Determination of Methanol Content in Hydrate Inhibitor Solutions Using Raman Spectroscopy

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Abstract. The use of methanol as an inhibitor of hydrate formation in the fields of the Far North is fraught with environmental risks and a threat to the health of personnel. Therefore, an urgent task is to find an analytical method for determining the methanol content in water-methanol solutions instead of the areometric method. One of such methods is Raman spectroscopy. In this work, water-methanol solutions used at the Otradninsky gas-condensate field are investigated. For the quantitative determination of the inhibitor content in water-methanol solutions samples, the stretching vibration bands of the CH groups of methanol molecules was selected, the intensity of which monotonously increases with increasing alcohol concentration. A comparison of the mass concentrations of methanol obtained by different methods showed that the presence of salts in water methanol solutions leads to an underestimation of the alcohol content. This entails an excessive consumption of inhibitors and an increase in the cost of gas companies to purchase and transport methanol.

1. Introduction

The exploitation of gas and gas condensate fields in the zone of permafrost almost generally is complicated by the formation and deposition of natural gas hydrates. At the fields of the Leno-Tunguska oil and gas province (LT OGP), the formation of hydrates in stratum manifold and slit columns is most often due to low stratum temperatures and pressures [1]. Currently, in these fields, the only way to struggle hydrate formation is the injection of methanol and its solutions into the slit [2, 3]. Methanol refers to traditional thermodynamic inhibitors that displace three-phase «gas-water-hydrate» equilibrium towards low temperatures [4-6].

The general use of methanol, especially in the gas industry of the Far North, is due to its relatively low cost compared to other inhibitors of hydrate formation (glycols, surfactants, water-soluble polymeric compositions). It is also the highest among the known inhibitors with antihydrate activity, which remains even at low temperatures, a very low freezing point of concentrated solutions of methanol and their extremely low viscosity at temperatures below –50 °C [4, 7].

However, methanol belongs to the category of highly dangerous substances that can cause great damage to the environment and the health of personnel [8, 9]. Pollution of the environment with methanol can occur as a result of its accidental releases or spills during the production, transportation and use of this substance. The maximum permissible concentration of methanol in water used for household drinking water is 3 mg/l [10]. The period of environmental objects restoration is not less than 30 years after complete disposal of the source of harmful effects [11]. When ingested, methanol
causes blindness and death due to damage to the central nervous and cardiovascular systems. Severe poisoning accompanied by blindness causes 5-10 cm³ of pure methanol, and the lethal dose of methanol is 30 cm³. In the air of the working zone, the maximum permissible concentration of methanol is 5 mg/m³. Therefore, personal protective equipment should be used [7, 12, 13] during working with methanol. Thus, the use of methanol in production is potentially dangerous to the health of personnel and the environment, which creates an additional load for management personnel in ensuring industrial and environmental safety during the operation of fields and gas pipelines.

In connection with the increase of the cost of production and delivery of methanol in the fields of the Far North, there is a practice of repeated use of the inhibitor by its regeneration. It allows to reduce environmental risks with transportation and storage of methanol, as well as reduce the cost of its purchase. However, the inhibitor before and after its purification contains salts of produced water, which change the density of the solution, therefore the use of the areometric method for determining the content of methanol in water-methanol solution is not accurate enough. In this regard, such an analytical method is needed to control the methanol content in water-methanol solution, which would ensure simplicity of sample preparation, expressivity and selectivity in the analysis of solutions with complex mineral composition, noncontact with breakdown for the safe operation of personnel. As such a method, the method of Raman spectroscopy can be used. This method allows contactlessly in glass or plastic containers without complicated sample preparation and tamper opening to perform a series of analyzes [14, 15].

2. Objects and research methods
Samples of return water-methanol solution (samples 13, 14 and 15) were used in the work. They were taken from a geological separator at three different (permissible, working and optimal) operating modes of slit number 314-3 of the Otradinskiy gas-condensate field.

To determine the total mineralization of the dry residue of the water-methanol solution samples, the methods used was PND F 14.1:2:4.261-2010 [16]. The obtained dry residues were diluted with distilled water to a salinity of 300 mg/l to determine the content of cations and anions in the samples.

The quantitative determination of inorganic ions in the samples was carried out according to PND F 14.1:2:4.167-2000 [17] and PND F 14.1:2:4.157-99 [18]. The determination of bicarbonate ions was carried out by the method of volume titration [19]. Water-methanol solution sample densities were determined by the areometric method [20].

The spectra were recorded on the SENTERRA Raman Microscope Spectrometer R 200-L (Bruker, Germany) using the OPUS program. The Raman spectra of the light were excited by radiation from an argon laser with a wavelength of 532 nm. The Raman spectra were recorded in the range of 400-4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹, the accumulation time of one spectrum was 10 seconds. The quantitative evaluation of the methanol content in the sample was carried out using the quant 1 software algorithm. To construct a calibration curve, standard solutions were prepared with a methanol content of 60-90 % by weight in 5 % increments.

3. Results and discussion
The water-methanol solution samples contain inorganic salts of produced water discharged from the well. The water phases from all samples according to Sulin's classification [21] belong to the calcium chloride genetic type with a predominant content of sodium and chlorine ions (table 1).

With increase in the mineralization of solutions, the density of water-methanol solution increases, and the content of methanol in them decreases. To reveal the effect of inorganic salts on the determination of the methanol content in water-methanol solution samples, Raman spectroscopy was used.
Table 1. Density and ion content in water-methanol solution samples.

| Number of sample | 13   | 14   | 15   |
|------------------|------|------|------|
| Density, g/ml    | 0.854| 0.878| 0.883|
| The methanol content, % mass. | 77.67 | 67.54 | 65.29 |
| Cations          |      |      |      |
| Potassium K⁺      | 26.23| 58.68| 136.94|
| Sodium Na⁺        | 1745.04| 2276.50| 5104.98|
| Lithium Li⁺       | 6.06 | 6.26 | 3.37 |
| Magnesium Mg²⁺    | 109.09| 154.22| 246.32|
| Strontium Sr²⁺    | 2.56 | 0.00 | 7.15 |
| Calcium Ca²⁺      | 356.92| 559.97| 849.39|
| The sum of cations is, mg/l | 2245.91| 3055.64| 6348.15|
| Anions            |      |      |      |
| Chlorides Cl⁻     | 3127.37| 4074.02| 9232.26|
| Nitrite NO₃⁻      | 4.83 | 10.53| 17.25 |
| Sulfates SO₄²⁻     | 5.02 | 10.02| 13.46 |
| Nitrates NO₃⁻     | 1.23 | 0.00 | 4.63 |
| Fluorides F⁻      | 23.39| 28.60| 6.52 |
| Phosphates PO₄³⁻   | 4.92 | 0.00 | 10.10 |
| Hydrocarbonates HCO₃⁻ | 119.00| 581.20| 264.30|
| The sum of anions, mg/l | 3285.77| 4704.47| 9548.54|
| The amount of ions, mg/l | 5531.67| 7760.02| 15896.54|
| Genetic type of water | calcium chloride. a subgroup of sodium |

Figure 1. Raman spectra of methanol (1) and samples of water-methanol solution Number 15 (2).

The Raman spectrum of 98 % methanol (figure 1, curve 1) consists of the following oscillation frequency: in the frequency range 1000-1100 cm⁻¹, the stretching vibrations of the C–O bond are observed; in the region of 1400-1600 cm⁻¹, the bending vibrations of the CH₃ and CH₂ groups; in the range of 2750-3100 cm⁻¹ - stretching vibrations of the CH-groups, and in the range of 3100-3600 cm⁻¹ - a wide band of stretching vibrations of the OH-groups of water and methanol. Curve 2 corresponds to the Raman spectrum of the sample water-methanol solution №15. The water-methanol solution sample contains complex ions (nitrates, sulfates, phosphates), which have their own vibrational lines in the region of 500-1700 cm⁻¹ [22-24]. It can be seen that the stretching vibration bands of the C–O bond in the frequency range 1000-1100 cm⁻¹ water-methanol solution overlap the bands of complex ions, since the intensities of their bands are small due to the low concentration of these ions (table 1). In the Raman spectrum of the water-methanol solution sample, a change is observed in the shape and position of the band of stretching vibrations of OH groups in the region of 3100-3600 cm⁻¹. Thus, the
band maximum shifted from 3353 cm\(^{-1}\) (curve 1) to 3430 cm\(^{-1}\) (curve 2). Such a change occurs due to the content in the water-methanol solution sample of simple ions (Cl\(^-\), I\(^-\), B\(^-\), Na\(^+\), K\(^+\)) that haven’t their own vibrational lines [25, 26]. Therefore, for quantitative determination of the inhibitor content in samples of water-methanol solutions, band-sided oscillations of the methanol CH groups were selected, which monotonously increases with increasing of alcohol concentration [17].

For making a calibration curve of the bands intensity of the CH groups valent oscillations in the frequency range 2750-3100 cm\(^{-1}\), they were compared with actual concentrations of the prepared standard solutions. The dependence obtained is approximated by a linear function (correlation coefficient 0.991) presented in figure 2, where \(x\) is real value of methanol concentration, \(y\) is the instrument reading. Then, according to the bands intensity of the CH groups stretching vibrations in the frequency range 2750-3100 cm\(^{-1}\), methanol concentrations were found in water-methanol solution samples.

![Calibration curve](image)

**Figure 2.** Calibration curve.

The table 2 shows the results of the methanol mass concentrations determining in water-methanol solution samples obtained by the areometric method and based on Raman spectra.

**Table 2.** The methanol content in water-methanol solution samples.

| Number of sample | 13   | 14   | 15   |
|------------------|------|------|------|
| Mineralization, mg/l | 5531.67 | 7760.00 | 15896.54 |
| Density of water-methanol solution, g/ml | 0.854 | 0.878 | 0.883 |
| Mass fraction of methanol, % mass | 77.67 | 67.54 | 65.29 |
| Determination by the areometric method | 77.67 | 67.54 | 65.29 |
| Determination from the intensity of the stretching vibration bands of CH groups in the frequency range 2750-3100 cm\(^{-1}\) | 83.12 | 79.11 | 79.15 |
| Determination of the intensity of bands of stretching vibrations of CO-groups in the frequency range 1000-1100 cm\(^{-1}\) | 84.39 | 81.95 | 82.26 |

In water-methanol solution samples, with increasing of mineralization, the density of solutions increases and the methanol content decreases (table 2). Concentrations of methanol, found from the Raman spectra are higher than those determined by the areometric method. Apparently, the presence of dissolved salts in water-methanol solution samples leads to an overestimation of the density and, consequently, to an underestimation of the methanol content. Concentrations of methanol found from the intensity of the C–O stretching vibration bands of the frequency range 1000-1100 cm\(^{-1}\) are higher than those determined from the intensity of the stretching vibration bands of the CH groups in the frequency range of 2750-3100 cm\(^{-1}\). This is apparently due to an increase in the intensity of the C–O
bond band due to the overlapping of the peaks of the complex ions with the peaks of methanol in this area.

4. Conclusions
Thus, the presence of dissolved salts in samples of water-methanol solution leads to the underestimated value of the methanol concentration when determining its content using areometric method. This entails an excessive consumption of inhibitors and an increase in the cost of gas companies to purchase and transport methanol. Therefore, it is necessary to use other additional analytical methods to determine the methanol content in water-methanol solution samples more accurately. As shown in this work, one of such methods can be Raman spectroscopy.

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