

## UNIFIED GAS CHROMATOGRAPHIC METHOD FOR DETERMINATION OF METHANOL IN NATURAL GAS AND RELATED PRODUCTS

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### Abstract

Method for determination of methanol traces in natural gas and the corresponding semi-products is developed. Method is based on pre-concentration of methanol from natural gas samples by passing it through two glasses containing water solution of sodium sulphate. Then the content of methanol was determined in the solutions obtained by analysis of their equilibrium gas phase at 60 °C. For this purpose, gas chromatography with a packed column filled with a modified polymer adsorbent was applied. When probe containers with a volume of 300 ml are applied, the method developed allows to determine methanol in natural gas in the range 0.010-5 mg l<sup>-1</sup> ( $1.3 \times 10^{-6} - 6.5 \times 10^{-4}$  vol%). This high sensitivity of the method is reached due to the pre-concentration of the analyte. Partial separation of methanol from the matrix components allows to decrease partial superposition of chromatographic peaks of methanol and iso-butane that improves correctness of the analysis and decreases the detection limit. With the corresponding changes in the sample preparation procedures, the method developed may be used for analysis of various technological semi-products (such as non-stable and stable condensate), as well as wastes.

*Keywords: natural gas, sewage, methanol, gas chromatography, head-space analysis.*

### 1. Introduction

Natural gas is an important fuel and raw material for modern industry, as well as a valuable export product of Russia. As a rule, the chromatographic methods developed allow to determine hydrocarbon components of the gas, together with some inorganic gases (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, Ar) (for review, see [1]). Meanwhile, methanol is widely used during production and processing of natural gas at main gas fields of Russia. Presently, application of methanol grows up because of more intensive exploitation of gas-condensate fields containing quite a lot of hydrocarbons heavier than methane [2]. Due to technology requirements, permanent control of concentration of methanol in semi-finished natural gas products is necessary. For this purpose, methods of classical chemical analysis are used. Before transporting, main part of methanol separates from the gas to be used further. However, one must control the rest traces of methanol in transporting gas because of its high toxicity. Then, methanol influences the value of Wobbe parameter and the calorific value of the gas, thus changing the price of the product. The methods of "wet" chemistry are not suitable for the determination of traces of methanol in natural gas because of their low sensitivity. The most appropriate method for solution of the problem is gas chromatography.

Up to date, there is a standardised method of the determination of methanol traces in liquefied gases [3]. According to the international standard [4], methanol is determined by direct analysis of the natural gas taken from its flow. However, this method is of a very limited applicability when the gas samples are transported to analytical laboratory in the special probe containers. If most widespread in former USSR countries probe containers made of stainless steel are used, significant part of methanol is being adsorbed on their walls during transportation (up to 10%). In this case, direct analysis of the gas phase only results to a systematically decreased values. Therefore, one had to develop a method that could be used both for the direct determination of methanol in a flow of natural gas and for error-free analysis of the gas kept in probe containers. Ideally, after slight modifications the same

method has to be suitable for the determination of methanol in semi-products of a gas industry, as well as in wastes.

## 2. Experimental

Reagents (except gases) of “chemically pure” grade and electrolytic hydrogen (“technical”, grade A and B) were used. The purity of the reagents towards methanol was very high (the values of control experiments were practically zero).

Computer-controlled gas chromatograph “Varian 3600” with a flame-ionization detector was used. The chromatograph was equipped with a stainless steel chromatographic column (length 1 m, inner diameter 2 mm). The column was filled with a sorbent Porapack R, modified with 5% PEG 20M. Other parameters of chromatographic determination of methanol are given in Table 1.

**Table 1.** Parameters of chromatographic determination of methanol.

Parameter	Values
Flow rate of transporting gas (hydrogen), ml min <sup>-1</sup>	30
Initial temperature of column thermostat, °C (hold time, c)	60 (4)
Heating rate of column thermostat, °C min <sup>-1</sup>	25
Final temperature of column thermostat, °C (hold time, c)	210 (10)
Temperature of vaporizer, °C	200
Temperature of detector, °C	250
Volume of sample, mm <sup>3</sup>	500

## 3. Results and discussion

For the determination of methanol in processed natural gas, content of the 300-ml probe container is passed through 2 glasses filled with a 12% solution of sodium sulphate (total volume of solutions is 40-50 ml). During this procedure, volume of the gas is measured as well. When container is empty, it is filled with 30 ml of the sodium sulphate solution and is shaken vigorously. Each of 3 solutions obtained is analysed separately (15 ml of each solution was taken for analysis).

For preparation of the calibration graph, solutions containing 5-200 mg l<sup>-1</sup> of methanol were prepared (in 12% aqueous solution of sodium sulphate). The methanol solutions were kept in a thermostat at 60 °C for 1 h. Five hundred mm<sup>3</sup> of the equilibrium vapour phase formed was taken for analysis by a microcylinder. The measurements were conducted under conditions given in Table 1. Determination of methanol in the analysed solutions was conducted under the same procedure. Repeatability of the parallel measurements was in the region 3-10% even for n=3. Unfortunately, we could not check accuracy of our method neither by analysis of the standard samples, not by the standard addition technique. The corresponding samples are quite unstable, mainly because of easy sorption of methanol traces on the walls of vessels used for their storage. As one can see from Table 2, total content of methanol in the natural gas sample analysed is 1.12 mg l<sup>-1</sup> (1.46x10<sup>-4</sup> vol.%). The method developed allows to determine methanol in the natural gas samples in the range 0.010-5 mg l<sup>-1</sup> (1.3x10<sup>-6</sup> – 6.5x10<sup>-4</sup> vol%). For P=0.95, reproducibility of the method is about 15%. Detection limit of the method calculated according to 2σ-criterium is 0.005 mg l<sup>-1</sup> (6x10<sup>-7</sup> vol%).

**Table 2.** Determination of methanol in natural gas and in components of non-stable condensate ( $\text{mg l}^{-1}$ ).

Sample	Gaseous phase (volume, l)	Stable condensate (volume, l)	Water layer (volume, l)	Adsorbed on the container surface*	Total content
Natural gas	1.09 (18.0)	--	--	0.03	1.12
Non-stable condensate 1	1.34 (8.0)	86.6 (0.0594)	30.3 (0.0504)	12.7	--
Non-stable condensate 2	12.8 (30.1)	2130 (0.0446)	--	49.0	--

\*Recalculated to the total sample volume.

The same method was used for analysis of two samples of non-stable condensate (a product formed during processing of original natural gas). The samples were taken from different points of the technological line. Together with the gaseous phase, these samples contained a liquid hydrocarbon fracture (stable condensate), as well as a water phase (sample 1).

In the water phase methanol was determined by the procedure discussed. In order to measure methanol in the stable condensate, 10 ml of it was shaken for 30 s with 16 ml of water. Then the phases were separated and 15 ml of water were used for the analysis as described above. During extraction, light hydrocarbons partially dissolve in the solution of sodium sulphate. As one can see from the chromatogram (see Fig. 1), peak of iso-butane is in the near of the methanol peak. Therefore, high concentrations of iso-butane in the sample result to partial superimposition of the peaks that, in turn, worsens the determination of methanol traces. Correctness of the analysis of stable condensate was checked by the standard addition techniques with very good results. As one can see from Table 2, content of methanol in the non-stable condensate depends greatly upon the sampling place.

Further, we plan to compare the method developed with the method [4], and to extend our method towards analysis of methanol-containing wastes.

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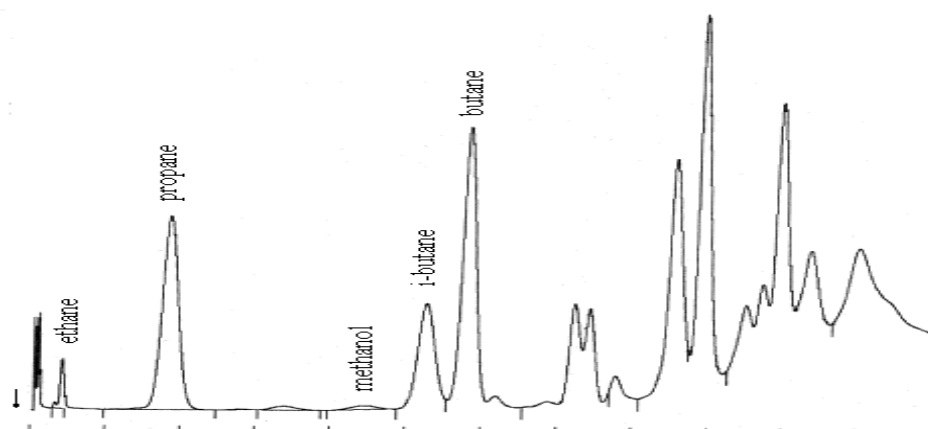


Fig. 1. Typical chromatogram of a sodium sulphate solution after its equilibration with a stable condensate

## References

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