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

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[ISO 23978:2020](https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba29f4860f2/iso-23978-2020)

<https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba29f4860f2/iso-23978-2020>



iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 23978:2020

<https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba29f4860f2/iso-23978-2020>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2020

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

	Page
Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Principle	2
4.1 Working principle of the laser Raman analyser	2
4.2 Calculation	3
5 Instruments	3
5.1 Laser Raman gas analyser	3
5.2 Laser specifications	4
5.3 Detection module	4
5.4 Signal processing and user interface	4
5.5 Sample filtration and probe	4
5.6 Gas pressure regulator	4
5.7 Sulfur compound absorber	5
6 Reagents and materials	5
6.1 Zero gas	5
6.2 Base span calibration gases	5
6.3 Working span calibration gases	5
7 Measurement procedures	5
7.1 preparation	5
7.2 Calibration	6
7.2.1 Calibration frequency	6
7.2.2 Calibration procedure	6
7.2.3 Zero calibration	6
7.2.4 Base span calibration	6
7.2.5 Working span calibration	6
7.3 Sampling and sample analysis	6
7.4 Data record	7
8 Repeatability	7
9 Uncertainty evaluation	7
9.1 General	7
9.2 Uncertainty of I_i and I_{Ri}	7
9.3 Uncertainty of C_{Ri}	8
9.4 Uncertainty of result	8
10 Test report	9
Annex A (informative) Statistical procedure for estimation of the repeatability	10
Bibliography	17

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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.

iTeh STANDARD PREVIEW (standards.iteh.ai)

[ISO 23978:2020](https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba29f4860f2/iso-23978-2020)

<https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba29f4860f2/iso-23978-2020>

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 23978:2020

<https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba29f4860f2/iso-23978-2020>

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*

ISO 23978:2020

3 Terms and definitions

<https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba29f4860f2/iso-23978-2020>

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

**3.3
avalanche photodiode**

APD
diode with an internal gain mechanism

Note 1 to entry: As in the case of standard diodes, photons generate electron-hole pairs, which are accelerated by the applied external voltage such that further electrons are introduced to the conduction band by means of impact ionization. These secondary electrons can in turn absorb sufficient energy to raise further electrons into the conduction band.

**3.4
signal intensity**

amount of Raman-shifted photons reaching the detection module

**3.5
external cavity**

measuring gas with a spectrograph outside the laser

**3.6
intracavity**

measuring gas inside the laser itself

**3.7
sulfur compound absorber**

container filled with basic solution for extraction of sulphur compounds

**3.8
base span calibration**

calibration process for eliminating cross-interference and Raman shift drift

**3.9
working span calibration**

calibration process for calculation of the concentration of sample

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 23978:2020

<https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-f622f98b-5668-4378-9741-70a294f80024/iso-23978-2020>

4 Principle

4.1 Working principle of the laser Raman analyser

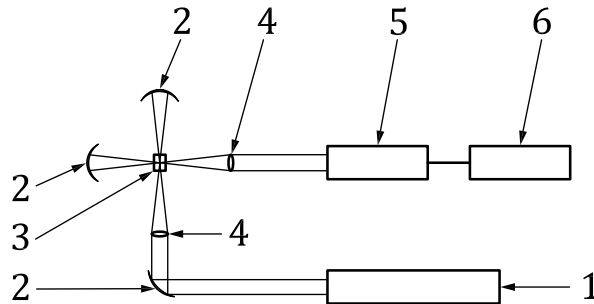
The sketch of the measuring principle is shown in [Figure 1](#). Monochromatic (single wavelength) light from a laser goes through the sample, these source photons interact with the molecules of the gas sample via the Raman effect to emit photons at a different wavelengths. These Raman shifted photons are quantified by wavelength in a detection module. The detection module can be external cavity or intracavity type, using a spectrograph or discrete detectors.

In external cavity, a spectrograph directs photons of different wavelengths to different pixels on multichannel photodetector, it can be charge-coupled device (CCD), complementary metal oxide semiconductor (CMOS) or other detectors. Each multichannel photodetector pixel stores the specific wavelength photons striking them, periodically creating digital signal intensity proportional to the number of photons collected. All pixels taken together generate a spectrum representing the number of photons detected at each wavelength. The spectrum can be mathematically processed to yield the molecular type and concentration in the gas sample.

In intracavity, a detector subsystem includes a focusing lens, an optical filter to select a specific Raman line and an APD or photomultiplier to capture the filtered light. The APD or photomultiplier separately collects and counts Raman photons emitted from individual gas species in millisecond time intervals.

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

iTeh STANDARD PREVIEW

Figure 1 — Working principle of the laser Raman gas analyser

4.2 Calculation

ISO 23978:2020

[https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-](https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba2944860f2/iso-23978-2020)

[7ba2944860f2/iso-23978-2020](https://standards.iteh.ai/catalog/standards/sist/f622f98b-5668-4378-9741-7ba2944860f2/iso-23978-2020)

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 H₂, *i*-C₄H₁₀, *n*-C₄H₁₀ 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](#).

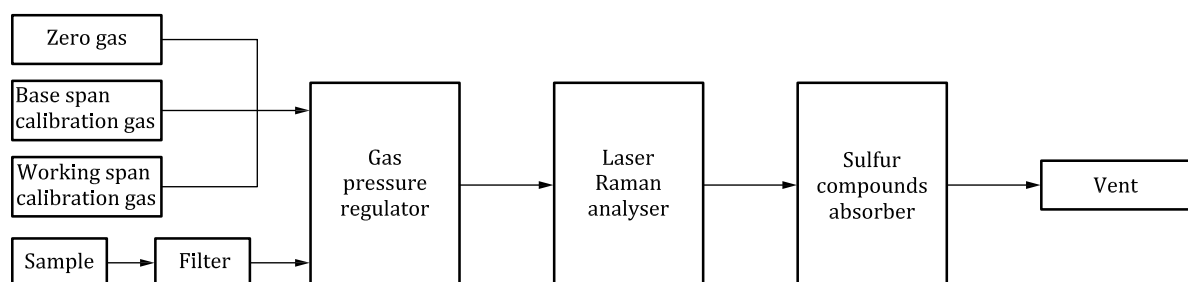


Figure 2 — Flowchart of the measurement procedures