THEORY AND PRACTICE OF FORENSIC EXAMINATION

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AN INTEGRATED APPROACH TO THE RESEARCH OF FIRE EXTINGUISHING POWDER AGENTS DURING FIRES EXAMINATION

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Abstract. The article discusses the possibility of using a set of instrumental methods, such as morphological analysis, elemental analysis, X-ray phase analysis, infrared spectroscopy, ion chromatography or capillary electrophoresis to study the chemical composition of fire extinguishing powders during fire-technical examinations. Examples of the use of these methods in the investigation of real fires are given. It is described in detail how studies of fire extinguishing agents are carried out to answer questions related to establishing their composition, as well as identifying the compliance of the fire extinguishing powder submitted for study with technical documentation. It is shown that in order to obtain complete information about the chemical composition of the fire extinguishing agent, it is necessary to use a set of methods, since each of the considered methods provides additional information during the study.

Keywords: fire extinguishing powder agents, fire extinguishing compositions, elemental analysis, morphological analysis, infrared spectroscopy, X-ray fluorescence analysis, X-ray phase analysis, scanning electron microscopy, infrared spectroscopy, fire-technical examination

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Introduction

Depending on the main component, fire extinguishing powder agents (OPF) can be divided into three groups: based on alkali metal carbonates, based on phosphorus-ammonium salts and based on alkali metal chlorides [1]. There are OPS of general and special purpose. General purpose powders are used to extinguish fires of classes A, B, C, E, and special purpose for extinguishing class D fires [2–5]. The joint use of different OPS groups within the same composition is not permitted.

Currently, cases of fire-technical products appearing on the market that do not meet the requirements of GOST and TU [6]. When conducting fire-technical examinations (FTE), questions arise related to with establishing the composition of fire extinguishing powders, identifying the compliance of the fire extinguishing powder submitted for research with the technical documentation, as well as the compliance of the composition of fire extinguishing powder for extinguishing fires of a certain class.

To answer these questions in the production of PTE, it is possible to use a complex of various physical and chemical research methods such as: elemental and phase analysis, study of the functional and ionic composition of the powder. For achieving this goal, it is possible to use scanning electron microscopy (morphological analysis) and X-ray fluorescence analysis, X-ray phase analysis, infrared spectroscopy, ion chromatography or capillary electrophoresis. Previously, the authors of [7, 8] studied the possibility of using the method of thermal analysis, infrared spectroscopy and X-ray diffractometric to identify OPS components in order to identify falsification.

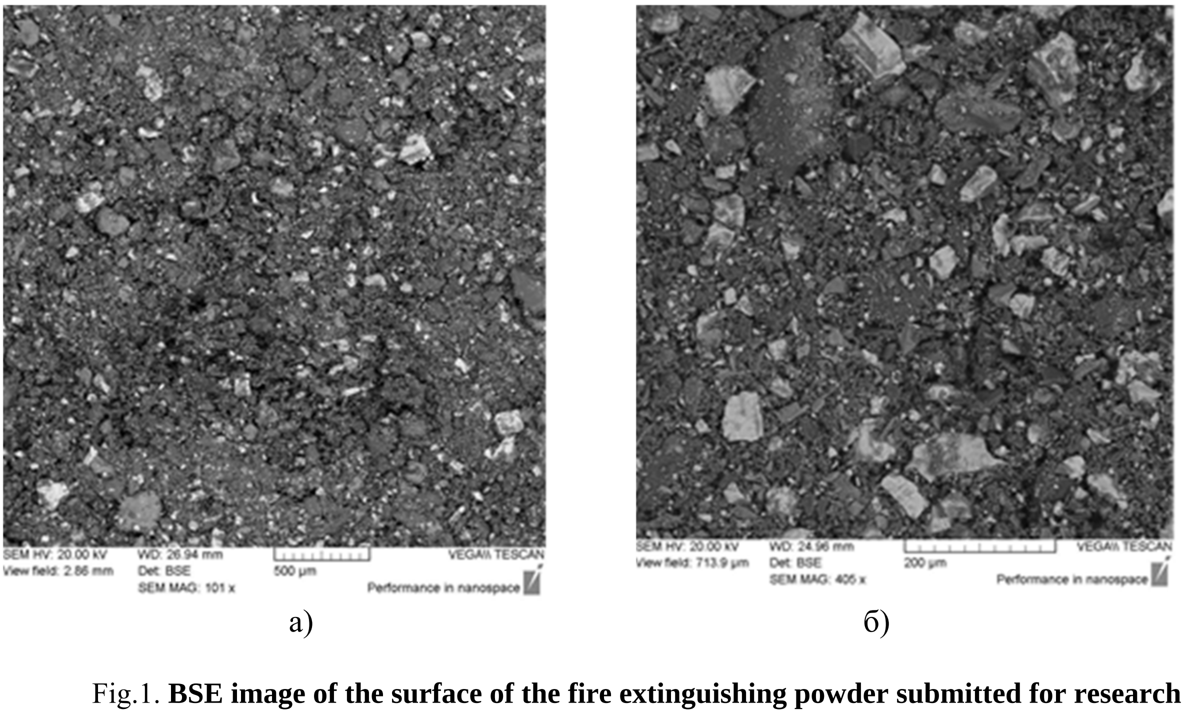
This article, using the example of real fires, examines the possibility of using the above methods, both in combination and separately, to study the compositions of hazardous substances and determine the compliance of the technical documentation submitted for study.

Main part

There was a fire at one of the enterprises. At the stage of the fire, employees of the enterprise used a fire extinguisher. During the inspection of the fire, this fire extinguisher was confiscated and the expert was asked whether the composition of the presented powder from the fire extinguisher complied with the regulatory documents (safety data sheet for chemical products). The technical documentation provided to the expert indicated the chemical composition of the fire extinguishing powder, which was a mixture of amorphous (a mixture of mono- and diammonium phosphate), quartz, amorphous silicon dioxide and ammonium sulfate.

At the first stage, a morphological analysis was carried out. The study was conducted on a Tescan VEGA//XMU scanning electron microscope equipped with an X–MAX 80 energy-dispersive detector with a crystal area of 80 mm^2, in high vacuum mode at an accelerating voltage of 20–30 kV, at a probe current of 2 pA–40 nA and working distance 20–27 mm. To obtain the images, a reflected electron detector (BSE) was used, which shows clearly defined differences in atomic weight between materials [1]. If there is a heterogeneous composition in the sample material, its image will have clearly visible areas with clear boundaries between them. Thus, light areas will correspond to material with a higher atomic number.

As a result of the morphological study, photographs of the surface of a sample of fire extinguishing powder were obtained (Fig. 1, 2).



a) б)

Fig.1. **BSE image of the surface of the fire extinguishing powder submitted for research at different magnifications: a) SEM 100^x; b) SEM 400^x**

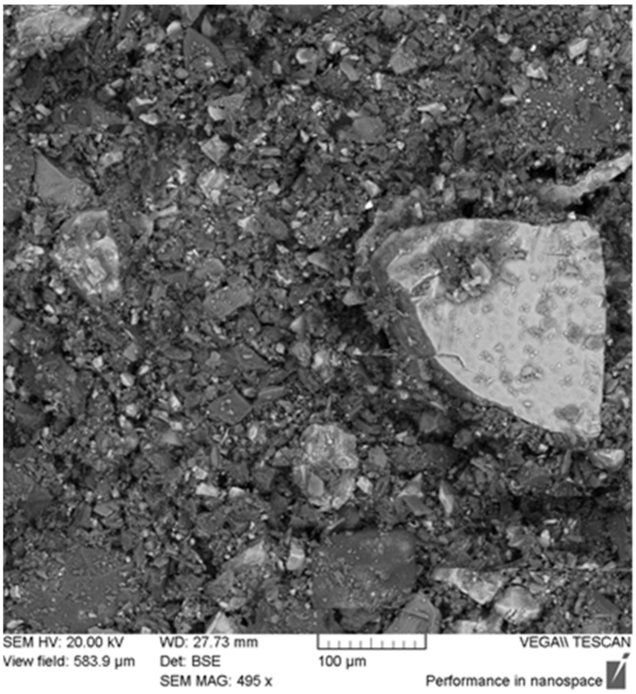


Fig. 2. **BSE close-up image of crystals on the surface of the presented for the study of fire extinguishing powder, SEM 500^x**

The obtained BSE images show that the surface of the fire extinguisher powder has pronounced differences in color (Fig. 1). This fact is due to the heterogeneity of the composition of the material under study. On the surface of the fire extinguishing powder there are many crystals in the shape of polyhedral.

The elemental composition and concentration of elements of the powder submitted for research were determined using X-ray fluorescence analysis.

As a result of elemental analysis of the entire surface of the powder (Table 1), oxygen (O), sulfur (S), silicon (Si), chlorine (Cl), nitrogen (N), sodium (Na), and trace amounts of magnesium (Mg), potassium (K), calcium (Ca) and iron (Fe).

Table 1

Elemental composition of the surface submitted for research fire extinguishing powder

Element	N	O	Na	Mg	Si	S	Cl	K	Ca	Fe
Mass fraction, %	6,79	47,86	6,76	2,27	13,18	10,59	10,95	0,26	0,66	0,68

Next, an elemental analysis of the crystals found in the composition was carried out powder (Fig. 2). It showed the presence of substances such as sodium (Na), chlorine (Cl), oxygen (O), carbon (C) and silicon (Si) (Table 2).

Table 2

Elemental composition of the crystal on the surface of the presented to study fire extinguishing powder

Element	C	O	Na	Si	Cl
Mass fraction , %	7,77	12,33	31,5	2,11	46,29

Based on the elemental composition of these crystals, as well as their shape, it can be assumed that these crystals are sodium chloride crystals. To confirm this fact, as well as to determine the chemical composition of a sample of powder from a fire extinguisher, its X-ray phase analysis was carried out.

The study was carried out using a DR-01 «Radian» diffractometer under the following conditions: anode material copper, angle range 18÷62°, voltage on the tube 30 kV, tube current 4,8 mA, detector step 0,05°, exposure time 3 sec., shooting mode with a turn.

The diffraction pattern of the powder under study is shown in Fig. 3. Information the observed analytical peaks from X-ray diffraction data are presented in table 3. According to [9], we can say that a certain phase is present in the substance under study if at least three peaks of the same phase are detected in the diffraction pattern.

In the obtained diffraction patterns, some of the analytical peaks were not deciphered. It was not possible to determine whether these peaks belonged to any phase.

Analysis of the obtained diffraction pattern showed that in the powder sample under study Sodium chloride, silicon dioxide (quartz), diammonium sulfate and ammophos (mono- and diammonium phosphate) were detected from the fire extinguisher.

To establish the functional composition of the fire extinguishing powder submitted for research, an infrared spectrum (IR spectrum) was obtained using the potassium bromide tableting method. IR spectra were recorded on an IR-Fourier spectrometer

FSM 1201 in the measurement range 4000–400 cm^{-1}. The IR spectra were interpreted in accordance with works [10–12].

Table 3

Crystallographic data of the main phases, present in the fire extinguishing powder submitted for research

Angle degree, 2θ	Interplanar distance, d/n, Å	Intensity, I,%	Estimated phase
$(NH_4)_2HPO_4$	3,04 2,54 2,00	86 57 46	Ammophos (diamonium phosphate)
$(NH_4)H_2PO_4$	3,07 2,67 2,00	100 9 27	Ammophos (ammonium monophosphate)
SiO_2	3,35 1,97 1,54	100 8 20	Quartz
$(NH_4)_2SO_4$	4,36 3,91 3,03 2,32	100 20 40 20	Diammonium sulfate
NaCl	2,81 1,98 1,61	100 55 15	Sodium chloride

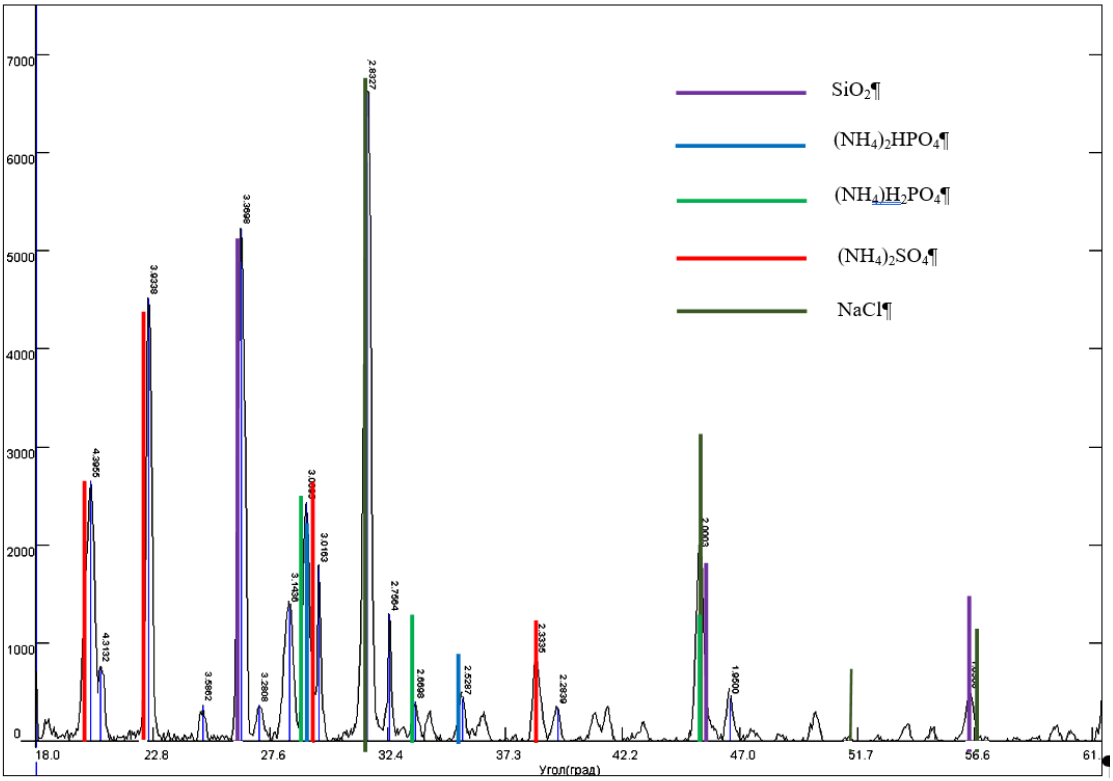


Fig. 3. **X-ray diffraction pattern of fire extinguishing powder submitted for research**

In the IR spectrum of the powder under study, absorption bands are observed in the region of 3500–3000 cm^{-1} (3220, 3050 cm^{-1}), 1410 cm^{-1}, 1110 cm^{-1}, shoulder 1023 cm^{-1}, 800 cm^{-1}, 670 cm^{-1}, 615 cm^{-1}, 466 cm^{-1} (Fig. 4). Absorption bands in the region of 3500–3000 cm^{-1} (3220, 3050 cm^{-1}) and the band at 1410 cm^{-1} are attributed to stretching and bending vibrations of the ammonium ion. The wide absorption band in the region of 1200–900 cm^{-1} can be attributed to both the stretching vibrations of the sulfate ion and the stretching vibrations of the Si-O bond in silicates and/or organosilicon compounds. Absorption band 615 cm^{-1} present on the IR spectrum of the sample under study, refers to the deformation vibrations of the sulfate ion, and the absorption bands at 800 cm^{-1} and 466 cm^{-1} are attributed to vibrations of the Si–O bond.

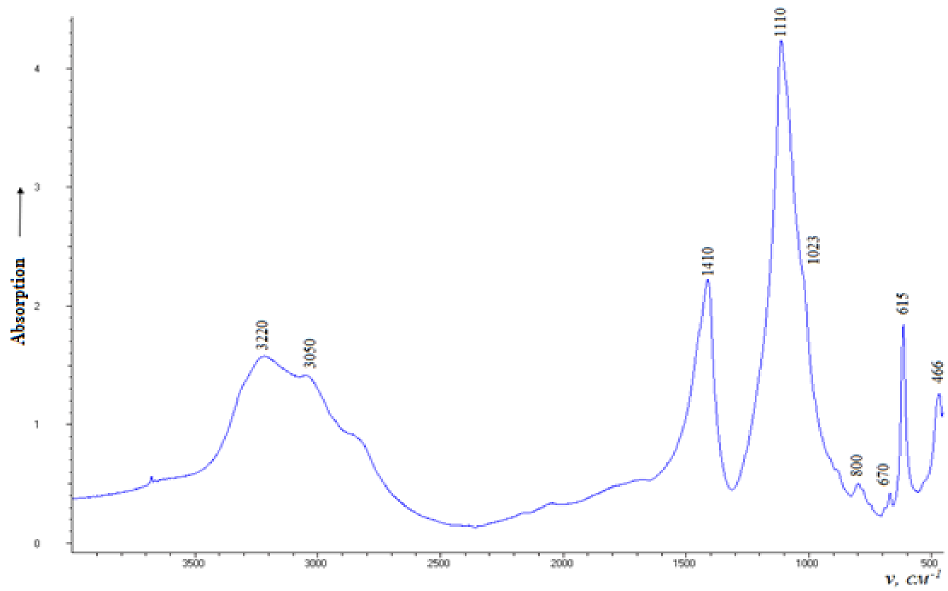


Fig. 4. **IR spectrum of the fire extinguishing powder submitted for research**

When comparing the IR spectra of the test sample of fire extinguisher powder and ammonium sulfate using the «fingerprint» method, it was revealed that most absorption bands (3220 cm^{-1}, 3050 cm^{-1}, 1110 cm^{-1}, 1410 cm^{-1}, 615 cm^{-1}) in the spectrum of the sample under study are similar in position to stripes of ammonium sulfate (Fig. 5). Also, when comparing the IR spectrum of the sample under study and the spectrum of silicon oxide (SiO_2), the colloidal (amorphous) absorption bands at 800 cm^{-1} and 466 cm^{-1} turned out to be similar in position (Fig. 6). Shoulder 1023 cm^{-1} and the absorption band 670 cm^{-1} also refer to vibrations of silicon oxide (Fig. 6).

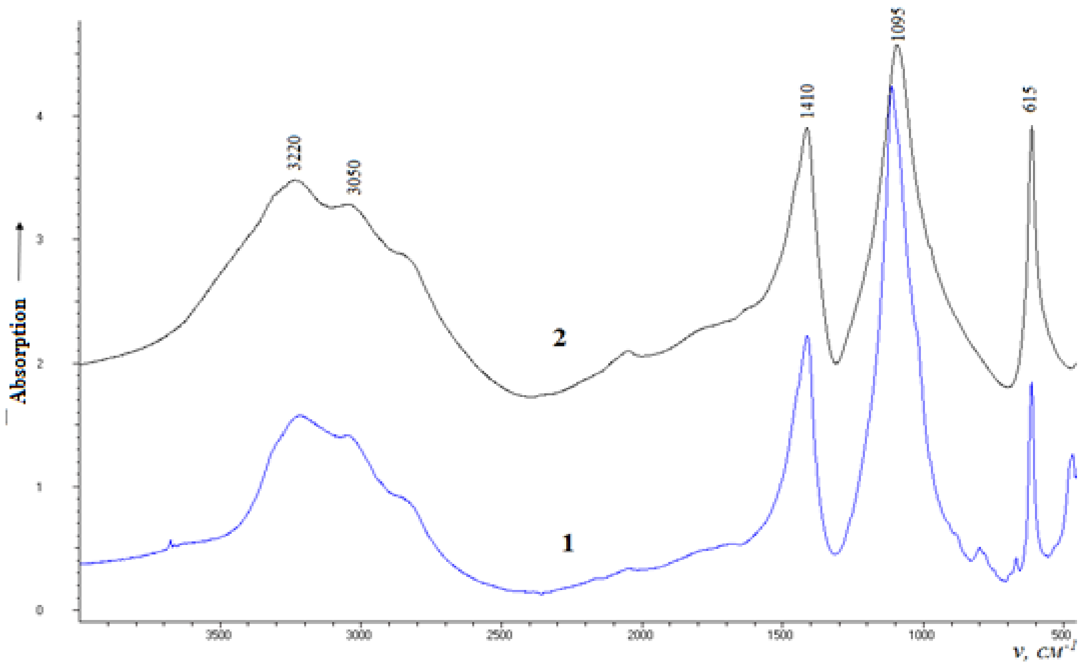


Fig. 5. **IR spectra:**
1 – fire extinguishing powder submitted for research; 2 – ammonium sulfate

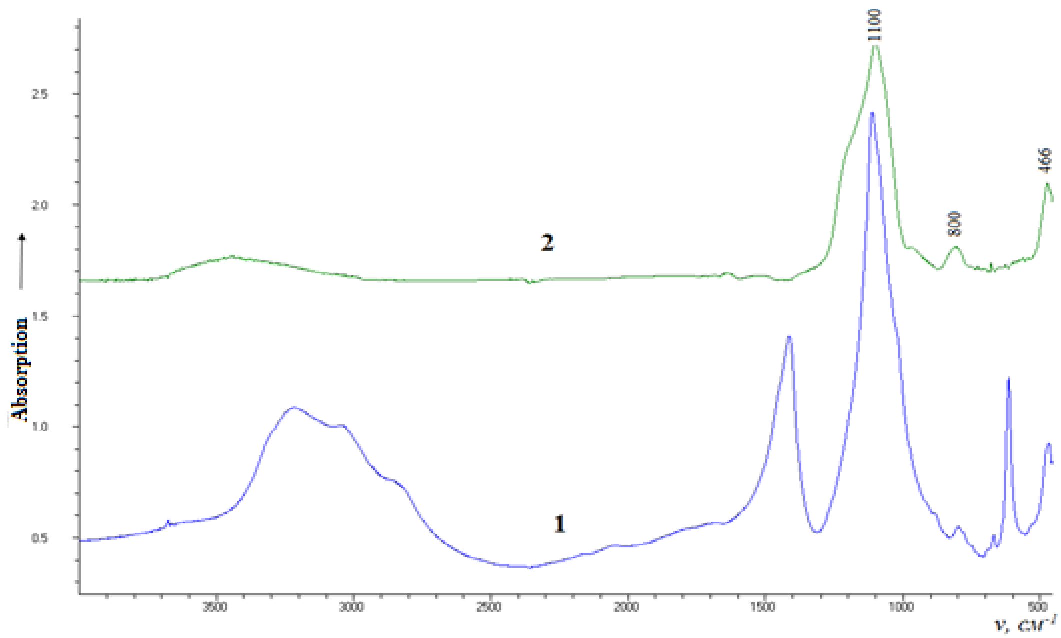


Fig. 6. **IR spectra:**
1 – fire extinguishing powder submitted for research;
2 – silicon oxide (colloidal)

In addition, the IR spectrum of the studied sample of fire extinguisher powder revealed low-intensity absorption bands at 896 cm^{-1} and 530 cm^{-1}, which most likely belong to the bands of phosphate ions (Fig. 7). Since the characteristic absorption bands of phosphates are in the region of 1100–900 cm^{-1}, they can be leveled when superimposed on the bands of sulfate ion and silicon oxide. Thus, the method IR spectroscopy detected ammonium sulfate, silicon oxide and trace amounts of phosphates, most likely ammonium phosphates, in a sample of fire extinguisher powder. Sodium chloride, identified by X-ray fluorescence and X-ray phase analysis, does not absorb IR radiation in the studied range, therefore this method was not detected.

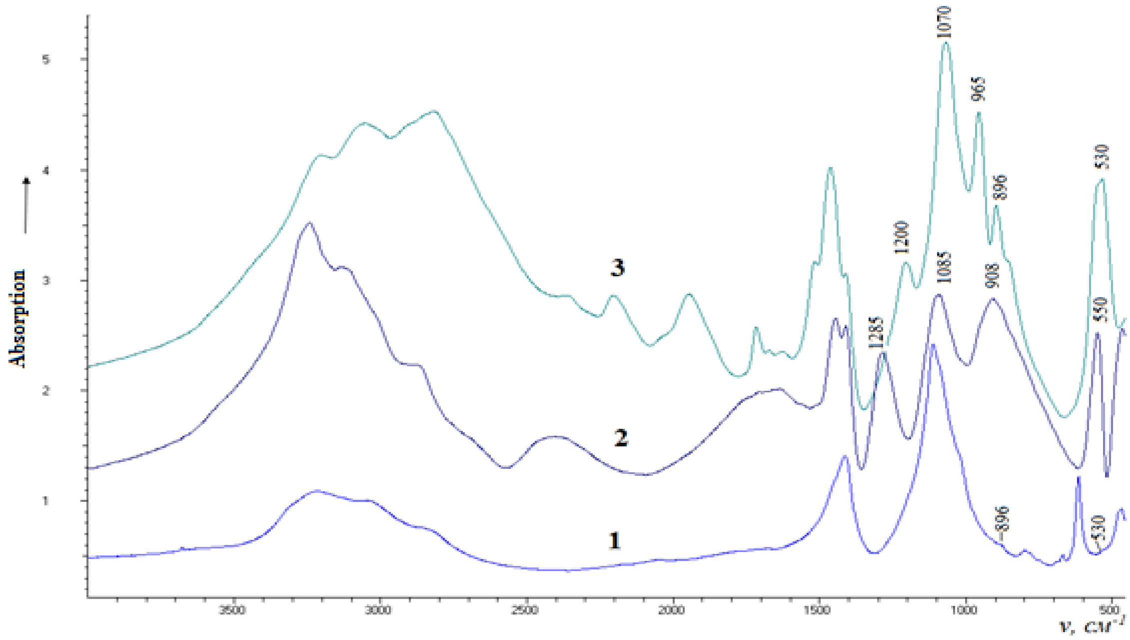


Fig. 7. **IR spectra:**
1 – fire extinguishing powder submitted for research;
2 – monoammonium phosphate; 3 – diammonium phosphate

Thus, when studying the composition of the presented fire extinguishing powder using infrared spectroscopy, elemental and X-ray phase analysis, silicon dioxide, ammonium sulfate, monoammonium phosphate, diammonium phosphate, and sodium chloride were discovered. Since the safety data sheet for chemical products.

The fire extinguishing powder submitted for research did not contain sodium chloride in its composition, therefore, it was concluded that the composition of the presented powder did not comply with the safety data sheet of chemical products.

Below is an example of an examination, where the expert was asked the question: «Does the OPS in the presented fire extinguisher correspond to the OPS sample of the PHC brand?» it is shown how, using a complex of infrared spectroscopy and ion chromatography methods, one can draw a conclusion about the compliance or non-compliance of a fire extinguishing powder with a specific brand.

It is known that PHC fire extinguishing powder is used to extinguish class D fires and is a mixture of several components, where the main component is potassium chloride.

In Fig. 8 shows the IR spectra of the OPS and OPS of the PKhK brand submitted for research.

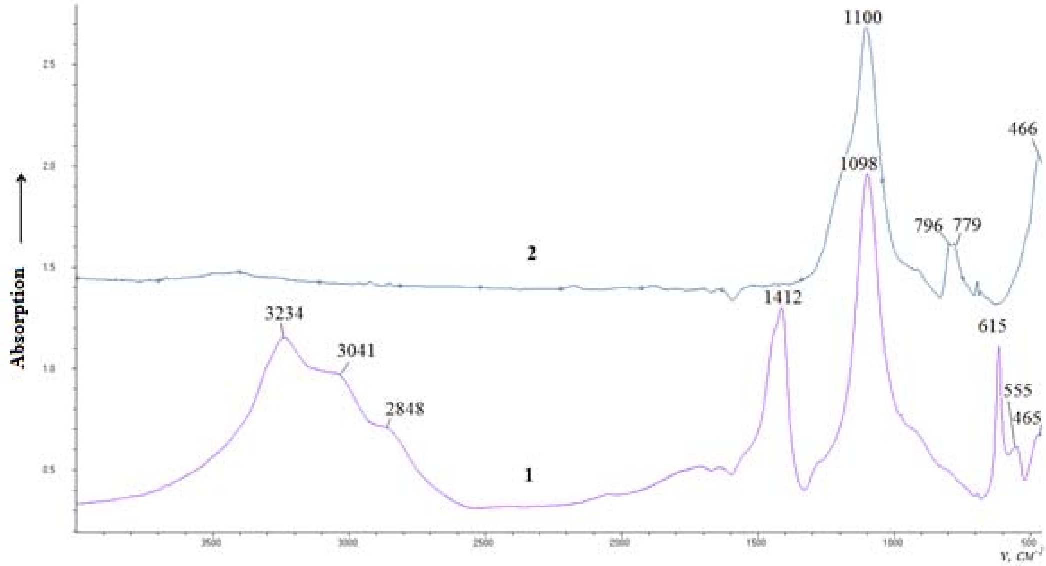


Fig. 8. **IR spectra:**
samples: 1 – OPS submitted for research; 2 – OPS brand PKHK

As can be seen from the presence of absorption bands and their intensity, the IR spectra turned out to be not identical.

When comparing the IR spectra of ammonium sulfate and ammonium phosphate with the IR spectrum submitted for OPS research, it was revealed that they coincide in the presence of characteristic absorption bands (Fig. 9, 10).

The absorption bands at 3234 cm^{-1}, 3041 cm^{-1}, 1412 cm^{-1}, 1098 cm^{-1} and 615 cm^{-1} in the IR spectrum of the OPS submitted for study are similar in position to the bands of ammonium sulfate (Fig. 9).

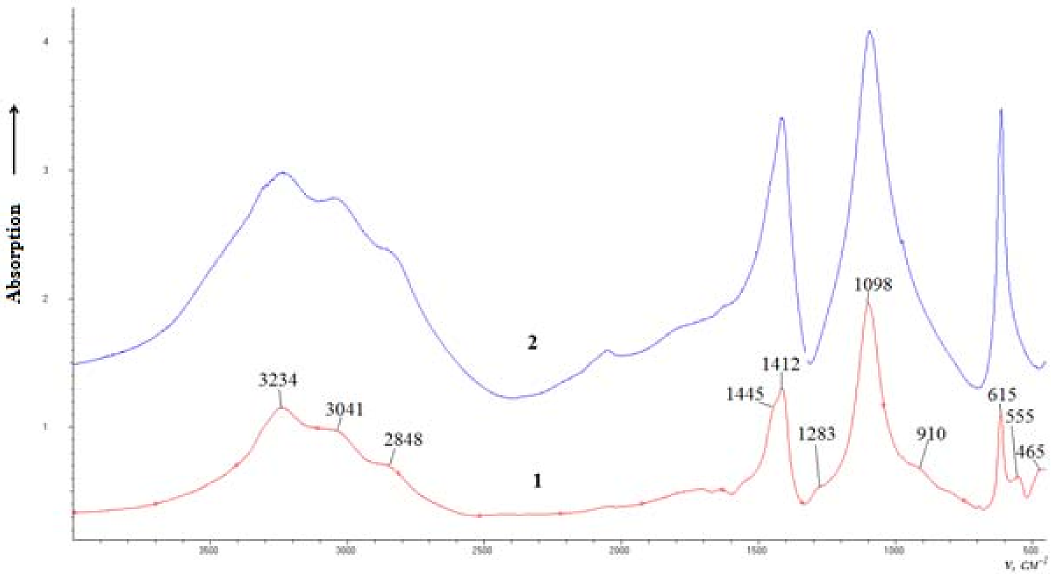


Fig. 9. **IR spectra:**
1 – OPS submitted for research; 2 – ammonium sulfate

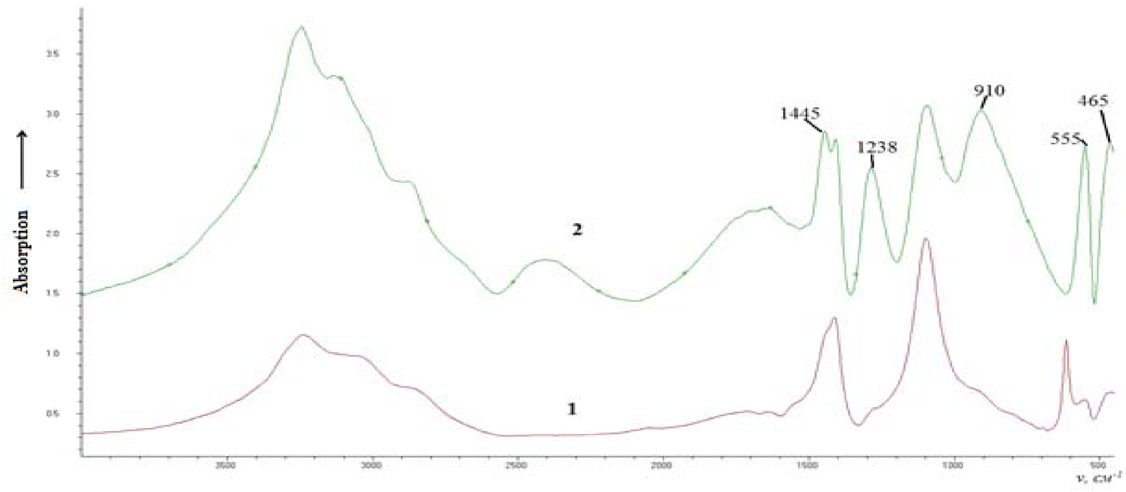


Fig. 10. **IR spectrum:**
1 – OPS submitted for research; 2 – diammonium phosphate

The absorption band at 555 cm^{-1} and the shoulder at 910 cm^{-1} are attributed to bending vibrations of the phosphate ion. The low-intensity absorption band at 465 cm^{-1} most likely refers to bending vibrations of the Si–O group. The stretching vibrations of the Si–O group in this spectrum can be overlapped by the stretching vibrations of the sulfate group.

When analyzing the IR spectrum of OPS brand PKhK, absorption bands were identified 1100 cm^{-1}, 796 cm^{-1}, 690 cm^{-1} and 466 cm^{-1}, most likely related to stretching and bending vibrations of the Si–O group (Fig. 11).

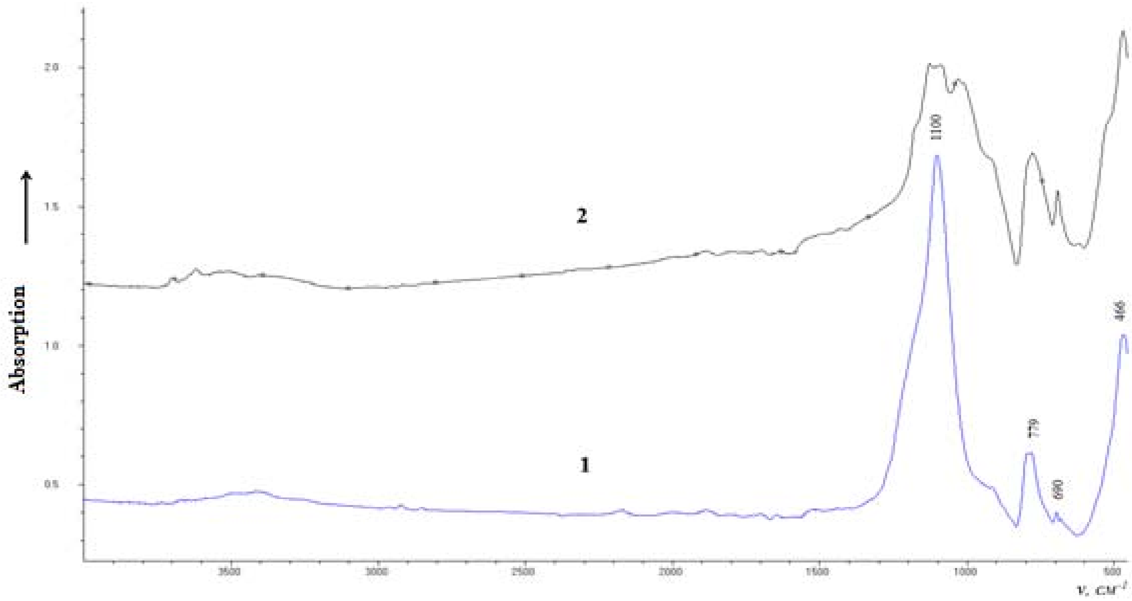


Fig. 11. **IR spectra:**
1 – OPS brand PKhK; 2 – silicon oxide (SiO_2)

Thus, based on the results of the study using IR spectroscopy, we can conclude that the OPS presented for the study and OPS of the PHC brand have different functional compositions. OPS from the fire extinguisher submitted for research is a substance containing ammonium sulfate, ammonium phosphate and silicon oxide, and OPS of the PKhK brand contains a silicon-oxygen compound.

Next, to clarify the chemical composition of the OPS submitted for research and OPS brand PKhK, aqueous solutions were analyzed by ion chromatography on a «Styer» chromatograph with a CD 510 conductometric detector included with columns for the determination of group I cations (ammonium, sodium and potassium) and anions (fluorides, chlorides, nitrites, nitrates, phosphates, sulfates).

The determination of group I cations was carried out on an AQUILINE C1 P 100x4,6 mm column, detection of anions on a STARION A300 100x4,6 mm column together with a STARION A300 protective column. 0,004 mol/L HNO3 was used as an eluent to separate group I cations, and a mixture of 1,8 mmol/L sodium carbonate and 1,7 mmol/L sodium bicarbonate was used to separate anions. The elution rate was 1,5 ml/min, the thermostat temperature was 30 °C, and the loop volume was 100 μL.

As can be seen from Table 4, the aqueous solution of the OPS presented for research contains trace amounts (no more than 5 mg/l) of sodium and potassium ions, as well as fluoride and chloride ions. In addition to the listed ions, the solution contains a high content of ammonium cation (513,0 mg/l), as well as phosphate (168,1 mg/l) and sulfate anions (53,9 mg/l).

A small amount of sodium ion was detected in an aqueous solution of OPS brand PKhK and ammonium (no more than 25 mg/l), as well as a high content of potassium cation (1096,5 mg/l) band chloride ion (200,0 mg/l).

Table 4

Cation-anion composition of aqueous solutions OPS and OPS of the PHC brand submitted for research

Example	Concentration of cations, mg/l			Anion concentration, mg/l			
	Na^+	K^+	NH_4^+	F^-	Cl^-	SO_4^{2-}	PO_4^{3-}
Composition presented for research	2,7	5,0	**513,0**	3,8	1,9	**168,1**	**53,9**
Composition of the PHC brand	24,9	**1096,5**	3,7	–	**200,0**	–	–

Data obtained by ion chromatography confirm the difference according to the chemical composition of the fire extinguisher from the fire extinguisher submitted for research and the fire extinguisher of the PKhK brand. The OPS from the fire extinguisher submitted for research contains water-soluble salts of ammonium sulfate and phosphate, and the OPS of the PHC brand contains a water-soluble salt – potassium chloride.

Summarizing the data obtained by a complex of methods of IR spectroscopy and ion chromatography, it was revealed that the OPS from the fire extinguisher submitted for research contains ammonium sulfate, ammonium phosphate, detected by ion chromatography, and silicon dioxide, detected by IR spectroscopy. This composition differs from the composition of PHC brand OPS, which consists mainly from potassium chloride detected by ion chromatography and silicon dioxide detected by infrared spectroscopy.

Conclusion

Summing up the results of the research, it can be stated that the study of fire extinguishing powder agents during fire-technical examinations is possible using the methods of morphological, elemental and X-ray phase analyses, infrared spectroscopy, thermal analysis, as well as ion chromatography or capillary electrophoresis. It is advisable to carry out research using a set of methods, since each method provides additional information on the chemical composition of the OPS. An integrated approach, using modern research methods, will allow us to obtain complete information about the elemental, phase, ionic and functional composition of OPS and answer questions related to their falsification.

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