

Improvement of the gas chromatographic method for diagnosing developing defects in oil-filled electrical equipment based on the analysis of furan compounds

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Abstract. During the operation of oil-filled electrical equipment under the influence of temperature, humidity and other negative factors, the destruction of paper insulation occurs. As a result of this destruction, furan compounds are formed, which get into the transformer oil. To identify the process of destruction of paper insulation, control of furan compounds in transformer oil is carried out by instrumental methods. Of these methods, the most widely used is gas chromatography using packed chromatographic columns, on the basis of which guidelines have been developed. To improve gas chromatographic methods for monitoring furan compounds, we used a highly efficient quartz capillary column filled with a polar stationary phase based on polyethylene glycol. The sample was injected into the injector of the chromatograph Chromos-GC1000 using an automated dosing system with a vial for 23 samples. Used transformer oil of the GK-1 brand of Almetyeysk electrical networks was taken as the object of research; The optimal retention characteristics of standard sorbates were preliminary determined, which were used as organic extractants of transformer oil and furan compounds. The effect of temperature on the process of chromatographic analysis of furfuryl alcohol and organic extractants was determined, on the basis of which it was established that the selectivity of separation is determined by the nature of intermolecular interactions in the sorbate-sorbent system, in particular, the formation of a hydrogen bond. It has been shown that the selectivity coefficient for the separation of furfuryl alcohol depends on the physicochemical nature of organic extractants, their boiling points and dipole moments and has the highest values for the analyzed pair of components: furfuryl alcohol - ethanol.

1 Introduction

At present, control over the technical condition of oil-filled electrical equipment is carried out by instrumental methods. In power enterprises of the Russian Federation, this control is carried out by chromatographic methods, which are characterized by a sufficiently high sensitivity and accuracy and allow the determination of the products of its destruction in transformer oil. Chromatographic methods for controlling transformer electrical equipment are included in the main regulatory documents that determine the main provisions of diagnostics.

During the operation of power transformers, gaseous substances are concentrated in them, which are products of the destruction of transformer oil. Therefore, usually the diagnosis of slowly developing defects in transformer electrical equipment is carried out by analyzing gases dissolved in transformer oil [1-4].

During the operation of oil-filled electrical equipment, as a result of the destruction of paper insulation due to thermal oxidative and hydrolytic transformation of cellulose, furan compounds are formed. To control these contents in transformer oil, chromatographic analysis methods are used. For the

extraction of furan compounds from transformer oil, it is more promising to use aliphatic alcohols with higher boiling points, which contain less water. To control the degree of destruction of solid insulation, the use of furfuryl alcohol is more promising [5-6].

To determine furfuryl alcohol in transformer oil, we used transformer oil sorption by various instrumental methods. For this purpose, the process of adsorption, obtaining chemical derivatives and extraction is used, which is subdivided into liquid, gas, solid-phase, supercritical fluid, as well as using low temperatures [7-9]. In addition, a promising direction is extraction in microwave, magnetic, electromagnetic and centrifugal fields, which makes it possible to separate the components of transformer oil into groups of substances. In this case, the process of sorption of transformer oil can be easily automated, which will lead to a decrease in the error in determining the analyzed components by eliminating the influence of the human factor [10-12].

2 Materials and methods

To process the results of chromatographic analysis, a computer program for the collection, storage and

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processing of chromatographic information “Chromos 2.24” was used with the possibility of printing the obtained experimental data on a printer. The chromatographic columns used were a capillary column 30 m long, 0,32 mm inner diameter, filled with a stationary phase based on polyethylene glycol “Vako BoHa VB WAX P / n CF 5903032050A”, with a film thickness of 0,5 μm . The analytes were dosed into an injector of a gas-liquid chromatograph using an automatic liquid dispenser “ALD-23”, with vials for 23 samples. The volume of the sample introduced into the chromatograph evaporator in all cases did not exceed 1,0 μl . The rate of sample collection into vials was 20 $\mu\text{l}/\text{sec}$, the rate of dosing was 30 $\mu\text{l}/\text{sec}$, and the time of sample accumulation in the evaporator of the chromatograph during dispensing was 10 sec. Chromatographic analysis was carried out both in isothermal mode and with linear programming of the temperature of the chromatographic column from 40°C to 250°C with a temperature rise rate from five to ten degrees per minute. The evaporator temperature was 200°C, the detector temperature was 240°C. Argon was used as a carrier gas. The hydrogen velocity was 25 cm^3/min , the air velocity was 250 cm^3/min .

3 Discussion result

Recently, for the analysis of complex organic mixtures, capillary gas-liquid chromatography has become widely used, which is more efficient, since it allows one to obtain narrower peaks. With the user of capillary columns, it is possible to carry out analysis in a wider range of boiling points of the analyzed components, since they do not contain sorption in the grains of a solid carrier, which exists in packed columns. To assess the chromatographic properties of organic solvents and furfuryl alcohol, we determined their absolute retention times on a capillary column at different temperatures and numerical values.

In figures 1 show chromatograms of separation of organic solvents and furfuryl alcohol, which is a marker for diagnostics of oil-filled electrical equipment, since it migrates into transformer oil as a result of destruction of paper insulation.

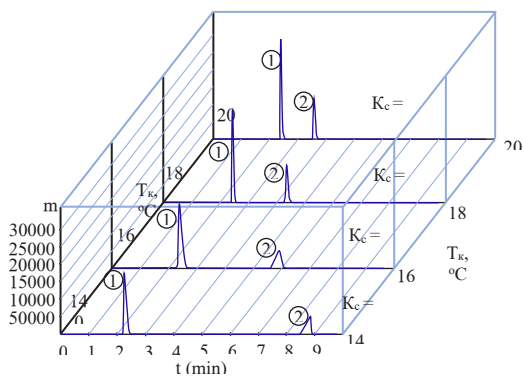


Fig. 1. Chromatogram of the separation of Ethyl acetate and Furfuryl alcohol at different temperatures of analysis in the coordinates: Response of the detector signal, mV; T_k - analysis temperature, °C. 1. Ethyl acetate, 2. Furfuryl alcohol.

As can be seen from the figures, in all cases there is a significant decrease in the retention time of all organic solvents with an increase in temperature in the range from 140 to 200°C. At the same time, at low temperatures of analysis, the peak of furfuryl alcohol turns out to be blurred, which is determined by its rather high boiling point. With an increase in the analysis temperature, the chromatographic peak of furfuryl alcohol becomes more symmetric. In this case, the selectivity of the separation of organic solvents and furfuryl alcohol also depends on temperature.

To assess the mechanism of chromatographic separation of organic solvents in gas-liquid chromatography, the relative retention characteristics are widely used, which are associated by a logarithmic dependence with the physicochemical properties of sorbents and stationary liquid phases. We used the retention time as a relative characteristic of the retention of organic solvents.

Table 1. Absolute dependence of the retention time of aliphatic alcohols and furfuryl alcohol on the temperature of the chromatographic column.

T_k °C	Retention time of aliphatic alcohols at temperature (t_R , min)				
	Methanol	Ethanol	n-Butanol	iso-Aminol	Furfuryl alcohol
40	5.21	6.17	24.55	39.81	-
60	3.47	3.91	12.08	15.67	-
80	2.75	2.90	6.68	7.94	90.99
100	2.45	2.46	3.89	4.74	35.89
120	2.34	2.43	2.95	3.31	16.60
140	2.27	2.38	2.69	2.95	8.82
160	2.29	2.39	2.60	2.73	5.81
180	2.34	2.43	2.57	2.67	4.40
200	2.40	2.53	2.57	2.71	3.73

In fig. 2. shows the dependence of the logarithm of the retention time of aliphatic alcohols of furfuryl alcohol on the temperature of the analysis

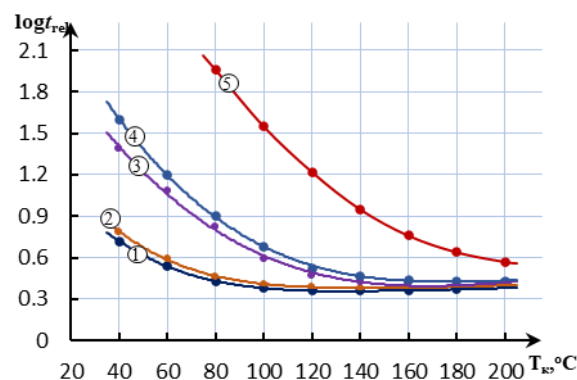


Fig. 2. Dependence of the logarithm of the retention time of aliphatic alcohols and furfuryl alcohol on the analysis temperature: 1. Methanol; 2. Ethanol; 3. n-Butanol; 4. iso-Aminol; 5. Furfuryl alcohol.

As seen from fig. with an increased separation temperature, the logarithm of the retention time of aliphatic alcohols and furfuryl alcohol significantly decreases. This is obviously associated with the formation of an intermolecular hydrogen bond of the hydroxy group of the alcohol with the structural

fragments of the polar stationary phase. Since the energy of the intermolecular hydrogen bond decreases with increasing temperature, the retention time of aliphatic alcohols and furfuryl alcohol decreases.

At a temperature exceeding 120°C, all aliphatic alcohols practically do not separate and their retention time does not depend on the temperature of the chromatographic column. This indicates a change in the chromatographic separation mechanism, when at an elevated temperature intermolecular hydrogen bonds are not formed in the sorbate-sorbent system, and the separation proceeds according to the dispersion mechanism, i.e. the stationary phase in the capillary column becomes non-polar. It is known that the extraction process of transformer oil can also be affected by various impurities contained in the organic extractant. For this purpose, organic solvents were analyzed for the content of associated impurities.

To determine furfuryl alcohol directly in the used transformer oil, a series of experiments was carried out. For this purpose, a direct analysis of transformer oil was carried out without preliminary sample preparation. For this purpose, furfuryl alcohol in an amount of 0,5% by weight and carbon tetrachloride were added to fresh transformer oil. The sample was injected directly into an injector of a gas-liquid chromatograph.

In fig. 3 (A) shows a chromatogram of the separation of used transformer oil from which it can be seen that furfuryl alcohol elutes in the form of a symmetrical peak against the background of a significant deviation from the baseline. This is obviously due to the fact that the used transformer oil contains asphaltenes and resins that have high boiling points, are characterized by high viscosity and, therefore, are washed out of the chromatographic column with great difficulty by an inert carrier gas. The chromatographic column is contaminated with high-boiling components of transformer oil; therefore, to clean it, it is necessary to carry out regular conditioning at an elevated temperature.

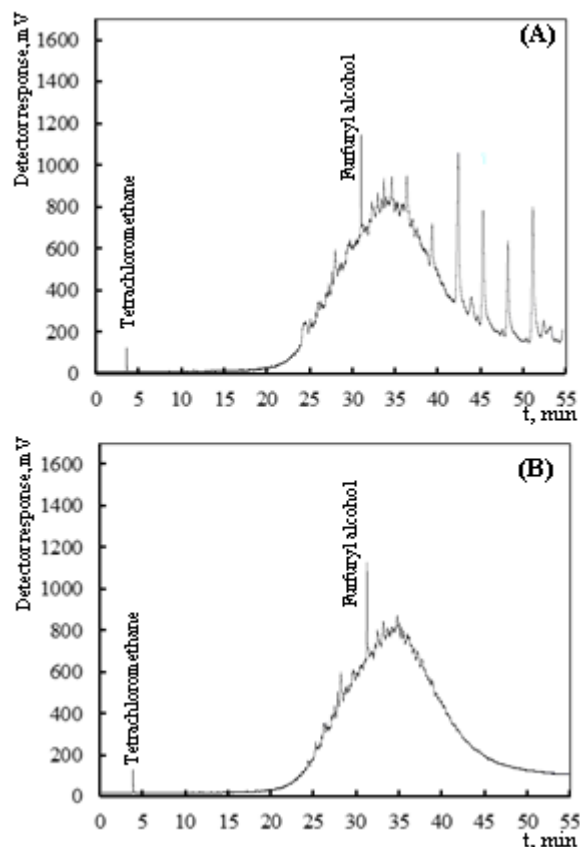


Fig. 3. Chromatogram of the separation of individual components of used transformer oil and furfuryl alcohol. The eluent is carbon tetrachloride. A. Used transformer oil; B. Transformer oil purified by sorption of the zeolite-containing rock of the Tatarsko-Shatrashanovskoye field.

As seen from fig. 3 (A), the transformer oil also contains peaks of higher boiling point components that are not identified.

To purify transformer oil from accompanying impurities, we used the adsorption method using zeolite-containing rocks of the Tatarsko-Shatrashanovskoye field. For this purpose, the spent transformer oil was passed through an adsorption chromatographic column filled with a zeolite-containing rock.

As seen from fig. 3 (B), the transformer oil is purified from accompanying impurities, since the “tail” of the peak lacks the components that make up the transformer oil. In this case, the analysis time of furfuryl alcohol does not exceed 30 minutes.

4 Findings

Based on the studies carried out, it has been shown that used transformer oil can be analyzed using gas-liquid chromatography, with which it is possible to determine their composition. Furfuryl alcohol resulting from degradation of paper insulation can be monitored by direct analysis on a capillary column with a polar stationary liquid phase.

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