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**APPLICATION OF RAMAN SPECTROSCOPY ANALYSIS
IN UNCONVENTIONAL NATURAL GAS RESERVOIRS –
DENSITY AND PRESSURE DEPENDENCE ON RAMAN SIGNAL
INTENSITY******

1. INTRODUCTION

According to an EIA reports, it is estimated that shale oil and shale gas resources are located in United States and in 137 shale gas formations in other 41 countries worldwide. Possible resources in these formations include about 345 billion barrels of world shale oil and 7,299 Tcf (trillion cubic feet) of world shale gas (Fig. 1) [1–3]. Furthermore over 85% of global resources of shale gas and over 72% of tight gas are located within fifteen countries. Despite the downturn in the global markets, unconventional natural gas production increased recently. Exploitation of main shale oil and gas basins is still more popular due to the higher reservoir potential and economically feasible drilling and exploitation [4–6].

Due to the energy policy implemented by the Polish government and the downturn in the global oil and gas industry, the situation in the Polish gas market has significantly changed in last few years. According to Polish Geological Survey reports, the number of granted concessions for exploration and exploitation remarkably diminished from January 2012 with only 30 concessions now active. For a better understanding of the current situation in Poland, 115 concessions were active in 2012 and 40 in 2015 [7–10].

However, amongst European countries Poland still has one of the most significant potentials for shale gas exploitation. Poland is in thirteenth position in the world and the first in Europe with the largest resources of shale gas. Given favorable conditions and market trends in the oil and gas industry, Poland could be a leader in the production of shale gas in the mid and long term future due its high-developed scientific and technical experience. The reported Polish shale gas resources could potentially cover demand for natural gas in the region of Central Europe [4].

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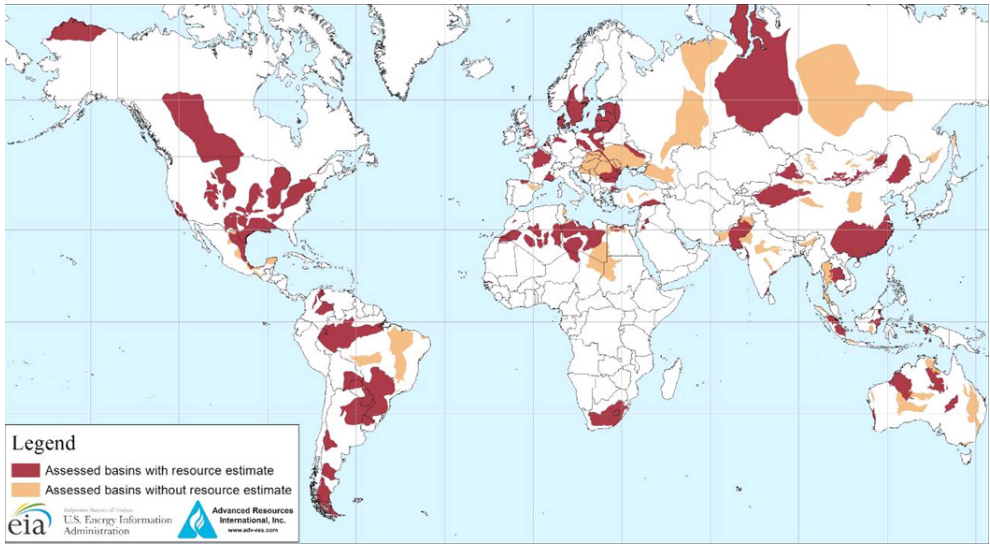


Fig. 1. World's shale oil and shale gas formations [1]

Table 1
Unproved technically recoverable resources of shale gas and tight oil [4]

Country	Wet shale gas [trillion cubic feet]	Tight oil [billion barrels]
China	1115.2	32.2
Argentina	801.5	27
Algeria	706.9	5.7
USA	622.5	78.2
Canada	572.9	8.8
Mexico	545.2	13.1
Australia	429.3	15.6
South Africa	389.7	0
Russia	284.5	74.6
Brazil	244.9	5.3
United Arab Emirates	205.3	22.6
Venezuela	167.3	13.4
Poland	145.8	1.8
France	136.7	4.7
Ukraine	127.9	1.1

2. SAMPLING AND ANALYSIS OF NATURAL GAS IN SHALE AND TIGHT RESERVOIRS

The classic method of measuring natural gas composition is gas chromatography. This method, although accurate, is impracticable when it is necessary to perform a quick measurement and to obtain results in a short time. In the case of in-situ conditions, it is often necessary to pre-take the sample and send it for analysis in the laboratory. This is the reason for finding new alternatives in which it will be possible to perform representative measurements for in-situ conditions in a short time without logistical challenges.

Several sampling methods can be used to collect reservoir fluids, including repeat formation tester (RFT) sampling, bottom hole sampling, separator sampling and wellhead sampling. The choice of method depends on whether the reservoir fluid is an oil or gas, whether the reservoir fluid is saturated at reservoir conditions or whether the well produces single phase fluid [11–14]. Then, compositional analysis and sample quality control is performed.

The Raman spectroscopy could be an alternative solution to those mentioned above. Raman spectroscopy has a wide scope of application in many fields of the oil and gas industry [15–21]. There is the possibility to apply this technology to oil and refinery products research, but in terms of research in natural gas engineering, analysis of natural gas composition is challenging from the Raman spectroscopy application point of view. This solution will allow the time required to measure the natural gas composition to be reduced from almost 30 min (gas chromatography) [22] to even 0.5 sec (Raman spectroscopy) [16] so it could be used as one of the alternative methods in oil and gas industry. Furthermore, this method allows to perform countless non-invasive tests and the chemical reaction detection in a particular sample at static or dynamic conditions in field or in-situ tests [23]. From a scientific point of view it is interesting for researchers to observe the complex phenomena related to the impact of adsorption and capillary condensation of gas-condensate systems in nanopores [24, 25]. It is a future challenge for Raman spectroscopy in-situ tests, as well as measurements in multiphase conditions.

Natural gas analysis with the use of Raman spectroscopy is safe thanks to the proper safeguards for the investigated fluid and apparatus. After construction of the Raman spectra data base, the composition of the natural gas can be determined for different pressure and temperature conditions with the application of prepared algorithms, with also the gas-oil ratio (GOR) for hydrodynamic conditions to be determined [15, 26]. Due to the high interest in unconventional natural gas production, the proposed method might be successfully implemented in the oil and gas industry because of its attractive price, equipment mobility, measurement quality, accuracy and possibilities of real time monitoring.

3. SYSTEM DESIGN AND EXPERIMENTAL LABORATORY TESTS

The main problem which occurs when Raman spectroscopy is applied to natural gas analysis is the low intensity of Raman signal [26, 27]. The system applied for this study was equipped with the NIR 785 nm diode laser with an output power of up to 400 mW. In our

opinion, a laser of this type is most preferable for Raman spectroscopy of natural gas mixtures with a probe at the end of a long fiber optic (low signal losses). Light from the laser travels along the optical fiber to a probe which is mounted to a high pressure and high temperature (HPHT) autoclave where laser light is focused on a natural gas sample. Backscatter radiation from the sample travels to a spectrograph through another fiber optic cable. The spectrograph used in the system is an $f/1.8$ axial transmissive type and focuses the Raman scattered radiation onto a charge-coupled device (CCD) detector. The CCD, cooled to -40°C , measures the intensity of the Raman scattered light. There are 1 024 pixels along the spectrograph dispersion axis and 256 pixels along the spectrograph slit height axis. Each pixel in the CCD detector is $26\ \mu\text{m} \times 26\ \mu\text{m}$.

The measurements were preceded by nitrogen flushing of the autoclave and pipes and valves. Before sample mixture injection, a vacuum was applied to the autoclave. Then spectra were collected for variant pressures at ambient temperature (Fig. 2).

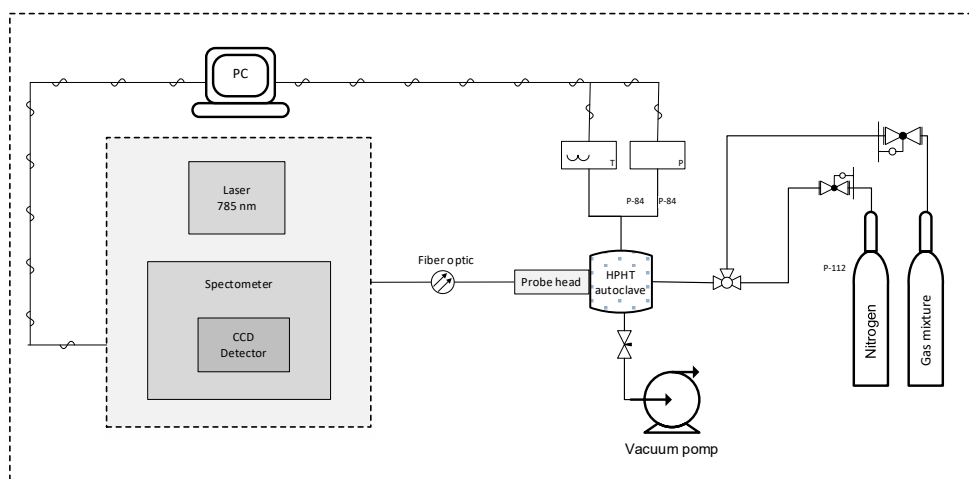


Fig. 2. Schematic diagram of the experimental system

4. DENSITY AND PRESSURE DEPENDENCE ON RAMAN SIGNAL INTENSITY

Density analysis of selected natural gas samples for the chosen conditions of pressure and temperature was based on the Peng–Robinson (PR) cubic equation of state (EOS) [28]. This equation (with its modifications) is one of the most popular equations for describing the PVT (Pressure, Volume, Temperature) behaviour of real, pure substances and mixtures. This equation has the following classic form:

$$p = \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m) + b_m(v - b_m)} \quad (1)$$

In this formula v is molar volume, a_m and b_m are parameters of PR EOS depending on sample composition.

From the general form of real gas equation of state density can be written as:

$$\rho = \frac{P}{ZR_i T} \quad (2)$$

where Z is compressibility factor, which is calculated from following formula (iterative PR EOS variant):

$$Z = \frac{Z}{Z - B} - \frac{A}{Z^2 + 2BZ - B^2} \quad (3)$$

where A and B are dimensionless PR EOS parameters.

The performed research was compared with Seitz studies [29] and their results are the basis for further studies of natural gas composition in changing temperature and pressure conditions. The Raman spectra measurements were performed at an ambient temperature. Conducted Raman spectra analysis for changing pressure conditions gave some information about the characteristic of a signal. Pressure has a significant impact on the characteristic bands for individual molecules in the mixture. Pressure growth is connected with the increase of a cross section of a scattering due to a higher density. It is the essential part for understanding the relationship between pressure and Raman spectrum behavior. Pressure growth causes also a shift of a characteristic band of a given vibration. Performing a similar analysis for a set of samples with different molar fractions allows one to create a intelligent algorithm which enable characterization of reservoir fluid through Raman spectra comparison [17, 20, 26, 29–33].

Table 2
Investigated mixture compositions

Component	Molar fraction [% mol]					
	Mixture no.					
	DHP7M	DHP7T	75865	75868	75871	75872
CH ₄	86.003	82.012	66.04	59.20	53.60	45.95
C ₂ H ₆	10.000	12.990	4.00	5.40	5.40	5.63
C ₃ H ₈	2.000	3.000	2.20	3.10	3.06	3.48
i-C ₄ H ₁₀	0.502	0.499	1.01	0.90	0.90	0.94
n-C ₄ H ₁₀	0.495	0.499	1.05	0.90	0.90	0.90
N ₂	1.000	1.000	25.70	30.50	36.14	43.10

This knowledge is fundamental for further reservoir fluid analysis. Based on identified relationships, molecules with defined mole fraction were tracked. During the research different hydrocarbons (methane, ethane, propane, isobutene, butane) and nitrogen were used as the components of the mixture. Tested compositions of mixtures' are presented in Table 2. Samples were prepared to avoid multiphase systems. All measurements were performed for single phase (vapor) conditions. For a better comparison also the pure methane was analyzed. In the first part of the analysis obtained changes in positions of methane 2917 cm^{-1} characteristic band, for a pure methane sample, were compared with a previous studies of other authors [34–41]. In the later part the impact of both pressure and density changes for characteristic band for other components are shown.

Table 3
Measured methane ν_1 band positions a elevated pressures compared with results obtained by Shang et al. [34]

Study	Pressure p [MPa]	Temperature T [°C]	Shift [cm ⁻¹]	Density [g/cm ³]	Band	Phase
This study	0.1203	23	2917.8	0.000786	methane ν_1	gas phase
	0.1595		2917.8	0.001043		
	0.2002		2917.8	0.001310		
	0.2472		2917.8	0.001619		
	0.3020		2917.8	0.001980		
	0.5026		2917.8	0.003309		
	0.9991		2917.6	0.006645		
	1.5020		2917.5	0.010093		
	1.9900		2917.4	0.013504		
	2.9910		2917.2	0.020703		
Shang et al.	0.041	22	2918.2	0.000271	methane ν_1	gas phase
	0.117		2918.2	0.000768		
	0.428		2918.2	0.002816		
	0.986		2918.1	0.006561		
	1.766		2917.9	0.011912		
	3.662		2917.6	0.025568		
	8.441		2916.5	0.063877		
	14.069		2916.3	0.11304		
	17.938		2914.5	0.14488		

In order to obtain bands' positions, a Voigt profile of the form was fitted to each line:

$$V(x; \sigma, \gamma) = \int_{-\infty}^{+\infty} G(x', \sigma) L(x - x'; \gamma) dx' \quad (4)$$

where:

$L(x)$ – Lorentzian distribution,

$G(x)$ – Gaussian distribution.

A suitable program was written using a peak fit package in a MATLAB software. In Figure 3, a comparison of a methane characteristic 2 917 cm^{-1} band position between this studies and other authors' works is shown. The measured sample was pure methane and the most prominent effect is a shift of the band's position towards lower values with an increase of pressure.

For pressures below 20 MPa, these dependences are approximately linear while for bigger pressures they are exponential. In this study we limited maximal pressure to 6 MPa. On the one hand, it ensures a single phase gaseous system and, on the other, it is sufficient to simulate the expected conditions in unconventional Polish gas reservoirs. Those linear dependences (in the pressure limit of 20 MPa) differ only in offset and have similar slopes. These differences can be connected with a spectrometer adjustment. Similar behavior presented by dependences of a position with respect to a samples' density are shown in Figure 4. Individual trends differ only in intercepts but not in slopes. However, in contrast to pressure dependencies, shift is also linear for higher pressures.

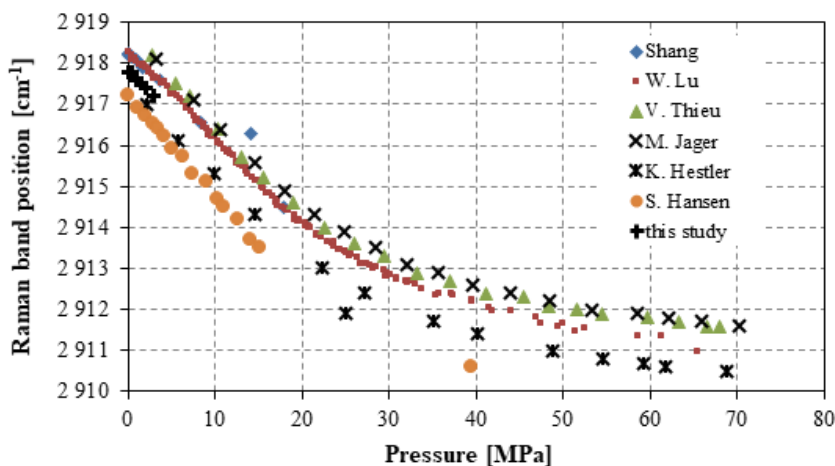


Fig. 3. Relations between Raman shift and pressure for methane 2 917 cm^{-1} band position data collected within this study and by other authors

According to Wanjun Lu, L. Shang and other research [34, 41] the peak position depends on pressure and temperature conditions. In case of increasing pressure at constant temperature, the peak position shifts to a lower wavenumber. Opposite changes were observed in case of temperature increase [41]. Different observations of peak position changes at ambient tem-

perature and at constant pressure, suggesting that a good solution is to find a function which connects both temperature and pressure. The density of the analyzed natural gas samples as a function of temperature, pressure and composition should be considered as the primary control parameter on a peak position [41].

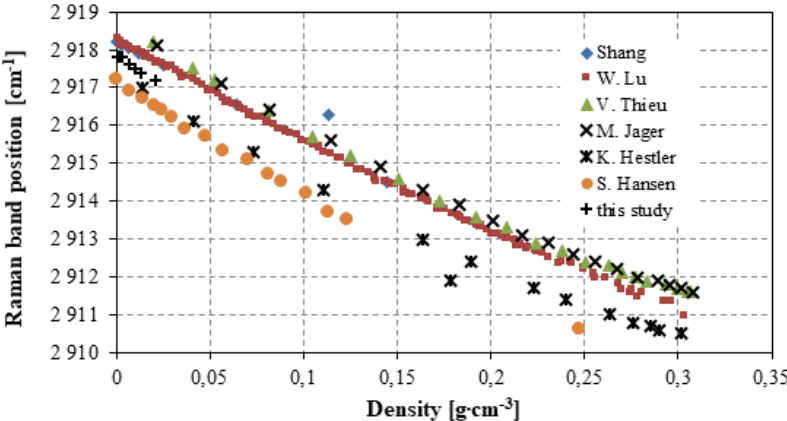


Fig. 4. Relations between Raman shift and density for methane 2917 cm⁻¹ band position – data collected within this study and by other authors

Figure 5 shows the obtained positions of a methane ν_1 2917 cm⁻¹ band for mixtures with compositions shown in Table 2. With the pressure change, the position of those band shifts linearly towards lower wave numbers. For each sample, this linear trend differs in both intercept and slope. Since the samples were measured using the same spectrometer with the same calibration, the mentioned differences have to be connected with differences in composition. Similar behavior can be seen for a position vs. density dependence shown in Figure 6.

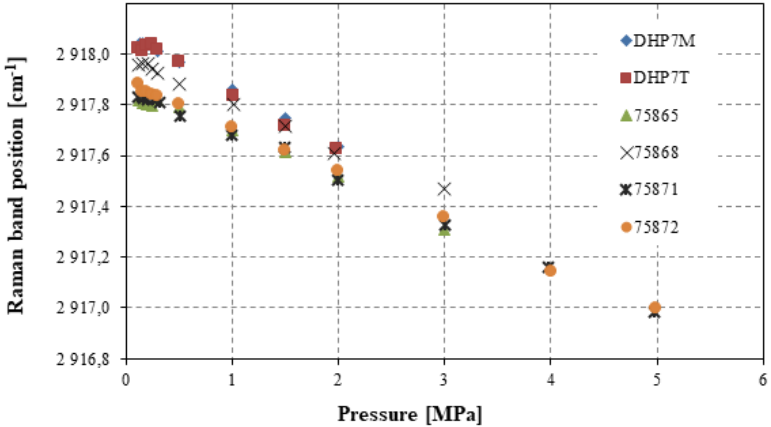


Fig. 5. Relations between methane 2917 cm⁻¹ peak position and pressure for analyzed natural gas mixtures

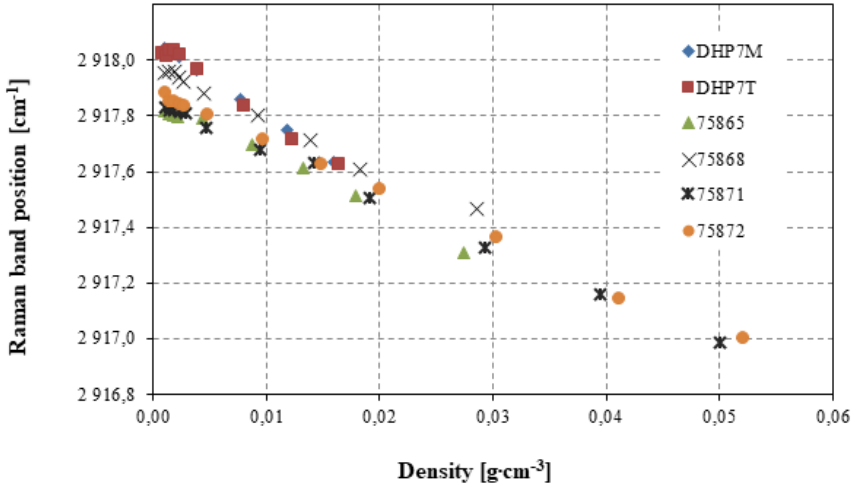


Fig. 6. Relations between methane 2917 cm⁻¹ peak position and density for analyzed natural gas mixtures

For each sample, methane is a major component and a 2917 cm⁻¹ band is a most intense peak in the whole spectra. Similar analysis can be performed for other (minor) components. Figures 7 and 8 show the positions of an ethane 995 cm⁻¹ band with the respect to pressure and density respectively. In each case, the position changes linearly with pressure. Considerable differences in an intercept can be seen between samples with a low nitrogen concentration i.e. DHP7M, DHP7T and a high nitrogen concentration. This clearly shows the impact of other components on the position of a given band.

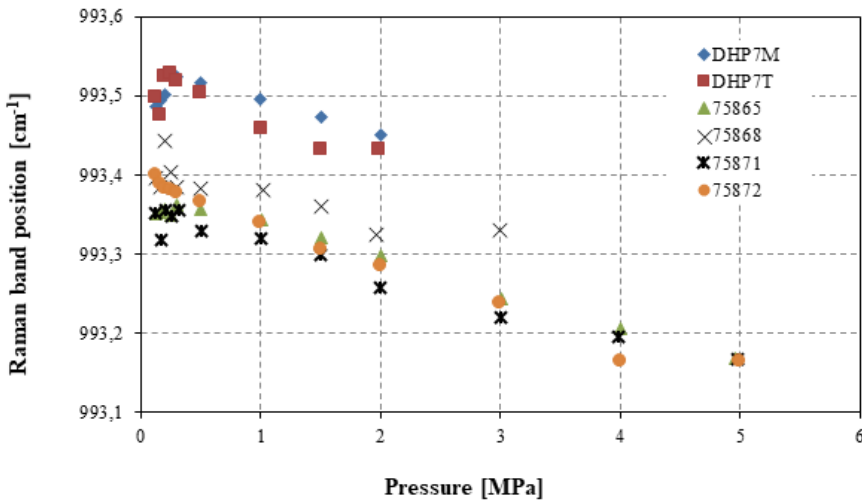


Fig. 7. Relations between ethane 995 cm⁻¹ (C-C stretch) peak position and pressure for analyzed natural gas mixtures

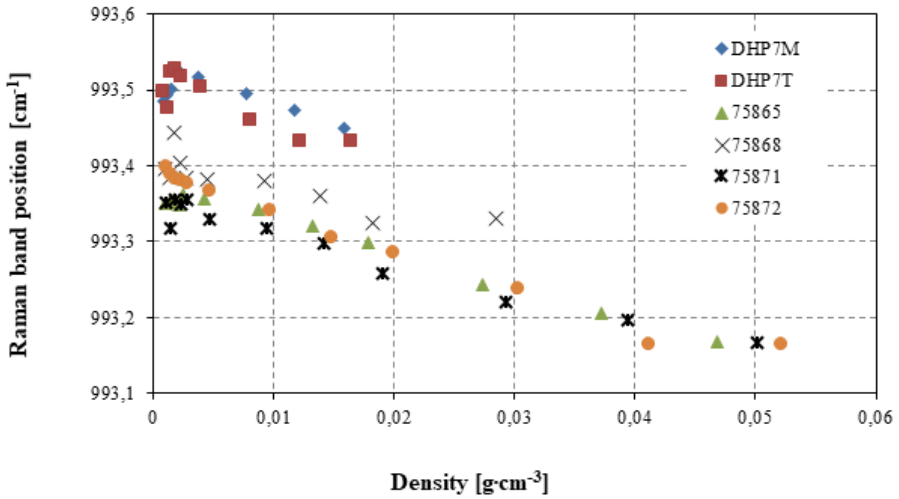


Fig. 8. Relations between ethane 995 cm^{-1} (C-C stretch) peak position and density for analyzed natural gas mixtures

Figures 9 and 10 show the analysis for a nitrogen 2 330 cm^{-1} band. This band can be used in order to present the sensitivity of a system. For higher pressure, the program is capable of detecting and fitting a model function for each sample. However, in the case of low pressure and low nitrogen concentration, the dispersion of results is high, making them unreliable. This problem can be resolved with an increase of accumulation time but this is not viable for in-situ applications. In order to obtain proper results at low concentrations and pressures, more accurate algorithm have be proposed. This illustrates the main limitations of the current analysis.

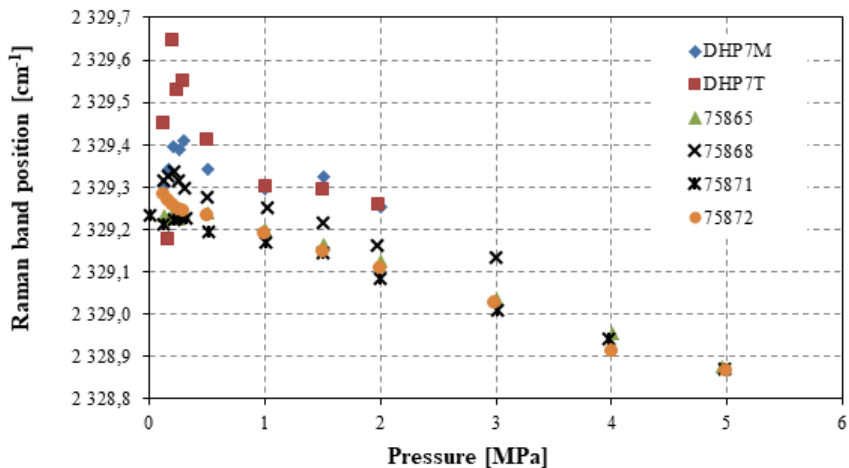


Fig. 9. Relations between nitrogen 2 330 cm^{-1} peak position and pressure for analyzed natural gas mixtures

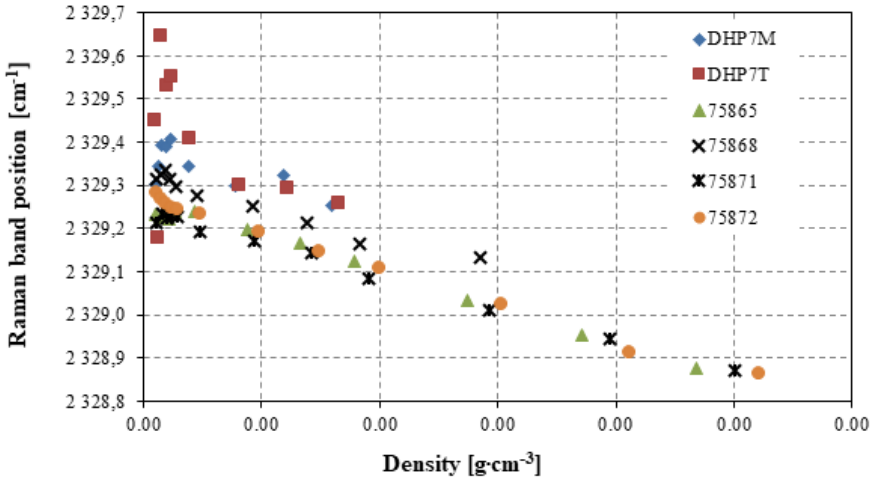


Fig. 10. Relations between nitrogen 2 330 cm^{-1} peak position and density for analyzed natural gas mixtures

5. CONCLUSIONS AND PERSPECTIVES

In this research we have shown the impact of pressure change on characteristic band positions. The conclusions stated in the articles of Shang and Buldakov [31, 34] showed that the characteristic Raman signal observed also changes at different temperature conditions. The higher the temperature measurement, the lower the Raman spectrum intensity. The distinctive methane ν_1 spectrum is a perfect example, where higher temperature and lower intensity is associated with a diminished area below the spectrum curve, smaller maximum intensity height and the smaller spectrum section width value. Simultaneously, the diverted wave numbers increase as the Raman scattering bands move away from the Rayleigh bands.

The correlation between temperature, intensity reduction and intensity is shown in the equation below called temperature correction and will in the future be calculated from the equation shown below during measurements. It needs to be done before any assignments of the peak are made. It is important due to the thermal population factor, which can mask peaks or bands of the spectrum.

$$I_{reduced} = \frac{I_{observed}}{\text{Exp}\left[\frac{\hbar\omega}{kT}\right] + 1} \quad (5)$$

In the case of in-situ measurements the impact of temperature should be taken into account yet such an analysis is beyond this study. The influence of a significant molecule to the spectrum form is analyzed as well. Moreover, it confirms the relationship between

particular parameters and characteristic features of Raman spectroscopy. Finally, it describes the key issues for making the algorithm based on the data base created and shows the limits of the proposed method. The collected spectra can be used to develop computer algorithms to determine the composition of natural gas samples.

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