

# Study of coulometric method of gas analysis for analytical control and monitoring of harmful components in the air environment

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**Abstract.** The results of research of the method of determination of toxic substances in the composition of gas-air medium providing high efficiency of continuous monitoring, control and management of the content of harmful components in gas mixtures on the examples of continuous monitoring of the content of mercaptans in the natural gas of technological lines of gas processing and chemical plants are presented. The basic regularities of the methods of direct and indirect coulometry in determining the concentration of mercaptans in a gas mixture have been studied. As a result of the study of the measurement conversion processes occurring in electrochemical cells with sensitive elements - gas-diffusion hydrophobised electrodes, the choice of a promising design of the gas analyser intended for determining the concentration of mercaptans in natural gas in the range of 0-100 mg/m<sup>3</sup> and hydrogen sulphide in the range of 0-50 mg/m<sup>3</sup> has been justified.

## 1 Introduction

Nowadays, almost all branches of the national economy are consumers of analytical gas analysis instruments. However, the gas analysers produced by the instrument-making industry do not meet the needs of the national economy either in terms of volume or purpose. First of all, it is connected with the specificity of gas analytical technique, dealing with a variety of composition of analysed gas mixtures in different industrial productions, a wide range of fluctuations in the concentrations of individual components, conditions of analysis in terms of temperature, pressure, humidity and flow rate of the gas mixture.

According to the international programme of the global environmental monitoring system, 145 substances and 25 combinations of substances are currently required to be monitored in atmospheric air.

The introduction of new technological processes, the need to process a significant amount of information for making managerial decisions in the production of various industries - all this requires the creation of new generations of analytical instruments and complex measurement systems based on modern physical and chemical principles of measurement using the latest achievements of science and technology [1].

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In this connection the complex scientific and technical task of development of automatic gas analysers for determination of mercaptans concentration in natural gas and the system of metrological support of gas analysis is undoubtedly topical and demanded.

## 2 Materials and methods

A comparativistic analysis of the characteristics of titrimetric, photometric, linear-colorimetric, chromatographic, luminescent and electrochemical methods of gas analysis and, in particular, methods for determining the concentration of mercaptans in a gas mixture has been carried out.

To determine the concentration of mercaptans, the most promising measuring instruments are those based on electrochemical methods of gas analysis. Among its varieties the coulometric method of measurement is more preferable, which belongs to the category of absolute methods and provides the required selectivity of the measuring process due to a reasonable selection of the catalyst composition of the sensing element. This method is favourably distinguished by the absence of temperature dependence of the output signal and the possibility of absolute graduation of the devices. These advantages together with the simplicity of hardware design and the possibility of long-term operation without maintenance predetermine the final choice of the coulometric method for determining the concentration of mercaptans in natural gas of technological lines of gas processing and chemical plants.

In this connection the problem of creation of new high-precision, fast-acting and selective devices for control of mercaptan concentrations in natural gas, possessing a high level of unification, a common design basis (with respect to the selected coulometric method), using modern element base, new materials and high-performance technological operations is solved.

The results of research of coulometric method of analysis for analytical control of mercaptan concentration in VGS are presented from unified theoretical and methodological positions [2].

When determining the concentration of mercaptans by coulometric titration we used coulometric cells of non-current type with internal generation of titrant. When determining the concentration of mercaptans using the direct coulometry method, we used a direct oxidation electrochemical cell.

The measurement principle consists in electrochemical oxidation of the analysed substance at a fixed value of its potential at the working electrode, which is a gas-diffusion hydrophobised electrode. The chosen method provides selective measurement of the concentration of almost any substance in a gas mixture by studying and selecting the redox potential of the substance to be analysed.

The measure of concentration is the oxidation (reduction) current of the determined substance. Polarisation curves in the range from 0 to 0.1 V were taken to determine the optimum value of the working electrode potential. The polarisation potential was changed stepwise every 0.05 V with holding at each potential value for four hours (the time required to establish the stationary state of the electrode).

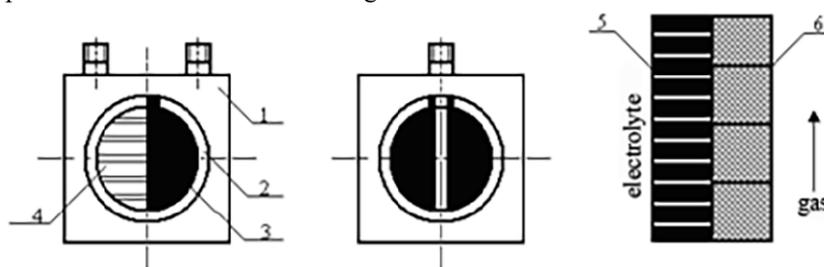
At the same time with the choice of potential the electrolyte composition was selected, for which the polarisation curves were taken in 5 % caustic soda solution and in 20÷30 % sulphuric acid solutions.

Based on the analysis of experimental data, the polarisation potential of the working electrode is chosen within 0.045-0.06 V relative to the reference electrode, which is similar to the working electrode in construction - with the only difference that the reference electrode is divided into two noncontacting parts, one of which serves as a reference electrode and the other as an auxiliary electrode.

The optimal electrolyte composition was found - 27.7% sulphuric acid solution. A stable value of the limiting diffusion current is observed in this electrolyte at the selected potential range [3].

For selective determination of mercaptan concentration, studies on selection of the catalyst composition of the sensing element were carried out. For this purpose, gas-diffusion hydrophobised electrodes with different catalyst composition were manufactured and their technical characteristics were determined [4]. Comparison of the latter allowed us to choose a gas-diffusion hydrophobised electrode (GHE) based on highly dispersed gold powder. The electrodes were made by applying hydrophobised catalyst, which is a homogeneous mixture of highly dispersed gold powder mixed with fluoroplastic suspension in a certain ratio, to a gas-permeable fluoroplastic base.

By introducing the required amount of hydrophobic substances, an optimal distribution of gas and liquid in the porous electrode is achieved. The design of the gas-diffusion hydrophobised electrode is shown in Fig. 1.



**Fig. 1.** Design of gas-diffusion hydrophobised electrode.

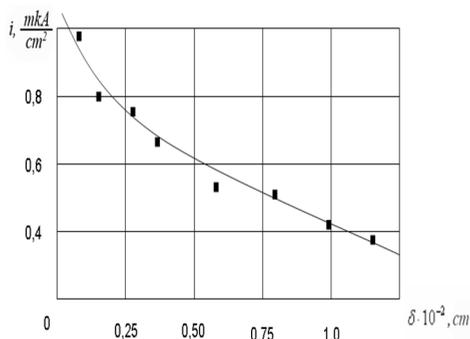
The sensing element consists of a body 1 and a porous fluoroplastic membrane 2 with a hydrophobised catalyst 3 applied thereto. The body 1 and membrane 2 form a hermetically sealed gas chamber with channels 4 for the passage of the analysed gas. The hydrophobised catalyst 3 is a mixture of hydrophilic catalyst and hydrophobic fluoroplastic and contains both hydrophilic 5 and hydrophobic 6 pores.

The analysed gas passes along the surface of membrane 2 (gas side), and the mercaptan contained in it diffuses to layer 3 and is oxidised to mercaptide. Due to the introduction of fluoroplastic into the catalyst, thin gas channels are formed and a high efficiency of utilisation of the inner surface of the catalyst is achieved.

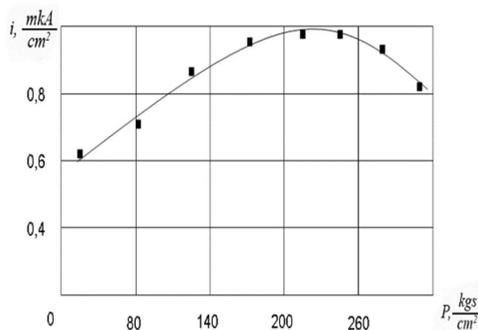
It is theoretically difficult to predict the optimal electrode design taking into account the least influence of the intra-diffusion stage [5]. However, by selecting the design parameters and appropriate manufacturing technology, it is possible to obtain electrodes in which the influence of limiting stages is the smallest and the limiting currents of mercaptan oxidation are the largest. Such an approach was implemented in the development of GGEs, on which the influence of the following factors on the value of the limiting current of mercaptan oxidation was studied: the thickness of the gas-permeable base, pressing pressure, the amount of hydrophobiser in the catalyst, and the method of application of the catalyst active mass [6].

### 3 Results and discussion

To study the dependence of the limiting current of mercaptan oxidation on the thickness of the gas-permeable substrate, 12 electrodes with substrate thicknesses of 0.25, 0.5, 0.75, and 0 mm1 were made. The results were evaluated by the value of specific current density (per unit surface area of the active mass) at passing of VGS N2 +RSH. The results of experiments are presented in Fig. 2.



**Fig. 2.** Dependence of the oxidation limit current on the thickness of the gas-permeable substrate.

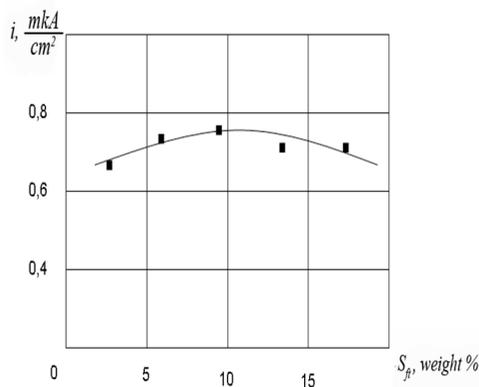


**Fig. 3.** Dependence of the oxidation current limit on the value of pressing pressure.

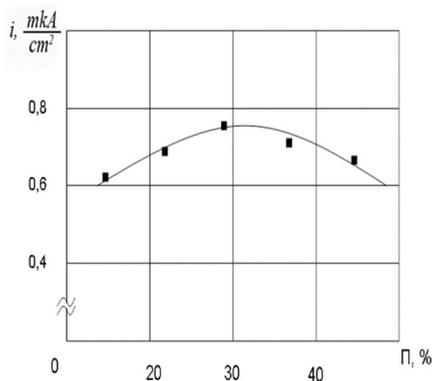
As expected, the limiting current of mercaptan oxidation decreased as the thickness of the gas-permeable substrate increased. The highest value of the limiting current was observed at the thickness of the substrate 0.25 mm, but the mechanical strength of the substrate was low, and the porosity was uneven, because after some time there was a through-flow of electrolyte. For further studies a gas-permeable substrate of  $0.5 \pm 0.1$  mm thickness was adopted (these electrodes have a lower limiting current for mercaptan oxidation, but at the same time provide sufficient mechanical strength).

The dependence of the limiting current of mercaptan oxidation on the base pressing pressure is shown in Fig. 3., from which it follows that the highest value of the value of the limiting current of mercaptan oxidation is observed at pressing pressure of 220 kgf/cm<sup>2</sup>. It should be noted that the pressing pressure also affects its porosity. As the pressing pressure increases, the porosity and thickness of the substrate decrease; at lower pressures, the substrate becomes loose and unstable.

The dependence of the mercaptan oxidation current on the concentration of hydrophobiser in the active mass of the catalyst is shown in Fig. 4. As can be seen, the concentration of hydrophobiser within the range of 5-13% does not affect the limiting current of mercaptan oxidation, but starting from the concentration of 15% and higher, the limiting oxidation current sharply decreases. This phenomenon is explained by an increase in the ohmic resistance of the active mass of the catalyst - due to complete isolation of the active mass by the hydrophobiser. Therefore, the electronic conductivity of the active mass decreases.



**Fig. 4.** Dependence of mercaptans oxidation current on hydrophobiser concentration.



**Fig. 5.** Dependence of the mercaptan oxidation current on the porosity of the gas-permeable substrate.

The dependence of the limiting current of mercaptan oxidation on the porosity of the gas-permeable base is shown in Fig. 5.

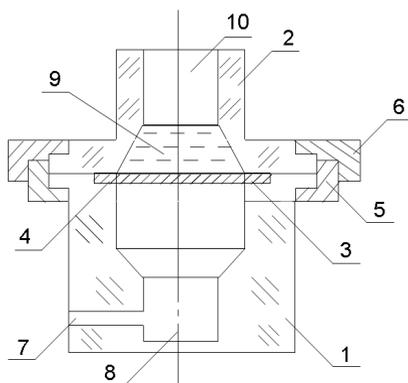
The choice of necessary porosity is carried out experimentally, for this purpose gas-permeable bases with different porosity in the range of 20÷40 % were produced. The latter was determined from the following expression:

$$\Pi = [1 - G / ((G - G_g) \cdot 2.15)] \cdot 100, \quad (1)$$

where  $G$  - weight of gas-permeable base in air, g;  $G_g$  - weight of gas-permeable base in water, g; 2.15 - density of fluoroplastic F-4, g/cm<sup>3</sup>.

Studies have shown that the use of a gas-permeable base with porosity less than 25% leads to a decrease in the limiting oxidation current due to a decrease in the contact of the controlled substance with the surface of the active mass, which is accompanied by a decrease in the catalytic activity of the electrode. The use of a base with porosity more than 35% causes the controlled substance to slip through the base and impairment of the electrode tightness.

On the basis of generalisation of experimental data, an electrode with the following design parameters was chosen as a sensitive element: thickness of gas-permeable base -  $0.5 \pm 0.1$  mm, concentration of hydrophobic agent in the active mass - 10 weight %, porosity of the base -  $30 \pm 5$  %.



**Fig. 6.** Device for uniform application of active mass on the substrate.

The active mass of the catalyst was applied to the surface of the gas-permeable base (substrate) by the rubbing method. This method of catalyst application is labour intensive. In this case there is uneven application of the catalyst layer on the surface of the substrate, which leads to a decrease in the catalytic activity of the electrode [7].

For uniform application of the active mass on the substrate, a method was proposed whereby the active mass was applied to the substrate by filtering the sol using the device shown in Fig. 6. The device has a collapsible body formed by a beaker 1 and a lid 2, separated from each other by a perforated partition 3, on which a gas-permeable substrate 4 is placed. The cup and cover are connected by means of a sleeve 5 and a coupling nut 6. The beaker has a socket 7 for creating a vacuum and a chamber 8 for collecting the mother liquor. The salt of the active mass containing the required amount of catalyst and fluoroplastic suspension diluted in the ratio 1:100 is mixed and poured into the chamber 9 through the hole 10 on a gas-permeable base. In the chamber 8 through the connector 7 a vacuum is created, due to which the ash with active mass is filtered. Fine particles of the catalyst are deposited in an even layer on the surface of the base, and the mother liquor is collected in the chamber 8.

The degree of uniformity of distribution of the catalyst active mass on the surface of the gas-permeable base of the electrode is determined by measuring the resistance between any two points of the active mass, the value of which should not exceed 20 Ohm. Table 1 shows the values of the ohmic resistance of the electrode depending on the method of application of the active mass (the weight of the catalyst for all electrodes was taken equal and was 2052 g0).

**Table 1.** Ohmic resistances of electrodes made by different methods.

Ohmic resistances of the electrode, Ohm	
machined	made by filtration
4-40	3-6
3-4	2-5
12-24	4-5
71-208	4-5
16-60	4-6
240-940	0-5
4-8	0-2
2-5	2-3
9-20	2-3

The comparative analysis of experimental data indicates that the electrodes made by filtration method have high sensitivity, good dynamic characteristics due to low ohmic

resistance and uniform distribution of active mass on the surface of the base, as well as the absence of scrap [8].

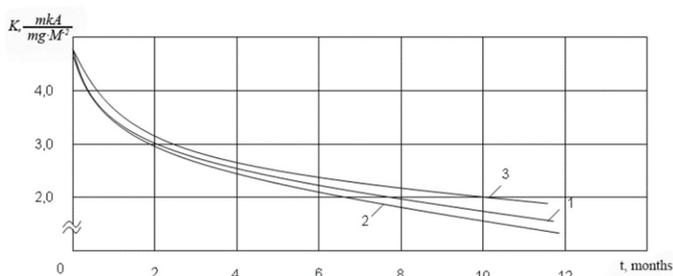
In order to determine the suitability of the electrochemical cell (ECC) with GGE for the tasks of measuring mercaptan concentration, the dependence of the rate of change of the conversion coefficient to a certain lower limit on the electrode operation time was taken. The controlled parameter was the conversion coefficient, the value of which was 1.5-2.0  $\mu\text{A}/\text{mg}\cdot\text{m}^{-3}$  [9-10]. The lowest permissible value of the conversion coefficient  $K(n)$  should be not less than 1.0  $\mu\text{A}/\text{mg}\cdot\text{m}^{-3}$ . Calculation of  $K(n)$  was performed by the formula:

$$K(n)=J/C. \quad (2)$$

where J - value of mercaptan oxidation current,  $\mu\text{A}$ ; C - value of mercaptan concentration,  $\text{mg}\cdot\text{m}^{-3}$ .

The above data indicates that the cells' operating resource has not yet been exhausted by the end of the tests.

Figure 7 shows the results of studies of the dependence of the conversion coefficient on the electrode operation time.



**Fig. 7.** Dependence of the conversion coefficient on the electrode operation time: 1 - electrochemical cell No. 1; 2 - electrochemical cell No. 2; 3 - electrochemical cell No. 3.

Three mock-ups of electrochemical cells have also been developed, which differ in design, supply of the analysed gas, and electrolyte composition:

- ECHN with forced feeding of the analysed gas and with electrolyte make-up chamber;
- ECN with diffusion feeding of the analysed gas;
- small-sized ECN with diffusion gas supply and thickened electrolyte [11].

## 4 Conclusion

Analysing the results of the performed research, it is possible to propose as a primary converter of automatic gas analysers for determining the concentration of mercaptans in natural gas the electrodes in which a catalyst consisting of a highly dispersed powder is proposed as the active mass, and the auxiliary electrode and the reference electrode are made of platinum niello.

The characteristics and capabilities of titrimetric, photometric, linear-colorimetric, chromatographic, luminescent and electrochemical methods for determining the concentration of mercaptans in gas mixtures are analysed. The method of determining the concentration of mercaptans in CBC is proposed, based on the method of potentiostatic amperometry, which belongs to the category of absolute and provides the required metrological characteristics of the gas analyser.

Selection of qualitative and quantitative composition of the catalyst of the sensitive element of the electrochemical transducer, providing the required selectivity of the measuring process, was carried out.

The main metrological characteristics of electrochemical cells based on gas-diffusion hydrophobised electrode with optimally selected catalyst composition and taking into account the least influence of the limiting intra-diffusion stage of the measuring conversion process have been studied experimentally.

A universal electrochemical cell with gas-diffusion hydrophobised electrodes has been developed.

A rational method of uniform application of the catalyst active mass layer on a porous gas-permeable base is substantiated, due to which a high efficiency of using the inner surface of the catalyst is achieved.

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