

During the operation of power plant equipment, technological media are used – water, turbine oils. Diagnostics of equipment by gas chromatographic determination of diagnostic components (gases  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$ ), water, "Ionol" in these media is urgent. For this, 5 chromatographs are used. An increase in the reliability of the main circulation pumps of a nuclear power plant can be due to an increase in the reliability of its oil system. The influence of ultrasonic vibrations on the generation of gases in the systems "oil – diagnostic gas", "oil – water – diagnostic gas" with the use of turbine oil Tn-22s is studied. Gas concentrations increase with an increase in the duration of exposure for 1600 s at a frequency of 35–125 kHz and a power of 20 W. The dependences of the concentrations  $C_i$  of dissolved gases on the irradiation time  $\tau$  of technological media is expressed by the equation  $C_i = A \cdot \tau + B$ . Coefficients  $A$ ,  $B$  and correlation coefficients  $R^2$  have specific values for each dissolved gas. So,  $0.95 \leq R^2 \leq 0.995$ , which indicates the adequacy of the obtained equations to the experimental data. This makes it possible to determine turbine oil in water after irradiation and subsequent gas chromatographic determination of the generated dissolved gases. The technical requirements for a 5-channel gas chromatograph were established and its structural diagram was developed. This makes it possible to reduce the number of measurement operations and chromatographs. The thresholds for determining the diagnostic components in the corresponding technological environments have been determined: 2 ppm ( $H_2$ ); 1 ppm ( $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ); 0.5 ppm ( $C_2H_2$ ); 5 ppm ( $CO$ ,  $CO_2$ ); 1.5 ppm ( $O_2$ ,  $N_2$ ); 0.05 wt. % ("Ionol"); 2 g/t (water in turbine oil) 0.02 mg/dm<sup>3</sup> (turbine oil in water).

The basic technological scheme of the oil system for the main circulation pumps of the NPP has been developed. It is proposed to continuously: degassing the turbine oil flow; sorption purification of cooling water, analysis of turbine oil and cooling water by gas chromatography methods. This will reduce the degradation of turbine oil and increase the reliability of the oil system of the NPP main circulation pumps

**Keywords:** gas chromatography, turbine oil, cooling water, diagnostic component, nuclear power plant

# DEVELOPMENT OF METHODS OF GAS CHROMATOGRAPHIC ANALYSIS OF TECHNOLOGICAL MEDIA OF THE MAIN CIRCULATION PUMPS OF A NUCLEAR POWER PLANT

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## 1. Introduction

During the operation of power plant equipment, technological media are widely used: water, mineral turbine and transformer oils [1].

This requires an assessment of the actual technical condition of the power plant equipment installed in the process flow diagrams of circulating oil and water supply, based on the determination of the content of diagnostic components in samples of these process media taken from the appropriate equipment [2].

To determine the content of diagnostic components in these technological environments, various methods are used, including gas chromatography (GC), using several measurement techniques and chromatographs, which complicates and increases the cost of measurements. Thus, gas chromatographs can be used to determine the content of gases  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$  in mineral

insulating oils, including turbine oils [3]. Gas chromatographs can be used to determine the content of these gases in cooling water [4]. At the same time, the influence of the operating temperature of the gas chromatograph columns on the GH reliability of analyzes of  $C_2H_2$  gas concentrations was not taken into account [5]. To determine the content of the additive "Ionol" in mineral turbine oils in international practice, it is recommended to use liquid chromatographs [6] or gas [7], which requires the use of expensive and harmful in operation liquid extractants. In Ukraine, it is recommended to use gas chromatographs to determine the content of the "Ionol" additive in mineral turbine oils [7, 8]. The threshold for determining the content of the "Ionol" additive is 0.05 % by weight (% by weight). These works do not provide requirements for calculating the values of measurement errors of the "Ionol" concentration in energy oils and requirements for the numerical values of these errors. At the same time, the influence of analyzes of "Ionol" concentrations at different

operating temperatures of GC columns of a gas chromatograph on the GC reliability was not taken into account [5]. Gas chromatographs can be used to determine the water content in mineral insulating oils, including turbine oils [9]. The threshold for determining the water content is 2 g/t. This work does not provide requirements for calculating the values of errors in measuring the concentration of water in energy oils and requirements for the numerical values of these errors. In this case, rather complex operations are required for the preparation and storage of graduated mixtures of water in insulating oil under isothermal ambient conditions.

To determine the content of petroleum products with a concentration of petroleum products in water of at least 0.02 mg/dm<sup>3</sup>, it is recommended to apply the GC methods [10]. These methods are distinguished by the complexity of execution, the use of expensive and harmful extractants and reagents, and sophisticated auxiliary equipment.

All this requires the use of at least 5 chromatographs to determine the content of gases, water, Ionol additive and turbine oil in water in the corresponding liquid technological media. This increases the cost of taking measurements, complicates their performance, requires several operators to perform the measurement, or increases the time for taking measurements when performed by one operator.

Therefore, the task is to develop a multichannel gas chromatograph for analyzing samples of turbine oils for the determination of gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, water, "Ionol" additives. Another task is to develop a multichannel gas chromatograph for analyzing cooling water samples to determine the gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, turbine oils.

In technical systems of oil and water supply of the main circulation pumps (MCP) of the reactor block of a nuclear power plant with a pressurized water reactor, turbine oil degrades under the influence of atmospheric oxygen and loses its technological properties [5, 11]. In this case, the "acid number" indicator can reach the value of 0.6 mg KOH per 1 g of oil, exceeding the requirements of the norms [5, 11]. In addition, turbine oil often enters oil coolers of the "cooled oil – cooling water" type into the cooling circulating water and loses its technological properties [12]. This happens in the event of defects associated with a violation of the sealing of units of oil coolers of the type "energy oil – cooling water" [12]. In the circulating oil supply system, the MCP equipment of this oil system is subjected to intense vibration. In this case, degradation of the turbine oil under the influence of acoustic cavitation is possible [5]. Such defects can arise under the influence of: equipment vibration; contamination of the inner surface of heat exchange tubes (HET) in oil coolers; loss of tightness of the tube bundle oil coolers due to loss of tightness of previously plugged damaged HET; hydraulic shocks. Similar defects arise under the influence of: thermal stresses on rolled HET joints; air ingress into the oil cooler housing; erosive wear and fatigue phenomena of HET metal under the action of oncoming flows of liquids [12].

At present, the determination of the presence and content of turbine oils in the flow of cooling water from the oil cooler is not standardized; this reduces the reliability of the circulating oil and MCP water supply system [13].

Therefore, the task is to develop a new conceptual technological scheme of circulating oil and water supply using GC of analyzes of turbine oil and cooling water samples for the oil system equipment in the MCP operation. Also, the

tasks are to control the content of turbine oil in the cooling water during the operation of the oil system of the main circulation pump of the NPP pressurized water power reactor.

Requirements for diagnosing electrical equipment based on the results of GC analyzes of the contents of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in insulating oils refer to electrical equipment (EE) of voltage classes 35–750 kV [14]. This requires a separate gas chromatograph. Requirements for the determination of water in insulating oil also apply to EE of the same voltage classes [9]. This also requires a separate gas chromatograph. This makes it expensive and difficult to take GC measurements. Therefore, it is necessary to develop one multichannel gas chromatograph, which can be used to determine the content of diagnostic components in technological media.

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## 2. Literature review and problem statement

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In [15], the results of diagnosing equipment with insulating oils based on the results of their GC analysis are considered. The paper presents a method of GC measurements using complex and expensive equipment using flame ionization detectors and a vacuum attachment for extracting gases from insulating oil. This requires the development of economic and simplified GC methods for determining the content of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in insulating oils.

In [16], the results of online diagnostics of equipment with insulating oils based on the results of their IR spectrometric analysis are considered. The paper presents a method of GC measurements using expensive equipment with spectrometric detectors. This requires the development of economic and simplified GC methods for determining the content of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in insulating oils.

In [17], the results of diagnosing equipment with insulating oils based on the results of their GC analysis are considered. The paper presents a method of GC measurements using complex and expensive equipment with the use of IR spectrometric or sound-acoustic detectors. This requires the development of economic and simplified GC methods for determining the content of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in insulating oils.

In [18], the results of diagnosing equipment with insulating oils based on the results of their GC analysis are considered. The paper presents a complex method of GC measurements using expensive hardware and software. This requires the development of more economical and simple GC methods for determining the content of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in insulating oils.

In [19], the results of diagnosing equipment with insulating oils based on the results of their GC analysis are considered. The paper presents the GC measurement method, which is difficult to perform using complex equipment. This requires the development of simplified GC methods for determining the content of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in insulating oils.

The work [20] presents the results of the development of methods for extraction-gas chromatographic (EG) determination of the content of dissolved gases, ionol in such energy oils as transformer, condenser, cable, turbine grade AZMOL Tp-22s. The values of the distribution coefficients for the dissolved diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub> in

the systems “energy oil – gaseous extractant” are given. The conditions for performing measurements are established. For the widely used turbine oil Tp-22s (grade 1), no such results are given. This work does not provide the requirements for calculating the values of the measurement errors of the concentrations of dissolved gases and ionol in energy oils and the requirements for the numerical values of these errors. This work also does not show the technological scheme of the proposed multichannel gas chromatograph. This requires the development of EG methods for determining the content of dissolved gases and ionol in turbine oil Tp-22s (grade 1) and the technological scheme of a multichannel gas chromatograph.

In [21], the influence of the water-chemical regime (WCC) indicators on the quality assurance of cooling water (corrosion processes, the presence of biological and organic impurities (turbine oil) in the cooling water, gas generation, etc.) is considered. This work does not provide methods for the determination of gases in cooling water. This requires the development of methods for determining the content of diagnostic gases  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$  and turbine oil in cooling water, for example, by the GC method.

In [22], the GC method for the determination of oil products in water using capillary GC columns is considered. This method is distinguished by the complexity of execution, the use of expensive and harmful extractants and reagents, and sophisticated auxiliary equipment. This requires the development of a method for GC measurements using packed GC columns, does not require the use of expensive and harmful extractants and reagents, and complex auxiliary equipment.

In [23], the results of diagnosing equipment with insulating oils based on the results of their GC analysis are considered. In this work, the GC measurement method is presented, which is characterized by the complexity of execution, the use of expensive reagents, and sophisticated equipment. This requires the development of economic methods for determining the content of diagnostic gases  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$  in insulating oils.

In [24], the results of diagnosing equipment with insulating oils based on the results of their GC analysis are also considered. In this work, the GC measurement method is presented, which is also difficult to perform using expensive reagents and equipment. This requires the development of economic methods for determining the content of diagnostic gases  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$  in insulating oils.

Thus, it is necessary to conduct studies aimed at increasing the reliability of determinations by GC methods of the contents of diagnostic components in samples of mineral turbine oils and cooling water. This will make it possible to diagnose power plant equipment according to standardized diagnostic models. This implies a study of the influence of ultrasonic vibrations on the artificial generation of diagnostic components in the systems “turbine oil – dissolved diagnostic gas” and “turbine oil – water – dissolved diagnostic gas”. It is necessary to determine the main technical requirements for a gas chromatograph to determine the content of diagnostic components, water, and the “Ionol” additive in the corresponding technological media. It is necessary to develop a block diagram of a multichannel gas chromatograph for the analysis of technological media. It is necessary to develop a new conceptual technological scheme of the circulating oil and water supply system of the NPP MCP with a pressurized water power reactor.

### 3. The aim and objectives of research

The aim of research is to improve the accuracy of GC methods for analyzing technological media for diagnostics of equipment in the oil system of the MCP based on the results of GC measurements of diagnostic components in technological media using a multichannel chromatograph. This will improve the reliability of oil and water supply systems for oil-to-water coolers when operating the equipment of the MCP oil system of the NPP pressurized water-cooled power reactor and reduce the oxidative degradation of turbine oil.

To achieve the aim, the following objectives are set:

- to study the influence of ultrasonic (US) vibrations on the generation of diagnostic components  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$  in turbine oil and in a mixture of turbine oil with water;
- to determine the main technical requirements for a gas chromatograph to determine the content of turbine oil in samples, in a mixture of turbine oil with water and in cooling water of diagnostic components;
- to develop a structural diagram of a multichannel gas chromatograph for determining the content of diagnostic components in turbine oil samples, in a mixture of turbine oil with water and in cooling water;
- to determine the value of the thresholds for determining the concentrations of diagnostic components in liquid technological media when performing measurements by GC methods;
- to develop a basic technological scheme of the circulating oil and water supply system during the MCP operation of the NPP pressurized water power reactor.

### 4. Materials and methods for studying the ultrasonic decomposition of turbine oil and its aqueous mixture

The research was carried out using: fresh mineral turbine oil Tp-22s (grade 1); distilled water; a mixture of fresh mineral turbine oil Tp-22s (grade 1) with distilled water at a turbine oil concentration of  $5 \text{ mg/dm}^3$ ; dissolved diagnostic components  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$  in mineral turbine oil, distilled water and in mixtures of distilled water with turbine oil.

When performing the measurements, the following were used: gas chromatograph with gas dispensers, methanator (for converting  $CO$  and  $CO_2$  into  $CH_4$ ), thermal conductivity detector (TCD), flame ionization detector (FID), liquid evaporators; Ultrasonic generator (irradiation frequency 35–125 kHz, power 20 W) for acoustic irradiation of turbine oil, water and a mixture of turbine oil with water; a device for accelerating the achievement of equilibrium with a rotating drum for placing syringes with a volume of  $20 \text{ cm}^3$  or  $50 \text{ cm}^3$  with analyzed samples of liquid technological media and gaseous extractants for establishing phase equilibria in the systems “technological medium – extractant”; extractant – gaseous argon (Ar) graduated gaseous mixtures of  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$  in argon; saturated solution of  $H_2$  in distilled water; a mixture of turbine oil with distilled water.

The measurements were carried out at a temperature of  $(20 \pm 0.5) \text{ }^\circ\text{C}$ . Duration: gas extraction of components from liquid technological media – 10 minutes; Ultrasonic exposure to turbine oil, distilled water or a mixture of turbine oil and water – up to 25 minutes. In the chromatograph, the registration of the components is performed using: TCD – for  $H_2$ ,  $O_2$ ,  $N_2$ ,  $H_2O$ ; FID – for  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ .

When determining the content of diagnostic components in turbine oil, cooling water and in a mixture of turbine oil with water, the following was used: a static version of the GC measurement method using a gaseous extractant and the corresponding versions of methods for analyzing the equilibrium gas phase in the “liquid technological medium – dissolved component – gaseous extract” systems; method of absolute calibration when determining the content of diagnostic components in gaseous extracts using the corresponding gaseous graduated mixtures [3, 4].

When determining the concentration  $C_0$  of a dissolved component in liquid technological media, the calculation formulas used for double sequential gas isothermal extraction [3]

$$C_0 = \frac{S_c}{K_g} \cdot \left( K_d + \frac{V_e}{V_{ev}} \right), \tag{1}$$

where  $S_c$  – area of the GC peak for the considered component after its first gas extraction;  $K_g$  – graduated coefficient for a gas chromatograph FID or TCD detector for the component under consideration;  $V_{ev}$  – sample volume of the analyzed liquid technological medium;  $V_e$  – volume of the gaseous extractant;  $K_p$  – distribution coefficient for the considered component in the system “liquid technological medium – dissolved component – gaseous extract”.  $S_1, S_2$  – areas of GC peaks for the considered component after its first and second sequential gas extraction from the liquid process medium.

The distribution coefficient  $K_d$  is determined by the formula [3]

$$K_d = \frac{S_1}{S_2 - S_1} \cdot \frac{V_e}{V_{ev}}, \tag{2}$$

where  $S_1, S_2$  – areas of GC peaks for the component under consideration after its first and second sequential gas extraction from the liquid process medium. Each value of the concentration of the dissolved gas was obtained as a result of five ( $n=5$ ) parallel measurements with a confidence level of  $p=0.95$ . In this case, the coefficient of normalized deviations depending on the number of degrees of freedom  $f=n-1$ , for  $n=5$  has a value  $t=2.78$ .

### 5. Research results of ultrasonic decomposition of turbine oil and its mixture with water

Determination of the content of diagnostic components in turbine oil and in its mixture with water was carried out by the GC method using the calculation formulas (1) and (2). The results of studying the effect of ultrasonic vibrations on the generation of diagnostic components  $H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, CO_2$  in turbine oil and in a mixture of turbine oil with water are presented in Table 1.

In a graphical form, the dependences of the values of the concentrations of dissolved gases  $C_i, \%$  volumetric, with time  $\tau, s$ , ultrasonic irradiation of turbine oil or a mixture of turbine oil – water are shown in Fig. 1–4. Fig. 1 shows the dependence of the values of the concentration of dissolved gases  $C_i$ , volume %, for gases  $C_2H_4, H_2, CH_4, C_2H_6$  on time  $\tau, s$ , ultrasonic irradiation of the “turbine oil” system.

Fig. 2 shows the dependence of the values of the concentrations of dissolved gases  $C_i, \%$  volumetric, for gases  $C_2H_4, H_2, CH_4, C_2H_6$  on the time  $\tau, s$ , ultrasonic irradiation of the “turbine oil – water” system.

Table 1

The values of the concentration of gases  $C_i$  in turbine oil and in a mixture of turbine oil with water on the duration  $\tau$  of ultrasonic irradiation

| $\tau, s$           | $C_i, \%$ volumetric |          |       |          |          |        |        |
|---------------------|----------------------|----------|-------|----------|----------|--------|--------|
|                     | $CH_4$               | $C_2H_4$ | $H_2$ | $C_2H_6$ | $C_2H_2$ | $CO$   | $CO_2$ |
| Turbine oil         |                      |          |       |          |          |        |        |
| 0                   | 0.001                | 0.004    | 0     | 0        | 0        | 0.0009 | 0.0003 |
| 200                 | 0.07                 | 0.29     | 0.18  | 0.025    | 0.05     | 0.02   | –      |
| 600                 | 0.15                 | 0.40     | 0.32  | 0.046    | 0.08     | 0.055  | –      |
| 1000                | 0.25                 | 0.98     | 0.50  | 0.075    | 0.11     | 0.088  | 0.04   |
| 1500                | 0.46                 | 1.60     | 0.60  | 0.14     | 0.20     | 0.1    | 0.05   |
| Turbine oil – water |                      |          |       |          |          |        |        |
| 0                   | 0.001                | 0.0004   | 0     | 0        | 0        | 0      | 0.0003 |
| 200                 | 0.005                | 0.025    | 0.015 | 0.005    | 0.004    | 0.002  | 0.003  |
| 600                 | 0.01                 | 0.041    | 0.030 | –        | –        | 0.004  | 0.005  |
| 1000                | 0.020                | 0.080    | 0.040 | 0.085    | 0.08     | 0.007  | 0.007  |
| 1500                | 0.035                | 0.16     | 0.060 | 0.10     | 0.12     | 0.01   | 0.009  |

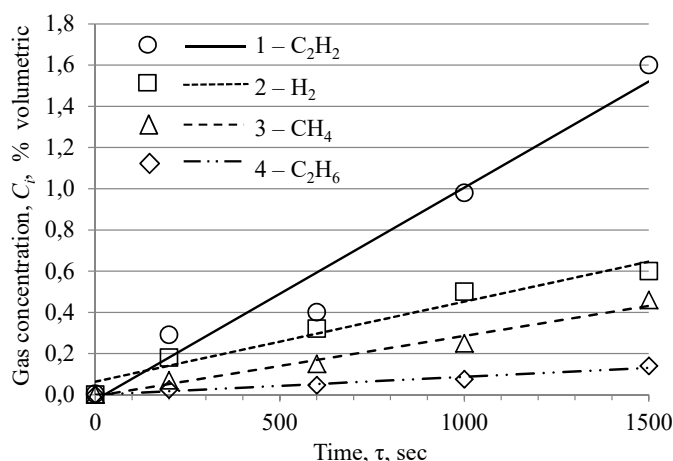


Fig. 1. Dependence of the values of the concentration of dissolved gases  $C_i, \%$  by volume, for gases  $C_2H_4, H_2, CH_4, C_2H_6$  on time  $\tau, s$ , ultrasonic irradiation of the “turbine oil” system

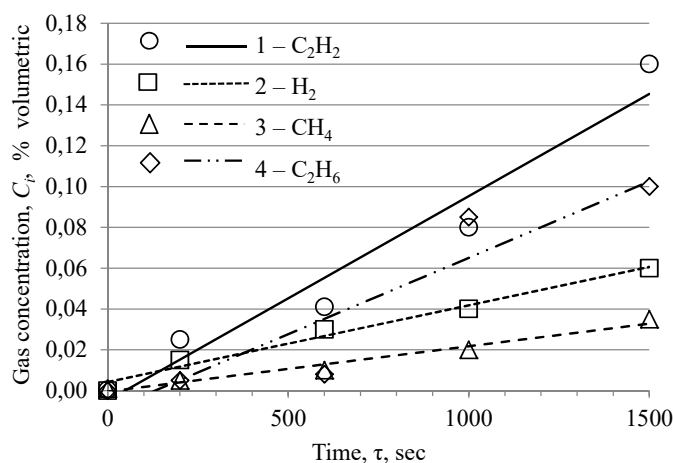


Fig. 2. Dependence of the values of the concentration of dissolved gases  $C_i, \%$  volumetric, for gases  $C_2H_4, H_2, CH_4, C_2H_6$  on time  $\tau, s$ , ultrasonic irradiation of the “turbine oil – water” system

Fig. 3 shows the dependence of the concentration of dissolved gases  $C_i, \%$  volumetric, for gases  $C_2H_2, H_2, CO, CO_2$  on time  $\tau, s$ , ultrasonic irradiation of the “turbine oil” system.

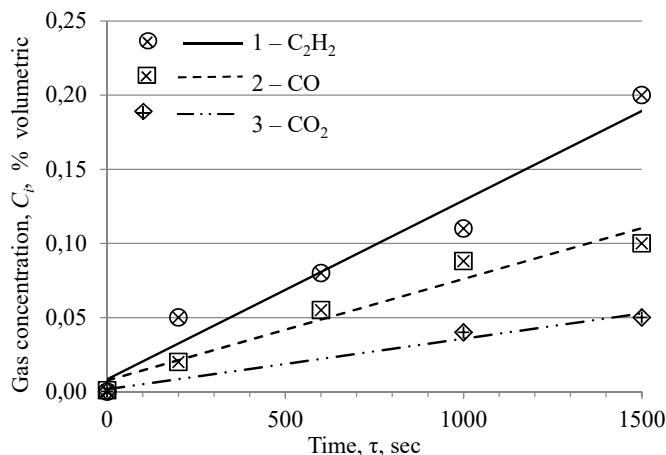


Fig. 3. Dependence of the values of the concentration of dissolved gases  $C_i$ , % volumetric, for gases  $C_2H_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$  on time  $\tau$ , s, ultrasonic irradiation of the "turbine oil" system

Fig. 4 shows the dependence of the values of the concentration of dissolved gases  $C_i$ , % volumetric, for gases  $C_2H_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$  on time  $\tau$ , s, ultrasonic irradiation of the "turbine oil – water" system.

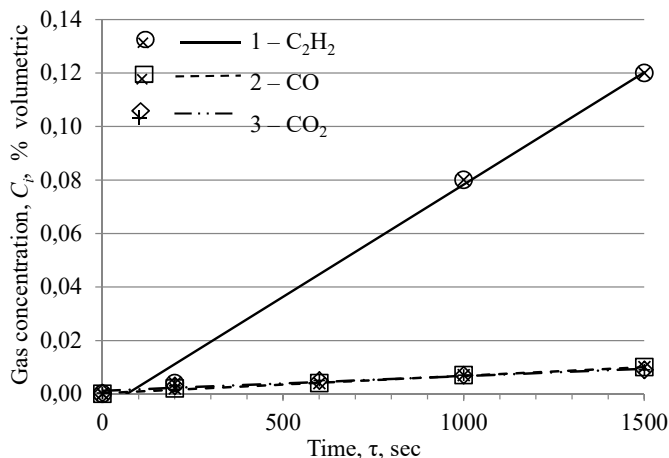


Fig. 4. Dependence of the values of the concentration of dissolved gases  $C_i$ , % volumetric, for gases  $C_2H_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$  on time  $\tau$ , s, ultrasonic irradiation of the "turbine oil – water" system

In mathematical form, the dependence of the values of the concentration  $C_i$  of dissolved gases on the time of ultrasonic irradiation  $\tau$  of turbine oil or a mixture of turbine oil – water can be expressed by the equation

$$C_i = A \cdot \tau + B, \tag{3}$$

where  $C_i$  – concentration of dissolved gas in the process medium, % volumetric;  $\tau$  – ultrasonic irradiation time, s.

Table 2 shows the values of the coefficients A, B, equation (3) and the correlation coefficients  $R^2$  for the "turbine oil" system.

Table 3 shows the values of the coefficients A, B, equation (3) and the correlation coefficients  $R^2$  for the "turbine oil – water" system.

Table 2

Values of coefficients A, B, equation (3) and correlation coefficients  $R^2$  for the "turbine oil" system

| No. | Gas      | A                    | B                     | $R^2$ |
|-----|----------|----------------------|-----------------------|-------|
| 1   | $C_2H_4$ | $1.03 \cdot 10^{-4}$ | $-2.54 \cdot 10^{-2}$ | 0.965 |
| 2   | $H_2$    | $3.89 \cdot 10^{-4}$ | $6.35 \cdot 10^{-2}$  | 0.955 |
| 3   | $CH_4$   | $2.91 \cdot 10^{-4}$ | $-6.39 \cdot 10^{-3}$ | 0.978 |
| 4   | $C_2H_6$ | $8.75 \cdot 10^{-5}$ | $-5.68 \cdot 10^{-4}$ | 0.972 |
| 5   | $C_2H_4$ | $1.21 \cdot 10^{-4}$ | $8.37 \cdot 10^{-3}$  | 0.962 |
| 6   | $CO$     | $6.85 \cdot 10^{-5}$ | $7.57 \cdot 10^{-3}$  | 0.954 |
| 7   | $CO_2$   | $3.41 \cdot 10^{-5}$ | $1.71 \cdot 10^{-3}$  | 0.980 |

Table 3

Values of coefficients A, B equation (3) and correlation coefficients  $R^2$  for the system "turbine oil – water"

| No. | Gas      | A                    | B                     | $R^2$ |
|-----|----------|----------------------|-----------------------|-------|
| 1   | $C_2H_4$ | $1.0 \cdot 10^{-4}$  | $-4.80 \cdot 10^{-3}$ | 0.950 |
| 2   | $H_2$    | $3.75 \cdot 10^{-5}$ | $4.21 \cdot 10^{-3}$  | 0.980 |
| 3   | $CH_4$   | $2.22 \cdot 10^{-5}$ | $-4.35 \cdot 10^{-4}$ | 0.974 |
| 4   | $C_2H_6$ | $7.34 \cdot 10^{-5}$ | $-2.06 \cdot 10^{-3}$ | 0.962 |
| 5   | $C_2H_4$ | $8.39 \cdot 10^{-5}$ | $-5.62 \cdot 10^{-3}$ | 0.992 |
| 6   | $CO$     | $6.54 \cdot 10^{-5}$ | $2.87 \cdot 10^{-4}$  | 0.995 |
| 7   | $CO_2$   | $5.48 \cdot 10^{-6}$ | $1.25 \cdot 10^{-3}$  | 0.960 |

Before preparing a mixture of turbine oil with distilled water, the latter was degassed in an argon flow to remove  $CO$  and  $CO_2$  from it below a concentration of 5 ppm as determined by the GC method.

During ultrasonic irradiation of degassed distilled water for  $\tau=1,500$  s (25 minutes), no accumulation of diagnostic components was detected.

It was found that under the action of ultrasonic irradiation, turbine oil and a mixture of turbine oil with water decompose with the formation of gases  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CO$ ,  $CO_2$ . This corresponds to a similar result noted in [5] for transformer oils.

## 6. Results of determining the main technical requirements for a gas chromatograph for the determination of diagnostic components

The main technical requirements for a gas chromatograph for determining the content of diagnostic components in technological media are given in Table 4.

In the Table 4,  $t_{GC}$ ,  $t_{TCD}$ ,  $t_{FID}$ ,  $t_m$ ,  $t_{ev}$ ,  $t_{GC outlet}$ ,  $v$  – GC column temperature, TCD, FID, methanator, evaporator, GC column outlet temperature, respectively;  $v$  – velocity of GC column temperature programming.

The sorbent "CaA" is possible to be manufactured by Russian Federation. The following countries as Germany "Merck KGaA, Darmstadt"; USA Supelco, USA; Agilent Technologies" is supposed to be the manufacturers of the sorbent «Porapak N 80/100». For the sorbent "Chromosorb P + SE-30" countries of origin may be Meinhard, USA; AgilentTechnologies, USA; SCP SCIENCE CONOSTAN Canada; CPI International, USA; Elemental Microanalysis, UK; Elemental Scientific, USA.

Table 4

Basic technical requirements for a gas chromatograph for determining the content of diagnostic components in technological media

| No. | Characteristics  |
|-----|--|
| 1   | Measurement channel No. 1 for defining (detection) H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> in water; turbine oil; mixture of turbine oil and water. Elements: GC column position 2 – sorbing agent «CaA» (USA); $t_{GCc}=40\text{ }^{\circ}\text{C}$ , $t_{TCD}=200\text{ }^{\circ}\text{C}$ , TCD detectors (operating chamber) position 4   |
| 2   | Measurement channel No. 2 for defining water in turbine oil. Elements: GC column no. 6 – sorbing agent «Polisorb-1» (Russia Federation); $t_{ev}=300\text{ }^{\circ}\text{C}$ , $t_{GCc}=120\text{ }^{\circ}\text{C}$ , $t_{TCD}=150\text{ }^{\circ}\text{C}$ , TCD detectors (reference chamber) position 4   |
| 3   | Measurement channel No. 3 for defining CO, CH <sub>4</sub> , CO <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>2</sub> in: water; turbine oil; mixture of turbine oil and water. Elements: GC column position 8 – sorbing agent «Porapak N 80/100»; $t_{GCc}=40\text{ }^{\circ}\text{C}$ , $t_m=325\text{ }^{\circ}\text{C}$ , $t_{FID}=200\text{ }^{\circ}\text{C}$ , $v=12\text{ }^{\circ}\text{C}/\text{min}$ from $t_{GCc}=40\text{ }^{\circ}\text{C}$ to $t_{GCc\text{outlet}}=180\text{ }^{\circ}\text{C}$ , FID detector, position 11 |
| 4   | Measurement channel No. 4 for defining additive «Ionol» in turbine oil. Elements: GC column position 13 – sorbing agent «Chromaton N-AW+SE-30» (Czech Republic); $t_{ev}=200\text{ }^{\circ}\text{C}$ , $t_{GCc}=150\text{ }^{\circ}\text{C}$ , $t_{FID}=240\text{ }^{\circ}\text{C}$ ; $v=20\text{ }^{\circ}\text{C}/\text{min}$ from $t_{GCc}=150\text{ }^{\circ}\text{C}$ to $t_{GCc\text{outlet}}=200\text{ }^{\circ}\text{C}$ , FID detector position 15 (argon line)   |
| 5   | Measurement channel No. 5 for defining turbine oil in water. Elements: GC column position 17 – sorbing agent «Chromosorb P +SE-30»; $t_{ev}=400\text{ }^{\circ}\text{C}$ , $t_{GCc}=50\text{ }^{\circ}\text{C}$ under isotherme 5 min, $t_{FID}=350\text{ }^{\circ}\text{C}$ , $v=10\text{ }^{\circ}\text{C}/\text{min}$ from $t_{GCc}=50\text{ }^{\circ}\text{C}$ to $t_{GCc\text{outlet}}=320\text{ }^{\circ}\text{C}$ , FID detector position 15 (hydrogen line)  |

7. Results of the development of a block diagram of a multichannel gas chromatograph for gas chromatographic analysis of technological media

Fig. 5 shows a block diagram of the developed five-channel gas chromatograph with TCD and FID modules for determining the content of diagnostic components in samples of turbine oils and cooling water.

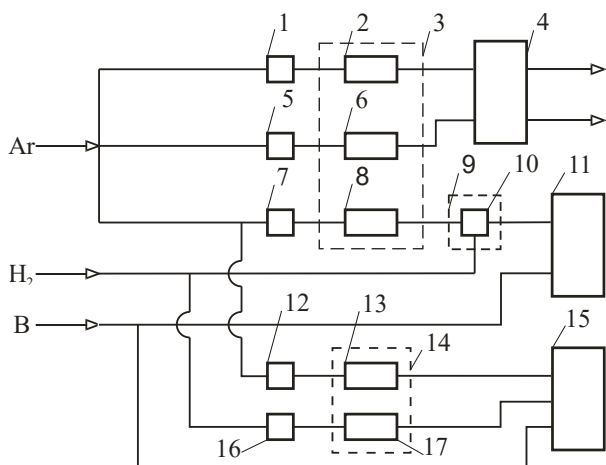


Fig. 5. Block diagram of a five-channel gas chromatograph for determining the content of diagnostic components in samples of turbine oils and cooling water:

- 1, 7 – gas metering valves with calibrated metering loops;
- 2, 6, 8, 13, 17 – chromatographic columns;
- 3, 9, 14 – thermostats; 4 – TC; 5, 12, 16 – evaporators;
- 10 – methanator; 11, 15 – FID; Ar, H<sub>2</sub>, B – argon, hydrogen, air, respectively

To determine the content of turbine oil in water, a water sample is introduced into the evaporator pos. 16. To determine the water content in the turbine oil, a water sample is introduced into the evaporator pos. 5. To determine the additive «Ionol» in the turbine oil, the extract from the turbine oil is introduced into the evaporator pos. 12. To determine the gases H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in water, turbine oil and in a mixture of turbine oil and water, the gas extract from these liquids is introduced into the metering valve pos. 1. To determine gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub> in water, turbine oil and in a mixture of turbine oil and water, the gas extract from these liquids is introduced into the metering valve pos. 7.

8. Research results of the values of the thresholds for determining the concentrations of components in liquid technological media during measurements

Table 5 shows the experimentally obtained values of the thresholds for determining the concentrations of diagnostic components in technological environments when performing measurements by GC methods. Each value of the concentration of a component in technological media was obtained as a result of five ( $n=5$ ) parallel measurements with a confidence level of  $p=0.95$  with a coefficient of normalized deviations depending on the number of degrees of freedom  $f=n-1$ , for  $n=5$ ,  $t=2.78$ .

The relative standard deviations of the output signals of the chromatographic detectors of the gas chromatograph (height or area of the chromatographic peak, the retention time of the chromatographic peak) when determining the content of the additive «Ionol» in turbine oil, water in turbine oil, turbine oil in water did not exceed 10 %.

Table 5

Thresholds for determining the concentrations of diagnostic components in liquid technological media when performing measurements by GC methods

| No. | Component   | $C_{no}$                |
|-----|---|-------------------------|
| 1   | H <sub>2</sub>  | 2 ppm                   |
| 2   | CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> | 1 ppm                   |
| 3   | C <sub>2</sub> H <sub>2</sub>   | 0.5 ppm                 |
| 4   | CO, CO <sub>2</sub>   | 5 ppm                   |
| 5   | O <sub>2</sub> , N <sub>2</sub>   | 1,5 ppm                 |
| 6   | «Ionol» additive in turbine oil   | 0.05 % mass             |
| 7   | Water in turbine oil  | 2 g/t                   |
| 8   | Turbine oil in water  | 0.02 mg/dm <sup>3</sup> |

Table 6 shows the values of the permissible relative error  $\delta_i$ , 5, determination of the concentration of dissolved gases  $C_i$  based on the results of GC analyzes of turbine oil, a mixture of turbine oil with water, water, depending on the concentration range.

These results are in line with those reported in [3] for mineral transformer oils.

The relative standard deviations of the output signal of the chromatographic detectors of the gas chromatograph (height or area of the chromatographic peak, the retention time of the chromatographic peak), depending on the range of gas concentrations, do not exceed the values given in Table 7.

Table 6

The value of the permissible relative error  $\delta_i$  of determination of the concentration of dissolved gases  $C_i$  based on the results of GC analyzes of turbine oil, a mixture of turbine oil with water, water, depending on the concentration range

| Dissolved gas concentration range, $C_i$ , % volumetric |   |                               |                             | $\delta_i$ , % |
|---|---|-------------------------------|-----------------------------|----------------|
| H <sub>2</sub>  | CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> | C <sub>2</sub> H <sub>2</sub> | CO, CO <sub>2</sub>         |                |
| <5·10 <sup>-3</sup>                                     | <10 <sup>-3</sup>   | <5·10 <sup>-4</sup>           | <5·10 <sup>-3</sup>         | ≥50            |
| (5...25)·10 <sup>-3</sup>                               | (1...3)·10 <sup>-3</sup>  | (5...15)·10 <sup>-4</sup>     | (5...25)·10 <sup>-3</sup>   | <50            |
| (25...50)·10 <sup>-3</sup>                              | (3...50)·10 <sup>-3</sup>   | (1,5...25)·10 <sup>-3</sup>   | (25...100)·10 <sup>-3</sup> | ≤20            |
| >5·10 <sup>-2</sup>                                     | >5·10 <sup>-2</sup>   | >5·10 <sup>-2</sup>           | >0,1                        | ≤10            |

Table 7

The value of the relative standard deviations of the output signal of the chromatographic detectors of the gas chromatograph

| Gas volume fraction, % volumetric | By 0.0001 | Above from 0.0001 to 0.01 | Above from 0.01 to 1 | Above from 1 to 10 |
|-----------------------------------|-----------|---------------------------|----------------------|--------------------|
| Relative standard deviation, %    | 10        | 4                         | 2                    | 1                  |

These results are consistent with similar results reported in [25].

Table 8 shows the values of the permissible relative error  $\delta_i$  of determination of the concentration of dissolved gases O<sub>2</sub> and N<sub>2</sub> in turbine oil, a mixture of turbine oil with water, water, depending on the concentration range.

Table 8

The value of the permissible relative error  $\delta_i$  of determination of the concentration of dissolved gases O<sub>2</sub> and N<sub>2</sub> in turbine oil, a mixture of turbine oil with water, water, depending on the concentration range

| $C_i$ , % volumetric | <1.5·10 <sup>-3</sup> | (1.5...7.5)·10 <sup>-3</sup> | (7.5... 15)·10 <sup>-3</sup> | >1.5·10 <sup>-2</sup> |
|----------------------|-----------------------|------------------------------|------------------------------|-----------------------|
| $\delta_i$ , %       | ≥50                   | <50                          | ≤20                          | ≤10                   |

These results are in line with those reported in [3] for mineral transformer oils.

Table 9 shows the values of the errors in determining the concentrations of the “Ionol” additive in turbine oil depending on the concentration range.

Table 9

Values of errors in determination of  $C_{ion}$  concentrations of the “Ionol” additive in turbine oil depending on the concentration range

| $C_{ion}$ , % mass         | 0.05  | 0.10  | 0.20  | 0.45  | 0.6   | 0.8   |
|----------------------------|-------|-------|-------|-------|-------|-------|
| $\pm\Delta_{ion}$ , % mass | 0.014 | 0.013 | 0.012 | 0.014 | 0.011 | 0.012 |
| $\delta_i$ , %             | 28    | 13    | 6     | 3     | 1.8   | 1.5   |

Note:  $\delta_{ion}$  – limits of permissible relative error, %,  $\Delta_{ion}$  – absolute error, % mass.

These results are consistent with similar results reported in [26].

Table 10 shows the values of errors in determining the concentration of water in turbine oil, depending on the concentration range.

Table 10

The values of the errors in the determination of water concentrations in turbine oil in depending on the concentration range

| $C_a$ , g/t         | 2    | 10   | 20   | 25   | 30   | 50   | 60   | 80  |
|---------------------|------|------|------|------|------|------|------|-----|
| $\pm\Delta_a$ , g/t | 0.79 | 3.4  | 5.7  | 6.3  | 6.6  | 7.2  | 7.3  | 7.4 |
| $\Delta_a$ , %      | 39.5 | 34.2 | 28.3 | 25.1 | 22.0 | 14.3 | 12.0 | 9.2 |

Note:  $\delta_{ion}$  – limits of permissible relative error, %,  $\Delta_a$  – absolute error, g/t.

These results are consistent with similar results reported in [26].

When determining the presence of turbine oil in water at concentrations of this oil from 0.02 mg/dm<sup>3</sup> to 5 mg/dm<sup>3</sup>, the permissible relative error at a confidence level of  $p=0.95$  at the level of 50 %, and at concentrations of this oil from 5 mg/dm<sup>3</sup> and above the permissible relative error at a confidence level of  $p=0.95$  – at the level of 25 %. These results correspond to the standardized requirements, presented in [10].

To determine the thresholds for determining the concentrations of components in technological media, mixtures were used: gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> in argon gas at a concentration of each gas at the level of 0.5 % by volume; additives “Ionol” in turbine oil at concentrations of “ionol” from 0.05 % by weight; up to 1.0 % by weight; turbine oil in water at turbine oil concentrations of 0.02 mg/dm<sup>3</sup>, 5 mg/dm<sup>3</sup> and 10 mg/dm<sup>3</sup>; water in turbine oil at a water concentration of 2 g/t to 80 g/t; hydrogen in water at a hydrogen concentration of 0.089 % by volume, 0.178 % by volume, 0.89 % by volume and 1.78 % by volume at a temperature of 20 °C.

### 9. Results of the development of the conceptual technological scheme of the oil and water supply system of the NPP main circulation pumps

Fig. 6 shows the developed flow diagram of the circulating oil and water supply system during the MCP operation of the pressurized water power reactor of the NPP with full or partial degassing of the flow of mineral turbine oil and the analysis of turbine oil and cooling water samples by GC methods.

This schematic flow diagram of the circulating oil and water supply system has been improved in comparison with the schematic flow diagram of the circulating oil and water supply system given in [5] during the MCP operation of the NPP pressurized water-cooled power reactor due to the introduction into this scheme: blocks of sorption purification of cooling water pos. 12, 16; unit of vacuum-thermal degassing of turbine oil flows pos. 27; sampling points of turbine oil (pos. 18–20, 28) and cooling water (pos. 21–26).

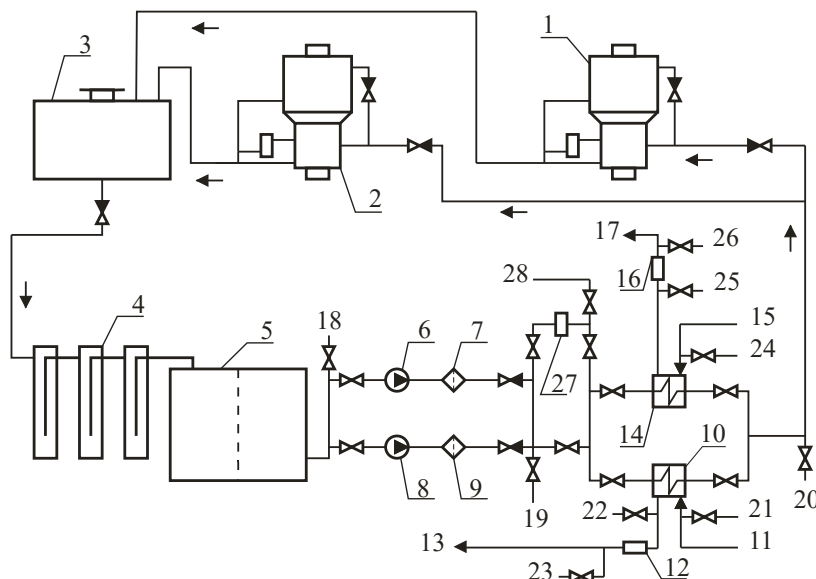


Fig. 6. Principal flow diagram of circulating oil and water supply during MCP operation of the NPP pressurized water power reactor and the analysis of samples of mineral turbine oil and return cooling water by GC methods:  
 1, 2 – MCP; 3 – oil tank for emergency discharge of turbine oil; 4 – liquid seal;  
 5 – oil tank; 6, 8 – oil pumps; 7, 9 – oil filters; 10, 14 – oil coolers;  
 11, 15 – inlets of cooling water flows; 12, 16 – blocks of sorption purification of cooling water; 13, 17 – outlets of cooling water flows;  
 18–20, 28 – turbine oil sampling points; 21–26 – sampling points of cooling water; 27 – unit for vacuum-thermal degassing of mineral turbine oil streams

**10. Discussion of the research results of the implementation of gas chromatographic analysis methods of technological media of the main circulation pumps**

The influence of ultrasonic vibrations on the generation of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub> in turbine oil Tp-22s (grade 1) at irradiation frequencies in the range 35–125 kHz and a radiator power of 20 W. This shows the degradation of turbine oil under the influence of acoustic vibrations in the conditions of acoustic cavitation in the volume of turbine oil and the generation of diagnostic gases dissolved in this oil. From the Table 1 it follows that the values of the concentration of dissolved diagnostic gases in the turbine oil increase with an increase in the duration of ultrasonic irradiation of this oil during the entire study time – 1500 s. In graphical form, the dependences of the values of the concentration of dissolved gases on the time of ultrasonic irradiation of the turbine oil have the form of straight lines (Fig. 1, 3). In the mathematical form, the dependences of the values of the concentration of dissolved gases C<sub>i</sub> on the time of ultrasonic irradiation τ of turbine oil have the form of a linear equation of the form C<sub>i</sub>=A·τ+B. Coefficients A and B of this equation have specific values for each diagnostic gas. Correlation coefficients R<sup>2</sup> have values in the range of 0.955–0.980, which indicates the adequacy of the obtained equations to the experimental data. This makes it possible to obtain solutions of diagnostic gases in turbine oil for their use when calibrating a gas chromatograph and determining the metrological characteristics normalized for it. In this case, there is no need to use expensive certified calibration mixtures. These results make it possible to reveal the cavitation mode of operation of the oil pumps of the cir-

culating oil supply system of the MCP and the degree of development of this mode on the basis of GC for determining the content of diagnostic gases before and after the oil pumps. The results correspond to similar results noted for mineral transformer oils [5].

The influence of ultrasonic vibrations on the generation of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub> in a mixture of turbine oil Tp-22s (grade 1) with water is investigated. The concentration of this oil is 5 mg/dm<sup>3</sup>, the irradiation frequency is in the range of 35–125 kHz, and the emitter power is 20 W.

This also shows the degradation of turbine oil under the action of acoustic vibrations in the conditions of acoustic cavitation in the volume of turbine oil and the generation of diagnostic gases dissolved in water. From the Table 1 it follows that the values of the concentration of dissolved diagnostic gases in a mixture of turbine oil and water increase with an increase in the duration of ultrasonic irradiation of this mixture during the entire study time – 1500 s. In graphical form, the dependences of the values of the concentration of dissolved gases on the time of ultrasonic irradiation of this mixture also have the form of straight

lines (Fig. 2, 4). In the mathematical form, the dependences of the values of the concentration of dissolved gases C<sub>i</sub> on the time of ultrasonic irradiation τ of turbine oil have the form of a linear equation of the form C<sub>i</sub>=A·τ+B. Coefficients A and B of this equation have specific values for each diagnostic gas. The correlation coefficients R<sup>2</sup> have values in the range of 0.95–0.995, which indicates the adequacy of the obtained equations to the experimental data. These results make it possible to reveal the cavitation mode of operation of the oil coolers of the circulating oil supply system of the MCP and the degree of development of this mode on the GC basis for determining the content of diagnostic gases before and after the oil coolers in the cooling water. This mode of operation can lead to depressurization of the heat exchange tubes and the penetration of turbine oil into the cooling water. The presence of turbine oil in the cooling water is determined in samples of this water by ultrasonic disintegration products of turbine oil in the form of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>. When determining turbine oil in the cooling water, oil coolers are based on the presence of dissolved gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub> in the cooling water, it is sufficient to perform ultrasonic irradiation for 1500 s.

From the Table 4 it follows that the main technical requirements for a gas chromatograph for determining the content of diagnostic components in technological media comply with the requirements of regulatory documents. These documents are: for gases in turbine oil and water [3]; for “Ionol” in turbine oil [7]; for turbine oil in water [10]; for water in turbine oil [9].

From Tables 5–10 it follows that the obtained results of the values of the thresholds for determining the concentra-



tions of diagnostic components meet the requirements for metrological characteristics, which are given in the regulatory documents. These documents are: for gases in turbine oil and water [3]; for "Ionol" in turbine oil [7]; for turbine oil in water [10]; for water in turbine oil [9]. The obtained values of the detection thresholds in turbine oil and cooling water: 2 ppm for H<sub>2</sub>, 1 ppm for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, 0.5 ppm for C<sub>2</sub>H<sub>2</sub>. Also, the obtained values of the detection thresholds in turbine oil and cooling water are 5 ppm for CO and CO<sub>2</sub>, 1.5 ppm for O<sub>2</sub>, N<sub>2</sub>. The value of the determination threshold in the turbine oil of the "Ionol" additive at the level of 0.05 % by weight was obtained. The value of the detection threshold in the turbine oil of water at the level of 2 g/t was obtained. The value of the detection threshold in the cooling water of the turbine oil at the level of 0.02 mg/dm<sup>3</sup> was obtained.

The block diagram of the developed five-channel gas chromatograph with TCD and FID modules for determining the content of diagnostic components in turbine oils and cooling water includes several main elements (Fig. 5). These include gas metering valves with calibrated metering loops, column head, thermostats, TCD, FID, evaporators, methanator, lines of gaseous argon, hydrogen, air. The principle of operation of a similar circuit for the operation of individual measuring channels is described in [5].

A feature of the proposed scheme is the additional placement of the evaporator (pos. 16) and the column head (pos. 17) in the supply line of the FID (pos. 15) with gaseous H<sub>2</sub> to determine the turbine oil in the cooling water.

In addition, it was proposed to preliminarily perform ultrasonic irradiation of cooling water for the disintegration of turbine oil in it and further determination of the obtained diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>.

Such technical solutions make it possible to use one gas chromatograph to perform measurements and provide the metrological characteristics given in Tables 5–10.

A schematic flow diagram of the circulating oil supply system with turbine oil and with the use of cooling water during operation of the NPP MCP has been developed (Fig. 6). This scheme includes MCP, turbine oil emergency discharge oil tank, liquid seal, oil tank, oil pumps, oil filters, oil coolers, cooling water flow inlets, cooling water sorption treatment units, cooling water flow outlets. This scheme also includes sampling points for turbine oil and cooling water, a unit for vacuum-thermal degassing of turbine oil flows.

It is proposed additionally in this scheme to place a unit for vacuum-thermal degassing (UVTD) of turbine oil flow (item 27) for its continuous complete or partial degassing. This helps to reduce the oxidative degradation of the turbine oil and the corrosion of the interior of equipment and pipelines.

It is proposed to additionally place blocks for sorption treatment of cooling water (BSTCW) (pos. 12, 16) in this scheme to clean the flow of cooling water from oil products. This also allows cleaning the cooling water from the turbine oil, it can penetrate into this water during the operation of oil coolers (pos. 10, 14) when the heat exchange tubes are depressurized.

It is suggested additionally in this scheme to place sampling points of turbine oil (pos. 18–20, 28) for measuring concentrations in it using the GC methods of diagnostic gases, water, and the Ionol additive.

It is proposed additionally in this scheme to place cooling water sampling points (pos. 21–26) for measuring concen-

trations in it by the GC method of diagnostic gases and the presence of turbine oil.

This presence of turbine oil is determined by the products of its accelerated ultrasonic disintegration in the cooling water sample in the form of H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>. Such technical solutions make it possible to establish the presence of the occurrence of a cavitation mode of operation of oil pumps (pos. 6, 8) and oil coolers (pos. 10, 14). In this case, it is possible to determine the operability of the UVTD (pos. 27), BSTCW (pos. 12, 16) and oil coolers (pos. 10, 14), taking into account the depressurization of the heat exchange tubes and the penetration of turbine oil into the cooling water. In general, such technical solutions ensure the reliability of operation of the equipment of the circulating MCP oil and water supply systems.

When examining the content of components in technological environments, the conditions for performing measurements should not exceed the values typical for the operation of the corresponding GC columns of the chromatograph. When examining the content of diagnostic gases in technological environments, the limitations are that the concentration range of  $5 \cdot 10^{-4}$  – 1.60 % by volume has been studied. When investigating the content of the "Ionol" additive in turbine oil, the limitations are in the fact that the concentration range of 0.05–0.8 % by weight was studied. When examining the water content in turbine oil, the limitations are that the concentration range of 2–80 g/t is investigated. When examining the content of turbine oil in water, the limitations are that the concentration range is 0.02–5 mg/dm<sup>3</sup>. When using formulas (1) and (2) for calculating the values of the concentrations of components in technological media, the values of the distribution coefficients should not depend on the values of these concentrations. In the study of the technological scheme of circulation oil and water supply during the NPP MCP operation, the limitations are that the sampling of technological media and the performance of GC measurements are performed periodically. This is due to the dangerous effect of radioactive radiation on personnel during sampling of technological media.

The research can be developed in the direction of determining the effect of acoustic vibrations on: generation of water, organic acids, solid carbon, hydrogen sulfide, nitrogen oxides, degradation of the Ionol additive and aromatic compounds in mineral turbine oil. This will make it possible to develop methods for diagnosing defects in equipment associated with acoustic cavitation using GC methods for analyzing liquid technological media. The study can be developed in the direction of developing methods for monitoring the content of diagnostic components in technological environments using automatic chromatographs and other measuring equipment.

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## 11. Conclusions

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1. The study revealed the influence of ultrasonic vibrations on the generation of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub> in turbine oil Tp-22s (grade 1) and in a mixture at a turbine oil concentration of 5 mg/dm<sup>3</sup> in distilled water at irradiation frequencies in the range of 35–125 kHz and a radiator power of 20 W. This shows the degradation of turbine oil under the influence of acoustic vibrations in the conditions of acoustic cavitation in the volume of turbine oil and the generation of diagnostic gases dissolved in this oil.

It was found that the values of the concentration of dissolved diagnostic gases in the turbine oil increase with an increase in the duration of ultrasonic irradiation of this oil during the entire study time – 1500 s. In this case, the concentrations of dissolved gases reach values (% vol.): 0.46 – for CH<sub>4</sub>, 1.6 – for C<sub>2</sub>H<sub>4</sub>, 0.6 – for H<sub>2</sub>, 0.14 – for C<sub>2</sub>H<sub>6</sub>, 0.20 – for C<sub>2</sub>H<sub>2</sub>, 0, 1 – for CO, 0.05 – for CO<sub>2</sub>. In graphical form, the dependences of the values of the concentration of dissolved gases on the time of ultrasonic irradiation of turbine oil have the form of straight lines. In the mathematical form, the dependences of the values of the concentration of dissolved gases C<sub>i</sub> on the time of ultrasonic irradiation τ of turbine oil have the form of a linear equation of the form  $C_i = A \cdot \tau + B$ . Coefficients A and B of this equation have specific values for each diagnostic gas. Correlation coefficients R<sup>2</sup> have values in the range of 0.955–0.980, which indicates the adequacy of the obtained equations to the experimental data. This makes it possible to obtain solutions of diagnostic gases in turbine oil for their use when calibrating a gas chromatograph and determining the metrological characteristics normalized for it. In this case, there is no need to use expensive certified calibration mixtures. These results make it possible to reveal the cavitation mode of operation of the oil pumps of the circulating oil supply system of the MCP and the degree of development of this mode on GC basis for determining the content of diagnostic gases before and after the oil pumps.

It was found that the values of the concentrations of the dissolved diagnostic gases in the mixture of turbine oil and water increase with an increase in the duration of ultrasonic irradiation of this system throughout the entire study period – 1,500 s. at the same time, the concentration of dissolved gases reaches values (% vol.): 0.035 – for CH<sub>4</sub>, 0.16 – for C<sub>2</sub>H<sub>4</sub>, 0.06 – for H<sub>2</sub>, 0.10 – for C<sub>2</sub>H<sub>6</sub>, 0.12 – for C<sub>2</sub>H<sub>2</sub>, 0.01 – for CO, 0.009 – for CO<sub>2</sub>.

In graphical form, the dependences of the values of the concentration of dissolved gases on the time of ultrasonic irradiation have the form of straight lines. In mathematical form, the dependences of the values of the concentration of dissolved gases C<sub>i</sub> on the time of ultrasonic irradiation have the form of a linear equation of the form  $C_i = A \cdot \tau + B$ . Coefficients A and B of this equation have specific values for each diagnostic gas. The correlation coefficients R<sup>2</sup> have values in the range of 0.95–0.995, which indicates the adequacy of the obtained equations to the experimental data. These results make it possible to reveal the cavitation mode of operation of the oil coolers of the circulating oil supply system of the MCP and the degree of development of this mode on the GC for determining the content of diagnostic gases before and after the oil coolers in the cooling water.

The presence of turbine oil in the cooling water is determined in samples of this water by ultrasonic disintegration products of turbine oil in the form of diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>. In this case, it is sufficient to perform ultrasonic irradiation for 1,500 s.

The results obtained make it possible to develop GC methods for determining the accumulation of turbine oil in the flow of cooling water by the presence of dissolved gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub> as a result of artificial ultrasonic disintegration of a sample of this oil in cooling water. This, in turn, makes it possible to identify violations of the sealing of oil cooler assemblies and to simplify and reduce the cost of measurement processes.

2. As a result of the study, the main technical requirements for the structural diagram of a five-channel chro-

matograph with TCD and FID modules for GC analysis of mineral turbine oils and cooling water and determination of the content of diagnostic components in them were determined. These requirements for a gas chromatograph meet the requirements of regulatory documents for determining the content of: gases in turbine oil and water; “Ionol” in turbine oil; turbine oil in water in turbine oil. These requirements for a gas chromatograph relate to such indicators as: training temperatures of GC columns, TCD, FID, methanator, evaporators, final temperatures of GC columns; v – speed of temperature programming of GC columns; types and physico-chemical characteristics of the chromatographic sorbent and liquid phases on these sorbents. The diagnostic components are: turbine oil contains H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, water, “Ionol” additive; in cooling water – H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, turbine oil. This allows to develop a block diagram of a single gas chromatograph for performing measurements using different GC columns and measurement techniques. This simplifies and reduces the cost of the measurement process.

3. As a research result, a structural diagram of a five-channel gas chromatograph with TCD and FID modules was developed for GC analysis of turbine oils and cooling water and determination of diagnostic components in them.

In the developed scheme, it is proposed to additionally place an evaporator and a GC column in the supply line for a gas mixture of H<sub>2</sub> to determine turbine oil in the cooling water.

It is proposed to preliminarily perform ultrasonic irradiation of cooling water for the disintegration of turbine oil in it and further determination of the obtained diagnostic gases H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>. This allows the presence of turbine oil in the water to be detected. Such technical solutions allow using one gas chromatograph to perform measurements, provide standardized metrological characteristics, simplify and reduce the cost of measurement processes.

4. As a research result, the value of the thresholds for determining the concentrations of diagnostic components in liquid technological media when performing measurements by GC methods was determined. The obtained values of the detection thresholds in turbine oil and cooling water: 2 ppm for H<sub>2</sub>, 1 ppm for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, 0.5 ppm for C<sub>2</sub>H<sub>2</sub>. Also, the obtained values of the detection thresholds in turbine oil and cooling water are 5 ppm for CO and CO<sub>2</sub>, 1.5 ppm for O<sub>2</sub>, N<sub>2</sub>. The value of the determination threshold in the turbine oil of the additive “Ionol” at the level of 0.05 % of the mass was obtained. The value of the detection threshold in the turbine oil of water at the level of 2 g/t was obtained. The value of the detection threshold in the cooling water of the turbine oil at the level of 0.02 mg/dm<sup>3</sup> was obtained. The obtained results correspond to the standardized requirements for the metrological characteristics of the GC results for determining the concentrations of diagnostic components in the corresponding liquid technological media.

5. As a research result, a schematic flow diagram of the circulating oil supply system with turbine oil and with the use of cooling water during the NPP MCP operation was developed.

It is proposed in this scheme to place a unit for vacuum-thermal degassing of the turbine oil flow for its continuous complete or partial degassing. This helps to reduce the oxidative degradation of the turbine oil and the corrosion of the interior of equipment and pipelines.

It is proposed to place blocks of sorption cleaning of cooling water in this scheme for cleaning the flows of cooling water from oil products. This also makes it possible to purify

the cooling water from the turbine oil, it can penetrate into this water during the operation of oil coolers when the heat exchange tubes are depressurized.

It is proposed to place sampling points of turbine oil in this scheme for measuring concentrations in it using the GC methods of diagnostic gases, water, and the Ionol additive.

It is proposed to place cooling water sampling points in this scheme for measuring concentrations in it by the GC method of diagnostic gases and the presence of turbine oil.

This presence of turbine oil is determined by the products of its accelerated ultrasonic disintegration in the cooling water sample in the form of dissolved gases

H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>. Such technical solutions make it possible to establish the occurrence of a cavitation mode of operation of oil pumps and oil coolers. At the same time, it is possible to determine the operability of the installation for vacuum-thermal degassing of the flow of turbine oil, blocks of sorption purification of cooling water and oil coolers, taking into account the depressurization of heat exchange pipes and the penetration of turbine oil into the cooling water. In general, such technical solutions ensure the reliability of operation of the equipment of the circulating oil and water supply systems of the MCP.

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