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INSTRUMENTAL METHODS IN MODERN FIRE-TECHNICAL EXPERTISE. 5. CHROMATOGRAPHIC RESEARCH METHODS

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Abstract. The possibilities of using chromatographic methods in fire-technical expertise are considered. The advantages and disadvantages of thin-layer, high-performance liquid, gas-liquid and ion chromatography methods are presented. The use of linear retention indices and the «fingerprint» method in gas-liquid chromatography to establish the nature of organic residues of unknown origin and assign them to a specific class (type) of a flammable and combustible liquid by component composition is described in detail. Examples of the application of the method of gas-liquid and ion chromatography for the study of objects of various nature and the solution of identification problems in fire-technical expertise in the investigation of real fires are given. It is shown that the most popular methods for solving expert problems in the investigation of fires in order to study flammable and combustible liquids, special incendiary compositions and flame retardant wood are the methods of ion and gas-liquid chromatography.

Keywords: chromatography, gas chromatography, gas-liquid chromatography, ion chromatography, thin-layer chromatography, high-performance liquid chromatography, fire-technical expertise, research objects

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This article is a continuation of a series of articles on the analytical capabilities of various instrumental methods in solving problems of forensic fire and technical expertise [1–4]. The article deals with the application of chromatographic methods in fire-technical expertise.

Chromatography is a physicochemical method for separating complex mixtures into components, based on repeated repetition of the distribution of components between two phases – mobile and stationary. In forensic activities, chromatographic methods are widely used to detect and study residues of combustible and flammable liquids (FL, flammable liquids) [5, 6], special incendiary compositions [7], and fire retardants on wood [8].

For a long time, thin-layer chromatography [9, 10] was used in expert practice to detect residues of flammable liquids and liquids, where oil products were detected by the presence of characteristic spots on plates with a sorbent using various eluents. Thin-layer chromatography is used to separate oil residues into paraffinic, naphthenic, olefinic, aromatic hydrocarbons, as well as to separate oil products from extractive substances of carrier objects (wood, fabrics, etc.). In addition to color, during development, each substance is characterized by the location of the spot on the chromatogram by the so-called Rf value – the ratio.

The distance traveled by the spot from the start to the distance traveled from the start by the solvent (eluent) front. However, this method has not been widely used in expert practice due to low sensitivity, limited resolution, poor reproducibility and toxicity. Many reagents used in thin layer chromatography are toxic.

Another widely used method in the detection and study of petroleum products is high performance liquid chromatography [11–14]. This method has high sensitivity and the ability to detect various classes of organic compounds, depending on the detector used. In the study of petroleum products, UV-spectrometric, fluorimetric and refractometric detectors, which allow you to determine the total content of aromatic hydrocarbons.

Gas chromatography is one of the most popular instrumental methods in analytical chemistry. In forensic science, the method is widely used to establish the nature of organic remains of unknown origin and assign them to a specific type of combustion intensifiers.

Chromatographic separation in gas-liquid chromatography consists of a number of dissolution and elution processes occurring in the stationary liquid phase layer inside the chromatographic column along its entire length. As a result of the interaction for each component of a complex mixture with a stationary liquid phase (SLP), a new state of dynamic equilibrium is created at the interface between the stationary and mobile phases [15–17].

To study oil products, standard methods have been developed for determining the total content of oil products in water, as well as their identification by comparing the obtained chromatograms with chromatograms of oil products of various types using the «fingerprint» method [18]. Identification of hydrocarbons by the «fingerprint» method makes it possible to draw a conclusion about the contamination of an object with a specific type of oil product, which leads to a simplification of the procedure for determining the source of pollution.

The gas chromatographic method [19, 20] makes it possible to establish with high accuracy the type of oil product by hydrocarbon composition and determine the content of oil products in natural and waste waters. As a rule, the calculation of the fractional composition is performed on the basis of a linear relationship between the retention time of hydrocarbons and their boiling point [21–26].

In the procedure [5], developed for the study of organic residues after fires in the testing fire laboratories of the Forensic laboratory EMERCOM of Russia, a ZB-50 capillary column is used, and a universal flame ionization detector is used as a detecting device. The separation of complex mixtures into separate components to reduce the analysis time is carried out by programming the column temperature in the temperature range from 40 °C to 280 °C at a temperature rise rate of 4 °C per minute and holding at the initial column temperature for 5 min. Identification of peaks in the chromatogram of a sample of unknown origin is carried out by the coincidence of the chromatographic parameters of the peaks (times or retention indices) with the parameters of the peaks of the reference mixtures of hydrocarbons and oxygen-containing compounds. To do this, chromatograms of reference mixtures of alkanes, arenes, and oxygen-containing compounds are taken in the chromatography mode developed for the study of liquid samples according to the procedure [5].

To identify arenes that are part of petroleum products and butyl acetate, which is part of mixed solvents, it is sufficient to calculate the linear retention indices of peaks on the chromatogram of a sample of unknown composition, and to identify oxygen-containing compounds such as alcohols (methanol, ethanol, propanol-1 and butanol-1) and esters (ethyl and propyl acetates), logarithmic retention indices should be used, since the separation of these substances in the column proceeds in the isothermal temperature regime of the column, namely, for 5 min at 40 °C.

The coincidence of the retention parameters serves as the basis for the identification of the compound. Chromatographic characteristics of substance indices are calculated in a unified scale of Kovacs indices of alkanes. Almost all substances can be represented on the Kovacs index scale for alkanes.

The table shows the linear retention indices of arenes calculated for the stationary liquid phase of the ZB-50 brand relative to the retention times and Kovacs indices of alkanes.

Thus, to calculate the linear retention indices of arenes and iso-alkanes in the case of petroleum products and oxygen-containing compounds that are part of non-petroleum technical fluids (mixed solvents and alcohol-based ignition fluids), integer values of the Kovacs retention indices for alkanes are used, which depend on only on the number of carbon atoms in the alkane molecule and do not depend on the nature of the stationary liquid phase in the column and its geometric parameters (length, inner diameter, layer thickness), as well as on the chromatography conditions (temperature regime of the column, nature and pressure of the carrier gas – mobile phases).

Table

Linear indices of arenes and isoprenoid alkanes calculated for NZhF brand ZB-50 relative to the retention times of normal alkanes C_8–C_{18}

Component Name	Linear index	Group arena
Toluene	865	Monoalkylbenzene
Ethylbenzene	965	Monoalkylbenzene
P-xylene	969	Dimethylbenzene
M-xylene	972	Dimethylbenzene
O- xylene	1005	Dimethylbenzene
Propylbenzene	1058	Monoalkylbenzene
1-methyl-3 (4)-ethylbenzene	1069	Dialkylbenzene
1,3,5-trimethylbenzene	1073	Trimethylbenzene
1-methyl-2-ethylbenzene	1095	Dialkylbenzene
1,2,4-trimethylbenzene	1105	Trimethylbenzene
1,2,4,5-tetramethylbenzene	1235	Tetramethylbenzene
1,2,3,5-tetramethylbenzene	1245	Tetramethylbenzene
2,6,10-trimethylpentadecane	1630	Iso-alkane
Prystane	1680	Iso-alkane
Fitane	1786	Iso-alkane

As an example, in fig. 1 shows a chromatogram of organic residues of unknown origin from the fire site. As can be seen from fig. 1, the chromatogram contains intense peaks in the retention time interval from 15 min up to 42 min, indicating the multicomponent nature of the analyzed organic residues. The peaks are located with almost the same time step, which indicates that they belong to the same class of compounds. Moreover, the retention times of the peaks in this chromatogram coincide with the retention times of the alkane peaks from undecane to nonadecane in the chromatogram of the reference mixture of alkanes (C11–C19), which makes it possible to identify these peaks as the peaks of C11–C19 alkanes. As a result of calculating the retention indices of additional low-intensity peaks in the region of alkanes from hexadecane to octadecane, it was found that these peaks have linear retention indices of 1 630 units, 1 680 units. and 1 786 units, respectively. According to the table, these peaks belong to isoprenoid alkanes, namely, 2,6,10-trimethylpentadecane, pristane, and phytane, respectively. It should be noted that the chromatogram shown in fig. 1, there are no peaks belonging to low-boiling alkanes (octane, nonane, and decane).

It is known that the presence of normal alkanes from octane to nonadecane and isoprenoid alkanes in mixtures of diesel fuels is characteristic of diesel fuels [27, 28].

On fig. 2 shows a typical chromatogram for diesel fuels. Comparison of the chromatogram of a sample of unknown composition with the chromatogram of diesel fuel (fig. 2) using the «fingerprint» method confirms that organic residues of unknown origin belong to diesel fuel subjected to thermal treatment during a fire.

As a second example in fig. 3 shows a chromatogram of organic residues (a fragment of a mattress) that came from a fire in the attic of a residential building, from which it can be seen that the chromatogram is a set of peaks of different intensities located in the range of retention times from 3 to 43 min. To establish the nature of these organic residues, the peaks on the chromatogram were processed with respect to the retention times of alkanes (fig. 1, curve 2) and their linear retention indices were determined (fig. 3). Comparison of the obtained values of the linear retention indices of the peaks in the chromatogram of unknown composition with the values of the linear retention indices from the table made it possible to identify the peaks and establish the presence of arenes and isoprenoid alkanes in the organic residues. The set of arenes found in the course of the GLC study in a sample of unknown origin (hexane extract from a fragment of a mattress) received from the fire site coincides with the values of the linear indices of the peaks

on the chromatogram of the arbitration sample of Regular-92 motor gasoline (fig. 4), and the region of the peaks from 30 min and more reproduces the area of the diesel fuel chromatogram (fig. 2). This unequivocally indicates the presence of residues of a mixture of motor gasoline and diesel fuel in the sample.

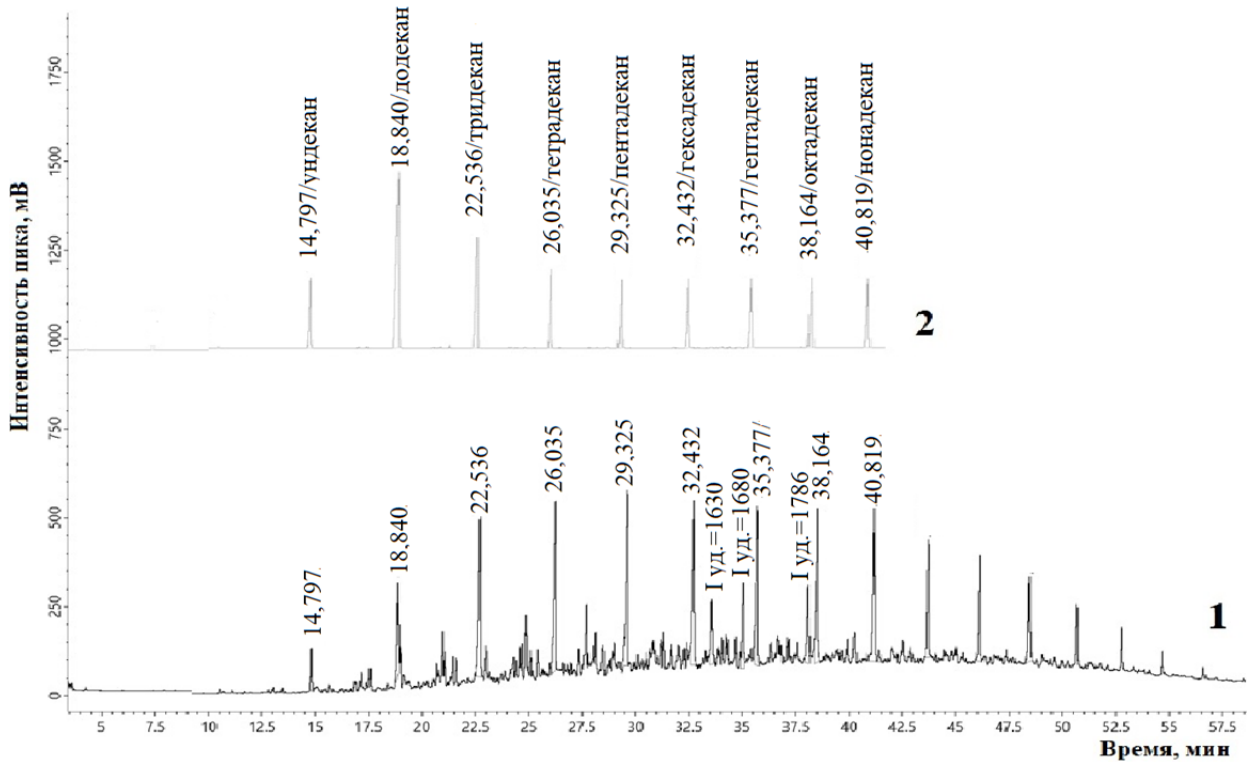

Fig. 1. **Comparison of the chromatogram of organic residues of unknown origin (1) with the chromatogram of a mixture of alkanes (C_{11}–C_{18}) (2)**

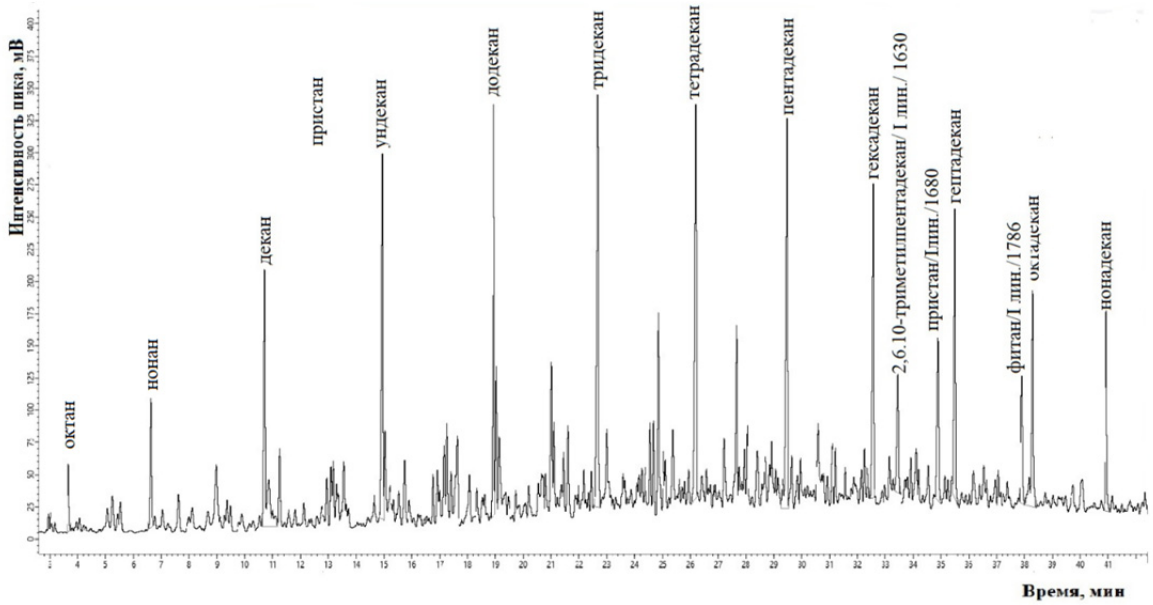

Fig. 2. **Chromatogram of DTZ diesel fuel**

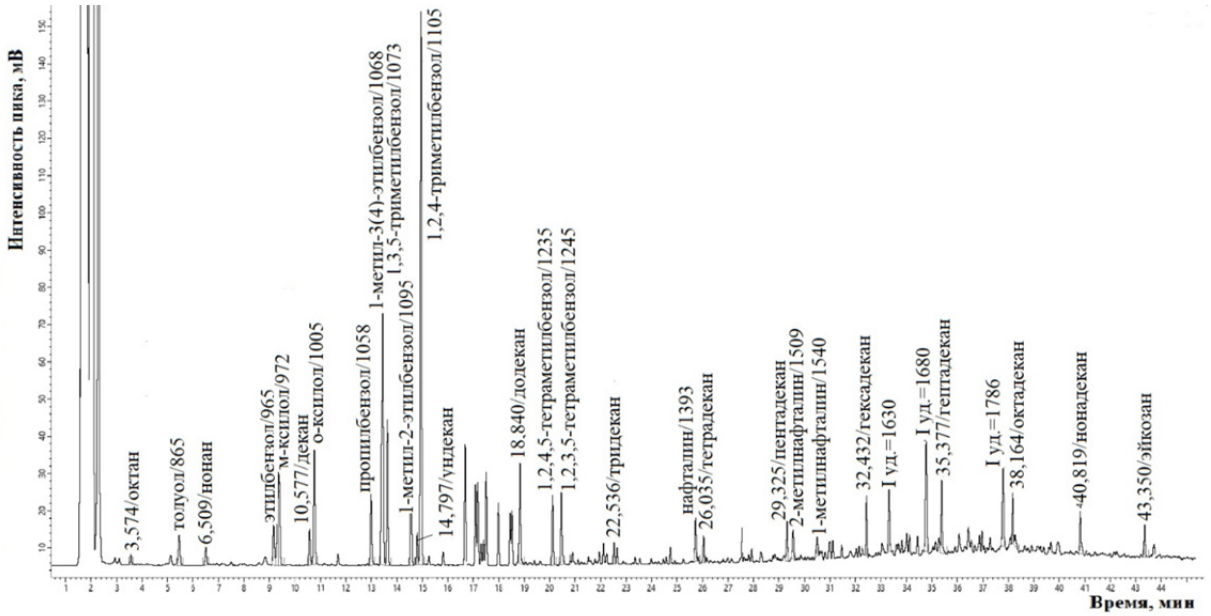

Fig. 3. **Chromatogram of a hexane extract of organic residues from a fragment of a mattress that came from a fire in the attic of a residential building**

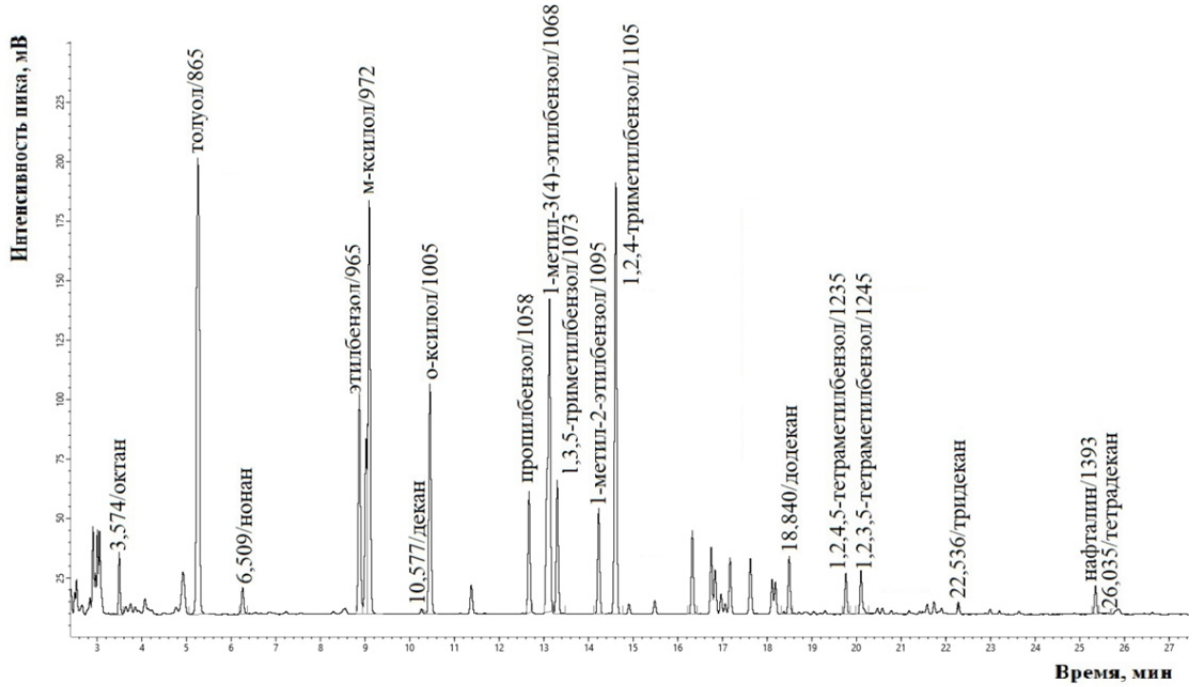

Fig. 4. **Chromatogram of the arbitration sample of unleaded gasoline of the Regular-92 brand, GOST R 51105–97, manufacturer «Kinef» LLC**

Thus, using the relative peak retention parameters (linear retention indices) and the «fingerprint» method, when comparing chromatograms of compositions of unknown nature with arbitration samples of oil products of a known composition, the nature of organic residues of unknown origin is established during a fire and technical examination, and the component composition allows us to assess the belonging them to LVZH and/or to GZH.

Chromatographic methods, as mentioned above, in expert practice can also be used to study flame retardant wood and special incendiary compositions. For this, ion chromatographs with a conductometric detector are used. Ion chromatography is a highly sensitive and efficient method for studying the cation-anion composition of aqueous solutions.

As you know, during arson, various chemical compositions are often used to initiate the ignition process. The composition of such incendiary compositions includes a strong oxidizing agent and a combustible substance. Inorganic oxygen-containing salts (nitrates, permanganates, chlorates, perchlorates, sulfates, chromates, bichromates, etc.) are most often used as oxidizing agents, and organic carbon-containing materials (charcoal, sugar, glycerin, alcohol, acetone, etc.) are used as combustible substances. acetic acid, turpentine, etc.), inorganic substances, including such non-metallic elements as sulfur, red phosphorus, carbon, as well as reactive metals (aluminum, magnesium, titanium, etc.). The components of incendiary compositions, as well as the products of their chemical interaction, are mainly water-soluble compounds, and can be detected at the fire site by ion chromatography. This method can detect not only the most common ions, such as Cl^-, NO_3^-, NO_2^-, Br^-, SO_4^{2-}, PO_4^{3-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, but also the detection of ions that form the basis of the components of incendiary mixtures CrO_4^{2-}, $Cr_2O_7^{2-}$, ClO_3^-, Mn^{2+}, Cr^{3+}, Pb^{2+} etc.). The conditions and procedure for conducting research for the detection of incendiary compositions after a fire by ion chromatography are described in detail in the manual [7].

It must be remembered that when examining objects that came from the scene of a fire in order to detect incendiary compositions, it is desirable to have a «control sample».

Also, the method of ion chromatography has become widespread in forensic practice in the detection and study of flame retardants for wood. It is known that water-soluble compositions based on salt flame retardants are the most commonly used as fire retardants for wood [29]. These are mainly compositions based on ammonium and sodium phosphates, ammonium chloride and sulfate, borates, carbonates, phosphoric and boric acids, urea, etc. A significant content in the study of phosphates, sulfates, chlorides, fluorides, ammonium, sodium and potassium cations in water extracts of wood indicates the presence of a fire-retardant composition on wood.

On fig. 5 and 6 show chromatograms of an aqueous extract of wood presumably treated with a flame retardant. As can be seen from the chromatograms, the analysis of the ionic composition revealed a high content of the phosphate ion and the ammonium ion. This indicates the presence of fire-retardant impregnation on the wood. In addition, it can be assumed that the composition of this impregnation includes ammonium phosphates, as well as phosphoric acid, since the content of the phosphate ion is 1,3 times higher than that of the ammonium ion. To confirm this conclusion, it is necessary to carry out additional research methods, such as IR spectroscopy, qualitative analysis, and pH-metry.

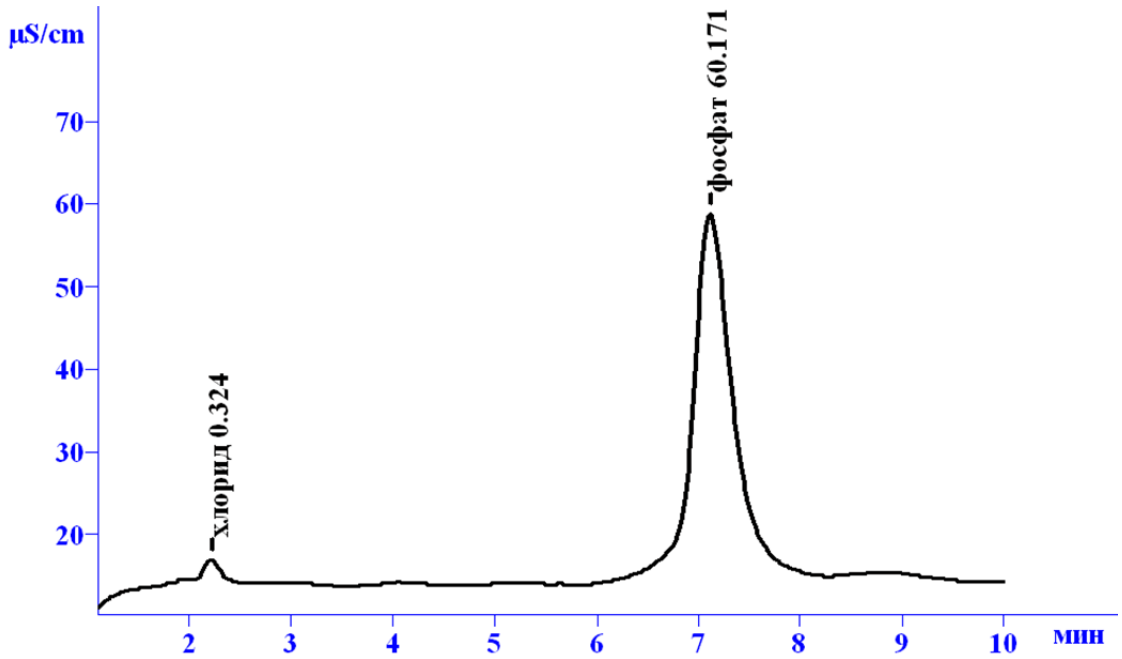

Fig. 5. **Chromatogram of the anionic composition of the aqueous extract of flame retardant wood**

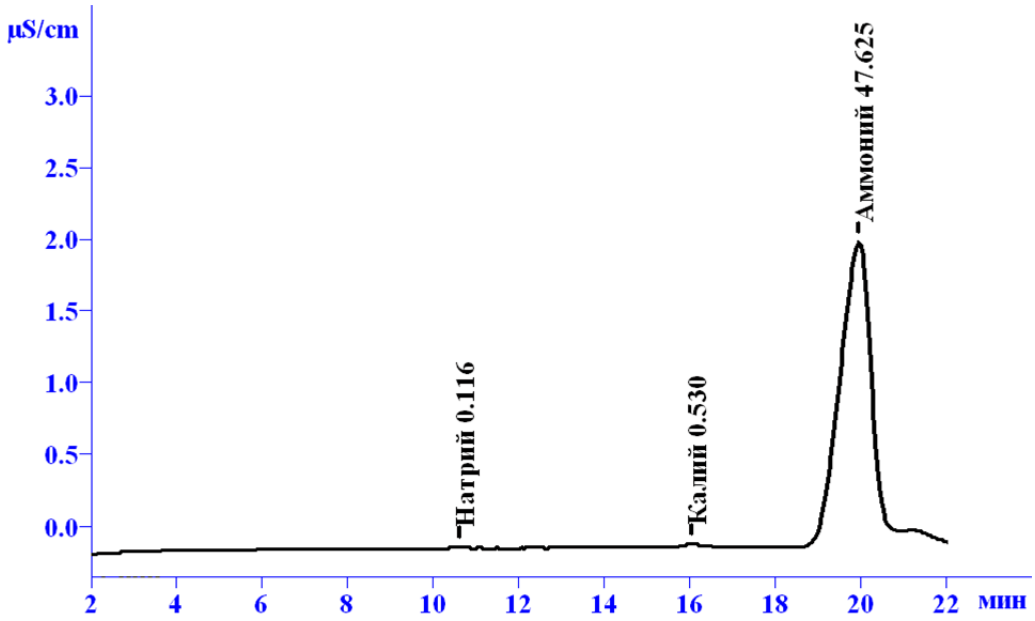

Fig. 6. **Chromatogram of the cationic composition of the aqueous extract of flame retardant wood**

After thermal exposure, the ionic composition of aqueous extracts of wood treated with a flame retardant composition change. This reduces the content of all ions present in the extract. However, with surface charring of wood, it is still possible to detect chlorides, phosphates, sulfates, as well as potassium and sodium cations. After «deep charring», ammonium cations and fluorides are not found in the extracts of flame retardant wood.

Thus, the above review of chromatographic methods shows that the most popular in forensic practice in the examination of fires are gas and ion chromatography. The listed complex of research methods allows for expert support of the activities of units involved in the investigation of fires.

With the advent of new tasks and new instrumental equipment for their implementation, the series of articles on instrumental methods for the purposes of fire and technical expertise can be continued.

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