



BSI Standards Publication

Natural gas — Upstream area — Determination of composition by Laser Raman spectroscopy

National foreword

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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 3, *Upstream area*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Gas chromatography methods for determination of composition in natural gas already exist as [ISO 6974-1](#) to [ISO 6974-6](#) or ISO/TR 14749.

Gas laser Raman spectrometry is a simpler and more direct analysis method than gas chromatography. Gas laser Raman offers a faster and more convenient means of determining composition of upstream area natural gas because it is an entirely optical method operating at the speed of light with no moving parts. Natural gas exploration and development benefits from fast determination of gas composition and real-time monitoring of gas composition better optimizes natural gas treatment processes.

Gas laser Raman spectrometry enables rapid and simultaneous analysis of multiple gas species because each type of gas molecule emits unique light frequencies shifted from the frequency of laser light striking it. This "Raman scattering" is instantaneous and directly proportional to the number of molecules the light impacts. This simple principle allows continuous on-site real-time data monitoring and control, it will bring tremendous improvements to gas exploration, well operations, transport, and processing.

Natural gas — Upstream area — Determination of composition by Laser Raman spectroscopy

1 Scope

This document describes a laser Raman spectroscopy method for the quantitative determination of chemical composition of natural gas in upstream area.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

[ISO 6142-1](#), *Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures*

[ISO 6144](#), *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*

[ISO 6145](#), *Gas analysis — Preparation of calibration gas mixtures using dynamic methods*

[ISO 10715](#), *Natural gas — Sampling guidelines*

[ISO 11095](#), *Linear calibration using reference materials*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

3.1

Raman effect

process, in which photons from a light source are absorbed by the electrons surrounding polyatomic molecules and result in a new photons being emitted at wavelengths higher or lower than the source photon wavelength

Note 1 to entry: The resulting wavelength changes are called Raman shifts. The Raman shifts are determined by the vibrational and rotational frequencies of the atomic bonds within each molecule.

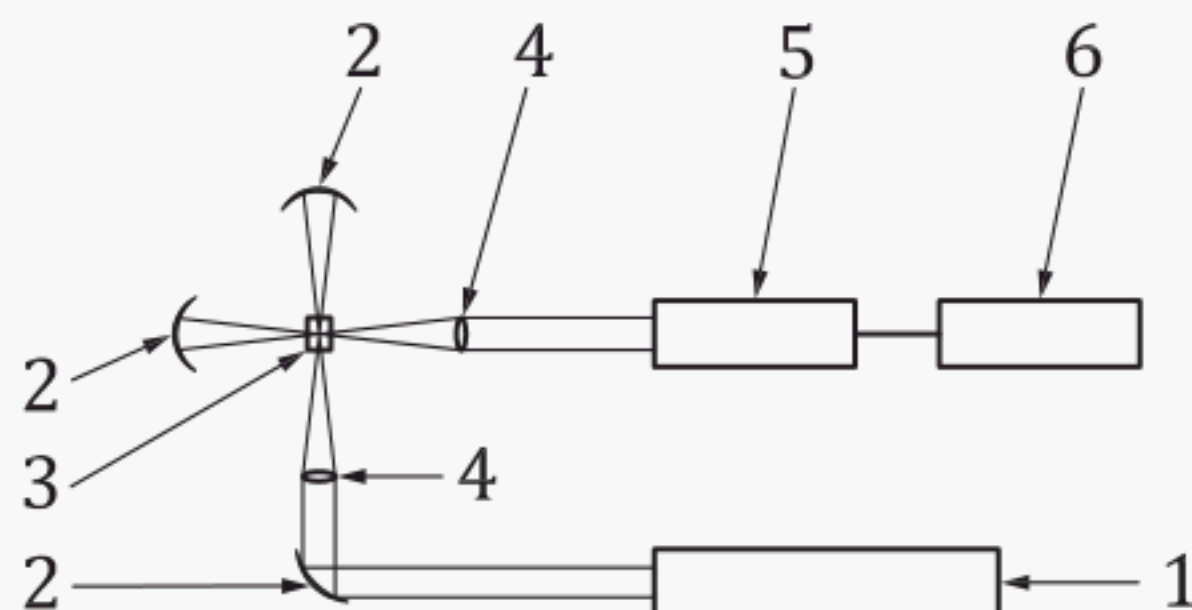
3.2

multichannel photodetector

photosensitive semiconductor device that transports electric charge from one capacitor to another, allowing serial output of parallel data, typically used for digital image capture

Gas concentrations are calculated for a specified period. Because each discrete detector collects photons at one wavelength, one detector position is typically needed to detect each natural gas species.

NOTE Currently, only analysers with 8 APD detector positions per module are available. 8 is sufficient for some natural gas applications, however, if more than 8 gases need to be measured, two or more detectors can be operated in parallel.



Key

- 1 laser generator
- 2 mirror
- 3 gas chamber
- 4 lens
- 5 detection module
- 6 user interface

Figure 1 — Working principle of the laser Raman gas analyser

4.2 Calculation

Because the gas concentration is directly and linearly proportional to the signal intensity expressed by photon counts, the concentration of components in the sample can be calculated by [Formula \(1\)](#):

$$C_i = \frac{I_i}{I_{Ri}} \times C_{Ri} \quad (1)$$

where

- C_i is the concentration of component i in the sample;
- I_i is the signal intensity of component i in the sample;
- I_{Ri} is the signal intensity of component i in the reference gas;
- C_{Ri} is the concentration of component i in the reference gas.

5 Instruments

5.1 Laser Raman gas analyser

The type of Raman gas analyser is selected according to the types of gases and the natural gas concentration ranges of interest. The base analyser unit contains a laser, optical path control, gas detection chamber, photon detection and processing, signal processing, and human/machine interface. The analyser should have sensitivity sufficient to detect the components in the analytical range given in [Table 1](#). It should keep a stable state after zero calibration.

Table 1 — Natural gas components and range of composition covered

Component		concentration (10 ⁻² mol/mol)	
		min.	max.
Nitrogen	N ₂	0,02	10
Carbon dioxide	CO ₂	0,02	30
Hydrogen sulfide	H ₂ S	0,02	30
Methane	CH ₄	50	100
Ethane	C ₂ H ₆	0,02	20
Propane	C ₃ H ₈	0,02	10
NOTE 1 The ranges in this table do not indicate detection limits, but indicate that the specified precision can be achieved. The range can be wider when precision is not limited.			
NOTE 2 Other gases such as H ₂ , <i>i</i> -C ₄ H ₁₀ , <i>n</i> -C ₄ H ₁₀ can also be desired. For some gas Raman technologies, multiple detector modules can be required.			

5.2 Laser specifications

The laser shall have a narrow-enough line width with a stable-enough power output and wavelength so as not to compromise the generation and analysis of the Raman spectra. Laser power should be high-enough to ensure sufficient sensitivity.

- laser wavelength should be in the range of 500 nm to 800 nm, and a laser of wavelength 785 nm is generally suggested;
- laser wavelength stability, initially less than ±0,005 nm, less than ±0,05 nm after 10 000 h of operation;
- laser power is typically 0,5 W to 5,0 W depending on Raman photon collection and detection efficiency;
- Laser power stability, short term (seconds) ±0,5 % average power, less than 20 % after 10 000 h of operation.

5.3 Detection module

The detection module should be capable of sufficient resolution, high throughput and stability.

5.4 Signal processing and user interface

Raman spectroscopy software is included as a part of the analyser to process the detector data and provide a user interface. Software should be able to indicate gases measured, calculate the gas concentrations, track key diagnostic factors such as temperatures, spectral intensity, and laser power, and maintain and check instrument calibration and drift.

5.5 Sample filtration and probe

Particulates and aerosols larger than 0,2 µm should be removed by filtration prior to entering the detector. The filter housing and sample probe shall be made of a material which is inert, non-adsorptive and non-permeable to components in the gas sample, stainless steel is preferred.

5.6 Gas pressure regulator

For sulfur-containing natural gas, hydrogen sulfide corrosion resistant gas pressure regulators should be selected.

5.7 Sulfur compound absorber

Beakerflask, flask etc. filled with basic solution can be used as sulfur compound absorber in order to eliminate sulfur compounds discharged to the atmosphere. Sodium hydroxide solution (200 g/l), prepared by dissolving sodium hydroxide (chemically pure) in water is suggested as the basic solution.

6 Reagents and materials

6.1 Zero gas

Pure argon or other monatomic gas is used to set the zero level of the Raman analyser. The purity should not be less than 99,999 %.

6.2 Base span calibration gases

Base span calibration gas used to set software parameters shall be working standard pure gases or binary mixtures in accordance with [ISO 6142-1](#), [ISO 6144](#) or with [ISO 6145](#). Binary gas mixtures consisting of blending zero gas and a single gas component present in natural gas are preferred when their typical concentrations in natural gas are below 75 %. For typical natural gas upstream area samples, 1 % H₂S/Ar, 5 % CO₂/Ar, 3 % N₂/Ar, 3 % C₃H₈/Ar, 2 % C₂H₆/Ar, are suggested. As base span calibration gases for all but CH₄ which can be pure (100 %) or Ar diluted.

6.3 Working span calibration gases

Regular calibration shall perform using working standard gas mixtures in accordance with [ISO 6142-1](#), [ISO 6144](#) or with [ISO 6145](#). The working standard gas mixtures shall contain appropriate concentrations and cover the analytic range of the analyser. All components in the reference standard shall be homogenous in the vapour state at the time of use. The concentration of a component in the reference standard gas shall be close to the actual sample gas concentration, shall be less than relatively 20 % of the corresponding component in the test gas, the minimum concentration shall be greater than 0,02 %.

7 Measurement procedures

7.1 preparation

Make sure the analyser placed on a flat, horizontal surface, in a clean location that maintained at a relatively constant environmental conditions:

- temperature: 15 °C to 35 °C;
- relative humidity: 10 % to 75 %.

Set up the laser Raman gas analyser according to the manufacturer's instructions, connect zero gas, base span calibration gas, measurement calibration gas, and sample in sequence to the instrument as shown in [Figure 2](#).

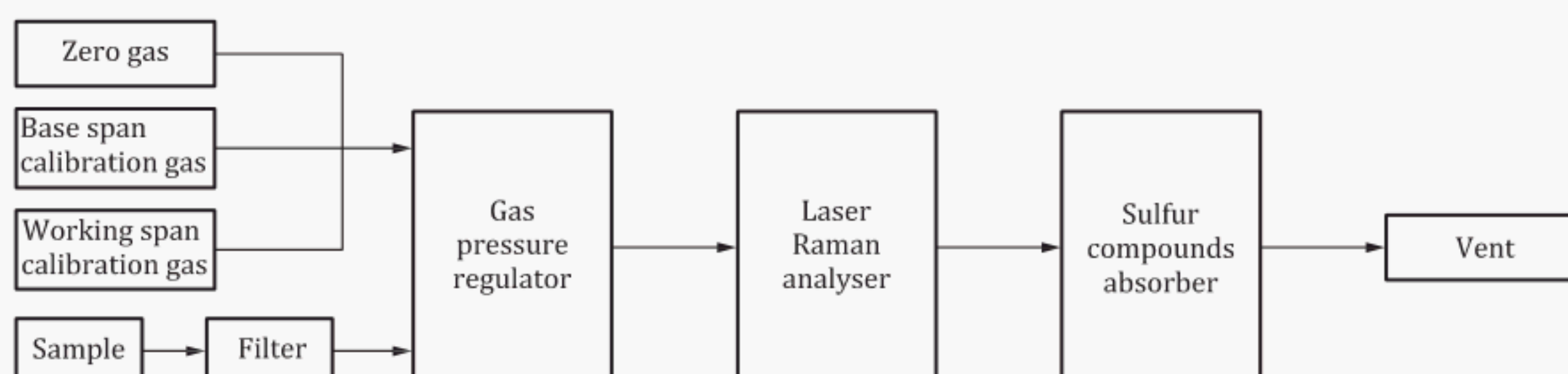


Figure 2 — Flowchart of the measurement procedures

7.2 Calibration

7.2.1 Calibration frequency

Calibration should be carried out when experimental conditions were changed. And it should be recalibrated according to the needs of the user.

7.2.2 Calibration procedure

Connect the calibration gas with the analyser according to [Figure 2](#). Adjust the input pressure and temperature to a stable condition. Sweep the analyser with the gas flow for at least 2 min.

After the sulfur-containing calibration gas is injected, it should go through the absorption solution before it is vented.

7.2.3 Zero calibration

According to [7.2.2](#), connect zero gas with the analyser, start calibration, update the background when the signal values are stable.

7.2.4 Base span calibration

Before sample measurement, base span calibration should be done to overcome the instrument drift caused by temperature, pressure and general electronic fluctuations, and the cross-interference caused by the multiple components in the gas could be maximum eliminated by calibrating the cross-interference factors. According to [7.2.2](#), connect base span calibration gas to the analyser, start calibration, observe the signal values, adjust the cross-interference factors till the interference signal to a reasonable value (usually in a range of -1 to 3).

7.2.5 Working span calibration

Using [ISO 11095](#), the user shall choose the calibration method depending on the analytical accuracy that is required. The following are candidate methods and their requirements:

- bracketing calibration: the difference between calibration gas and analytical result should be less than relatively 20 %;
- response formula simulation: no less than three calibration gas should be used to cover the analytical range;
- one point calibration: the difference between calibration gas and analytical result should be less than relatively 20 %.

If the method is used to monitor fixed natural gas source, one point calibration or bracketing calibration should be applied. If the method is used to analyse a non-constant natural gas source, response formula simulation should be applied.

7.3 Sampling and sample analysis

Connect gas sample, gas pressure regulator, filters, and analyser in sequence adjust pressure and flow to the experimental conditions, start sample analysis, the sample will be automatically measured. Sampling shall be in accordance with [ISO 10715](#).

Sulfur-containing sample should go through the absorption solution before it is vented.

7.4 Data record

In measurement mode, the results are automatically calculated out by [Formula \(1\)](#), the listed result is the content of the analysis, and testing result should be read directly.

NOTE The reference conditions of the test results are the same as that of working span calibration gas. Conversion between reference conditions is according to [ISO 13443](#).

8 Repeatability

In the analytical range given by this document, under repeatability conditions, the difference of two successive test results in a short time interval (10 s) should not exceed the values listed in [Table 2](#) at a 95 % level of confidence. [Annex A](#) gives an example of the statistical procedure of the repeatability estimation.

Table 2 — Repeatability of different concentration ranges

Component	Content range (10 ⁻² mol/mol)	Repeatability limits (10 ⁻² mol/mol)
C ₂ H ₆	0,02 to 1	0,01
	above 1 to 20	0,07
C ₃ H ₈	0,02 to 1	0,01
	above 1 to 10	0,03
N ₂	0,02 to 1	0,01
	above 1 to 15	0,04
CO ₂	0,02 to 1	0,02
	above 1 to 30	0,10
H ₂ S	0,02 to 1	0,02
	above 1 to 30	0,05
CH ₄	above 50	0,18

9 Uncertainty evaluation

9.1 General

The component concentration is calculated using [Formula \(1\)](#). The uncertainty of the final result shall be based on [Formula \(1\)](#) with some mathematical computing in accordance with ISO/IEC Guide 98-3.

9.2 Uncertainty of I_i and I_{Ri}

The uncertainty of I_i is the standard deviation of the analytical data, I_i , and the relative uncertainty of I_i is calculated by [Formula \(2\)](#):

$$u_{\text{rel}}(I_i) = \frac{\sqrt{\frac{\sum_{j=1}^n (I_{ij} - \bar{I}_i)^2}{n(n-1)}}}{\bar{I}_i} \quad (2)$$

where

$u_{\text{rel}}(I_i)$ is the relative standard uncertainty of the signal intensity of component i of sample gas;
 I_{ij} is the signal intensity of component i of sample gas in each test;
 \bar{I}_i is the mean of all the signal intensity values of component i of sample gas.

The uncertainty of I_{Ri} depends on the calibration procedure. In the one point calibration procedure, the relative uncertainty of I_{Ri} is calculated by [Formula \(3\)](#):

$$u_{\text{rel}}(I_{Ri}) = \frac{\sqrt{\frac{\sum_{j=1}^n (I_{Rij} - \bar{I}_{Ri})^2}{n(n-1)}}}{\bar{I}_{Ri}} \quad (3)$$

where

$u_{\text{rel}}(I_{Ri})$ is the relative standard uncertainty of the signal intensity of component i of reference gas (working span calibration gas);
 I_{Rij} is the signal intensity of component i of reference gas in each test;
 \bar{I}_{Ri} is the mean of all the signal intensity values of component i of reference gas.

9.3 Uncertainty of C_{Ri}

The standard relative uncertainty of C_{Ri} is given by the producer of the calibration gas, which are listed in the certificate of the calibration gas.

9.4 Uncertainty of result

As the test result is related to I_i , I_{Ri} and C_{Ri} as shown in [Formula \(1\)](#), according to ISO/IEC Guide 98-3, the relative standard uncertainty of the result is calculated by [Formula \(4\)](#):

$$u_{\text{rel}}(C_i) = \sqrt{u_{\text{rel}}^2(I_i) + u_{\text{rel}}^2(C_{Ri}) + u_{\text{rel}}^2(I_{Ri}) + 2r(I_i, I_{Ri})u_{\text{rel}}(I_i)u_{\text{rel}}(I_{Ri})} \quad (4)$$

where

$u_{\text{rel}}(C_i)$ is the relative standard uncertainty of the final analytical result;
 $u_{\text{rel}}(I_i)$ is the relative standard uncertainty of signal intensity of component i of the sample;
 $u_{\text{rel}}(I_{Ri})$ is the relative standard uncertainty of signal intensity of component i of the reference gas;
 $u_{\text{rel}}(C_{Ri})$ is the relative standard uncertainty of component i of reference gas;
 $r(I_i, I_{Ri})$ is correlation factor between I_i and I_{Ri} .

NOTE $r(I_i, I_{Ri})$ is estimated by experience, to simplify the calculation, the degree of correlation between I_{Ri} and I_i is set nearly independent, and then $r(I_i, I_{Ri}) = 0$.

10 Test report

The test report shall include the following information:

- a) the sample identification including:
 - time/date of sampling;
 - sample point (location information);
- b) a reference to this document, i.e. [ISO 23978:2020](#);
- c) the date of analysis, name of laboratory and signature of the analyst;
- d) the calibration information including:
 - the traceability of the certified- Base span calibration gases used for calibration;
 - the date of last calibration and the calibration frequency;
 - the composition of the working span calibration gases used to calculate the sample composition;
- e) the most recent test data on stability and response for the measuring system;
- f) the sample composition in mole fraction, expressed as a percentage, including normalized sample composition to the number of digits appropriate to the certificate of working span calibration gases and size of error including the result of uncertainty calculation.

Annex A (informative)

Statistical procedure for estimation of the repeatability

A.1 Background

In order to test the repeatability of the method, a series of experiments was carried out based on three instruments in three laboratories. The instruments used in the experiments are listed in [Table A.1](#).

Table A.1 — The analytical instruments used in these experiments

Laboratory	Analytical component	Analytical range (mol/mol)	Repeatability	Instrument Model
A Research institute of Yanchang Petroleum(Group)CO.LTD	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , H ₂ S, H ₂ O, CO ₂ , N ₂ , CO ₂ , C ₄ +	50 × 10 ⁻⁶ to 100 %	≤2,5 % F.S.	RGLA 4141
B RINGT. PetroChina	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , H ₂ S, O ₂ , CO ₂ , SO ₂ , N ₂	50 × 10 ⁻⁶ to 100 %	≤2,5 % F.S.	RGLA 2811T
C Oil Industry Natural Gas Quality Supervision and Inspection Center PetroChina	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , H ₂ S, O ₂ , CO ₂ , SO ₂ , N ₂	50 × 10 ⁻⁶ to 100 %	≤2,5 % F.S.	RGLA 2811T* (using a new laser and Laser cavity)

A.2 Calibration gas and test sample

Prior to test, zero calibration was done with pure Argon with purity of 99,999 %, and then base span calibration was done with 3 cylinders of calibration gas with Argon as balance gas, whose composition and uncertainty are shown in [Table A.2](#).

Table A.2 — Cylinders of calibration gas used for base span calibration in the experiments

Sample No.	Component, concentration (10 ⁻² mol/mol)							Uncertainty (<i>k</i> = 2)
	C ₂ H ₆	C ₃ H ₈	CH ₄	CO ₂	N ₂	H ₂ S	SO ₂	
1	-	-	94,200	-	-	-	-	Rel 2,5 %
2	3,090	1,080	-	-	-	0,943	-	Rel 2,5 %
3	-	-	-	5,320	15,100	-	0,555	Rel 2,5 %

All of the test objects are the same batch of calibration gases, 11 cylinders of calibration gases are used as test samples, and the different concentrations of components and related uncertainty are listed in [Table A.3](#). And the corresponding measurement calibration gases are listed in [Table A.4](#). 7 cylinders of H₂S/CH₄ calibration gases with methane as balance gases are used as both sample and measurement calibration gas. The different concentrations of components and related uncertainty are listed in [Table A.5](#). In the H₂S test, gas No.2 is used as measurement calibration gas when gas No.1 is tested, and gas No.3 is used as measurement calibration gas when gas No.2 is tested, and so on.

NOTE The reference conditions are 20 °C, 101,325 kPa.

Table A.3 — Cylinders of calibration gas used as sample in the experiments

Sample No.	Component concentration (10^{-2} mol/mol)					Uncertainty ($k = 2$)
	C ₂ H ₆	C ₃ H ₈	CH ₄	CO ₂	N ₂	
1	0,005	0,302	99,683	0,005	0,005	Rel 2,5 %
2	5,030	0,503	94,447	0,010	0,010	Rel 2,5 %
3	0,020	0,989	98,951	0,021	0,020	Rel 2,5 %
4	0,051	2,010	97,831	0,050	0,058	Rel 2,5 %
5	0,091	0,010	99,687	0,102	0,110	Rel 2,5 %
6	0,502	4,960	93,539	0,501	0,496	Rel 2,5 %
7	1,000	0,050	96,958	1,000	0,992	Rel 2,5 %
8	2,010	0,099	79,770	3,020	15,100	Rel 2,5 %
9	0,010	9,990	84,818	0,302	4,880	Rel 2,5 %
10	10,000	0,020	71,990	15,000	2,990	Rel 2,5 %
11	19,900	0,005	49,893	30,000	0,202	Rel 2,5 %

Table A.4 — Cylinders of measurement calibration gas in the experiments

Sample No.	Component concentration (10^{-2} mol/mol)					Uncertainty ($k = 2$)
	C ₂ H ₆	C ₃ H ₈	CH ₄	CO ₂	N ₂	
1	0,004	0,402	99,586	0,004	0,004	Rel 2,5 %
2	5,880	0,586	93,515	0,009	0,010	Rel 2,5 %
3	0,030	1,520	98,391	0,029	0,030	Rel 2,5 %
4	0,060	3,000	96,810	0,060	0,071	Rel 2,5 %
5	0,200	0,020	99,371	0,201	0,208	Rel 2,5 %
6	0,592	5,990	92,225	0,599	0,594	Rel 2,5 %
7	1,510	0,059	95,431	1,500	1,500	Rel 2,5 %
8	3,010	0,200	79,800	4,990	12,000	Rel 2,5 %
9	0,020	11,900	81,853	0,397	5,830	Rel 2,5 %
10	8,020	0,030	74,920	12,000	5,030	Rel 2,5 %
11	18,000	0,004	56,795	24,900	0,301	Rel 2,5 %

Table A.5 — Cylinders of H₂S/CH₄ calibration gas in the experiments

Sample No.	Concentration (10^{-2} mol/mol)	Uncertainty ($k = 2$)
1	0,005	Rel 2,5 %
2	0,010	Rel 2,5 %
3	0,020	Rel 2,5 %
4	0,100	Rel 2,5 %
5	1,000	Rel 2,5 %
6	10,000	Rel 2,5 %
7	30,000	Rel 2,5 %

A.3 Experiments

A total of 11 tests were performed on each test gas.

The following procedure was used:

Do zero calibration and base span calibration;

- Before starting the 11 tests of each test gas, do measurement calibration, then connect the test gas with the instrument, sweep the pipe and instrument for more than 2 min, and then record the analytical result every 10 s;
- After completing 11 tests, do another measurement calibration and 11 tests.

A.4 Raw data of the test

Each sample was tested at least 11 times continuously. Two consecutive values from these results were randomly selected according to [ISO 4259-1](#) and [ISO 4259-2](#). Rounding off is used to get the final results. Which are listed in [Table A.6](#) to [Table A.11](#)

Table A.6 — Original data of CH₄ (10⁻² mol/mol)

Laboratory	Sample										
	1	2	3	4	5	6	7	8	9	10	11
A	99,732	94,590	99,231	97,549	99,375	93,486	96,892	79,726	84,597	72,011	49,999
	99,615	94,489	99,045	97,658	99,193	93,677	96,754	79,872	84,794	71,860	49,816
B	99,728	94,685	99,072	97,305	99,556	93,698	97,035	79,673	84,789	72,260	49,964
	99,554	94,589	99,145	97,491	99,415	93,581	97,188	79,817	84,892	72,100	50,082
C	99,644	94,821	98,920	98,327	99,243	93,937	96,754	79,865	84,800	72,100	49,819
	99,790	94,663	99,006	98,133	99,070	93,856	96,546	79,706	84,601	71,812	49,987

Table A.7 — Original data of C₂H₆ (10⁻² mol/mol)

Laboratory	Sample										
	1	2	3	4	5	6	7	8	9	10	11
A	0,011	5,020	0,007	0,035	0,096	0,491	1,003	2,006	0,011	10,050	20,080
	0,018	5,025	0,014	0,043	0,098	0,493	0,984	1,995	0,003	10,035	20,001
B	0,011	5,040	0,014	0,034	0,101	0,494	0,994	2,004	0,013	10,073	20,039
	0,013	5,037	0,007	0,036	0,097	0,484	1,000	1,998	0,007	10,058	20,106
C	0,015	5,019	0,015	0,040	0,098	0,476	0,984	2,006	0,011	10,058	20,015
	0,015	5,037	0,011	0,039	0,098	0,484	0,991	2,004	0,007	10,037	20,011

Table A.8 — Original data of C₃H₈ (10⁻² mol/mol)

Laboratory	Sample										
	1	2	3	4	5	6	7	8	9	10	11
A	0,295	0,507	0,981	1,990	0,018	4,956	0,055	0,098	9,984	0,023	0,001
	0,298	0,508	0,984	2,000	0,016	4,955	0,052	0,095	9,984	0,013	0,004
B	0,305	0,503	0,986	1,992	0,022	4,958	0,046	0,091	9,981	0,008	0,000
	0,302	0,498	0,984	1,997	0,019	4,966	0,041	0,101	10,014	0,010	0,000
C	0,301	0,501	0,987	2,014	0,020	4,956	0,052	0,091	9,996	0,010	0,000
	0,303	0,507	0,983	2,015	0,011	4,962	0,044	0,093	9,984	0,021	0,006

Table A.9 — Original data of CO₂ (10⁻² mol/mol)

Laboratory	Sample										
	1	2	3	4	5	6	7	8	9	10	11
A	0,000	0,015	0,004	0,073	0,105	0,487	1,011	3,035	0,271	14,780	29,830
	0,000	0,021	0,012	0,066	0,115	0,494	1,006	3,044	0,280	14,757	29,743
B	0,000	0,004	0,017	0,067	0,120	0,486	1,007	3,041	0,285	14,827	29,890
	0,003	0,006	0,020	0,043	0,118	0,487	1,001	3,027	0,280	14,815	29,951
C	0,000	0,012	0,013	0,043	0,117	0,500	1,006	3,047	0,283	14,815	29,771
	0,001	0,008	0,009	0,049	0,121	0,494	1,014	3,041	0,269	14,745	29,887

Table A.10 — Original data of N₂ (10⁻² mol/mol)

Laboratory	Sample										
	1	2	3	4	5	6	7	8	9	10	11
A	0,009	0,010	0,018	0,056	0,108	0,488	0,981	15,066	4,874	2,978	0,200
	0,012	0,009	0,018	0,054	0,111	0,492	0,984	15,095	4,886	2,972	0,201
B	0,013	0,012	0,020	0,055	0,109	0,487	0,983	15,060	4,877	2,989	0,200
	0,013	0,008	0,020	0,055	0,108	0,485	0,982	15,079	4,904	2,981	0,202
C	0,009	0,010	0,020	0,052	0,113	0,486	0,984	15,081	4,890	2,981	0,201
	0,012	0,010	0,021	0,059	0,110	0,487	0,975	15,035	4,881	2,966	0,200

Table A.11 — Original data of H₂S (10⁻² mol/mol)

Laboratory	Sample						
	1	2	3	4	5	6	7
A	0,004	0,009	0,018	0,118	1,003	10,005	29,946
	0,006	0,012	0,014	0,107	1,020	10,027	29,964
B	0,007	0,012	0,019	0,105	1,014	10,002	29,905
	0,003	0,010	0,021	0,111	1,005	10,019	29,898
C	0,008	0,010	0,022	0,106	1,012	10,021	29,898
	0,005	0,009	0,021	0,113	1,008	10,001	29,951

A.5 Data processing

The reported data of [Table A.6](#) to [Table A.11](#) were inspected for outliers by the following formulae:

Test the repeatability results of the same sample by Cochran rule.

$$C = \frac{e_{\max}^2}{\sum_{i=1}^L e_i^2} \quad (\text{A.1})$$

where

- L is the number of labs;
- i is the subscript which represents the No. of lab;
- e is difference of two repeated results;

Calculate the standard deviation of [Table A.6](#) to [Table A.11](#) according the following formulae:

Repeat standard deviation for sample j :

$$d_j = \sqrt{\sum_{i=1}^L e_i^2 / 2L} \quad (\text{A.2})$$

The results of inspection for outliers and standard deviation calculation are shown in [Table A.12](#) to [Table A.17](#).

Table A.12 — Data processing of CH₄

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
1	99,677	0,463 8	0,104 3
2	94,640	0,562 5	0,086 0
3	99,070	0,729 5	0,089 0
4	97,757	0,346 0	0,134 5
5	99,309	0,398 8	0,117 8
6	93,706	0,645 8	0,097 1
7	96,861	0,507 1	0,119 5
8	79,777	0,374 9	0,106 2
9	84,745	0,445 3	0,121 7
10	72,024	0,630 6	0,148 2
11	43,253	0,549 8	0,100 6

Table A.13 — Data processing of C₂H₆

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
1	0,014	0,924 5	0,003 0
2	5,030	0,905 0	0,007 7
3	0,011	0,465 1	0,004 3
4	0,038	0,930 5	0,003 5
5	0,098	0,741 7	0,001 5
6	0,487	0,563 9	0,005 5
7	0,993	0,829 0	0,008 6
8	2,002	0,720 6	0,005 0
9	0,009	0,594 1	0,004 6
10	10,052	0,463 3	0,012 2
11	20,056	0,535 2	0,044 3

Table A.14 — Data processing of C₃H₈

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
1	0,301	0,409 1	0,001 9
2	0,504	0,580 6	0,003 2
3	0,984	0,514 0	0,002 1
4	2,001	0,818 1	0,004 7
5	0,018	0,819 5	0,004 1
6	4,959	0,568 0	0,004 0

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
7	0,048	0,674 6	0,004 2
8	0,095	0,859 1	0,004 4
9	9,985	0,500 3	0,019 4
10	0,010	0,842 2	0,004 7
11	0,001	1,000 0	0,001 2

Table A.15 — Data processing of CO₂

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
1	0,001	0,900 0	0,001 3
2	0,013	0,800 0	0,001 8
3	0,012	0,787 6	0,003 9
4	0,057	0,864 5	0,010 3
5	0,116	0,897 7	0,004 3
6	0,491	0,583 8	0,004 0
7	1,008	0,526 4	0,004 5
8	3,039	0,619 4	0,007 3
9	0,278	0,625 5	0,007 4
10	14,790	0,880 4	0,030 4
11	29,845	0,545 0	0,064 3

Table A.16 — Data processing of N₂

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
1	0,011	0,500 0	0,001 7
2	0,010	0,818 2	0,001 4
3	0,019	0,465 8	0,000 7
4	0,055	0,938 1	0,002 8
5	0,110	0,621 0	0,001 5
6	0,488	0,889 9	0,002 0
7	0,981	0,860 3	0,003 8
8	15,069	0,642 4	0,023 3
9	4,885	0,765 4	0,012 5
10	2,978	0,682 3	0,007 1
11	0,201	0,723 7	0,000 9

Table A.17 — Data processing of H₂S

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
1	0,005	0,637 5	0,001 9
2	0,011	0,561 0	0,001 6
3	0,019	0,795 4	0,002 1
4	0,110	0,581 4	0,006 0

Sample	Mean (10 ⁻² mol/mol)	Uniformity of repeatability <i>C</i>	Repeatability standard deviation <i>d_j</i>
5	1,010	0,739 7	0,007 9
6	10,013	0,419 1	0,014 0
7	29,927	0,877 5	0,022 9

When the laboratory number $n = 3$, the repeatability test critical values = 0,993 3, in the range of 0,02 % to 100 %, values $C < 0,794 5$ in the above six tables, so, the results obtained were effective.

A.6 Repeatability results

The total standard deviation was calculated by the method of subsection induction, and then the repeatability of the method was calculated. The total standard deviation d_t is calculated in accordance with the [Formula \(A.3\)](#):

$$d_t = \sqrt{\sum_{j=1}^S d_j^2 / S} \quad (\text{A.3})$$

where S is the number of sample = n .

Then, the repeatability limit ($r = 2,8d_t$) were calculated in the respective concentration range, the result are shown in [Table 2](#).

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