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Recent Achievements in Development of Chalcogenide Optical Fibers for Mid-IR Sensing

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Abstract: Recent results of research of passive and active optical waveguides made of high-purity chalcogenide glasses for middle infrared fiberoptic evanescent wave spectroscopy of liquid and gaseous substances are presented. On the basis of selenide and telluride glass fibers, novel types of highly sensitive fiber probes are developed. On the basis of Pr(3+)- and Tb(3+)-doped Ga(In)-Ge-As-Se and Ga-Ge-Sb-Se glass fibers, the 4.2–6 μm wavelength radiation sources are created for all-fiber sensor systems. Successful testing of chalcogenide glass fiber sensors for the analysis of some liquid and gaseous mixtures was carried out.

Keywords: fiber evanescence wave spectroscopy; middle infrared; chalcogenide glass fiber; sensing probe; rare earth elements

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1. Introduction

Fiber optic evanescent wave spectroscopy (FEWS) of the middle infrared (mid-IR) range is a rapidly developing method of analysis. The FEWS method is based on recording the absorption spectrum of a fiber in contact with the analyzed liquid, powder, paste, gas, biological tissue, etc. Due to the partial exit of radiation beyond the boundaries of the fiber, selective absorption bands of analyte components appear in the spectrum. The first reports on the use of fibers as optical sensors date back to the 1980s [1–3]. The use of fibers for analytical purposes expands the possibilities of IR spectroscopy, since it makes it possible to study samples that, for some reason, cannot be placed in the measuring chamber of a spectral instrument. Waveguides significantly reduce the restrictions on the minimum size and shape of samples. Remote measurements with the help of optical fibers make it possible to analyze substances online directly in the system under study and without additional sampling.

Silica glass fiber sensors operating in spectral range up to 2.5 μm have insufficiently high sensitivity and selectivity, since, in the short-wavelength IR region, only weak overtones and combined absorption bands of molecular species are present. The fundamental absorption bands of most organic and inorganic functional groups (saturated, unsaturated, aromatic hydrocarbons, ketones, aldehydes, alkyl, carboxyl, carbonyl, amino groups, etc.) with large extinction coefficients are in the 3–15 μm spectral range. In the mid-IR, the absorption spectra of even structurally similar homologues of organic substances reliably differ from each other. This advantage provides a sensitive chemical analysis and allows us to determine a large number of substances in complex mixtures, including petroleum products and environmental and biological objects.

The main materials of commercial mid-IR FEWS sensors are polycrystalline materials based on silver halides [4–6] transparent in the 4–15 μm range. FEWS sensors based on chalcogenide fibers have recently competed with polycrystalline silver halides. They have significantly better chemical resistance and photostability, and, as a result, an increased

service life [7–10]. These advantages are used for the analysis of aggressive media, such as concentrated organic solvents, dilute solutions of mineral acids, oil and products of its processing, waste water, etc. An important advantage of chalcogenide fibers is the great variability of the glass compositions which makes it possible to vary their properties over a wide range of values. Sulfide fibers are transparent in the 1–6 μm spectral range that is inaccessible to polycrystalline halide fibers. Selenide fibers are transparent in the 2–10 μm range; and fibers based on germanium tellurides are transparent in the 4–15 μm range [11,12]. An additional advantage of chalcogenide sensors is the ability to set a complex geometric shape and vary the detector element diameter (fiber tip) in a wide range (10–1000 μm), providing the required sensitivity and detection limit of analyzed object.

One of the first studies of single-index chalcogenide fiber for FEWS analysis of the curing kinetics of polyimide resin is presented in [13]. In the early 1990s, the authors of [14,15] used telluride fibers to measure the evanescent absorption spectra of water, methanol, ethanol, isopropanol, acetone, ethanoic acid, hexane, and chloroform. Scientists from the University of Rennes (France) observed the fermentation of alcohol using a chalcogenide fiber [16]. Since that time, a fairly large number of publications on the use of chalcogenide fibers for the analysis of the chemical composition of inorganic and organic liquids and biological tissues have appeared in the literature [17–22]. Chalcogenide fiber probes have been tested in biomedicine to determine the difference between healthy and damaged tissues and organs, and in medical diagnostics, including early cancer detection [21,22].

For preliminary tests, a chalcogenide fiber sensor element had a simple linear shape [15,23]. One of the ways to improve the sensitivity is to change the sensor geometry for increasing the path of radiation penetration into the analyzed sample [23]. For this purpose, the sensing element is made in the form of one or more loops [24–26], in the form of a tapered fiber [27,28], or in the form of a side-polished chalcogenide fiber [29,30].

Sensor systems with the use of laboratory IR spectrometers are rather bulky and expensive, which hinders their widespread use. To create compact sensor systems, laser diodes and quantum cascade lasers can be used as sources of mid-IR radiation. Recently, the idea of creating all-fiber sensor systems using active fibers as sources of IR laser radiation, broadband spontaneous (luminescent) radiation, and supercontinuum has been actively developed [31–39]. Rare-earth element (REE)-doped chalcogenide glass fibers are suitable materials for mid-IR sources because they exhibit intense broadband mid-IR luminescence [33,34] and lasing, which we recently demonstrated for the first time in the Tb(3+)-doped chalcogenide glass fiber at 5.38 μm wavelength [35]. The use of emission sources makes it possible to create an all–fiber sensor scheme for substance detection by studying the vibrational modes of some bonds (for example, C-H, C-O, S-H, C-S, N-O, C-Cl [25,36–39]) to identify chemical compounds. Fiber sensors based on REE-doped chalcogenide glasses were tested for detection of CO_2 and chloroform [36–39].

We have presented some results for an all-fiber sensor for the identification and quantitative analysis of organic compounds in [25]. The advantages of such a sensor system using the mid-IR luminescent fiber source are high stability of optical parameters, selectivity, and low cost.

Previously, we carried out a theoretical assessment [23] of absorption pattern for evanescent waves in chalcogenide fiber placed in aqueous solutions of acetone and crude oil, using a rigorous electrodynamic model of a multimode optical fiber with an infinite absorbing cladding. It has been established that the functioning of the fiber-sensing element significantly depends on the mode composition of the radiation propagating through the fiber. Based on computer models [26,40,41], the basic characteristics of chalcogenide sensor were optimized in terms of the geometry of fiber-sensing elements to increase the sensitivity of the FEWS method.

The purpose of this paper is to present the recent experimental results on the development and testing of chalcogenide glass fibers for mid-IR FEWS. The presented results

can be useful both for specialists in the field of IR optical materials and for the chemical analysis of industrial products and medicine.

2. Materials and Methods

2.1. Materials for Fiber Sensors

To develop mid-IR fiber sensors, a large number of chalcogenide glasses of various compositions were synthesized, as well as the fiber samples on the base of these glasses were drawn and studied [24,25,33–35,42]. The most important functional parameter of the optical fiber sensor is the low level of optical losses in the operating spectral range. To prepare the high-purity glass samples that provide low-loss fibers we developed special purification methods [25,42–48]. Particular attention in our work was paid to methods for removing limiting impurities (hydrogen, oxygen, carbon), since these impurities absorb radiation in the transparency range of glasses.

On the base of prepared high-purity glasses, single-index and core-clad fibers were drawn by crucible and double-crucible techniques.

To fabricate the single-index fibers for FEWS sensing elements, chalcogenide glasses of $Ge_{20}Se_{80}$, $Ge_{20}Se_{70}Te_{10}$, $Ge_{10}As_{30}Se_{38}Te_{22}$, $Ge_{28}Sb_{12}Se_{60}$, and $Ga_{10}Ge_{15}Te_{73}I_2$ compositions were chosen [23–26,42]. The choice is due to the wide range of transparency of these materials in the mid-IR range, their good stability against crystallization, and good mechanical strength.

To create mid-IR fiber sources, high-purity Ga(In)-Ge-As(Sb)-Se core glasses doped with various REE ions were prepared. For the cladding of step-index fibers, the Ge-As-S, As-S, Ge-As-Sb-S, or Ge-As-Se-S glasses, with compositions that provides close viscous and thermal properties, and the required numerical aperture were chosen. More detailed studies of these glasses are described in our papers [34,35,45,46,48,49].

2.2. Schemes and Functional Elements for Mid-IR FEWS Analysis

On the bases of prepared chalcogenide fibers, three types of sensor designs were proposed and used for FEWS analysis: (1) a fiber-sensing element in the form of an extended piece of a fiber (of linear form or curved ones (Figure 1)) connected to an IR Fourier spectrometer using lens systems (Figure 2); (2) a fiber sensor probe connected to an IR Fourier spectrometer through a probe attachment (Figure 3); (3) a fiber-sensing element combined with a luminescent source of mid-IR radiation from the REE-doped chalcogenide glass fibers or a lasing source from the same ones (Figure 4).

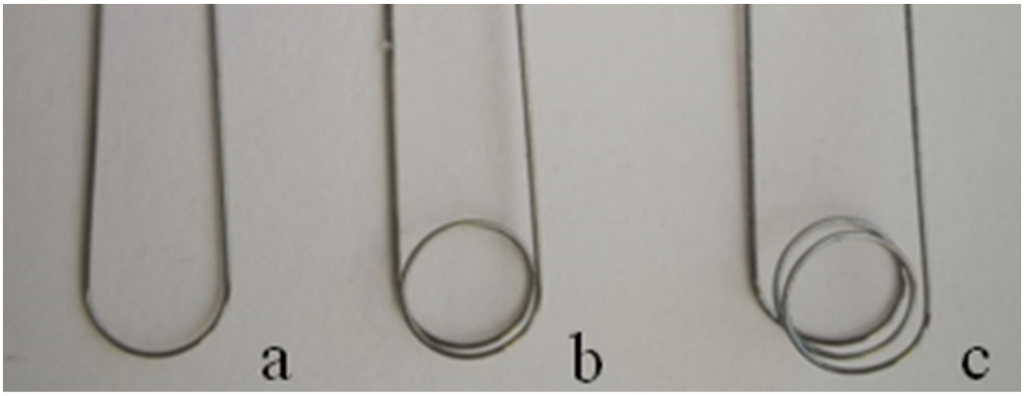


Figure 1. Different shapes of the probe sensing zone: (**a**) U-shaped; (**b**) one loop; (**c**) two loops.

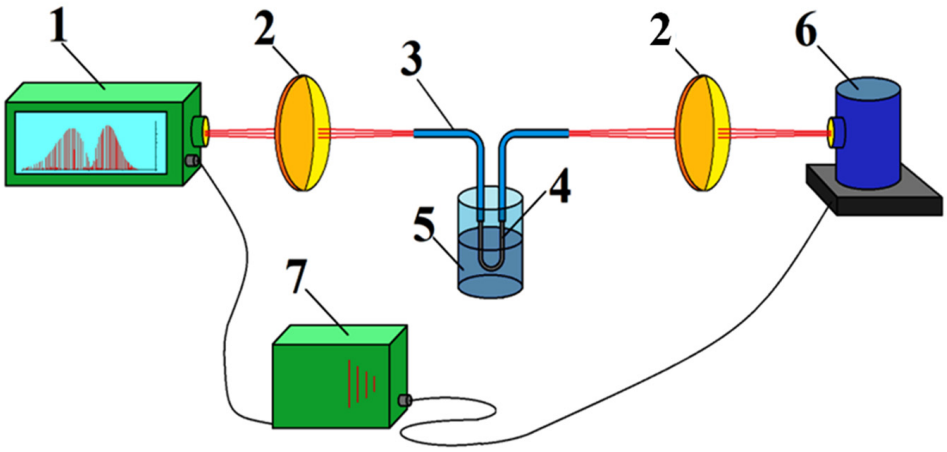
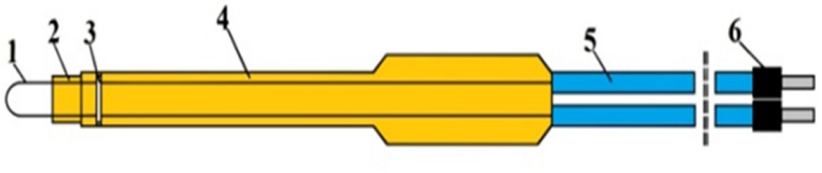
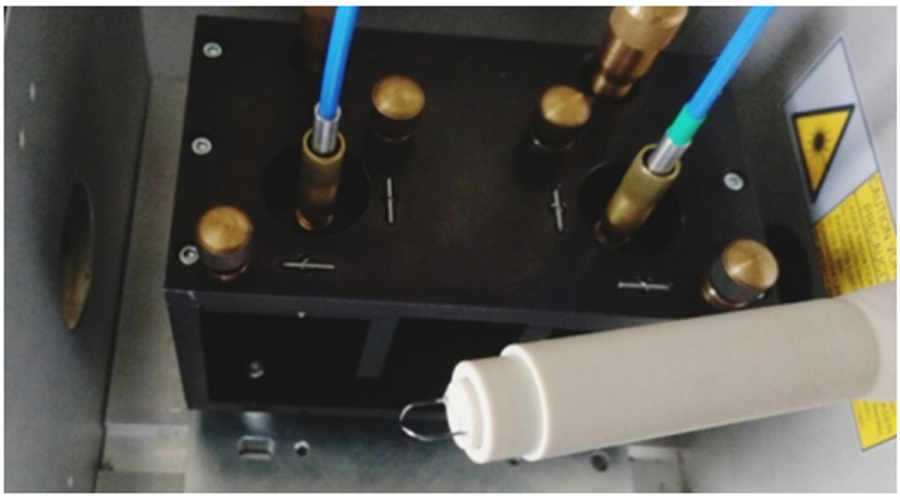


Figure 2. Setup for FEWS analysis: 1—IR Fourier spectrometer; 2—ZnSe focusing lenses; 3—chalcogenide fiber with polymer coating; 4—sensing part of the fiber without coating; 5—container with analyzed liquid; 6—HgCdTe detector; 7—amplifier.



(a)



(b)

Figure 3. Scheme and photo of fiber probe: (**a**) sensor scheme: 1—U-shaped fiber-sensing element; 2—removable tip; 3—the area of the sensor docking with the inlet and outlet fibers; 4—protective PEEK polymer shaft; 5—inlet and outlet fibers in protective polymer tubes; 6—SMA 905 optical connectors. (**b**) Photo of the sensor probe connected with IR spectrometer using special attachment.

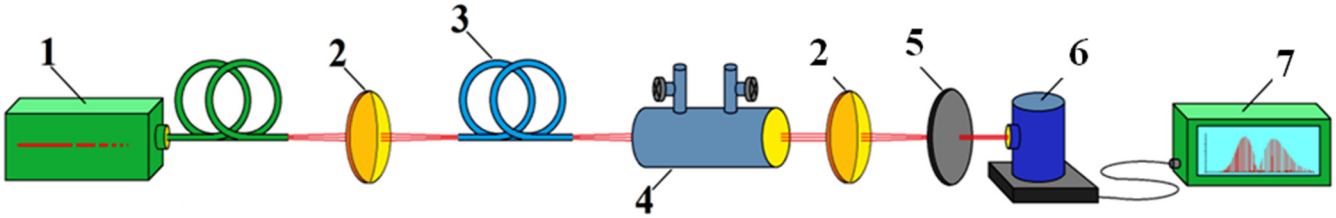


Figure 4. Setup for recording the spectra of gases that absorb in the emission range of REE ions: 1—pump laser with fiber output; 2—ZnSe focusing lens; 3—REE doped chalcogenide fiber; 4—container with analyzed gas; 5—optical filter; 6—HgCdTe/InSb detector; 7—IR Fourier spectrometer.

For the first and second types of sensor design, the single-index fibers based on high-purity $Ge_{20}Se_{80}$, $Ge_{20}Se_{70}Te_{10}$, $Ge_{10}As_{30}Se_{38}Te_{22}$, $Ge_{28}Sb_{12}Se_{60}$, and $Ga_{10}Ge_{15}Te_{73}I_2$ glasses were used. The fiber diameter varied in the range of 150–500 μm. The advantage of smaller diameter fibers of sensing elements is increased sensitivity due to the excitation of higher-order modes with greater penetrating power, as shown in our theoretical assessment mentioned above [26]. Fibers of 500 μm diameter make it possible to fabricate sensing elements with increased resistance to mechanical stress. The optical losses in the $Ge_{20}Se_{80}$ fiber did not exceed 0.5 dB/m in the 5.0–7.5 μm spectral range; the losses in the $Ge_{26}As_{17}Se_{25}Te_{32}$ fiber did not exceed 0.7 dB/m within 5.5–8.5 μm. The optical losses in the $Ga_{10}Ge_{15}Te_{73}I_2$ fiber were quite high (22 dB/m in the 10.5–13.5 μm spectral range; minimum value is 20 dB/m). For fibers made of glasses based on germanium and gallium tellurides, the losses in our fibers are among the lowest [50].

The all-fiber sensor probe (Figure 3) consists of a chalcogenide fiber-sensing element, a replaceable polyetheretherketone (PEEK) tip, and a pair of flexible supply multimode fibers for connecting with IR spectrometer.

Polycrystalline silver halide fibers or multimode arsenic selenide glass fibers were used as flexible supply ones. The $As_{38}Se_{62}/As_{35}Se_{65}$ fiber had optical losses lower than 500 dB/km in the 1.5–8.6 μm spectral range, and the minimum losses were 40 dB/km at 2.8 μm. Photo of the all–fiber probe with the tip and the special attachment for connection with FT-IR spectrometer is shown in Figure 3b. Such scheme makes it possible to carry out the FEWS analysis of substances for a short time under well-reproducible conditions [24,25].

For the third type of fiber sensor design, we used the REE-doped chalcogenide glass fibers emitting in the mid-IR (Figure 4). The peculiarity of this scheme (Figure 4) is the use of such fibers as a source of mid-IR broadband luminescence [33–37,45,46], as well as a source of mid–IR lasing, which we recently achieved [35,49,51]. REE-doped glass fiber materials make it possible to significantly expand the number of objects to be detected and also to simplify the analytical control procedure.

3. Results and Discussion

3.1. Testing the First Type of the Sensor Design

Chalcogenide fiber pieces of up to 70 cm length were used as sensing elements. The fiber-sensing elements had a linear form, a U-shaped form, or loop forms (Figure 1). To record IR absorption spectra, the sensing element was placed in the container with analyzed liquid (Figure 2). Globar source radiation was entered into one end of the fiber using lens systems, and the radiation from the other end was focused onto the HgCdTe/InSb detector of the IR-Fourier spectrometer. The absorption spectrum of the analyzed liquid was calculated by the equation:

$$A(\lambda) = -\log(I_s/I_{ref}),$$

where $A(\lambda)$ is absorption at wavelength λ; and I_{ref} and I_s are the intensity of idle radiation signal and the signal transmitted through the analyte, respectively.

Different kinds of sensing elements and various liquids were used for testing the sensor system. Figure 5 shows the absorption spectra of diesel fuel in the range of 2800–3000 cm^{-1}, recorded using sensors with different geometries of the sensing zone. In the case of a double loop, the integrated intensity of the absorption bands of diesel fuel increases by an order of magnitude compared to the linear form of the sensing element because of the greater penetration of light waves into an external medium at a fiber bend and the increase in attenuation coefficients of the bent fiber modes, as was shown in [26], as well as due to the coupling between all propagating modes. When the fiber modes are excited by a long-focus lens, the lower-order modes have greater amplitudes, but at a fiber bend, they can exchange their energy with higher-order modes, which have greater penetration depth into an analyte, even in a straight fiber [52]. The bending is very efficient for increasing the light penetration depth in chalcogenide fibers with a large refractive index, resulting in the strong confinement of light. For a multimode single-index fiber, attenuation coefficients of lower-order modes can be increased up to one order of magni-

tude and attenuation coefficients of higher-order modes can increase up to two orders of magnitude at the fiber bend [26].

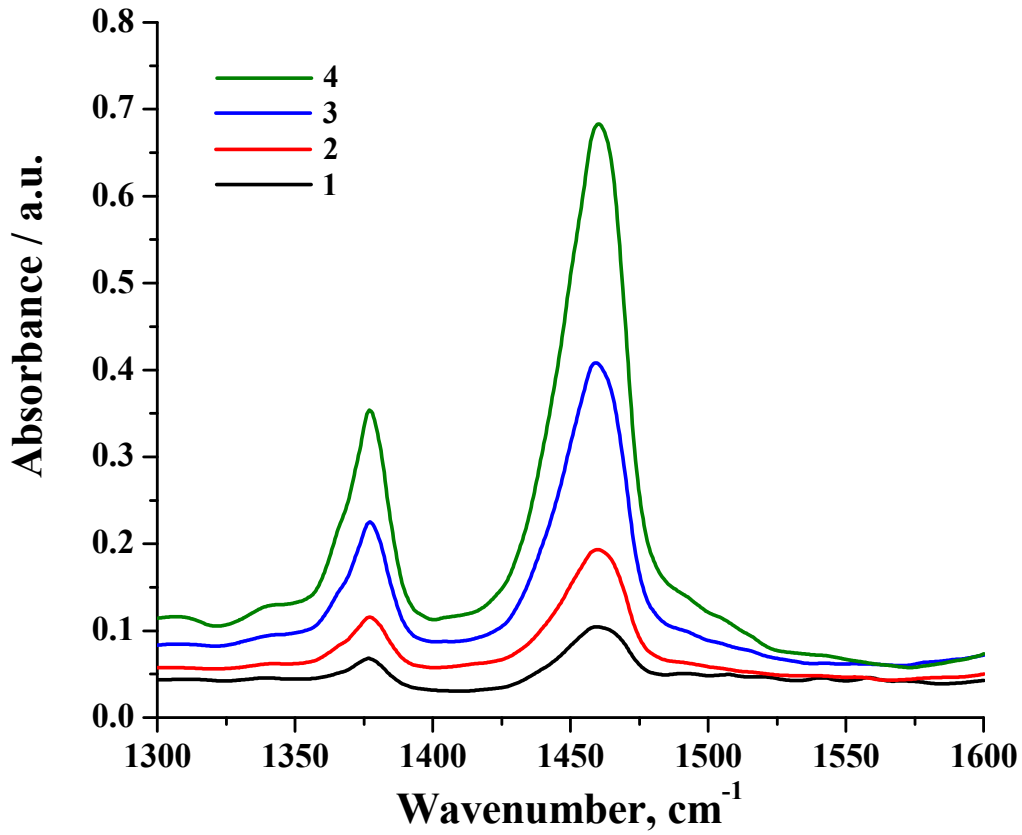


Figure 5. Diesel fuel absorption spectra (geometries of fiber sensitive zone are: 1—linear; 2—U-shaped; 3—two loops; 4—three loops).

Using the $Ge_{10}As_{30}Se_{38}Te_{22}$ glass fiber-sensing element in the form of U-shaped loop, the method for FEWS determination of an antigel additive content in diesel fuel has been developed. The antigel additive, which reduces fuel viscosity, gives sufficiently intense absorption bands that do not overlap with the bands of the main substance (Figure 6a). These bands correspond to carboxyl groups (1749 cm^{-1}), carboxylate anion (1636 cm^{-1}), and esters (1240 and 1276 cm^{-1}). The ester absorption bands were used to quantify the additive in diesel fuel. Figure 6b shows the dependence of the integral intensity of the absorption band centered at 1240 cm^{-1} on the concentration of the additive in the range of 0–1.0 vol.%. (The absorption bands of the additive are marked with arrows.) The detection limit of the additive in diesel fuel was 0.02 vol.%, whereas the 0.05–1.0 vol.% concentration values are recommended as a production process standard. The random error of additive determination was less than 10 % in the specified concentration range at a confidence level of 0.95.

Recently, we have observed an original result in the study of M-shape sensing zones with three multidirectional bends that were prepared based on $(GeTe_4)_{75}(AgI)_{25}$ and Ge_xSe_{100-x} single-index fibers. This sensing element design provides the ability to adjust the sensitivity by changing the number of element bends that are immersed in the analyte. An additional advantage of this M-shaped element is the ability to measure the time-varying composition of liquids with a high adsorption of one of the components on the fiber surface. The overall sensitivity of the M-shaped element, according to the results of the determination of methanol in the oil mixture (Figure 7), exceeds the result for the linear fiber-sensing element by 8–10 times, which is comparable to the previously obtained results for the double loop [25].

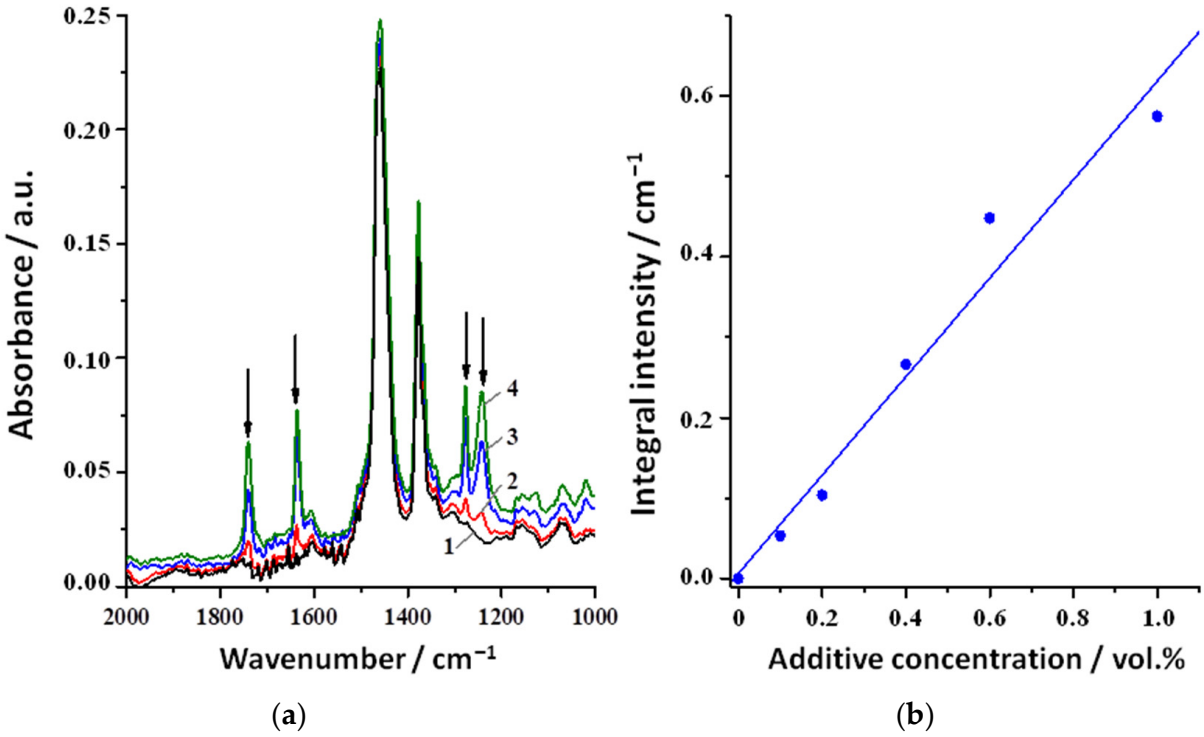


Figure 6. (**a**) Absorption spectra of diesel fuel with an antigel additive: 1—fuel without additive; 2—0.2 vol.% additive; 3—0.6 vol.%; 4—1 vol.%. (**b**) Dependence of absorption band intensity (1240 cm^{-1}) on the additive concentration. Figure is adapted from [25].

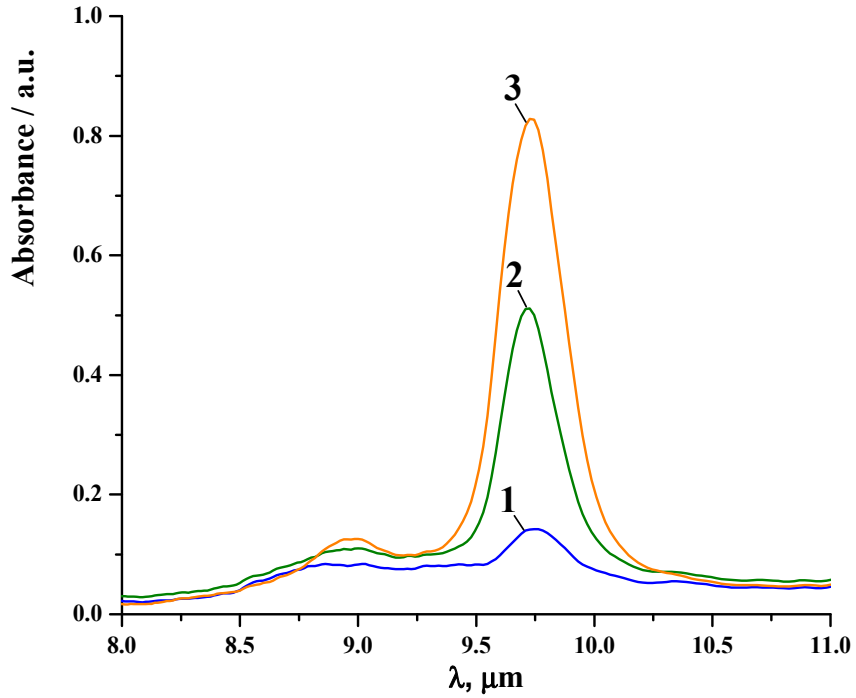


Figure 7. Absorption spectra of methanol in the oil mixture: a linear form of sensing element (1); a U-shaped loop form (2); a M-shaped loop form (3).

3.2. Testing the Second Type of Sensor Design

Sensor probes with removable sensing elements with the following combinations of flexible supply fibers and sensitive tips are of interest: polycrystalline silver halides (AgX)/AgX;

AgX/$Ge_{20}Se_{80}$; AgX/$Ga_5Ge_{15}Te_{73}I_2$; AgX/$Ge_{28}Sb_{12}Se_{60}$; ($As_{38}Se_{62}$/$As_{35}Se_{65}$)/$Ge_{20}Se_{80}$. Previously [42], we have shown that chalcogenide glass tip probes are more sensitive than crystalline silver halide ones (Table 1). The instrumental sensitivity of probes with chalcogenide tips is 1.6–1.8 times higher than that of polycrystalline ones, due to the higher refractive index and smaller diameter of chalcogenide fibers. The tip of the $Ge_{20}Se_{80}$ fiber probe with a waist at the center of the U-shaped bend demonstrated the highest sensitivity. The advantage of the $Ga_5Ge_{15}Te_{73}I_2$ glass fiber as a sensing element is a wider transmission region (4–15 μm) compared to the $Ge_{20}Se_{80}$ fiber (2–10 μm). The fiber made of $Ge_{28}Sb_{12}Se_{60}$ with a glass transition temperature of 285 °C is promising for FEWS analysis at elevated temperatures (study of exothermic reactions, quality control of engine motor oil, etc.). Due to the greater mechanical strength of the silver halide waveguides, the combined fiberoptic sensor consisting of polycrystalline silver halide (for connection to the spectrometer) and a chalcogenide fiber-sensitive element turned out to be the best probe design.

Table 1. Sensor performances in the determination of isopropyl alcohol [42].

Material of Flexible Fiber and Tip	Spectral Range, μm	Sensitivity $\times 10^3$, cm^{-1}/vol.% (947 cm^{-1})	Signal Linearity ($R^2 \times 10^2$) [1]	C_{min}, vol.% [2]
AgX/AgX	4–15	7.0 ± 0.2	99.63	0.2
AgX/$Ge_{20}Se_{80}$	4–12	12.0 ± 0.2	99.96	0.5
AgX/$Ge_{28}Sb_{12}Se_{60}$	4–12	13.5 ± 0.2	99.95	0.5
AgX/$Ge_{20}Se_{80}$ with taper	4–12	21.3 ± 0.2	99.93	0.3
AgX/$Ga_{10}Ge_{15}Te_{73}I_2$	4–15	12.8 ± 0.2	99.68	0.5
$As_{38}Se_{62}$/$Ge_{20}Se_{80}$	2–12	11.2 ± 0.2	99.88	0.5

[1] R^2 is the square of the approximation coefficient, [2] C_{min} is the detection limit.

Besides organic substances, an important application of FEWS spectroscopy is the determination of the content of inorganic salts in aqueous solutions. The combined AgX/$Ge_{20}Se_{80}$ fiber sensor probe was used to determine the concentration of iron sulfate in water (Figure 8). In the sulfate ion concentration range of 0.16–16 g/L, a linear calibration function was obtained that provides a relative analysis error of 2–5% at a confidence level of 0.95.

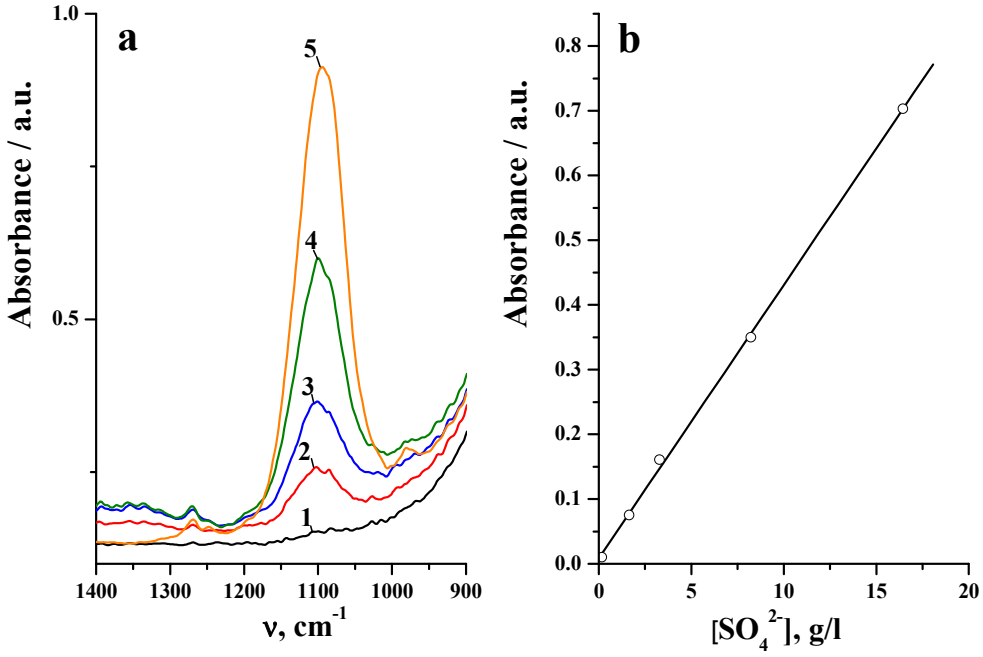


Figure 8. (**a**) Absorption spectra of SO_4^{2-} ions: 1–0.16 g/L; 2—1.6 g/L; 3—3.2 g/L; 4—8.0 g/L; 5—16 g/L. (**b**) Dependence of absorption band intensity centered at 1080 cm^{-1} on the sulfate-ions concentration.

An actual direction of application of the FEWS analysis is the determination of the ionic composition of sparingly soluble salts in the form of powders. This task is of particular importance for the oil industry because over time, oil pipelines become covered with a salt layer, which worsens their performance and can lead to breakdown of expensive equipment. Figure 9a shows the absorption spectra of calcium sulfate, sodium carbonate, and ammonium dihydrogen phosphate in the form of powders. Figure 9b gives the absorption spectra of the actual sediment from the inner surface of the oil pipeline recorded using a fiber-optic sensor (2) and a bulk attenuated total refection chalcogenide prism (1). The spectrum of the precipitate shows absorption bands of sulfate ions, carbonate ions, and water, apparently of a crystalline nature. The X-ray phase analysis, traditionally used to solve such problems, reliably detects only sodium chloride as the main component of the mixture in the analyzed precipitate. For FEWS analysis, this salt has no interfering effect, which makes it possible to reliably establish the presence of other salts.

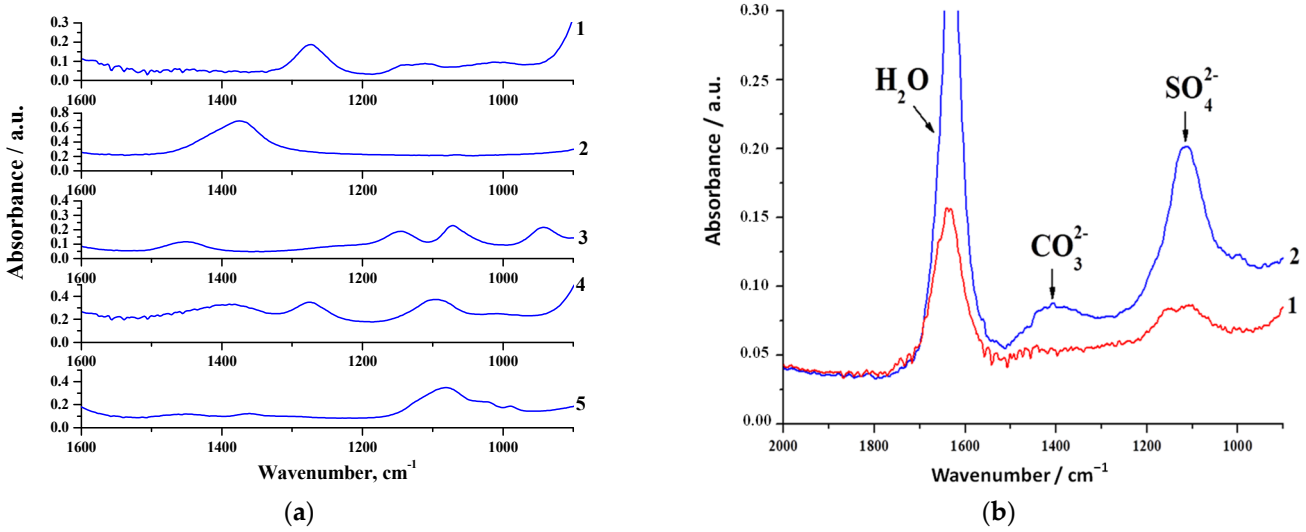


Figure 9. Absorption spectra of various anions: (**a**) model mixtures of salts (1—$CaSO_4$; 2—Na_2CO_3; 3—$NH_4H_2PO_4$; 4—$CaSO_4$ + Na_2CO_3; 5—$CaSO_4$ + Na_2CO_3 + $NH_4H_2PO_4$); (**b**) actual sediment. The spectra were recorded using a fiber-optic sensor (spectrum 2b) and a bulk attenuated total refection chalcogenide prism (spectrum 1b).

In real production conditions, the most demanding task is to measure the chemical composition of liquids directly in the stream. To establish the fundamental possibility of such measurements with the help of the fiber probes, a pipeline layout was constructed, consisting of a system of soldered polypropylene pipes with valves to control the flow rate. The forced flow of the liquid mixture with a linear velocity of 0.5–1 m/s was set using a submersible pump. The fiberoptic sensor was hermetically integrated into the system using a threaded plug and a PTFE seal (Figure 10, inset). As the analyzed liquid, the "water-isopropyl alcohol" mixture with the alcohol concentration of 1–10 vol.% was used. High sensitivity, linearity of the analytical signal, and resistance to mechanical loads in the turbulent flow regime indicate the promise of such sensors for in-line measurements of the chemical composition of liquid mixtures in real production processes.

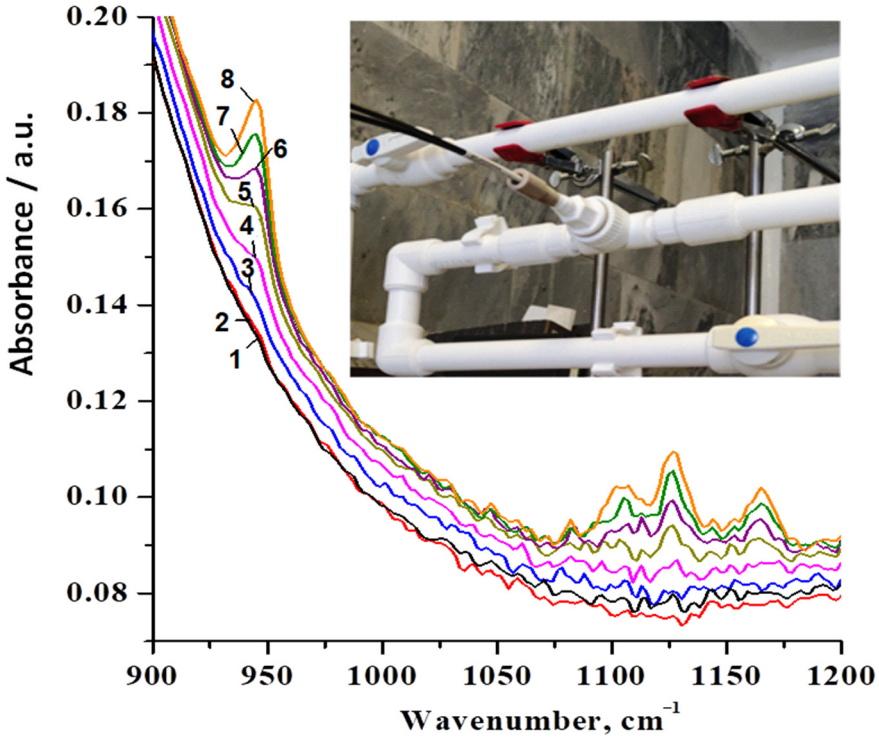


Figure 10. Photo of an experimental layout for testing the sensor "in situ". Absorption spectra of isopropyl alcohol in a water/alcohol mixture: 1—pure water; 2—0.1% vol. isopropyl alcohol; 3—0.5% vol.; 4—1.0% vol.; 5—2.0% vol.; 6—3.0% vol.; 7—4.0% vol.; 8—5.0% vol.

3.3. Testing the Third Type of the Sensor Design

Previously [25], we implemented a scheme for detecting acetonitrile using the Pr(3+)-doped glass fiber as a radiation source and determined the optimal configurations of the sensing element that make it possible to increase the measurement sensitivity. A distinctive feature and advantage of this scheme is the use of two fibers of different chemical compositions as the source and conductor of radiation. In the development of this work, we continued the search for the compositions of active glass matrices and the choice of rare earth additives in order to expand the range of substances to be detected.

Recent achievements in the development of Tb(3+)-doped glass fibers as the sources of spontaneous emission and laser generation in 4.2–5.5 μm wavelengths [34,35,49] make it possible to use these fibers for an all-fiber sensor scheme for determining the number of gas mixture components, which is extremely important for many industrial processes and environmental monitoring systems. The results of this approach are shown in Figure 11. Gaseous NO, N_2O, and CO_2 can be detected simultaneously, using the same active fiber. The absorption of the N_2O molecule [53] "cuts out" a section in the 4.4–4.6 μm region in the luminescence band of the Tb(3+)-doped chalcogenide fiber (a,b). Using a 30-cm-long optical cell, the minimum detectable N_2O concentration was about 10 ppmV. CO_2 can be determined by absorption in the 4.2–4.4 μm region which manifests in the emission spectra (Figure 11b). The absorption bands of the NO molecule are in the range of 5.1–5.6 μm, which corresponds to the active fiber generation range (Figure 11c).

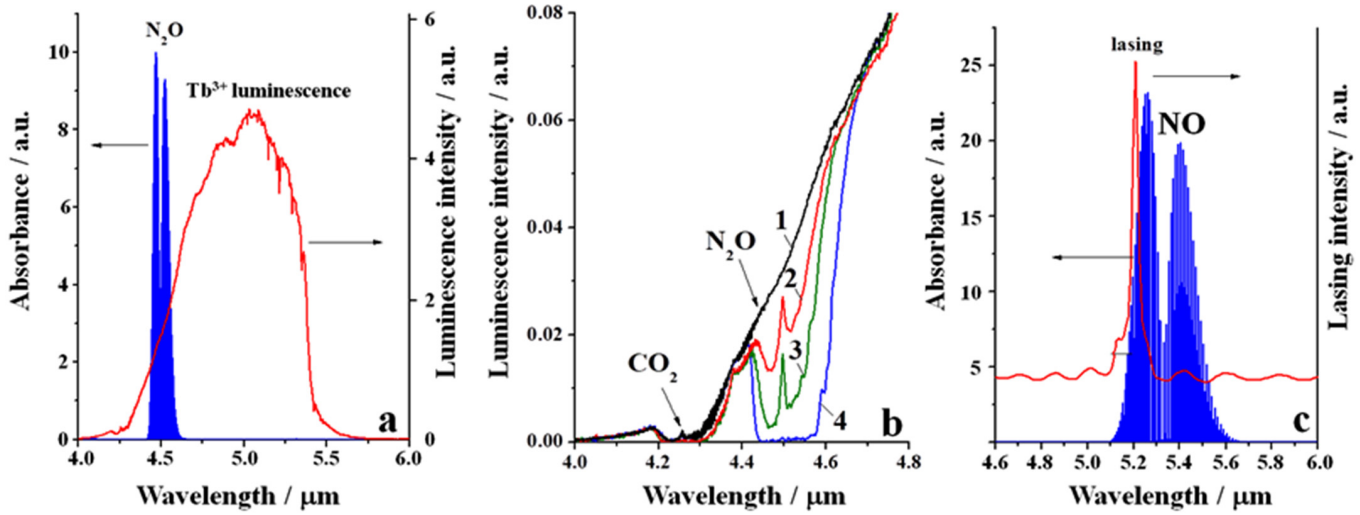


Figure 11. Emission spectrum of Tb(3+)-doped chalcogenide fiber and fragment of N_2O absorption spectrum (**a**). Absorption bands of gas mixture in emission spectrum (**b**) (concentration of N_2O: 1—0; 2—10 ppmV; 3—20 ppmV; 4—100 ppmV). Lasing spectra of Tb(3+)-doped chalcogenide fiber and fragment of NO absorption spectrum (**c**) ([53]).

Laser generation in Tb(3+)-doped chalcogenide fibers, which we recently demonstrated [35,49,51], opens up new possibilities for using the same active fiber as a mid-IR radiation source for monitoring several components simultaneously, expanding the spectral range of detection. Work in this direction is promising and will continue.

4. Conclusions

High purity chalcogenide glass fibers for mid-IR fiber-sensing elements have been developed. Such fibers show promise in determining the chemical composition of liquids, powders, and gases using FEWS spectroscopy. Various designs of sensing elements have been proposed. On the bases of selenide and telluride glasses, optical fibers—transparent in the 2–15 μm range—have been prepared. Testing these fibers as sensing elements of various configurations for different types of analytes has shown their advantages over previously known sensor materials. First of all, chalcogenide FEWS sensors have high sensitivity and the ability to determine the qualitative and quantitative composition of several components simultaneously with a low detection limit directly "in situ".

Glasses of the proposed compositions for fiber sensors are resistant to aggressive environments compared to commercially available polycrystalline silver halides and have better photostability. Thus, they show promise in the development of sensors for a wide range of analyzed objects and increase the service life of the sensor element. Combined AgX/$Ge_{20}Se_{80}$, AgX/$Ga_5Ge_{15}Te_{73}I_2$, AgX/$Ge_{28}Sb_{12}Se_{60}$, and ($As_{38}Se_{62}$/$As_{35}Se_{65}$)/$Ge_{20}Se_{80}$ fibers turned out to be the most successful solution for the design of the sensor probe, which was tested for different analyzed objects.

On the base of the Pr(3+)- and Tb(3+)-doped Ga(In)-Ge-As-Se and Ga-Ge-Sb-Se glass fibers, all-fiber sensor schemes were developed for the detection of gas components at the level of units of ppmV concentration, which gives the better results, to our knowledge. The high emission characteristics of the proposed doped glass fibers, functioning as sources of spontaneous and laser radiation at 3–6 μm, open up new prospects for the development of analytical spectral methods and expand the range of detectable substances.

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