

Measurement of molecular humidity and oxygen in natural gas

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Abstract. The coulometric method of measuring humidity and oxygen on the basis of an electrolytic cell with a film of phosphorus oxide for continuous analysis of natural gas in pipelines of its transportation is considered. On the basis of the method the device is implemented that is designed to determine the mass concentration of water vapor $\text{mg}\cdot\text{m}^{-3}$, the dew point temperature in water at absolute pressure of the analyzed natural gas, as well as the volume fraction of oxygen. Measurements of the mass concentration of water vapor is from 1 to 100 $\text{mg}\cdot\text{m}^{-3}$, and the volume fraction of oxygen is from 10 to 10000 ppm at a gas pressure from 0.16 to 25 MPa. The main reduced measurement inaccuracy is from 3 to 6 %.

1. Introduction

Natural gas used as fuel and industrial raw materials in the production of various organic substances. Water vapor contained in the gas can condense under certain conditions and during its transportation in the pipeline (especially in winter conditions) leads to the formation of ice deposits, which leads to disruption of gas transportation systems. To solve the problem of humidity control in the gas, there are a number of methods along with which it is possible to distinguish the coulometric method.

2. Coulometry of gases

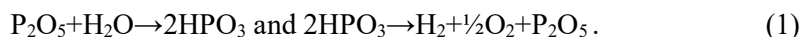
The coulometric method is based on the principle of absorption of moisture by the sorbent (a film of the substance of the sensing element) at a certain dosed flow of the analyzed gas, as well as electrolytic decomposition of this moisture into hydrogen and oxygen. The amount of moisture in the gas is determined by the electric current of the electrolysis process and the amount of gas flow.

The implementation of the coulometric method is carried out by means of a moisture electrolytic cell with a sensitive element (SE) from the sorbent film when a constant flow of the analyzed gas is passed through the coulometric electrolytic cell (CEC) [1, 2].

In SE cells GEC1 as a sorbent is used, the film partially hydrated phosphoric anhydride P_2O_5 . A direct current (DC) voltage is applied to the cell electrodes. In SE cells are continuously taking place two processes: the almost complete absorption of moisture with a film of phosphoric anhydride P_2O_5



with the formation of phosphoric acid and electrolytic decomposition of water into hydrogen and oxygen with regeneration of phosphoric anhydride according to the reactions:



At a constant gas flow rate according to Faraday's law, the value of the electrolysis current is a measure of the moisture content of the gas. In this case, all the moisture in the flow of the analyzed gas is practically absorbed by the SE cell. The absorption of moisture and its electrolysis by the film of phosphorus oxide of SE cell occurs when an external DC voltage is applied to its electrodes, the value of which exceeds the decomposition potential of water. When operating in continuous operation, such a coulometric electrolytic cell performs electrolytic regeneration of phosphorus oxide SE, which provides a long service life of the cell.

3. The system of preliminary gas treatment

For pre-purification of natural gas from mechanical particles, droplet particles of oils, hydrogen sulfide, ethylene glycol and other organic compounds interacting with phosphorus anhydride SE in the measuring device implemented gas treatment system (GTS) (Figure 1).

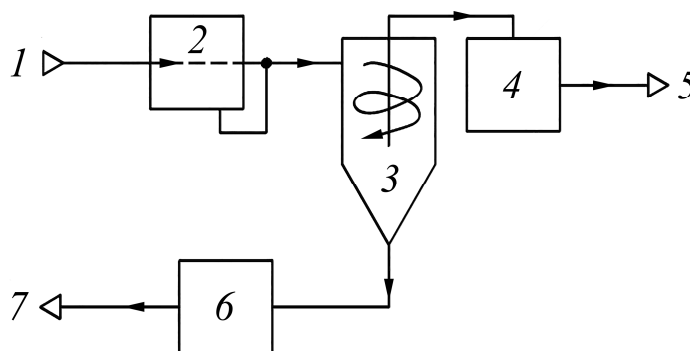


Figure 1. Block diagram of the primary gas flow preparation system GTS: 1 – gas input; 2 – pressure stabilizer; 3 – dynamic filter; 4 – fine filter; 5 – pure gas outlet; 6 – throttle; 7 – outlet to the collector drainage.

The work of the GTS (Figure 1) is to reduce the analyzed gas pressure stabilizer 2 and its purification from impurities. Block 2 provides an accurate output gas pressure within a predetermined value of $\pm 30\%$, adjusts the output pressure and reduces the influence of sorption processes in the volume of the gas path. The gas after the gas pressure stabilizer 2 enters the dynamic filter 3, where due to centrifugal forces it is cleaned from mechanical and droplet particles, and is divided into two streams. The purified gas through the filter 3 enters the fine filter 4, where heavy hydrocarbons and compressor oil vapor are removed. Further, the purified gas stream 5 is fed to the input of the analyzer (Figure 2). The second part of the impurity flow through the choke 6 is diverted to the drainage line 7 of the collector. This impurity part of the gas comes out at a flow rate of up to $2000 \text{ cm}^3 \cdot \text{min}^{-1}$ (at atmospheric pressure).

The lighter components of natural gas from the dynamic filter 3 are lifted up by a small flow through the filter 4 with a nominal flow rate of $50 \text{ cm}^3 \cdot \text{min}^{-1}$, which then enters the gas analyzer input into the first CEC1.

In blocks 2 and 3 and 4 of the primary gas flow preparation system (Figure 1) used not sorption thin organic coatings based on fluoropolymers and Parylene F, are applied to the inner surface elements and nodes from an active gas phase in a low vacuum [3, 4]. The coating thickness is $100 \div 1000 \text{ nm}$. The wettability angle of the surface on the water of such coatings is not less than 95° degrees.

4. Gas analyzer of moisture and oxygen

The gas analyzer implemented on the basis of a coulometric electrolytic cell includes a gas treatment system GTS unit and the analyzer of molecular water and oxygen content (Figure 2). Here, natural gas is supplied to the inlet A of the GTS (Figure 1) block where it is divided into two streams: the separation of moisture from impurities and the gas flow for molecular analysis at the inlet C.

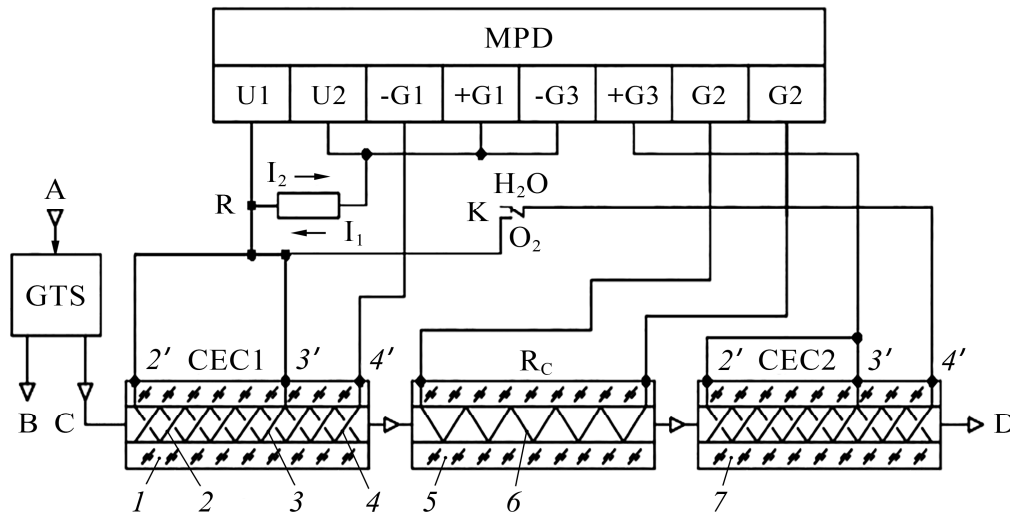


Figure 2. Block diagram of the gas analyzer: GTS – gas treatment system; MPD – microprocessor device; U1 and U2 – input information of ΔI in the microprocessor; G1 and G3 – direct current sources; G2 – alternating current source; R – precision resistor; K – measuring mode switch; R_c – reactor; CEC1 and CEC2 – coulometric electrolytic cell; 1, 5 and 7 – glass tube; 2', 3' and 4' – working, control and common electrodes, respectively; 6 – platinum coil heater.

Next, the analyzed natural gas with a constant flow rate passes through the first coulometric electrolytic cell CEC1 with an internal diameter of the channel 0.8 mm, and then through the R_c reactor enters the second same coulometric electrolytic cell CEC2. In the channel of the cylindrical glass tube 1 cell A1 electrodes are placed, made in the form of non-contacting spirals of radium: working 2', control 3' and total 4' contact electrodes. On the inner surface of the tube channel 1 is an electrode 3 with a film of sorbent-partially hydrated phosphorus oxide P_2O_5 , which has a high sorption capacity of water molecules.

Under normal operating conditions, the moisture in the natural gas is absorbed by the SE sorbent film in cell CEC1 to the electrodes of which a DC source G1 is connected. The applied constant voltage exceeds the water decomposition potential. Simultaneously with the absorption of moisture in the film, a continuous electrolysis occurs with the formation of oxygen and hydrogen according to the reactions (1). In the steady-state mode, the amount of absorbed and decomposed moisture per unit time is equal and, consequently, the electrolysis current I_1 of the coulometric electrolytic cell CEC1 is a measure of the moisture content in the natural gas and is determined:

$$I_1 = B_{H_2O} \cdot Q \cdot P_0 / K_1 \cdot T, \quad (2)$$

where I_1 – current electrolysis of water in GEC1, mA; B_{O_2} – volume fraction of moisture in the analyzed gas, ppm; Q – flow rate of the analyzed gas, $\text{cm}^3 \cdot \text{min}^{-1}$; P_0 – barometric pressure, kPa; T – ambient temperature, K; K_1 – normalizing coefficient due to the choice of units of physical quantities in the measurement of moisture, $\text{ppm cm}^3 \cdot \text{kPa} \cdot \text{K}^{-1} \cdot \text{min}^{-1} \cdot \text{mA}^{-1}$.

The current I_1 flows in this direction through the precision resistor R , which creates a voltage drop recorded by the microprocessor device MPD. From the outlet of the first cell CEC1, the hydrogen, oxygen and dry natural gas formed enter the reactor R_c . In the cylindrical channel of the

glass tube 5 of the reactor R_C , a platinum spiral of the heater 6 is placed, connected to the alternating current source G2. Under the action of the heated catalyst 6, the reaction of the interaction of the micro-impurities of oxygen with hydrogen with the formation of water molecules takes place.

Then natural gas is obtained in the catalyst micro preemies moisture enters the second similar to the first cell of the CEC2 in a glass tube 7 with the inner channel diameter of 4.0 mm. Electrodes of the cell are made of platinum-iridium wire and connected to the constant current source G3. Through the output D, the output of the analyzed gas at atmospheric pressure is provided.

5. Experimental result

In the steady-state operation of the gas analyzer (Figure 2) the amount of moisture absorbed and decomposed per unit time is equal. In this case, the electrolysis current of the coulometric electrolytic cell is a measure of the total volume fraction of moisture in the natural gas to the CEC1 cell, and moisture additionally formed in the R_C reactor due to the interaction of natural gas oxygen to GEC1 and the resulting trace oxygen with hydrogen.

The electrolysis currents of I_1 cell CEC1 and the electrolysis current of I_2 cell CEC2 in the mode of measuring the volume fraction of oxygen O_2 flow through the precision resistor R in opposite directions, creating a difference current $\Delta I = I_2 - I_1$. The value of the current ΔI is due to the current of electrolysis of moisture, which was formed in the reactor R_C in interaction with the oxygen of the analyzed natural gas. The difference current ΔI is a measure of the oxygen concentration in natural gas in the mode of measuring the volume fraction of oxygen O_2 and is determined by the formula:

$$\Delta I = I_2 - I_1 = B_{O_2} \cdot Q \cdot P / K_2 \cdot T, \quad (3)$$

where I_1 – current electrolysis of water in GEC1, mA; B_{O_2} – volume fraction of moisture in the analyzed gas, ppm; Q – flow rate of the analyzed gas, $\text{cm}^3 \cdot \text{min}^{-1}$; P – barometric pressure, kPa; T – ambient temperature, K; K_1 – normalizing coefficient due to the choice of units of physical quantities in the measurement of moisture, $\text{ppm cm}^3 \cdot \text{kPa} \cdot \text{K}^{-1} \cdot \text{min}^{-1} \cdot \text{mA}^{-1}$.

Table 1 shows the results of experimental studies of the molecular moisture content in natural gas using the element-by-element method of verification.

Table 1. Experimental data of volume fraction of moisture in natural gas (VFM)

№	Absolute gas pressure, MPa	I_1 , mA	VFM, ppm	VFM, mg/m^3	$^{\circ}S_{t,r}$
1	2.2	4483	670.6	503	11.9
2	2.6	2505	374.7	281	5.8
3	3.0	137.7	20.6	15.5	-25.0
4	3.4	474.6	71.0	53.3	-11.3
5	3.8	4171	623.9	468	10.7
6	4.2	1473	220.3	165	4.3
7	4.6	35.7	5.3	3.98	-32.7
8	5.0	846.4	126.6	95.0	-0.6
9	5.4	259.9	38.8	29.1	-13.0
10	5.8	71.24	10.7	8.03	-24.7
11	6.2	19.99	3.0	2.25	-34.8

The volume fraction of moisture and oxygen is determined after appropriate transformations by the microprocessor device and displayed on a digital display indicating the type of gas (H_2O or O_2).

The performance of the system sample gas is provided at pressures up to 25 MPa. The dew point temperature of the moisture $^{\circ}S_{t,r}$ is from minus 69.4 to plus 31.3 $^{\circ}C$ with the basic absolute error ± 2 $^{\circ}C$, and in the measurement range from minus 69.4 $^{\circ}C$ to minus 20 $^{\circ}C$ is ± 1.5 $^{\circ}C$.

Performed analyzer in ppm at atmospheric ambient pressure values $^{\circ}S_{t,r}$ when the pressure in pipeline transport. The deviation of the real gas humidity from the humidity of its ideal model increases with decreasing temperature and increasing pressure [5].

Figure 3 shows graphs of experimental calibration data of the gas analyzer when measuring the concentration of oxygen N_{O_2} (curve 1) in natural gas, using the element-by-element method of verification and the corresponding difference current ΔI (curve 2) in the precision resistor R of the measuring circuit (Figure 2).

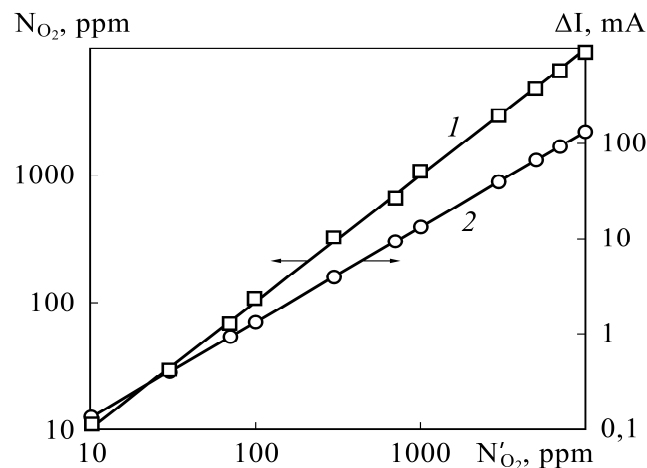


Figure 3. Graphs of gas analyzer calibration data for measurement of oxygen N_{O_2} (1) concentration in natural gas and difference current ΔI (2) in the precision resistor.

6. Conclusion

The method of coulometric electrolytic cell is implemented when creating a gas analyzer of moisture and oxygen of natural gas, which is designed to measure: the mass concentration of water vapor mg/m^3 , the dew point temperature of the water at the absolute pressure of the analyzed gas, as well as the volume fraction of oxygen. The gas analyzer in the hygrometer mode measures the mass concentration of water vapor from 1 to $100 \text{ mg} \cdot \text{m}^{-3}$, the volume fraction of oxygen from 10 to 10000 ppm at a gas pressure from 0.16 to 25 MPa. The main reduced error (to the upper value of the measurement range) from ± 4 to ± 6 %. The dew point temperature of the moisture $^{\circ}S_{t,r}$ is from minus 69.4 to plus 31.3 $^{\circ}\text{C}$ with the basic absolute error ± 2 $^{\circ}\text{C}$, and in the measurement range from minus 69.4 $^{\circ}\text{C}$ to minus 20 $^{\circ}\text{C}$ is ± 1.5 $^{\circ}\text{C}$.

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