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**CHARACTERIZATION OF NATURAL GAS
BY RAMAN SPECTROSCOPY
AND ITS APPLICATION FOR IN-SITU MEASUREMENTS****

1. INTRODUCTION

Since a year 2010 we can observe substantial increase of a shale gas production in the USA [1]. In Poland U.S. Department of Energy estimated shale gas recoverable resources to 4.1 Tcm [2]. This encouraged development of unconventional gas exploration and development of new analytical methods capable to perform in-situ composition determination and monitoring. Some of those fields of activity are part of a Polish National Research Program Blue Gas.

The analysis of natural gas system composition can be performed by means of several methods. The most prominent is a gas chromatography. Possibility of characterization of gas mixtures for liquids was show in several papers [3, 4] as well as a determination of natural gas composition [5]. Other methods are mass spectroscopy [6, 7], IR spectroscopy [8] and for heavier hydrocarbons NMR [8]. In-situ experiments are predominantly carried out in high pressure and high temperature condition. Therefore application Raman spectroscopy is more perspective. Implementation of this method in a well can be achieved by two methods: lowering spectrometer by wireline in a coiled tubing, or use of a fiber optic probe.

Adaptation of this technology in the field of natural gas can allow analysis of composition of fluid contained in a reservoir under hard conditions in a wellbore in a real time.

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Another application is a monitoring of a performance of new and old wells by indicating water zones, or identification of treatments chemicals (solvents, corrosion inhibitors). In this work a series of laboratory tests for different gas compositions were performed in specially designed high pressure resistant autoclave. A portable spectrometer consist probe with a fiber optic was designed. The autoclave can provide simulated in-situ condition.

The analysis of behavior of characteristic peaks for high pressure have been performed only for simple hydrocarbons mixtures [9–11]. In this study analysis for more complicated hydrocarbon mixtures is shown. Those mixtures were tested in pressures range from 1 to 150 bar. For a peak analysis a computer algorithm was developed by authors. It automatically detects and determines changes of Raman bands for different pressures and different composition. It is also capable to deconvolve of overlapping bands in the spectra. In a perspective based on those studies a determination of composition of natural gas can be carried out.

2. HIGH PRESSURE RAMAN SYSTEM

Spectrometer

Current Raman system (shown in a Figure 1) was designed as a movable working station. Its weight is of the order of 20 kg. It has integrated spectrometer with high throughput f/1.8 optics configured for coverage from 450 cm^{-1} to 3550 cm^{-1} and resolution of $\sim 1.6\text{ cm}^{-1}/\text{pixel}$. The system includes low noise back-illuminated Charge Coupled Device (CCD) camera with 2048×512 , 13.5×13.5 micron pixels. The camera is devoted for quantitative scientific imaging. It has thermoelectric cooling (TE) down to -75°C . Application of such device is ideal for demanding, low light applications such as Raman spectroscopy, LIBS, absorbance, emission, fluorescence and reflectance spectroscopy. The setup is also equipped with a 21 meter 100 micron fiber with a SMA/SMA coupling between 532 nm laser and a connected to a probe. Another twenty meter 400 micron fiber for a back scattering collection with a SMA/SMA coupling between the probe and spectrometer. The source is an integrated 532 nm single longitudinal mode, continuous wave (CW) monolithic diode-pumped solid-state (DPSS) laser. Power is adjustable through software (max 120 mW). Gas sample is injected into analytical high pressure cell (up to 250 bar) with a sapphire window.

The first part of studies was a determination of an influence of the fiber on collected signal. As a test sample liquid cyclohexane was used. The same sample was used in the further calibration of the spectrometer. In Figure 2 spectra collected for a 1 and 21 m long fiber are shown. The most prominent effect is a drop of intensity for characteristic

lines. For the current fiber losses are of the order of 0.15 dB/m. The length of the fiber is one of the main factors affecting signal quality. The second feature is a displacement of the whole spectra towards lower Raman wavelengths. The displacement is of the order of 6 cm^{-1} . For this reason each change of the length of the fiber requires new calibration of a spectrometer.

Fig. 1. High pressure Raman system with a fiber optics probe

Fig. 2. Measured Raman spectra of liquid cyclohexene with a probe fitted with a 1 m and 21 m long fiber. The insert shows enlarged area of a $2600\text{--}3200\text{ cm}^{-1}$ region

3. RAMAN MEASUREMENT CHALLENGES FOR HYDROCARBONS MULTICOMPONENT SYSTEM

Natural gas as a mixture of hydrocarbons often contains certain amount of heavier hydrocarbons (such as butane, pentane, hexane). Molar fraction of these components has a significant impact on thermodynamic properties of the whole mixture. Under certain conditions of pressure and temperature natural gas mixtures occurs as a two-phase system (liquid-vapor). Higher molar ratio of heavier hydrocarbons in a natural gas

mixture causes increase of a dew point temperature. As a result a range of conditions of pressure and temperature for two-phase system occurrence is much wider. Measurement of a natural gas composition in these circumstances using Raman spectroscopy is a technological challenge. In this case the main problem is an implementation of a correct Raman measurement, because in two-phase system liquid phase exists separately. Liquid phase mainly consists heavier hydrocarbons whereas in gas (vapor) phase composition there are mostly light hydrocarbons (i.e. methane, ethane). One of drawbacks can be changes in gas phase composition especially changes in signal (peak) intensity for the components whose molar fraction in the gas (vapor) phase significantly changed. Another is an emergence of a light mist or larger drops of liquid. The mist is reducing signal from individual component and increasing background [12]. Large dew drops condensate on walls of the measurement cell or gravity flow down to the bottom of cell. While laser light is focused precisely at a focusing point, at this point the liquid phase may not be found. Therefore a Raman spectrum as a result of measurement will not contain characteristic signals from heavier hydrocarbons. In order to avoid these problems initial composition and maximal pressures in which measurement were performed were chosen to ensure a single-phase system in the cell.

Real gas equations of a state were used to determine conditions of pressure and temperature for two-phase system occurrence for a given mixture. The most popular equations of state for phase equilibria determination are cubic equation of state (CEOS) of Soave–Redlich–Kwong (SRK EOS) [13] or Peng–Robinson (PR EOS) (Eq. 2) [14]:

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2} \quad (1)$$

where:

- p – denotes pressure,
- T – temperature in Kelvin,
- v – molar volume,
- R – ideal gas constant.

a , b and α – constants specific for a substance given as:

$$a = \frac{0.45724R^2T_c}{P_c} \quad (2)$$

$$b = \frac{0.07780RT_c}{P_c} \quad (3)$$

$$\alpha = (1 + \kappa(1 - T_r^{0.5}))^2 \quad (4)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

$$T_r = \frac{T}{T_c} \quad (6)$$

where:

ω – ancentric factor,

p, T_c – critical pressure and temperature.

Calculations of a phase equilibrium with their thermodynamic interpretation based on equations of the state such as SRK and PR EOS are presented in a large number of original articles and reviews [15–17].

Phase equilibrium phenomena is described by phase envelopes i.a. p - T plots. Phase envelope is composed of two bubble point and dew point curves connected at a critical point. This plot sets boundaries between gas (vapor) phase or a liquid phase and a two-phase system. Due to physicochemical properties of heavier hydrocarbons the area for the two-phase system occurs at higher temperatures. p - T plots for measured samples are presented in a Figure 3. Measurements described in this paper were performed in a temperature higher than 20°C. Therefore we are ensured that only single gaseous phase was present.

Fig. 3. Phase envelopes (p - T plots) for investigated samples compositions with measurements points. Measurements were made using a Peng–Robinson EOS

3.1. Concentration determination

For an initial determination of composition for given mixtures gas chromatography was used. The GC instrument was an Agilent Model 6890 Gas Chromatograph. The system consisted of the following components: 6-port sample valve with 0.25 cc sample loop, capillary split/splitless injector with EPC, porous polymer capillary column PLOT-Q (30 m $\times$ 0.53 mm $\times$ 0.4 micron), thermal conductivity detector (TCD) with EPC. Helium and air used for the GC and TCD were high purity (99.9995% v/v) gasses. Helium was used at a constant flow of 6.9 mL/min and another flow rates were maintained by using electronic flow control. An injection port was in a split mode (1:15 split ratio) and held at 250°C. A temperature program consisted of the oven being initially set to a temperature of 60°C and held for 5 min, and then ramped at 20°C/min to 200°C, where a temperature was held for 1 min, thereby resulting in total run time of 13 min. The TCD was held at 250°C. Concentrations for measured samples are shown in Table 1.

Table 1
Compositions of investigated gas mixtures

Component\Sample	75873 [%]	DHP7E [%]	47787 [%]	DHP7K [%]	L56GF [%]	75867 [%]
Methane	71.39	86.00	83.29	90.00	16.06	41.90
Ethane	4.09	6.00	1.90	4.00	4.01	5.10
Propane	2.00	4.00	1.90	3.00	0	3.06
Butane	0.90	1.50	0.44	1.00	0	0.92
Iso-Butane	0.92	1.50	0.47	1.00	0	0.91
Pentane	0	0	0	0	0	0
Iso-Pentane	0	0	0	0	0	0
Hexane	0	0	0	0	0	0
Nitrogen	20.70	1.00	12.00	1.00	79.93	48.11

3.2. Methodology of measurements

During measurements the Raman spectrometer was equipped with a 21 m fiber optic. Calibration of the spectrometer was performed using a liquid cyclohexane. In order to performed background subtraction dark current was collected and a signal from the cell with vacuum measured. Gases were delivered to the cell directly from bottles. Pressures was adjusted using a manually controlled regulator. Total measuring time for each pressure was 1000 s. Single frame was integrated over 4 s and average of 200 frames were collected. Exemplary recorded spectra for a gaseous sample is shown in a Figure 4.

With an increase of pressure total cross section for Raman scattering increases resulting in higher intensity of peaks. Insert in the Figure 4 shows enlarged area of a methane 2917 cm^{-1} peak. Shift of the peak maxima can be observed with a change of the pressure. Analysis of positions and areas of peaks for various samples is a main goal of studies presented in following paragraphs.

Fig. 4. Measured Raman spectra of a gaseous sample 75873 in various pressures (values marked in bar). The insert shows enlarged 2917 cm^{-1} methane peak. With the increase of the pressure intensity increases as well as shift towards lower values of the maxima can be observed

4. SIGNAL PROCESSING

A single peak can be described by values such as position, full width at half maximum (FWHM) and area. In this work we limit analysis to position and area. For an automated spectra analysis a dedicated application in the MATLAB software was created.

Characteristic values of peak are calculated in two steps:

1. Automatic detection of a peak localization based on Raman Peak Database.
2. Fitting all detected peaks using theoretical peak formula.

For a peak fitting as signal shape a Voigt distribution function was used [18]. This function is a convolution of a Gaussian and Lorentzian distribution with the same values for amplitudes and centers. The model is given by formula (7):

$$V(x; \sigma, \gamma) = \int_{-\infty}^{+\infty} G(x', \sigma) L(x - x'; \gamma) dx' \quad (7)$$

where:

- $L(x)$ – Lorentzian distribution,
- $G(x)$ – Gaussian distribution.

The Lorentz distribution describes a natural shape of a Raman peak whiles Gaussian distribution taken into account an apparatus broadening. For overlapping peaks the sum Voigt distributions was fitted. The best fit was obtained by minimizing an error function. This function is defined as a difference between set of theoretical values and set of observed values. The objective function can given by formula (8):

$$f_i = \sum_{j=1}^N \left(\frac{V_{ij}^{obs} - V_{ij}^{theor}}{V_{ij}^{obs}} \right) \quad (8)$$

where:

- V_{ij}^{theor} – theoretical value,
- V_{ij}^{obs} – observed value,
- N – total number of detected peaks.

5. RAMAN BAND ANALYSIS

In order to determine an impact of pressure and composition on collected spectra, series of measurement for six samples were performed using the high pressure setup described in the second paragraph. Compositions of measured samples were shown in the Table 1. Concentration for methane and nitrogen varies in broad range from 16 to 90% for methane and 1 to 79.93% for nitrogen. These two components are the main fraction in mixtures. Higher hydrocarbons are minor components. This reflects a natural gas composition for methane-rich and nitrogen-rich deposits as well as ensure the single phase system.

Because of high concentration the most prominent in spectra is a 2917 cm^{-1} methane band (e.g. Fig. 4). It was shown that change in pressures results in the peak shift as well as change of peak intensity. Another factor to be considered is an influence of concentration. In Figure 5 spectra for three samples and pressure 80 bar are shown. For a better presentation of signal for higher hydrocarbons the figure presents an enlarged region for wavenumbers $700\text{--}1100 \text{ cm}^{-1}$.

Analysis of pure spectra can give some qualitative information about behavior of a signal for various concentrations of hydrocarbons. Intensities of bands correspond to theoretical concentration of given molecule. For an ethane band concentration of ethane varies is a range from 1.9% to 6% and its intensity is increasing significantly.

The most interesting is a propane band. Samples 75 873 and 47 787 has similar theoretical concentration of propane 2.00% vs. 1.90%. Intensity of this band for both samples

is almost equal despite differences in concentration of others species. It may lead to conclusion that the influence of others species do not have significant influence on Raman intensity of a given band. For DHP7E one can observe stronger background than for other samples. It can be connected with a fluorescence due to a higher concentration of higher hydrocarbons. In presented region characteristic signal for each component is well separated. It makes process a peak detection easier and robust.

Fig. 5. Comparison of Raman spectra of three measured samples in a pressure 80 bar. Increase of a intensity with a increase of a theoretical concentration of a given type of molecule is clearly seen

In order to present qualitative influence of pressure, trends for position and intensity are shown in Figures 6–8. For better clarity results are separated into two graphs for three samples each. Linear fits are also added in order to better presentation. Figure 6 shows results for a methane 2917 cm^{-1} band. For the first set of samples (Fig. 6a and 6b) concentration of methane differ by the order of 10%. Both position and area of the peak changes linearly over the change of pressure. In the case of position, slopes of fits are similar, only small shifts of intercepts are visible.

For an area also difference in slopes occur. For next set of samples (Fig. 6c and 6d) concentration of methane varies in bigger range, from a 16.06% to 90.00 % this reflects in significant difference in trends' slopes for area dependence (Fig. 6c). In the case of shift for a sample 75 867 trend has intercept differ significantly from other samples while slope is similar.

In similar manner we compare results for a ethane 994 cm^{-1} band (Fig. 7). Position of bands for a 75 867 and DHP7E has similar slope and intercept to each other despite

different concentration of ethane as well as other species. Position of band for the sample 47 787 in the case of a lower pressure differ significantly from high pressure resulting in prominent impact on the trend. The affect of the pressure on peak position is lower than for a methane line shown in Figure 7. In the case of sample DHP7K the position is shifted towards higher values. The area of peaks increases linearly with an increase of pressure

Fig. 6. Peak position and area for methane 2917 cm⁻¹ band with respect to pressure

Fig. 7. Peak position and area with respect to pressure for a ethane 994 cm⁻¹

Clearly area dependence corresponds to concentrations. Next set of samples (Fig. 7c and 7d) has similar concentration of ethane it results is similar peak area values, nevertheless position trend differ in both intercepts and slopes. This can be connected with a influence of other components.

Nitrogen band analysis is shown in the Figure 8. Similar to a methane its concentration in measured samples varies in a wide range from a 1% to a 79.93%. It is reflected in area dependences. For higher concentrations slopes are bigger. Position of a given band changes linearly with a pressure. However, concentration dependence is not straightforward e.g. samples DHP7E and DHP7K have the same nitrogen concentration but the slope of trends differ in signs. Samples 75 873 and DHP7E have the similar values of position despite different concentration.

Fig. 8. Peak position and area with respect to pressure for a nitrogen 2331 cm⁻¹. The positions and area of peaks changes linearly with a increase of pressure

Behavior of position for this band and for ethane we can conclude that influence of other components is not straightforward.

To clarify influence of composition in the Figure 9 are presented concentration dependences of position (left side panels) and area (rights side panels) for a chooses pressure of 80 bar. One can see that positions and concentration do not have linear relationship. In can be clearly seen especially for a panel (c). For a samples with an ethane concentration close to 4% position varies significantly. Therefore only reason for difference in position is an impact of other components. In contrast peak areas changes almost linearly with the increase of concentration. We can conclude that in this case interaction with other components has only minor effect on area.

Fig. 9. Peak position and area with respect to concentration of given component for methane 2917 cm^{-1} , ethane 994 cm^{-1} and nitrogen 2331 cm^{-1} lines for a pressure 80 bar. Area changes linearly with a change of a concentration while position do not follow any dependence

6. CONCLUSIONS

This preliminary analysis have shown that position and area of a Raman band are influenced by both pressure and composition of measured samples. The pressure impose a linear change of a position of a given Raman band. The value as well as a sign of the slope of this trend depends on composition. However, the influence of other components is not straightforward. Preformed analysis gave only qualitative description of this behavior. In contrast peak area is linearly changing with a both increase of the pressure and the concentration of a given component.

In a perspective based on studies of bands' intensities one can determined a composition of measured sample. In order to resolve this problem machine learning methods are promising, especially Artificial Neural Networks with complex topology. However,

those kind of analysis require at least 20–30 recorded reference spectra to represent the specific solution space in order to obtain robust results. Furthermore the construction of ANN structure using limited training data set is very complicated and laborious process. To resolve this problem the fully automated method based on nature-inspired heuristic optimization algorithms modified for a narrow domain of a Raman spectra analysis will be developed.

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