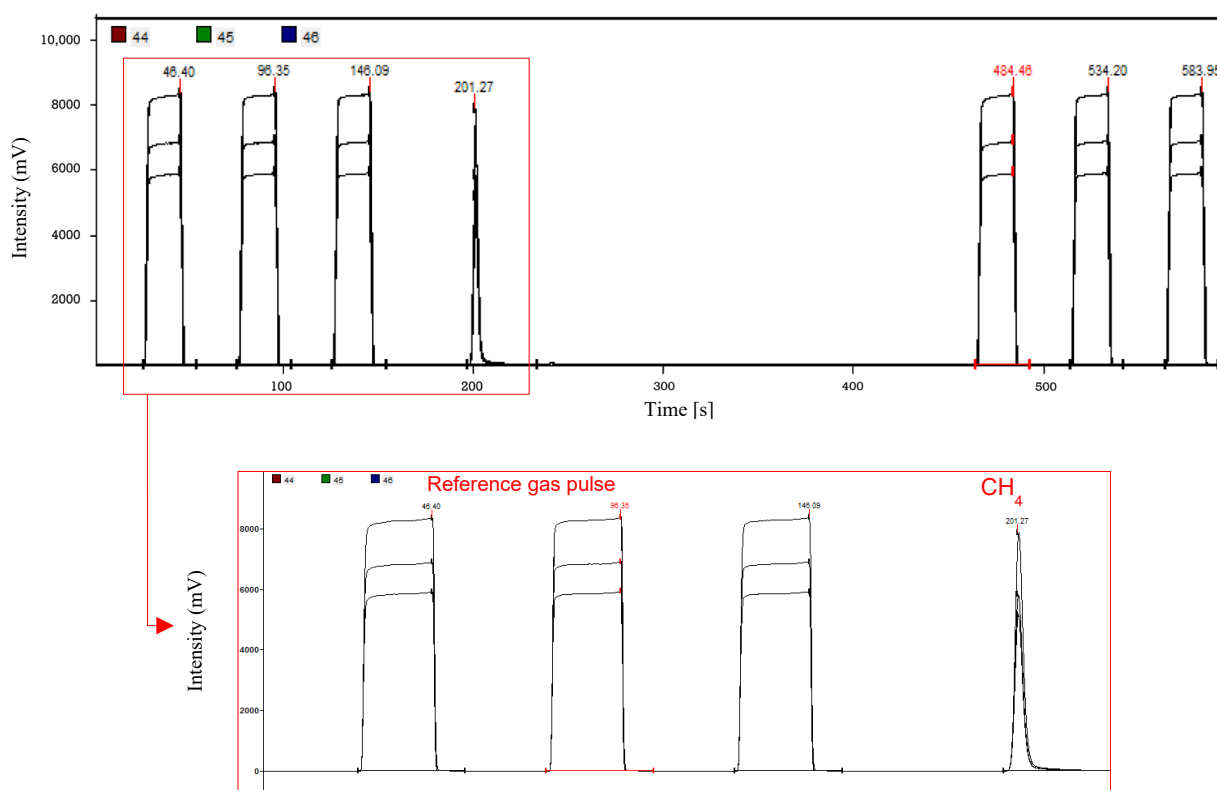


Figure 1. Representative GC-IRMS ion-current traces (m/z 44, 45 and 46) used to determine $\delta^{13}\text{C}$ of methane (CH₄), showing three reference-gas pulses and the CH₄-derived CO₂ peak (isotopologue signals summarized in Table 2).

Table 2. Relative abundance of carbon dioxide ‘CO₂’ isotopologue.

Isotopologues Detected	Molecules	Relative Abundance (%)
44	¹² C ¹⁶ O ₂	~98.4%
45	¹³ C ¹⁶ O ₂	~1.1%
	¹² C ¹⁷ O ¹⁶ O	~0.04%
46	¹² C ¹⁸ O ¹⁶ O	~0.39%
	¹³ C ¹⁷ O ¹⁶ O	~0.0005%
	¹² C ¹⁷ O ₂	~0.0001%

The molecular relative abundance is determined from the relative abundances of the respective isotopic species:

¹²C: ~98.93%, ¹³C: ~1.07%

¹⁶O: ~99.76%, ¹⁷O: ~0.04%, ¹⁸O: 0.20%

- IR δ²H

The same methodology is used for the determination of δ²H IR of methane, ethane and propane:

- δ²H methane CH₄ experimental parameters for IR determination: Fixed method, Direct injection using Gas-tight syringe, 10 µL, split 20:1, gas reference: 6000 mV.
- δ¹³C ethane C₂H₆ and propane C₃H₈ experimental parameters for IR determination: Fixed method, Headspace Injection ‘HS’, 100 µL, split 10:1, gas reference: 6000 mV.
- δ²H Hydrogen: the GC column (HP-Molesieve 5 A° 30 m × 0.32 mm × 25 µm), and oven program: 40 °C (10 min) have been changed for hydrogen approach in order to obtain a better separation and selectivity, the isotopic experimental parameters, Direct injection using Gas-tight syringe, 100 µL, split 10:1, gas reference: 6000 mV.

3. Results

3.1. Development of a GC-MS Method for Quantifying CO₂ and Light Alkanes

The chromatogram in Figure 2 depicts a good separation for all-natural gas compounds CO₂ and alkanes C₁–C₆ with a good Signal-to-Noise ‘S/N’ for each one according to chromatographic parameters summarized in Table A1. The first chromatogram peak is related to dinitrogen ‘N₂’, the separation of hydrogen and permanent gas is not possible with this column, a specific column is necessary for their separation such as molecular sieve Column.

- Linearity

The linear regression study is illustrated in Figure 3 and summarized in Table 3. The linearity of the GC–MS response was assessed for each compound by determining the coefficient of determination (R²), the Fisher statistic (F), and the standard errors associated with the slope (m) and intercept (b).

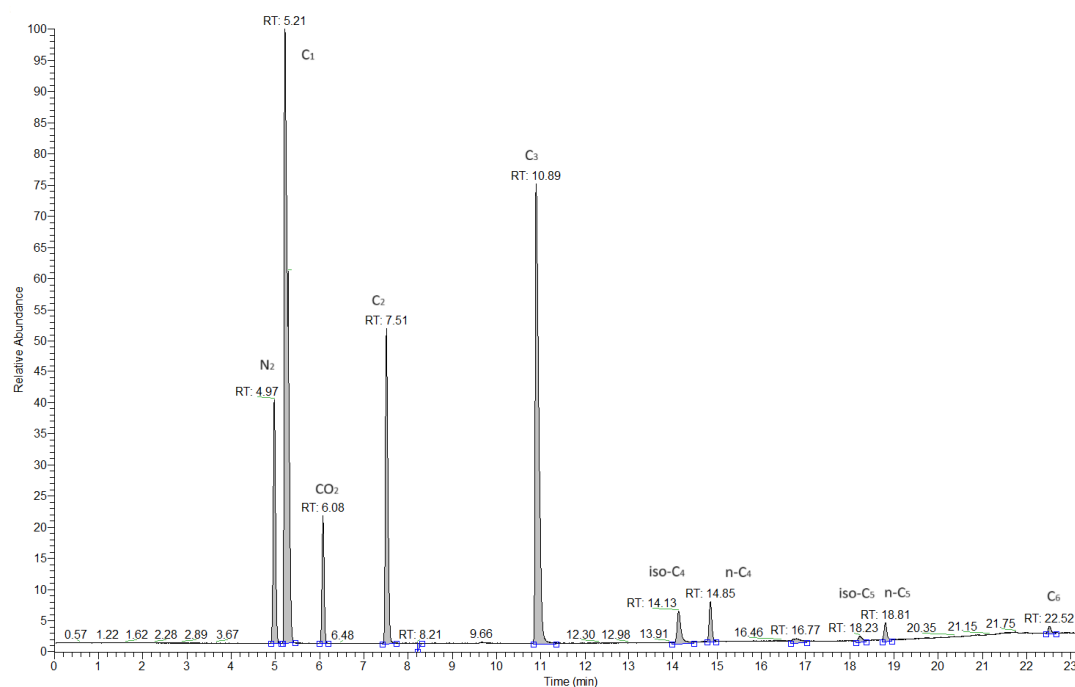


Figure 2. Representative GC-MS chromatogram of natural gas obtained using a PLOT column, showing baseline separation of permanent gases (N_2 , CO_2) and C_1 – C_6 hydrocarbons (C_1 , C_2 , C_3 , iso- C_4 , n- C_4 , iso- C_5 , n- C_5 , C_6); retention times are indicated above peaks.

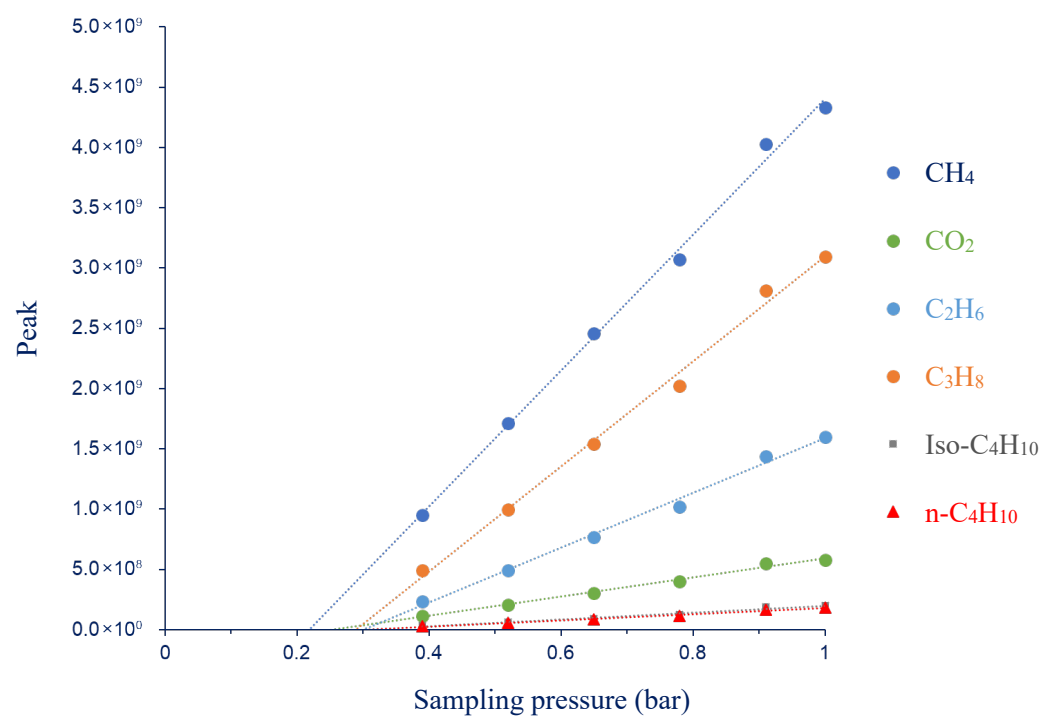


Figure 3. Linearity of detector response for a certified gas-mixture standard: peak area as a function of sampling pressure for CH_4 , CO_2 and C_2 – C_5 hydrocarbons.

Table 3. Statistical linear regression parameters.

Compound	Formula	Degree of Freedom	R ²	F (Fischer Test)	Linear Formula mx + b	Standard Error (m)	Standard Error (b)
Methane	CH ₄	4	0.996	1096	$5.6 \times 10^9 x - 1.2 \times 10^9$	1.70×10^8	1.26×10^8
Carbon dioxide	CO ₂	4	0.991	423	$7.9 \times 10^8 x - 2.0 \times 10^8$	3.85×10^7	2.85×10^7
Ethane	C ₂ H ₆	4	0.993	604	$2.3 \times 10^9 x - 6.9 \times 10^8$	9.26×10^7	6.85×10^7
Propane	C ₃ H ₈	4	0.994	701	$4.3 \times 10^9 x - 1.3 \times 10^9$	1.64×10^8	1.22×10^8
Iso-Butane	Iso-C ₄ H ₁₀	4	0.98	224	$2.8 \times 10^8 x - 8.6 \times 10^7$	1.91×10^7	1.41×10^7
n-Butane	n-C ₄ H ₁₀	4	0.99	335	$2.6 \times 10^8 x - 7.8 \times 10^7$	1.42×10^7	1.05×10^7

A minimum pressure of 0.39 bar was selected because it represents the lowest filling pressure at which all analytes are simultaneously detected and quantified with acceptable repeatability. While certain compounds remain detectable below this threshold, quantification is not consistently reliable across the full set of species, justifying 0.39 bar as the lower bound of the working range.

The calibration curves shown in Figure 3 display an apparent non-zero intercept, i.e., the linear fit does not pass through the origin. This behavior is consistent with a pressure-defined LOQ: below a certain filling pressure, the amount of substance in the vial becomes too small to yield a measurable and reproducible GC–MS peak area. Consequently, the low-pressure portion of the response is effectively truncated by the LOQ, and the regression performed over the quantifiable range yields a positive intercept rather than a line constrained to (0,0). The fact that methane and minor compounds exhibit different intercepts is also consistent with compound-specific detection/quantification limits, which depend on abundance and instrumental sensitivity/response for each species.

Within the validated working interval [0.39–1 bar], proportionality between GC–MS peak area and amount of substance is ensured using the calibration standard. Under constant vial volume and temperature, the amount of gas is proportional to pressure ($n \propto P$); therefore, a pressure-based LOQ can be expressed as an equivalent mole-fraction threshold at 1 bar by scaling the standard composition according to the LOQ pressure:

$$x_{LOQ,eq} = x_{std} \frac{P_{i\ LOQ}}{1\ bar} \quad (3)$$

For example, if ethane is 3% (mol/mol) in the standard and its compound-specific pressure range is [0.26–1 bar], the corresponding equivalent concentration range is [0.78–3% (mol/mol)]. Accordingly, for samples analyzed at 1 bar, ethane mole fractions below 0.78% (mol/mol) are operationally considered below quantification (i.e., “blank” with respect to ethane), because they correspond to an amount of substance lower than that produced by the LOQ pressure.

Finally, additional systematic contributions may arise from (i) reduced accuracy of the pressure gauge during low-pressure filling and (ii) possible losses during headspace sampling/transfer. Because these effects appear stable during method validation, their impact is treated as a constant bias and is considered negligible within the investigated pressure range.

For all gases, R² values above 0.98 and F values ranging from 224 to 1096 indicate an excellent linear relationship between signal intensity and gas pressure. The statistical significance of each regression was evaluated using the Fisher–Snedecor distribution, with one degree of freedom in the numerator and four in the denominator (corresponding to six calibration points). At a 95% confidence level, the critical value is $F_{(1,4)} = 7.71$. Since all experimental F values greatly exceed the critical threshold, the linear regressions can

be considered statistically significant, demonstrating that the GC–MS response behaves linearly across the tested concentration range for all compounds.

The slopes (2.6×10^7 to 5.6×10^9) reflect detector sensitivity, which varies among compounds according to their relative ionization efficiencies, and this ionization behavior is also strongly influenced by molecular structure. Linear alkanes, which share similar structural features, typically exhibit comparable ionization responses, whereas branched alkanes or compounds with distinct chemical structures such as CO₂ show markedly different ionization efficiencies.

The low standard errors on the slopes (generally below 5%) demonstrate the high precision and stability of the detector response. Similarly, the intercepts (b) are close to zero with small uncertainties, indicating a negligible background signal and effective baseline correction. The variability observed in signal intensity between compounds mainly results from concentration differences in the calibration mixtures rather than from deviations in instrumental linearity.

Overall, these results confirm that the GC–MS system provides a robust and reproducible linear response suitable for quantitative analyses. The calibration study is critical before any analysis sequence in order to ensure a good detector response and accurate quantification. The calibration method developed here, based on the proportional relationship between substance quantity and vial sampling pressures, provides a convenient and efficient solution for quantifying multiple components within gas mixtures. This approach obviates the necessity for multiple certified gas standards at varying molar concentrations, especially when gas calibration mixtures for some specific volatile organic compounds (VOCs) are unavailable.

- Repeatability

A repeatability assessment was performed to evaluate the precision of the GC–MS method for the quantification of hydrocarbon and non-hydrocarbon components in the tested gas mixture. The Equation (2) was employed to assess the repeatability of both quantification measurements and sampling. Five vials of a gas standard were sampled at 1 bar, with each vial injected twice.

The results reported in Figure 4 and Table S1 exhibited recoveries closely clustered around 100% for most compounds, with mean values ranging from 97.54% (C₆H₁₄) to 100.53% (n-C₄H₁₀). The relative standard deviations (%RSD) were generally low, between 2.96% (CH₄) and 7.11% (n-C₅H₁₂), except for neo-C₅H₁₂ which showed higher variability (16.82%), mainly due to isolated deviations in R_{%2} (122.51%), R_{%9} (64.17%) and R_{%10} (87.49%) for iso-C₅H₁₂. These anomalies may reflect compound-specific ionization fluctuations, transient chromatographic instabilities, or minor matrix effects. Overall, the narrow %RSD values for most compounds confirm the high repeatability and robustness of the method within the investigated concentration range, supporting its suitability for high-precision routine analyses in similar applications.

- Limit of quantification 'LOQ'

The limit of quantification (LOQ) for each compound was determined based on a linear calibration curve established by plotting peak area against the filling pressure of a gas standard mixture, ranging from 0.13 to 1.00 bar. The injection system was maintained at constant volume and temperature, ensuring that the molar amount of each component introduced into the GC-MS was directly proportional to the filling pressure. The gas standard composition at 1.00 bar was used as the reference, and the corresponding molar concentrations were expressed in mol%. The LOQ was defined as the lowest pressure at which the signal was reproducible (relative standard deviation < 20%) and provided a signal-to-noise ratio greater than 10. The corresponding molar concentration was then

calculated by proportionally scaling the known composition at 1.00 bar to the minimum validated pressure using the following equation:

$$\text{LOQ}(\text{mol/mol}\%) = C_{1\text{ bar}} \frac{P_{\text{LOQ}}}{1.00} \quad (4)$$

where $C_{1\text{ bar}}$ is the molar concentration (in mol%) of the compound in the standard at 1.00 bar, and P_{LOQ} is the lowest pressure (in bar) at which quantification is reliable. This approach allows for direct estimation of LOQ in mol% under experimental conditions identical to those used for sample analysis.

The limits of quantification (LOQ) values obtained for the developed GC–MS method are summarized in Table 4. The method exhibits low LOQs for most hydrocarbons and CO_2 , ranging from 0.04% to 0.78%, with the exception of methane (11.54%). The relatively higher LOQ observed for CH_4 mainly reflects its lower analytical sensitivity under the fixed injection and acquisition conditions used in this study. These parameters were deliberately kept constant to provide a single, robust method applicable to the full natural-gas matrix and to avoid saturation from major components, which inherently limits the extent to which methane can be optimized.

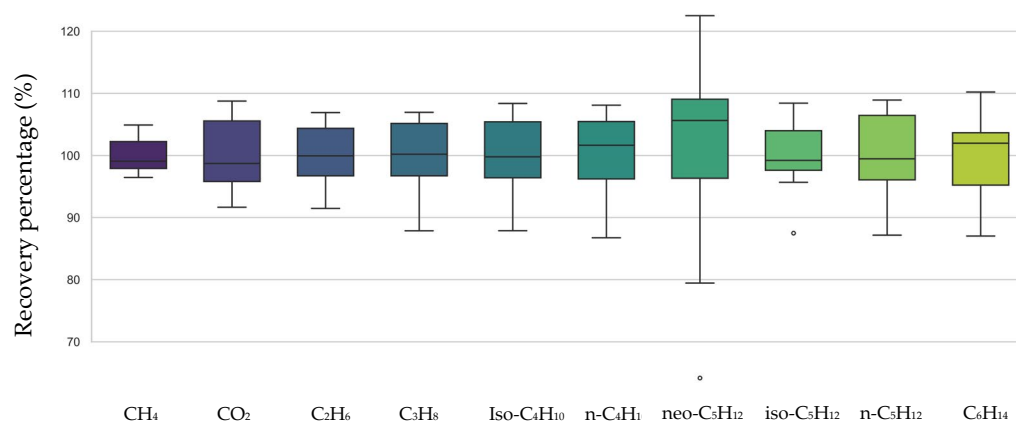


Figure 4. Assessment of Analytical Recovery Efficiency (%) Across Various Light Gaseous Species (C_1 – C_6) and carbene dioxide (CO_2). Data are presented as mean $\pm$ SD, $n = 10$.

Table 4. Limit of quantification estimation of carbon dioxide and alkanes ($S/N > 10$) in % mol/mol.

Compound	P_{LOQ} (Bar)	LOQ (% Mol/Mol)
CH_4	0.13	11.54
CO_2	0.13	0.13
C_2H_6	0.26	0.78
C_3H_8	0.26	0.78
iso- C_4H_{10}	0.39	0.04
n- C_4H_{10}	0.39	0.04

In comparison with standardized natural-gas composition protocols, the CH_4 LOQ achieved here (11.54% mol/mol) is lower than the lower applicability limit reported in ISO 6974-5:2014 (34% mol/mol) [24], indicating improved methane performance within a normalized framework. By contrast, when compared to a published GC–MS method developed outside such standardization, our CH_4 LOQ is of the same order of magnitude ($\approx 12.4\%$ mol/mol), while markedly lower LOQs for several heavier alkanes are obtained in this work [25]. These differences are consistent with changes in analytical objectives and instrument settings (e.g., injected amount, split ratio, and tuning strategy), which strongly control

sensitivity and dynamic range; therefore, apparent discrepancies in LOQ largely reflect differing methodological constraints rather than contradictory analytical performance.

Achieving a lower LOQ for methane is not critical for the objectives of this study, because CH₄ is the dominant component of natural gas and is quantified at concentrations far above the quantification limit in the investigated samples. Nonetheless, if lower methane LOQs were required for specific applications, they could be significantly improved by increasing the injected amount (e.g., larger sample volume and/or reduced split) and, where appropriate, by implementing a dedicated CH₄ protocol with acquisition settings optimized for methane.

Overall, the method developed here provides a robust and pragmatic compromise between sensitivity, dynamic range, and operational simplicity. In contrast to internationally standardized procedures that rely on stringent and highly constrained analytical setups, this approach preserves good analytical performance while remaining flexible and easy to deploy. It is therefore well suited for high-quality routine analyses in laboratory settings and can be readily leveraged for research studies spanning diverse themes in natural-gas characterization.

3.2. UGS Well Composition GC-MS Analyzes

The quantification method was applied to real gas samples collected from both the wellhead and annular space to assess its validity on field-collected samples. Table S2 presents the monitoring data from two gas wellheads (GW_WH_B_8 and GW_WH_A_2), with gas sampling performed using high-pressure cylinders as previously described. In contrast, the results shown in (Table S3) were obtained by directly connecting the sampling system either to the wellhead (under high pressure) or to the annular space (under low pressure). Across several years of sampling, the method demonstrated excellent repeatability for all measured compounds. These findings confirm both the reliability and robustness of the sampling system, regardless of the sampling approach employed.

The optimized parameter method represents the best compromise for analyzing all targeted compounds within a single run. However, the repeatability of methane (CH₄) measurements is less precise compared to other compounds. This reduced accuracy is attributed to the significantly higher concentration of methane relative to the other analytes, given that the injection parameters were specifically optimized for the determination of the minor components. To improve the accuracy of methane quantification, the method could be divided into two separate runs: one dedicated to methane and another for the less concentrated compounds.

Precise quantification of target gas species is critical for robust isotopic monitoring in gas well environments later, particularly in the annular space where concentrations may vary significantly. Such variations are closely linked to the origin and composition of the gas, necessitating methodological adjustments during analysis. For example, biomethane is typically enriched in carbon dioxide compared to thermogenic natural gas. This higher (CO₂) concentration requires the adaptation of injected gas volumes to ensure accurate and reproducible isotopic ratio determinations. Failure to account for such compositional differences may compromise the reliability of isotopic interpretations.

3.3. Development of Isotopic Ratio Analyzes Methods

- IR validation 'δ¹³C' and 'δ²H' for alkanes, carbon dioxide and hydrogen

The repeatability study for δ¹³C and δ²H IR shows a very good repeatability with a very low standard deviation (around) as depicted in Figures 5 and 6 for δ¹³C and δ²H of major compounds of natural gas, respectively.

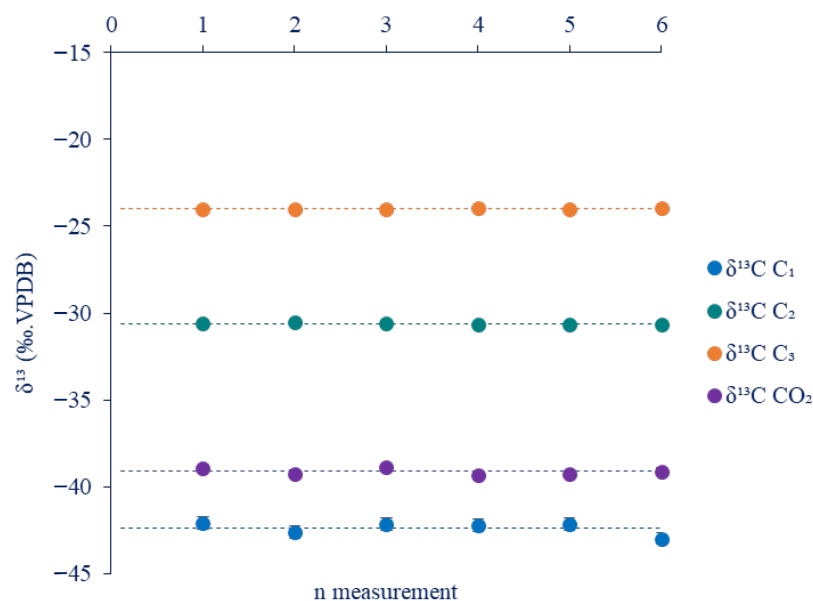


Figure 5. Alkanes repeatability study of $\delta^{13}\text{C}$ Isotopic Analysis. (Data are presented as mean $\pm$ SD, n = 6).

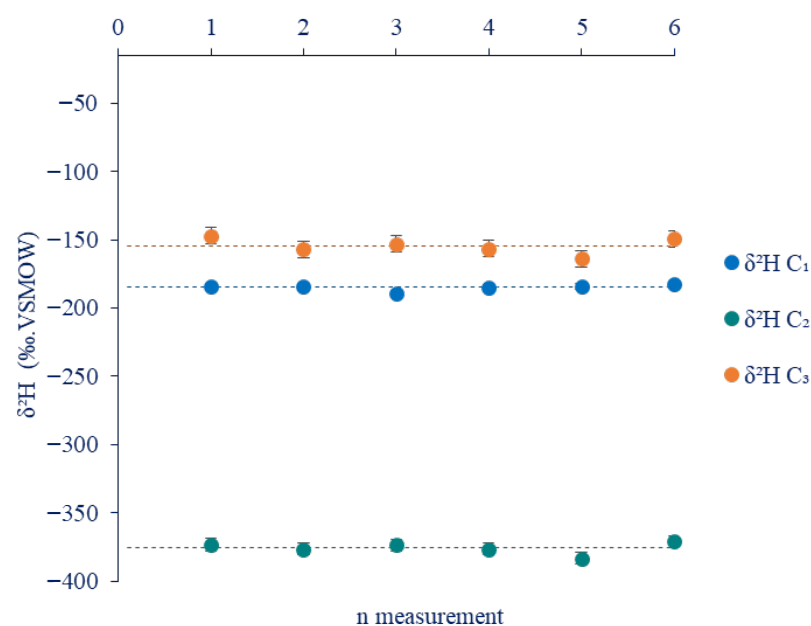


Figure 6. Alkanes Repeatability study of $\delta^2\text{H}$ Isotopic Analysis. (Data are presented as mean $\pm$ SD, n = 6).

The results demonstrate excellent measurement repeatability for all element isotopic ratio of analyzed compounds, including alkanes (C₁–C₃), carbon dioxide and molecular hydrogen ‘H₂’ (Figure 7), in both $\delta^{13}\text{C}$ and $\delta^2\text{H}$. Standard deviations for $\delta^{13}\text{C}$ were consistently low, typically below 0.2 ‰, while $\delta^2\text{H}$ measurements also showed high precision, with standard deviations generally below 2 ‰. This high level of analytical precision reinforces the robustness of the method and provides strong confidence in its ability to deliver reliable isotopic measurements for real samples in subsequent analyses.

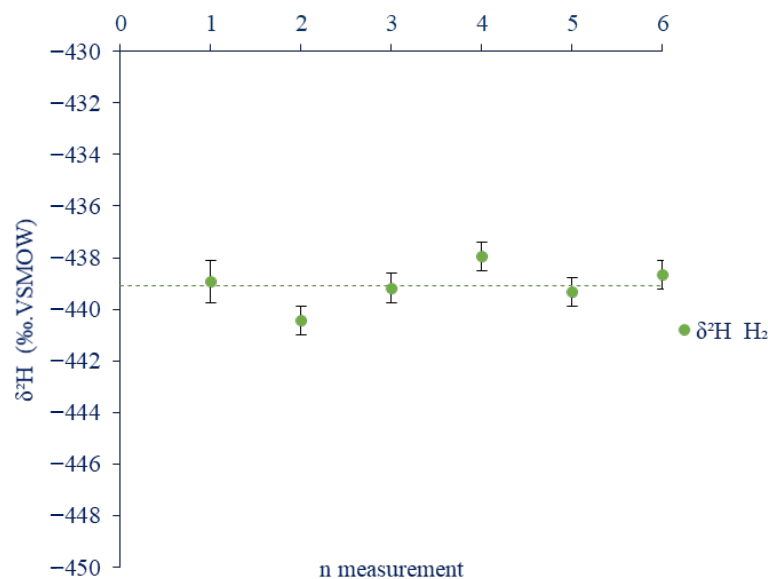


Figure 7. Hydrogen ‘H₂’ repeatability study of δ²H Isotopic Analysis (Data are presented as mean ± SD, n = 6).

The results obtained for these isotopic methods are insured with a typical natural gas composition around (90% of methane, 3% of ethane and propane and 1% of carbon dioxide). In case of a meaningful difference in the gas mixture, injection parameters need to be changed and adapted in order to obtain a coherent signal for samples and isotopic reference gas. Our IR analyses indicate that significant deviations in IR signal amplitude relative to the reference lead to biases in isotopic determinations, most noticeably in δ²H measurements. This effect highlights the sensitivity of δ²H to variations in signal intensity and suggests that careful signal normalization is required. Conversely, in cases where the IR response exhibits a clear linear relationship with the concentration of the target compound in the gas mixture, the injected volume can be directly inferred from the established injection parameters. For example, for a gas mixture containing 6% ethane, an injection volume of 50 µL with a 50:1 split is appropriate for δ¹³C analysis, in accordance with the fixed parameters (ii). This proportionality underscores the robustness of δ¹³C measurements under controlled injection conditions, in contrast to the greater susceptibility of δ²H to amplitude-related artifacts.

- UGS well IR ‘δ¹³C’ and ‘δ²H’ analyzes

The results shown in Tables 5 and 6 present the δ¹³C and δ²H isotopic ratios measured on several on-site gas samples collected over multiple years using the two sampling procedures (cylinder and direct sampling) described in the Section 2. These data correspond to repeated analyses of nominally identical samples and therefore document the analytical performance of the developed and validated on-site sampling and measurement method. Over several years of field campaigns, the pooled standard deviation of replicate measurements remains better than 0.3‰ (1σ) for δ¹³C and 4‰ (1σ) for δ²H, demonstrating the good long-term analytical precision and robustness of the whole procedure, from field sampling to laboratory isotope ratio determination. Higher standard deviations observed for some samples are mainly related to variations in the concentration of the measured compounds. Overall, the standard deviations obtained with the two sampling approaches are comparable, as illustrated in Tables 5 and 6, indicating that both cylinder and direct sampling provide similar analytical precision. The following results validate the accuracy of the analysis process including sampling at different field conditions, the variability of the targeted compound amount as shown in Table 6 and the various sampling campaigns across several years.

Table 5. Stable carbon and hydrogen isotope compositions ($\delta^{13}\text{C}$, $\delta^2\text{H}$) of field gas samples collected by high-pressure cylinder sampling at natural-gas wellheads (WH) and at a biomethanisation plant (biomethane).

Sample	Sampling Point	Sampling Day	$\delta^{13}\text{C}$ CH ₄	$\delta^{13}\text{C}$ C ₂ H ₆	$\delta^{13}\text{C}$ C ₃ H ₈	$\delta^{13}\text{C}$ CO ₂	$\delta^2\text{H}$ CH ₄	$\delta^2\text{H}$ C ₂ H ₆	$\delta^2\text{H}$ C ₃ H ₈	σ $\delta^{13}\text{C}$ CH ₄	σ $\delta^{13}\text{C}$ C ₂ H ₆	σ $\delta^{13}\text{C}$ C ₃ H ₈	σ $\delta^{13}\text{C}$ CO ₂	σ $\delta^2\text{H}$ CH ₄	σ $\delta^2\text{H}$ C ₂ H ₆	σ $\delta^2\text{H}$ C ₃ H ₈
GW_WH_B_8	Tubing	16 January 2024	−44.03	−32.613	−27.492	n.d	−186.489	−184.782	−150.08	0.055	0.049	0.235	n.d	0.522	0.257	1.783
GW_WH_B_8	Tubing	3 June 2024	−40.5	−31.91	−29.35	n.d	−179.2	−220	−105.08	0.2	0.008	0.03	n.d	0.4	4	0.2
GW_WH_B_8	Tubing	13 January 2025	−42.55	−30.95	−27.53	−7.58	−202	−271.5	−148	0.06	0.04	0.03	0.04	5	0.3	1
GW_WH_B_8	Tubing	31 January 2025	−42.66	−30.8	−27.78	−7.9	−192.9	−263	−151	0.3	0.03	0.04	0.3	0.6	2	2
GW_WH_A_2	Tubing	18 June 2024	−40.53	−30.76	−27.210	n.d	−173.5	−218	−120	0.06	0.01	0.06	n.d	0.6	2	2
GW_WH_A_2	Tubing	4 July 2024	−44.4	−31.66	−26.53	n.d	−192	−147	−122	0.4	0.04	0.03	n.d	2	2	3
GW_WH_A_2	Tubing	11 October 2024	−42.47	−30.61	−26.53	−4.7	−179	−235	−114	0.09	0.04	0.03	0.2	1	2	2
GW_WH_A_2	Tubing	13 January 2025	−42.4	−30.8	−27.47	−5.59	−204	−259.4	−151	−0.1	0.02	0.02	0.06	3	0.7	1
GW_WH_A_2	Tubing	31 January 2025	−42.7	−30.73	−27.5	−7.84	−198	−279	−176.5	0.1	0.04	0.05	0.09	3	5	0.7
BIOMETHANE	/	19 February 2024	−47.5	n.d	n.d	n.d	−326.5	n.d	n.d	0.14	n.d	n.d	n.d	0.4	n.d	n.d
BIOMETHANE	/	14 April 2025	−43.5	n.d	n.d	23.7	−334	n.d	n.d	0.3	n.d	n.d	0.2	3	n.d	n.d

Data are presented as mean $\pm$ SD, n = 3; n.d = non-detected.**Table 6.** Stable carbon and hydrogen isotope compositions ($\delta^{13}\text{C}$, $\delta^2\text{H}$) of field gas samples collected during a one-day direct-connection campaign: wellhead gas (WH; 40–60 bar) and annular-space gas (AS; 1–2 bar).

Sample	Sampling Point	Sampling Day	$\delta^{13}\text{C}$ CH ₄	$\delta^{13}\text{C}$ C ₂ H ₆	$\delta^{13}\text{C}$ C ₃ H ₈	$\delta^{13}\text{C}$ CO ₂	$\delta^2\text{H}$ CH ₄	$\delta^2\text{H}$ C ₂ H ₆	$\delta^2\text{H}$ C ₃ H ₈	σ $\delta^{13}\text{C}$ CH ₄	σ $\delta^{13}\text{C}$ C ₂ H ₆	σ $\delta^{13}\text{C}$ C ₃ H ₈	σ $\delta^{13}\text{C}$ CO ₂	σ $\delta^2\text{H}$ CH ₄	σ $\delta^2\text{H}$ C ₂ H ₆	σ $\delta^2\text{H}$ C ₃ H ₈
GW_WH_A_6	Tubing	16 January 2024	−39.8	−30.159	−25.58	n.d	−169.7	−252	−183	0.5	0.003	0.06	n.d	0.1	3	2
GW_WH_A_3	Tubing	13 January 2025	−43	−31.04	−26.54	n.d	−188.1	−222	−221	0.3	0.02	0.1	n.d	0.7	2	5
GW_WH_B_11	Tubing	31 January 2025	−42.75	−31.42	−28.41	−5.8	−198.67	−246	−175	0.03	0.05	0.04	0.2	0.78	2	1
GW_WH_A_5	Tubing	3 June 2024	−40.2	−32.9	−29.92	−3.9	−180.2	−214.7	−169	0.3	0.2	0.1	0.4	0.8	0.2	2
GW_WH_A_7	Tubing	18 June 2024	−41.65	−32.22	−29.24	−4.36	−185.5	−224	−192	0.02	0.03	0.05	0.06	0.7	2	2
GW_AS_A_3	AS1	4 July 2024	−41	−29	−26	n.d	−178.6	−227	−199.2	0.5	1	0.5	n.d	1	4	0
GW_AS_A_6	AS1	11 October 2024	−41	−30.38	−26.92	n.d	−181.3	−231	−193	0.2	0.01	0.08	n.d	2.3	3	8
GW_AS0_B_10	AS0	13 January 2025	−40.9	−30.16	−26.18	n.d	−199.62	−241.3	−201	0.2	0.05	0.09	n.d	0.76	0.7	1

Data are presented as mean $\pm$ SD, n = 3; n.d = non-detected.

This methodology has also been successfully applied to sampling from a biomethanisation plant (biomethane), as shown in Table 5. The results demonstrate that the approach can be extended to any type of gaseous source and site, regardless of composition. In the case of biomethane, which consists almost exclusively of CH₄ and CO₂, only the isotopic signatures of these major species are relevant. This confirms both the applicability and the robustness of the method, although its precision is inherently constrained by the chemical simplicity of the gas mixture.

- UGS well IR ‘ $\delta^2\text{H}$ ’ Hydrogen analyzes

The $\delta^2\text{H}$ isotopic composition of molecular hydrogen (H₂) was determined for three gas field samples (Table 7), using a sampling system directly connected to the annular space under low pressure (1 bar) and with a small gas volume.

Table 7. Hydrogen isotope composition ($\delta^2\text{H}$) of molecular hydrogen (H₂) in annular-space (AS) field gas samples.

Sample	Sampling Point	Sampling day	$\delta^2\text{H H}_2$	$\sigma \delta^2\text{H H}_2$
GW_AS1_A_5	AS1	12 March 2024	−744	2
GW_AS1_A_5	AS1	18 April 2025	−755	1
GW_AS1_B_12	AS1	18 April 2025	−755	3

Data are presented as mean $\pm$ SD, n = 3.

The results presented in Table 7 demonstrate good repeatability for $\delta^2\text{H}$ measurements of H₂. The standard deviations associated with $\delta^2\text{H}$ measurements are relatively small, ranging from $\pm 1\text{‰}$ to $\pm 3\text{‰}$, which indicates a good analytical precision despite the very low-pressure sampling conditions. The replicate measurements at the same sampling point on 18 April 2025 (−755‰ with $\sigma = 1$ and −755‰ with $\sigma = 3$) show excellent agreement within error margins, supporting the reliability of the data. Overall, the low variability in $\delta^2\text{H}$ compared to the analytical uncertainty suggests that the observed isotopic values are robust and not significantly influenced by measurement error. This methodology, applied to gaseous hydrogen, once again highlights the reliability of the implemented sampling protocol, as well as its versatility and suitability for application to various target molecules.

4. Discussion

The analytical work presented in this article is not a basic aleatory quantification and isotopic methods, it represents an ultimate guide to introduce a high-quality measurement for industrial gas fields research studies. It is the gate between the standardization of accurate analytical methods and the technical facilities requirement on-site and in the laboratory.

4.1. Gas Sampling Method

The optimized gas sampling system developed and validated in this study for multiple industrial applications—including a natural gas underground storage site (UGS-A) and a methanisation plant unit—demonstrates high robustness and versatility. The design allows for precise and reproducible sampling by maintaining accurate filling pressures and accommodating a wide range of experimental conditions, from high to low pressures and various sampling volumes. These features make the system a reliable sampling tool for high-precision industrial gas investigations, encompassing both chemical and isotopic analyses, in line with previous evaluations of vial-based sampling systems for free and dissolved gases in environmental studies [26].

While this work focused on the validation of the system for gaseous samples, its design is readily adaptable to more complex applications, such as the collection of dissolved gases

in aqueous matrices. The capability of the system to ensures airtight, contamination-free filling, which is particularly beneficial for trace gas and noble gas analyses, as highlighted in dedicated protocols for dissolved gas and noble gas sampling and measurement [27]. In addition, the use of gas vials offers significant safety and logistical advantages compared to conventional cylinder-based sampling methods, particularly when handling highly flammable gases such as hydrogen. Furthermore, it represents a cost-effective alternative to cylinder sampling, which is especially advantageous for large-scale field campaigns requiring the collection of numerous samples (e.g., >10 samples per day). This combination of analytical reliability, adaptability, and operational safety positions the system as a valuable asset for industrial and environmental gas studies.

4.2. Pressure Quantification Principle

The quantification approach based on the relationship between pressure and the amount of substance in a gas mixture offers a robust and versatile framework for the development and validation of standardized analytical methods for gaseous compounds. This principle enables the establishment of a well-defined or extended analytical range using a single, tailor-made gas standard, thereby eliminating the need for multiple calibration cylinders at various concentrations. Such simplification significantly reduces both costs and lead times typically associated with the preparation of gas standards, and is consistent with current metrological practice for standard gas mixtures and volumetric or gravimetric preparation techniques [28,29].

The optimized injection volume represents an ideal compromise for the simultaneous quantification of multiple compounds exhibiting a wide range of concentrations (0.09 to 88% mol/mol) within a single run. This compromise, however, affected the pressure calibration range, leading to a slight offset and a regression line that does not intersect the origin. Consequently, the calibration range was set between 0.2 and 1 bar for methane (88.765%) and between 0.3 and 1 bar for the other components. Despite this offset, proportionality between signal response and concentration remains valid across the investigated pressure and concentration ranges. Performing the analysis in two separate runs—one optimized for methane and another for the remaining compounds—would improve quantification accuracy and yield calibration lines passing through the origin.

In the present study, a custom gas mixture enriched in hydrogen was employed, enabling the investigation of variable gaseous energy systems (e.g., natural gas/hydrogen blends). This methodological choice is particularly relevant within the current context of the energy transition, where accurate and adaptable analytical tools are required to characterize evolving gas compositions and support the development of emerging energy technologies, as emphasized in recent studies on hydrogen-mixed natural gas transport and quality control [30].

4.3. Isotopic Ratio Measurement

Isotopic analyses are key tools for both geochemical investigations and gas-infrastructure monitoring. While $\delta^{13}\text{C}$ measurements of alkanes are now routine and widely reported in the literature, $\delta^2\text{H}$ determinations remain more challenging—especially for heavier alkanes ($\text{C}_2\text{--C}_3$)—because of the high analytical sensitivity of their isotopologues.

In this context, the $\delta^2\text{H}$ methodological development presented here provides a validated approach for on-site samples, delivering precision that is close to what is typically achieved for $\delta^{13}\text{C}$. This improved performance helps broaden the scope of geochemical studies by enabling a single, consistent sampling and a standardized analytical strategy, which in turn strengthens data comparability across sites and monitoring campaigns.

This integrated methodology also provides a solid analytical framework to support emerging energy transition challenges, particularly for the monitoring and management of renewable gases such as hydrogen and biomethane. Accurate isotopic determinations of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ in alkanes ($\text{C}_1\text{--C}_3$), CO_2 , and H_2 allow precise assessments of gas origin, mixing, and migration processes, which is consistent with established approaches for genetic classification of natural gas and dissolved hydrocarbons using combined carbon and hydrogen isotope systematics [31,32]. These assessments are essential for verifying the geological integrity of underground gas storage sites, CO_2 sequestration reservoirs, and hydrogen infrastructure.

The robustness of this approach has been demonstrated over multiple sampling campaigns, maintaining consistent isotopic results despite natural compositional variations. Similar combined use of gas composition, stable isotopes and noble gases has proven effective for long-term geochemical surveillance at underground gas and CO_2 storage sites, such as the Aquifer natural gas storage and the Rouse CO_2 pilot site [33]. Overall, this system offers a reliable and adaptable solution for geochemical surveillance in support of safe and sustainable subsurface energy storage and transport, in line with broader developments in hydrogen-mixed natural gas infrastructure [30].

5. Conclusions

The combination of the developed approaches—sampling and analytical—provides a comprehensive framework for large-scale monitoring of complex gaseous systems across diverse industrial environments and subsurface applications. The excellent reproducibility and accuracy achieved under both laboratory and field conditions demonstrate the robustness and versatility of the system, enabling extensive and long-term gas monitoring through a single high-performance methodology. The strong agreement between laboratory and on-site results confirms the complementarity of this approach with conventional gas cylinder sampling. Full compliance with ATEX safety standards ensures safe operation, while the implemented procedures effectively prevent contamination of the sampled gas. Furthermore, its capability to operate across a wide pressure range (1–250 bar), combined with a constant vacuum mechanism, ensures technical adaptability and preservation of sample integrity under a variety of field conditions.

Moreover, the developed methodology can be extended and adapted to a wide range of other compound studies, particularly those sensitive to atmospheric contamination, such as noble gas measurements. It is also suitable for applications requiring sampling at very low pressures and volumes, as well as for the collection and analysis of dissolved gases in water or other liquid matrices, further broadening its applicability in geochemical and environmental investigations.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/analytica7010014/s1>, Figure S1: Calibration Certificate of the Certified Natural Gas Reference Mixture (EffecTech, 2023); Figure S2: Gas chromatograph coupled to Isotopic Ratio Mass Spectrometer system (GC-IRMS); Figure S3: Isotopic ratio mass spectrometry analysis of $\delta^{13}\text{C}$ ethane ' C_2H_6 ' and propane ' C_3H_8 '; Table S1: Assessment of Repeatability for Natural Gas Compound Quantification ($n = 10$); Table S2: Quantification of gas well field samples, gas cylinder sampling ($n = 3$); Table S3: Quantification of gas well field samples, One day sampling campaign, direct plugging ($n = 3$); Table S4: Manometer Specifications; Table S5: Maximum Pressure Supported by the Different Components (bar); Data S1. Detailed Gas Sampling Protocol.

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Abbreviation

The following abbreviations are used in this manuscript:

A-UGS	Aquifer Underground Gas Storage
CSIA	Compound-Specific Isotopic Analysis
$\delta^{13}\text{C}$	$^{13}\text{C}/^{12}\text{C}$ isotopic ratio (expressed per mill ‰)
$\delta^2\text{H}$	$^2\text{H}/^1\text{H}$ isotopic ratio (expressed per mill ‰)
PTFE	Polytetrafluoroethylene
HS	Head-Space
GC	Gas Chromatography
MS	Mass Spectrometry
IR	Isotopic Ratio
PDB	Vienna Pee Dee Belemnite
V-SMOW	Vienna Standard Mean Ocean Water
S/N	Signal/Noise
VOCs	Volatile Organic Compound (s for semi)
TCD	Thermal Conductivity Detector
% mol/mol	Molar percent %
R^2	Determination factor
Std dev	Standard deviation
ATEX	potentially explosive atmospheres
LOQ	Limit of Quantification
GW	Gas Well
WH	Well-Head
AS	Annular Space

Appendix A

Table A1. Estimation of GC separation by chromatographic parameters.

Compound	Retention Time (R_t)	Resolution (R_s)	Capacity Factor (K')	Separation Factor α
N_2/t_0	5.0	/	/	/
CH_4	5.2	1.0	0.0	1.0
CO_2	6.1	3.6	0.2	1.2
C_2H_6	7.5	6.1	0.2	1.2
C_3H_8	10.9	8.9	0.5	1.5
iso- C_4H_{10}	14.1	7.6	0.3	1.3

Table A1. Cont.

Compound	Retention Time (R _t)	Resolution (R _s)	Capacity Factor (K')	Separation Factor α
n-C ₄ H ₁₀	14.9	2.2	0.1	1.1
néo-C ₅ H ₁₂	16.8	6.1	0.1	1.1
iso-C ₅ H ₁₂	18.2	4.8	0.1	1.1
n-C ₅ H ₁₂	18.8	2.6	0.0	1.0
C ₆ H ₁₄	22.5	17.3	0.2	1.2

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