A STUDY OF ELECTROCHEMICAL CONVERTER FOR A SYSTEM MEASURING THE CONCENTRATION OF HARMFUL SUBSTANCES IN GAS MIXTURES OF THE PAPER

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Abstract---*The paper presents the results of the development and study of the metrological characteristics of measuring transducers of the direct coulometry method — electrochemical cells of direct oxidation of the analyte with a fixed value of its potential on the working electrode, which is used as a gas diffusion hydrophobized electrode. The chosen measurement method provides selective determination of the concentration of almost any substance in the gas mixture by studying and selecting the redox potential of the analyte. The instrument implementation of the coulometric method of gas analysis of the content of toxic substances in industrial process media was carried out, which ensures high efficiency and reliability of the results of continuous monitoring of the composition of natural gas. The device and operation of gas diffusion hydrophobized electrochemical cells of automatic gas analyzers are described.*

Keywords--- *gas analysis, coulometric method, electrochemical cell, gas analytical technique.*

I. INTRODUCTION

In accordance with the international program of the global environmental monitoring system, it is necessary to ensure the control of 145 substances and 25 of their combinations in the air.

An introduction of new technological processes and the necessity for processing a significant amount of information for making managerial decisions in the industries of various industries require the creation of a qualitatively new generation of analytical instruments and complex measuring systems based on modern physicochemical principles of control and management using the latest achievements of science and technology.

In this regard, the complex scientific and technical task of developing new domestic and automatic gas analyzers for determining the concentration of harmful substances in natural gas and the metrological support system for gas analysis is considered to be crucial issue of today.

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II. THE STUDY OF COULOMETRIC METHODS OF ANALYSIS FOR ANALYTICAL CONTROL OF THE CONTENT OF HARMFUL SUBSTANCES IN GAS MIXTURES

Boulder tupe coulometric cell

To develop an automatic gas analyzer of an electrochemical type intended for continuous monitoring of the content of harmful substances in natural gas, the basic laws of direct and indirect coulometry were studied [1, 2].

When determining the concentration of mercaptans by coulometric titration, we used coulometric cells of a non-flow type with internal generation of titrant [3]. In fig. 1 shows a coulometric bubble cell.

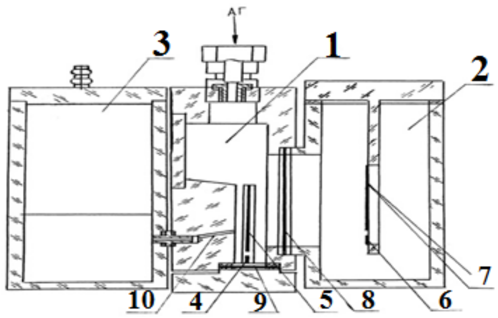

Fig 1: Coulometric cell of bubbled type:

1- measuring chamber; 2- auxiliary camera; 3- recharge chamber; 4-generator working electrode; 5-indicator working electrode; 6-generator auxiliary electrode; 7-indicator auxiliary electrode; 8 - ion exchange membrane; 9- polymer membrane; 10 - micro union.

It consists of three chambers: measuring 1, auxiliary 2 and make-up chamber 3. In measuring chamber 1 there are working electrodes (generator and indicator 5) installed on one frame, located at a short distance from each other and made of platinum mesh. Moreover, each of them is connected to its auxiliary electrode 6 and 7 located in the auxiliary chamber 2. The electrodes are discharged onto the upper part of the electrochemical cell (ECC). The findings are marked with the corresponding engraving: generator electrodes (+/- G), indicator (+/- I). Electrolytic contact between the measuring and auxiliary chambers is carried out through an 8-type MK-40 ion-exchange membrane. In the lower part of the measuring chamber 1, a membrane 9 is located on the path of the analyzed gas flow, made of a polymer material of a certain porosity to act on the flow of the analyzed gas in order to maximize its dissolution in the volume of the electrolyte. Due to the bubbling of the analyzed gas, intensive mixing of the electrolyte occurs in the measuring chamber. To increase the duration of the measurements, the measuring chamber 1 is connected to the make-up chamber 3 through the micro-nozzle 10. The analyzed gas is sucked into the ECC through the upper nozzle 11 and, breaking into small streams on the porous membrane 9, enters the measuring chamber 1. Citrate-phosphate buffer was used as the electrolyte with pH = 8, containing 120 g / l potassium bromide. In the measuring chamber on the generator electrode 4, a titrant is produced from bromide ion according to the equation

$$2Br^{-} - 2e \rightarrow Br_2 . \qquad (1)$$

The analyzed gas entering ECC enters into a chemical reaction with a titrant, reducing its concentration in the working solution

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$$2RSH + Br_2 \rightarrow R\text{-}S\text{-}S\text{-}P + 2HBr\,. \qquad (2)$$

When the test medium enters the ECC, the indicator current decreases by a value proportional to the concentration of the analyte. In this case, the concentration measurement can be carried out in two ways:

- fixing the current measurement on the indicator electrode [4];
- registering the current increment on the generator electrode [5].

When measured by the first method, the generator current remains constant, and the value of the indicator current decreases in proportion to the concentration of the analyte, i.e. $J_{ind} = f(s)$. When measuring the concentration of the analyte according to the second method, a feedback line is built in between the indicator and generator circuits in the measuring system. When the investigated substance enters the ECC, as in the first case, a decrease in the indicator current is observed. However, due to the presence of negative feedback. Variation of the indicator current causes the same measurement of the generator current. The system seeks to give the current on the generator electrode its original value, which leads to additional generation of titrant. The measure of concentration in this case is the increment of the current at the generator electrode $J_{gen} = f(s)$.

The free bromine obtained at the generator electrode at the indicator electrode is reduced to the bromide ion according to the equation

$$Br_2 + 2e^- \rightarrow 2Br^-\,. \qquad (3)$$

When determining the concentration of mercaptans using direct coulometry, the ECC of direct oxidation of CO was used [5], which is shown in Fig. 2.

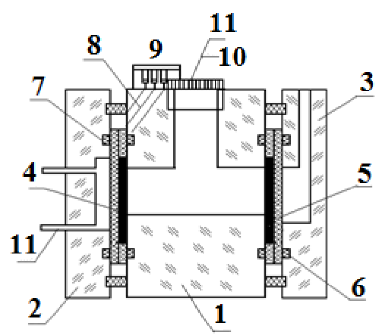

Fig 2: Electrochemical cell direct oxidation:

1 - housing; 2,3 - cover; 4 - working electrode; 5 - auxiliary electrode; and a reference electrode; 6 - rubber rings; 7 - platinum foil; 8 - wire tap; 9 - connector; 10 - cork; 11 - fitting.

It is a prefabricated plexiglass structure and consists of the following main parts: body 1, covers 2 and 3; electrodes 4 and 5. In the lid 2 there is a channel for the analyzed gas to pass along the surface of the working electrode 4. There is a hole in the lid 3 for communicating the reference electrode and the auxiliary electrode 5 with atmospheric air. The electrodes are sealed using rubber rings 6 by tightening the screws 7. The current collector is produced by pressing a portion of the active mass of the electrode to a platinum foil 8 soldered to the wires 9. The ECC is filled with an electrolyte solution through an opening 10 closed by a plug 11.

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Principle of operation of an electrochemical cell

The cell works as follows: the analyzed gas enters through the nozzle 12 into the working chamber and, passing along the surface of the working electrode 4, diffuses through the pores to the hydrophobized catalyst. The mercaptan contained in the analyzed gas is oxidized on it to mercaptide. The current passing through the cell is a measure of the concentration of mercaptans in the sample gas. [9]

Table 1 shows the technical characteristics of the studied electrochemical cells.

Table 1: Technical characteristics of the studied ECC

Specifications	**ECC bubbling type**	**ECC direct oxidation**
Range of measured concentrations, mg/m^3	0-20	0-150
The time of establishing readings, min	20	25
Stability for 24 hours of continuous operation, %	15	5
Permissible change in spatial position, degrees	-	5

Discussion of the results of studies of the operation of electrochemical cells

Based on the studies, we can conclude that:

- coulometric cells, for continuous quantitative determination of mercaptans are not suitable, because when determining large values of the concentration of mercaptans, passivation of the electrodes occurs;

- a direct oxidation cell can measure the concentration of mercaptans, because oxidation occurs at the working electrode. However, the technical and dynamic characteristics of the process of measuring mercaptans are not entirely satisfactory;

- it is necessary to conduct research on the selection of a catalyst ¬ sensitive element.

To selectively determine the concentration of mercaptans, studies were conducted to select the composition of the catalyst of the sensitive element. For this purpose, gas diffusion hydrophobized electrodes with various catalyst compositions were made and their technical characteristics were recorded. The electrodes were made by applying a hydrophobized catalyst to a gas-permeable fluoroplastic base.Comparative characteristics of cells with different catalyst compositions of the sensitive element are given in Table 2.

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Specifications	HGE cell based on 50% Au + 50% Pt	HGE cell based on 24% Au + 76% Pt	HGE cell based on Au
Conversion coefficient, μA/mg·m^{-3}	1.5	2.5	5.0
Transient time, min	2	10	0.5
Stability for 10 days of continuous operation, %	5	10	3

Table 2: Technical characteristics of cells with different composition of the catalyst

A comparison of technical characteristics made it possible to choose a gas-diffusion hydrophobized electrode based on highly dispersed gold powder. Therefore, an electrochemical cell with a HGE based on a gold catalyst was used as a primary converter in a gas analyzer.

The conversion characteristics of the studied electrochemical cells are shown in Fig. 3

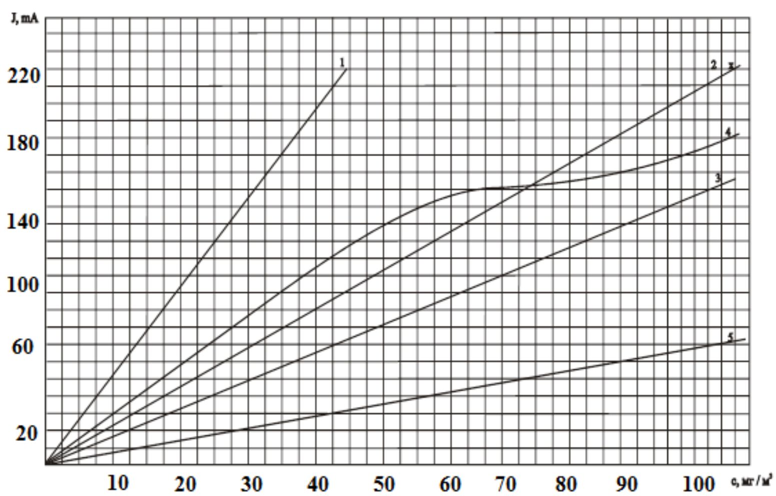

Fig3: The dependence of the cell current on the concentration of mercaptans on different electrodes:
1 - Au; 2 – 75% Au + 25% Pt; 3 - 50% Au + 50% Pt;4 - 24% Au + 76% Pt; 5 - 20% Au + 80% Pt.

III. CONCLUSION

Thus, invastigations were conducted on the selection of a catalyst for a sensitive element, and a comparison was made of the characteristics of a cell with gas diffusion hydrophobized electrodes with different composition of the catalyst. Investigations were made of the optimal operating modes of gas diffusion hydrophobized electrodes and electrode selection by comparison.

From the analysis of the studies, an electrochemical cell with gas diffusion hydrophobized electrodes is proposed as a primary converter in automatic gas analyzers, in which a catalyst made of finely dispersed gold powder is proposed as the active mass on the working electrode, and a platinum black is used as an auxiliary and reference electrodes.

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REFERENCES

[1] French patent, No. 2047665 b 01 27/00 Dispositif transporteur de feui Yes a reproduction dans un appareif a copier notamment une machine heliographigue / METEOR SIGEN APPARAT SCHMECK, 1971.
[2] Agronov H.I., Reiman L.V. Methods for the determination of gaseous pollution in the atmosphere. - M: Science, 1999. - 20 p.
[3] US Patent 4,220,415 Construction for Photometrik Analyzez / Hiroaki Yamaguchi, №1, 1980.
[4] Passport and photometer operation device. FL 5501. -M: 1997.
[5] A.S. No. 240318 A method for determining the micro-concentrations of carbon monoxide / Agral Kh.I. “Bulletin of inventions” No. 12, 1969.-52 p.
[6] Eshmatova B.I., Bandenok E.Yu. Development of an industrial gas analyzer for determining the micro-concentrations of carbon monoxide // Actual issues in the field of technical and socio-economic sciences: Rep. interuniversity. Sat Tashkent, 2008. -pp. 210-212.
[7] Bandenok E.Yu. Eshmatova B.I. Investigation of the temperature dependence of the oxidation rate of mercaptans on gas-diffusion hydrophobized electrodes // Olima ayllarning fan-tehnica taraqqiyotida tutgan o‘rni: Respublika ilmiy-amaliy anjumani ma’ruzalar to‘plami, II-qism. -Tashkent, 2008. –P.17-19.
[8] N.R. Yusupbekov, Sh.M. Gulyamov, E.Yu. Bandenok, B.I. Yeshmatova, N.Kh. Bobomurodov. Gas-diffusion hydrophobic electrodes for determining the concentration of carbon monoxide in gas mixtures Journal Sensors and Systems. 2010, №11, pp 30-33.
[9] Igamberdiyev H., Yusupbekov A., Zaripov O., Sevinov J. Algorithms of adaptive identification of uncertain operated objects in dynamical models. Procedia Computer Science. Volume 120, 2017, Pages 854-861.
[10] Ghosh A, Ghosh T. "Herbal Drugs of Abuse." Systematic Reviews in Pharmacy 1.2 (2010), 141-145. Print. doi:10.4103/0975-8453.75060

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