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

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Foreword

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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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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

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

4 Principle

4.1 Working principle of the laser Raman analyser

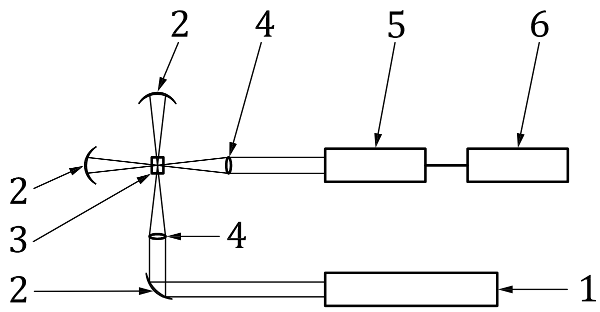
The sketch of the measuring principle is shown in Figure 1. Monochromatic (single wavelength) light from a laser goes through the sample, these source photons interact with the molecules of the gas sample via the Raman effect to emit photons at a different wavelengths. These Raman shifted photons are 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

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):

$$C_i = \frac{I_i}{I_{\mathrm{R}i}} \times C_{\mathrm{R}i} \tag{1}$$

where

C_i is the concentration of component i in the sample;

I_i is the signal intensity of component i in the sample;

$I_{\mathrm{R}i}$ is the signal intensity of component i in the reference gas;

$C_{\mathrm{R}i}$ 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_2S	0,02	30
Methane	CH_4	50	100
Ethane	C_2H_6	0,02	20
Propane	C_3H_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*-C_4H_{10}, *n*-C_4H_{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.

