

**Tomasz Włodek*, Szymon Kuczyński*,
Rafał Smulski*, Krzysztof Polański***

APPLICATION OF RAMAN SCATTERING ANALYZER FOR DETERMINATION OF NATURAL GAS COMPOSITION AT PROCESSING PLANT**

1. INTRODUCTION

Raman spectroscopy provides information about molecular vibrations that can be used for sample identification. The technique uses a monochromatic light source (i.e. laser) directed on a sample and detecting the scattered light. As a result, Raman spectroscopy provides an invaluable analytical tool for the molecular fingerprinting of chemical components in tested sample of material. This technique has a wide applications, due to a lot of advantages, e.g. it is a non-invasive method, the spectra are usually obtained without touching the sample, spectra can be obtained through transparent containers such as glass and only small amounts of samples are necessary for the measurements. Raman spectroscopy has a unique set of advantages when applied to gas phase process monitoring. The stability and speed of Raman instruments and their ease of calibration makes them an ideal candidate to replace the use of gas chromatography in natural gas processing and handling. Raman spectroscopy is additionally immune to measurement artifacts originating in variable pressures or flow rates, problems which plague other analytical approaches. Measurements are made quickly, and therefore timed sequential assays can be used to observe reaction progress, to ascertain endpoints and to understand the kinetics of some processes.

Natural gas as a solution to the world's economic and environmental challenges is the cleanest fuel of the hydrocarbons. Shale gas as a unconventional gas has an increasingly important role in the natural gas market. The documented resources of shale gas in the world are higher. Most of the shale gas is produced in the United States. Production of shale gas in the US increased from 2.3 Bcf/day in 2000 to about 43 Bcf/day in February 2016. Since February 2016 some decline is visible in shale gas production in the US probably connected with the crisis in the energy resources market and lower oil and natural gas prices. In 2011

* AGH University of Science and Technology, Drilling, Oil and Gas, Krakow, Poland

** This work has been prepared within the research cofounded by The National Centre of Research and Development (NCBiR) and industrial partners under Research Program BLUE GAS, project IRES no. BG1/IRES/13

optimistic forecasts for shale gas reached Poland. EIA initially forecasted 5.3 Tcm of potential shale gas resources in 2011 [1, 2], two years later predictions were verified to 4.2 Tcm, now the exact resources are difficult to estimate due to poor recognition of the potential of these deposits [1]. Nevertheless these forecasts began development and preparations for unconventional natural gas exploration in Poland including the development of a new measurement methods for qualitative and quantitative analysis of natural gas composition. Raman spectroscopy, which allows for the identification of different substances including hydrocarbons and other chemicals is a promising for application for providing non-invasive and quantitative analysis.

Research on techniques for measuring the composition of the natural gas with the use Raman spectroscopy are being developed under the research program BLUE GAS in Work Package 1 of the project IRES (Integrated Reservoir Exploration & Gas Extraction System for Shale Gas). Presentation of the proposed surface natural gas qualitative and quantitative measurement technique on natural gas plants or in the natural gas field is the main objective of this paper.

2. LABORATORY TESTS

Raman spectroscopy multi-component analysis of the natural gas is an important issue, but difficult, when one component (methane) or two components (methane and nitrogen) have a high molar fraction and others are at trace levels (higher hydrocarbons). Natural gas has varying concentrations of each component depending on the localization of a gas field. Spectroscopic techniques can provide real-time data, and allow *in situ* monitoring with spectroscopic selectivity and unprecedented sensitivity [3].

Before the stage of field tests a series of laboratory tests were performed, in which for several different tested natural gas compositions in spectroscopic measurements Raman spectra were obtained. In the next stage of the study a wide variability analysis of Raman spectra were performed depending on the gas composition and the temperature and pressure conditions. These analyzes are intended to prepare a dedicated algorithm determining the composition of the natural gas on the basis of the obtained Raman spectra and the known pressure and temperature conditions. The composition of tested exemplary natural gas sample is shown in Table 1.

The experimental setup consisted of Raman spectrometer with a 532 nm laser wavelength and high pressure cell with a sapphire window (Fig. 6). A laser beam were focused into the cell using objective. Spectra were collected in the range 100–4 325 cm^{-1} by a CCD detector with 5 cm^{-1} resolution. Integration time was 3 s with 5 accumulations for each single measurement. Exemplary measured spectra for the given mixture is presented in the Figures 1–5.

Before the laboratory tests an extensive literature research was performed to obtain reference data on the peak positions of the individual components of natural gas. The most known peak positions for selected components of natural gas are shown in Table 2. Each bond in the molecule gives a different excitation wavelength. For hydrocarbons the strongest excitations are commonly found for C-H and C-C bonds (symmetrical stretching). For a low resolution of spectra (Fig. 1) only the strongest excitations can be seen as symmetric stretch

(2 917 cm^{-1}), antisymmetrical stretch (3 020 cm^{-1}) and bend (1 534 cm^{-1}) for methane and symmetric stretch for nitrogen (2 330 cm^{-1}). In the Figures 2–5 fragments of Raman spectra are shown in higher resolution, there are more visible peaks especially for components at the trace level of molar fractions (butanes, pentanes and hexane). These measurements were performed for temperature 20°C (293 K) and pressure of 6 bar – tested mixture was in gas phase.

Table 1

Exemplary natural gas composition used for laboratory tests of field Raman spectrometer

Short symbol	Component	Molar fraction [% mol]
C1	methane	80.4838
C2	ethane	9.7
C3	propane	4.73
nC4	n-butane	0.975
iC4	iso-butane	1.201
nC5	n-pentane	0.4952
iC5	iso-pentane	0.501
C6	n-hexane	0.978
N2	nitrogen	0.936

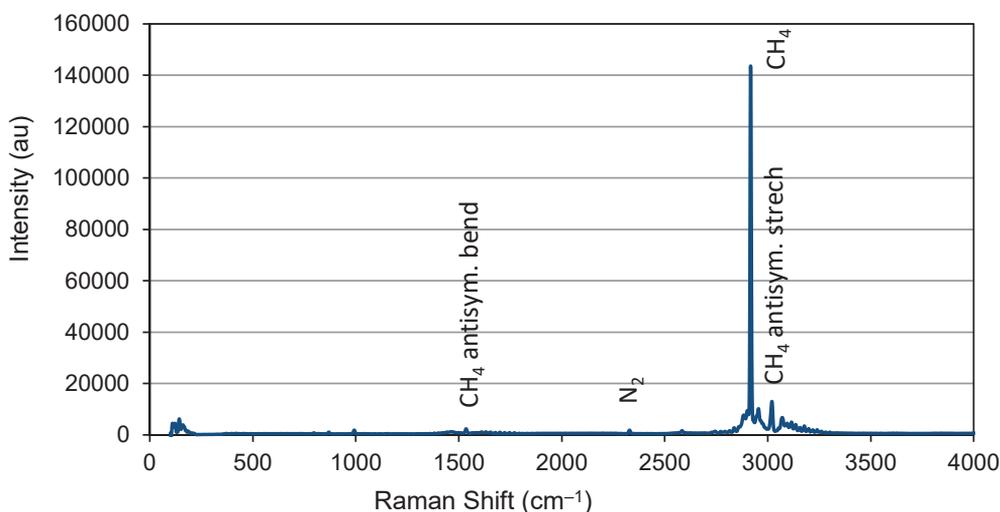


Fig. 1. Full Raman spectrum of analyzed sample of natural gas

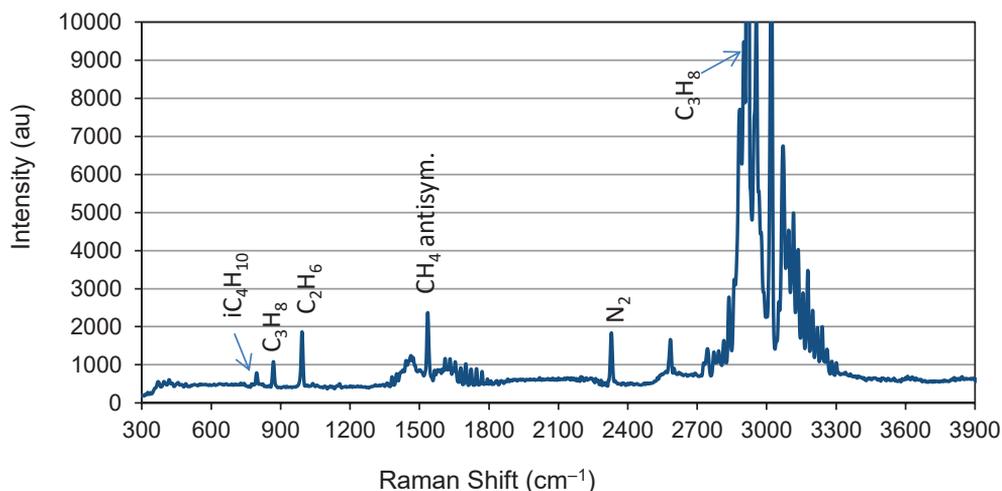


Fig. 2. Raman shift of analyzed sample of natural gas in higher resolution

In the region 2800–2950 cm⁻¹ peak maxima of C-H bond can be observed for hydrocarbons molecules. A qualitative analysis of natural gas with use of Raman spectroscopy on the basis only of this region is difficult because of the C-H bonds are essential in each hydrocarbon molecule and the peak position corresponding to the position of given hydrocarbon molecules can overlap. A qualitative analysis of the gas composition should be based on the analysis of the entire spectrum of Raman or at least the position of several characteristic peaks corresponding to Raman scattering for the different characteristic vibrations of bonds for a given compound. Figure 3 shows a detailed picture of the Raman spectra in the region 2 800–2 950 cm⁻¹.

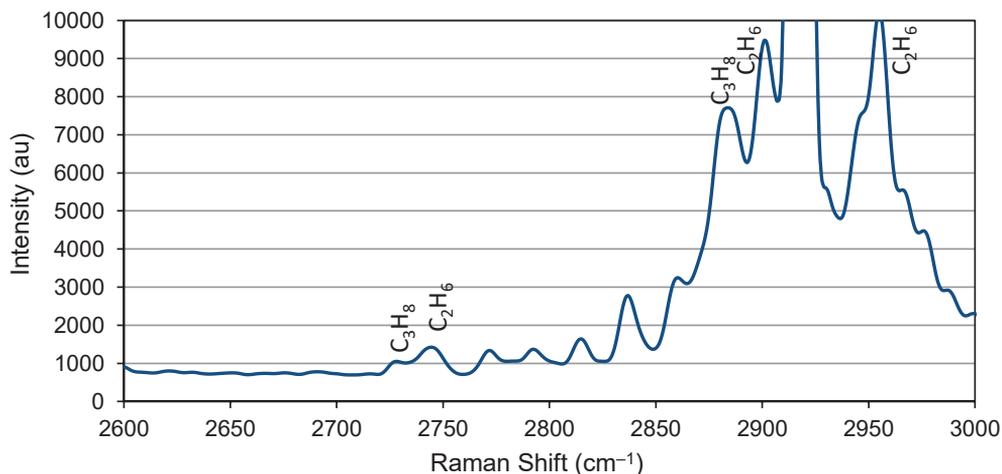


Fig. 3. Raman spectra for the region 2 600–3 000 cm⁻¹

The position of the peaks of ethane, propane and butanes in the region 600–1 100 cm^{-1} is characteristic and valuable for the overall compositional analysis of the natural gas (Fig. 4), furthermore the peaks characteristic for heavier hydrocarbons (pentane, hexane) may be found in the low frequency region (300 to 600 cm^{-1}) (Fig. 5).

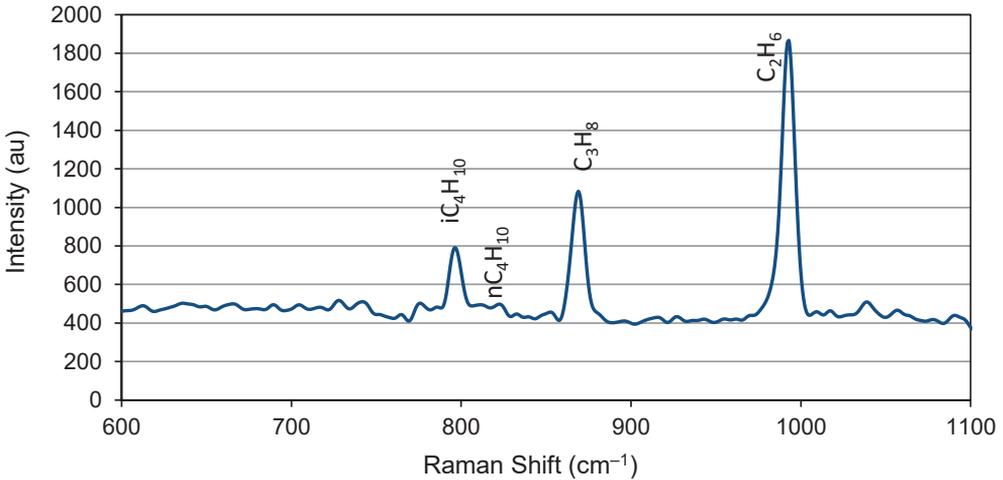


Fig. 4. Raman spectra for the region 600–1 100 cm^{-1}

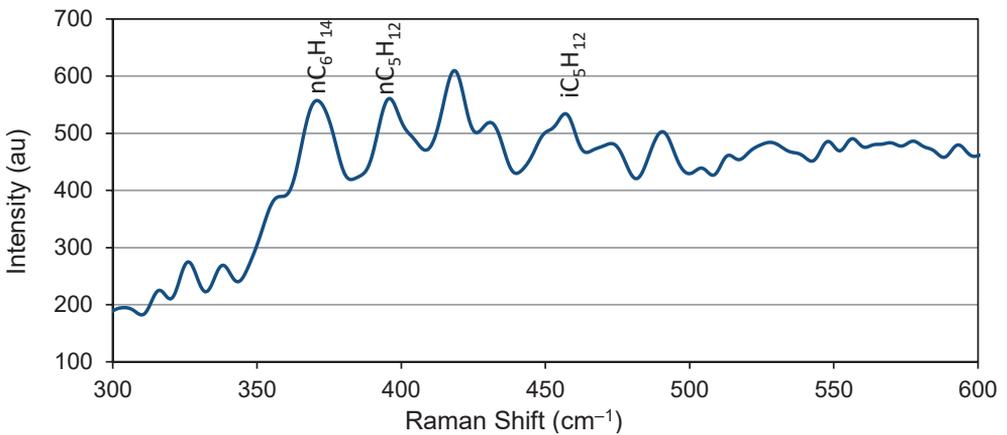


Fig. 5. Raman spectra for the low frequency region 300–600 cm^{-1}

Table 2
Reference data (selected peak positions)
for selected natural gas components [4–8]

Component	Symbol	Peak position [cm ⁻¹]	Type
Methane	CH ₄	1 534	antisym. bend
		2 916	C-H sym. stretch
		3 020	antisym. stretch
Ethane	C ₂ H ₆	995	C-C stretch.
		2 745	overtone
		2 896	C-H stretch.
Propane	C ₃ H ₈	867	C-C stretch. overtone C-H sym. stretch.
		2 740	
		2 887	
		2 910	
n-Butane	nC ₄ H ₁₀	827	–
		1 445	
		2 885	
		2 890	
iso-Butane	iC ₄ H ₁₀	794	–
		2 880	
Nitrogen	N ₂	2 330	N = N stretch.

3. MEASUREMENT TECHNICAL ASSUMPTIONS

The primary objective of the presented research is the implementation a tool by which the quick analysis and determination of the natural gas composition can be made in field conditions without sampling (eg. for chromatographic analysis). The main assumption for the technical measurements is the direct and continuous measurement into the stream of flowing reservoir fluid after the wellhead (after pressure reduction on limiting orifice) or a stream of natural gas or condensate after processing into the natural gas plant. The measurement technique with the use a Raman spectrometer in surface conditions should be resistant to the conditions of pressure of at least 10 MPa (in the case of in-situ measurements in a wellbore pressure limit should be at least several times higher) and temperature conditions from –30°C to +70°C.

4. PROPOSED MEASUREMENT METHODS

The proposed measurement methods are focussed on the use of:

- a laboratory cell (autoclave) with sapphire window mounted on a specially prepared bypass pipeline,
- a dedicated Raman probe mounted to the available installed stub pipe,
- the construction of a special measurement cell.

The first method of surface Raman spectra measurement is to use of a laboratory cell with a sapphire window. Raman probe would be applied into the sapphire window. This cell would be mounted on a special bypass between piping connections in the pipeline system. The main advantage of the use of the laboratory cell is the ability to use various types of Raman probes available on the market and probes designed specifically for this measurement.

The second method of measurement is similar to the first method. This method is simplified because the Raman probe is mounted directly to the connections available on the pipeline. An unquestionable advantage of this method is the short natural gas plant shutdown period during installation of the probe. The measurement is simpler, however, this solution has the basic disadvantage of the variety of types and sizes of the measurement stub pipes available on the different natural gas field plants. Raman probe is an element with precisely designed geometry. In case of the design and use it for a particular connection it will not be possible to mount it on a different type of connections or it will be required to design a special adapter to enable the installation of the probe.

The third proposed measurement technique is to use a specially designed measuring cell (Fig. 6–7). The measuring cell as part of the plant installation can be connected to the natural gas plant system by flange or hammered connections. The basic elements of this cell are mounted on the dedicated stub pipes (connectors) for the Raman probe (either on a threaded connections (1) and the flange connections (2)), and connectors for pressure and temperature measurement (3). The advantage of the presented solution is to enable the Raman probe installation to dedicated stub pipes mounted on the cell. The main disadvantage is a possible incompatibility of the cell with pipelines of various diameters, which may necessitate the use of orifices or adapters. Also the disadvantage is the necessity of a long shutdown periods during installation of the measuring cell.

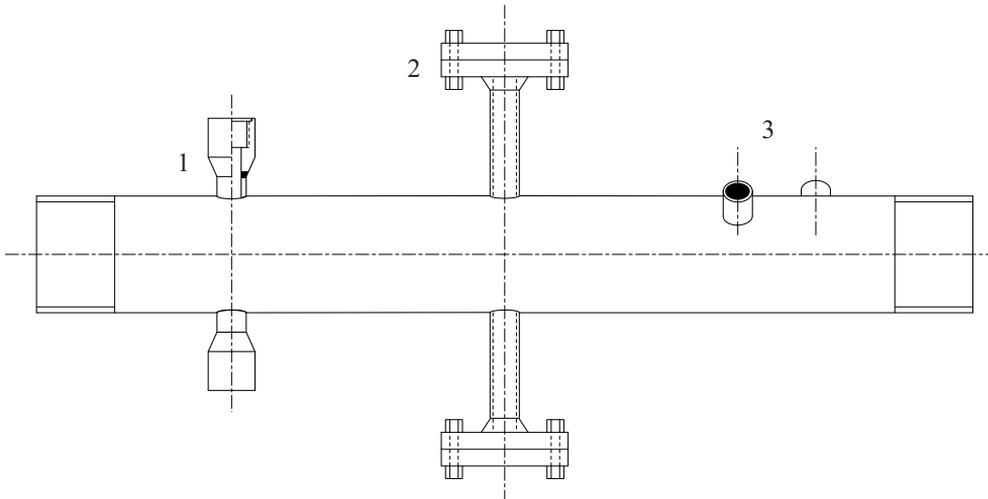


Fig. 6. Scheme of designed measurement cell with stub pipe connections (1), flange connections (2) for Raman probes and connectors for temperature and pressure measurements (3)

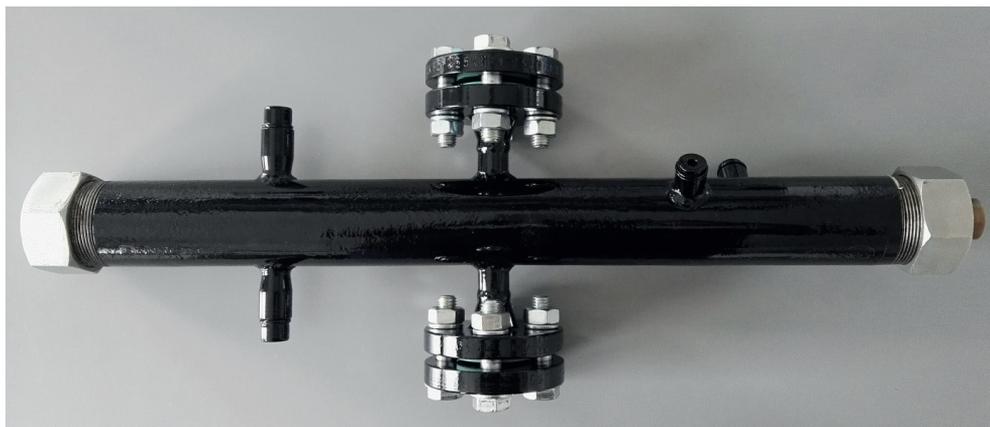


Fig. 7. Picture of measurement cell

5. CONCLUDING REMARKS

Development of conventional and unconventional natural gas reservoir management includes continuous monitoring of hydrocarbon exploitation processes and its impact on the reservoir and environment. Raman spectroscopy can be a very promising method for application of providing quick, non-invasive, nondestructive analysis of natural gas composition.

Before the stage of field tests laboratory tests for different gas compositions were performed in specially designed high pressure and high temperature autoclave. Typical natural gas mixture including heavier hydrocarbons C5–C6 were chosen for these tests. The mixture was tested at a temperature of 20°C and for pressure of 6 bar.

It is possible to apply the Raman method spectroscopy for measuring the composition of the natural gas in the natural gas field installation or on transmission pipelines. Three possible measurement techniques were proposed:

- a laboratory cell (autoclave) with sapphire window mounted on a specially prepared bypass pipeline,
- a dedicated Raman probe mounted to the available installed stub pipe,
- the construction of a special measurement cell.

In each of these methods: a laboratory autoclave, dedicated Raman probe or designed measurement cell should be designed to resist the high pressure in the case of surface measurements. Taking into account the typical pressures in natural gas plants and natural gas transmission pipelines the minimum operating pressure for this equipment should not be lower than 10 MPa.

The basic technical assumptions and the main advantages and disadvantages were presented for each of the proposed measurement methods. The most practical method from a technical point of view is the use of a dedicated Raman probe for direct measurement of the natural gas stream composition. The use of a specially designed measuring cell also enables the use of dedicated Raman probes, but this solution is very practical for the stage of operational tests.

REFERENCES

- [1] Hendel J., Kuczyński S., Sikora A.P.: *Shale gas revolution in Poland – challenges with replication of the US success*. Proceedings of the international conferences EEDE 2015: Zakynthos Island, Greece, July 16–20, 2015.
- [2] Nagy S., Siemek J.: *Shale gas in Europe: the state of the technology – challenges and opportunities*. Archives of Mining Sciences, vol. 56, iss. 4, 2011, pp. 727–760.
- [3] Kuczyński S., Włodek T., Polański K., Barbacki J., Dąbrowski K.: *Application of Raman Spectroscopy for shale gas compositions measurements in two-phase systems*. 8th ICAVS Conference, Vienna, Austria, July 12–17, 2015.
- [4] Buldakov M.A., Matrosov I.I., Petrov D.V., Tikhomirov A.A.: *Raman gas-analyzer for analyzing environmental and technogenic gas media*. Optical Instrumentation, Atmospheric and Oceanic Optics, vol. 25, iss. 4, 2012, pp. 298–303.
- [5] Corsetti S., McGloin D., Kiefer J.: *Comparison of Raman and IR spectroscopy for quantitative analysis of gasoline/ethanol blends*. Fuel, vol. 166, pp. 488–494, 2016.
- [6] Kiefer J.: *Recent Advances in the Characterization of Gaseous and Liquid Fuels by Vibrational Spectroscopy*. Energies, vol. 8, 2015, pp. 3165–3197.
- [7] Hansen S.B., Berg R.W., Stenby E.H.: *The Application of Raman Spectroscopy for Analysis of Multi-Component Systems*. Technical University of Denmark, 2000.
- [8] Seitz J.C., Pasteris J.D., Chou I.M.: *Raman spectroscopic characterization of gas mixtures; I. Quantitative composition and pressure determination of CH₄, N₂ and their mixtures*. American Journal of Science, vol. 293, 1993, pp. 297–321.
- [9] Kuczyński S., Włodek T., Hendel J.: *Development of a new monitoring system based on Raman spectroscopy and its application in a unconventional gas reservoirs*. XXIV International Conference on Raman Spectroscopy at the Friedrich Schiller University Jena, Germany, 2014, pp. 148.