**INTELLIGENT SYSTEMS FOR IMPROVING THE RELIABILITY OF SULFUR MEASUREMENT IN FUELS**

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The paper examines infrared spectroscopy as an effective tool for improving the reliability of intelligent analysis of sulfur-containing compounds in petroleum fuels. The feasibility of using this method is substantiated as a modern approach to determining the sulfur mass fraction in petroleum products, which combines high measurement accuracy with the capability of rapid express analysis without complex sample preparation procedures.

Special attention is devoted to the investigation of the mid-infrared range ($4000\text{--}400\text{ cm}^{-1}$), where characteristic absorption bands corresponding to the vibrations of S–H, C–S, S=O, SO₂, and S–S bonds are observed. These bands are associated with the functional groups of sulfur-containing compounds. It is shown that the application of narrow-band optical filters enables the isolation of informative spectral regions and reduces the influence of noise components, thus increasing the reliability of spectral measurements.

A conceptual optical scheme of an infrared analyzer is proposed, which includes a radiation source, a system of optical filters, a sample cuvette, focusing lenses, and a pair of detectors — working and reference. This architecture provides simultaneous registration of reference and measurement signals, allowing automatic correction of results and compensation of radiation fluctuations.

Based on the obtained experimental data, dependencies between fuel layer thickness, optical density, and transmittance have been constructed. The results confirm the linear correlation described by the Beer–Lambert–Bouguer law, forming the foundation for quantitative determination of sulfur concentration in low-sulfur fuel samples (5–10 ppm).

It has been demonstrated that the combination of infrared spectroscopy with the mathematical apparatus of chemometrics and multiple linear regression significantly enhances the accuracy of predicting the physicochemical properties of fuels, enables the creation of calibration models, and minimizes measurement errors. The results of the study form the scientific basis for the development of innovative intelligent express systems for monitoring the quality of petroleum products. Such systems are suitable for both laboratory and field applications, as well as for integration into the technical service infrastructure of fuel and energy complexes.

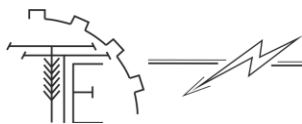
Key words: *infrared spectroscopy, sulfur-containing compounds, petroleum products, express measurement, optical density, transmittance, Beer–Lambert–Bouguer law, calibration model, intelligent analysis, fuel quality monitoring.*

Eq. 9. Fig. 5. Table. 2. Ref. 14.

1. Problem formulation

The problem of accurate and rapid determination of sulfur-containing compounds in motor fuels is extremely relevant. Firstly, an increased sulfur content during combustion leads to the formation of sulfur oxides, which, when interacting with moisture, form acids. In turn, this causes intensive corrosion of engine components, primarily of the fuel system (injectors, high-pressure pumps, turbochargers). Secondly, in several countries, the use of fuels with high sulfur content is still observed: for example, before the introduction of strict regulations in the United States, diesel fuel contained up to 5000 ppm of sulfur, and in marine transport, until 2020, fuels with sulfur content up to 3.5 % (35,000 ppm) were used, which exceeds the current IMO limit of 0.5 % [1].





Recent studies of A-95 gasoline conducted in 2025 by specialists of the Institute of Consumer Expertise (Table 1) showed that even in major fuel networks, there has begun to appear fuel that does not meet or is close to not meeting the requirements of the DSTU [2].

Table. 1

Data from the studies of the Institute of Consumer Expertise on A-95 gasoline as of early 2025

Filling stations (study according to DSTU 7687:2015)	Octane number	Sulfur content, mg/kg	Volumetric fraction of aromatic hydrocarbons (%)	Volumetric fraction of benzene (%)
	min 95	max 10	max 35	max 1.0
WOG	95,8	4	26,8	0,72
UKRNAFTA	95,3	5	25,3	0,77
AMIC	95,7	6	25,8	0,64
KLO	95,7	6	26,4	0,74
OKKO	95,6	8	31,2	0,65
PARALLEL	95,6	7	29,7	0,64
MARSHALL	95,4	8	32,4	0,80
SVR (Harkiv)	95,6	8	27,7	0,85
MOTTO	95,3	10	30,2	0,87
FAKTOR	95,0	10	28,3	0,98
BVS	95,7	9	33,0	0,91
VST	95,1	9	33,6	0,87
SVOI	95,0	10	32,7	0,99
BRCM-NAFTA	95,0	11	8,8	1,0
EVRO 5 (Zaporizhzhia)	95,3	21	10,8	2,95

As can be seen from the above-mentioned studies conducted by the specialists of the Institute of Consumer Expertise at the beginning of 2025, the A-95 gasoline market shows cases of exceeding DSTU standards (in the table, suppliers that exceed the DSTU limits and those that are close to the permissible values are highlighted). Typically, diesel fuels contain higher sulfur levels than gasoline [2].

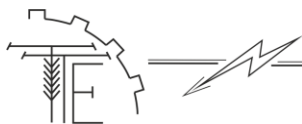
Therefore, infrared (IR) spectroscopy appears to be an effective method for monitoring both gasoline and diesel fuels: this method allows for rapid, non-contact measurements without complex sample preparation. However, the use of this method faces significant challenges: fuels contain dozens of organic and sulfur-containing components, spectral bands overlap, and weak peaks of sulfur groups can easily be lost in the noise background. To overcome these problems, correlation models, chemometric methods, and optimal selection of wavenumber ranges are required, which calls for further research.

2. Analysis of recent research and publications

Y. Biletsky, in two of his works [3, 4], dealt with the problem of measuring sulfur content, where all possible methods were systematically classified, with particular attention given to optical methods. V. Kapustian and A. Kovalsky studied the problems and prospects for the development of the petroleum products market in Ukraine. Their publications also indicate that the sulfur content in fuel depends on many factors, namely: the origin of crude oil, cracking processes, and preliminary treatment. Typically, diesel fuel contains more sulfur than gasoline, in the form of mercaptans, sulfides, disulfides, and heterocyclic compounds. During combustion in internal combustion engines, they are converted into SO₂, which in turn increases the risk of equipment corrosion, thereby reducing the service life of machinery [5, 6].

An important contribution to the study of sulfur analysis methods was made by foreign researchers such as Mohammadi M. and Nespeca M.G. who investigated optical and mass spectrometric techniques. According to these authors, a promising direction is the use of optical methods, which do not require sample preparation, are non-destructive, and enable measurements with high efficiency. In particular, they focused on infrared (IR) spectroscopy methods, which make it possible to detect and quantify sulfur-containing compounds by their characteristic absorption bands arising from the vibrations of chemical bonds [8, 9].

The author [10] noted that the main application area of infrared spectrophotometry in fuel analysis is the study of light and middle distillate fractions, although there are also examples of its use for heavy residual fractions. Most often, Fourier-transform spectrophotometers operating in the near-IR range are used; they



employ fiber-optic systems to transmit radiation from the source to the sample cuvette and to collect the reflected signal.

IR spectroscopy methods allow the detection and quantification of sulfur-containing compounds through specific absorption bands that occur due to the vibrations of chemical bonds. This technology has long been used for the analysis of gasoline, diesel fuel, and heavy fractions [11].

3. The purpose of the article

To substantiate the application of infrared spectroscopy as a tool for improving the reliability of intelligent analysis of sulfur-containing compounds in petroleum fuels, to investigate the possibility of detecting characteristic absorption bands of S–H, C–S, S=O, SO₂, and S–S bonds in the mid-IR range (4000–400 cm⁻¹), and to verify the adequacy of the Beer–Lambert–Bouguer law for low sulfur concentrations (5–10 ppm).

4. Results and discussion

Today, there is a continuous tightening of sulfur content requirements for automotive gasoline and diesel fuels worldwide. According to DSTU 7687:2015 for gasoline and DSTU 7688:2015 for diesel fuel, both standards set the permissible sulfur level in fuels at no more than 10 ppm, which complies with the European Euro-5 standard [3].

A comprehensive characterization of fuels requires performing multiple analyses, which demand a well-developed infrastructure, qualified personnel, and large sample volumes [12]. The use of chemometric methods based on IR spectra, however, allows for the rapid prediction of several parameters simultaneously, using a small sample volume (approximately 10 ml) [13].

Let us consider the schematic diagram of an optical infrared analyzer and perform the necessary calculations. Depending on the measurement tasks, the scheme may include additional elements designed to improve speed, accuracy, or other performance characteristics [14]. The structural diagram of the optical infrared analyzer is shown in Fig. 1.

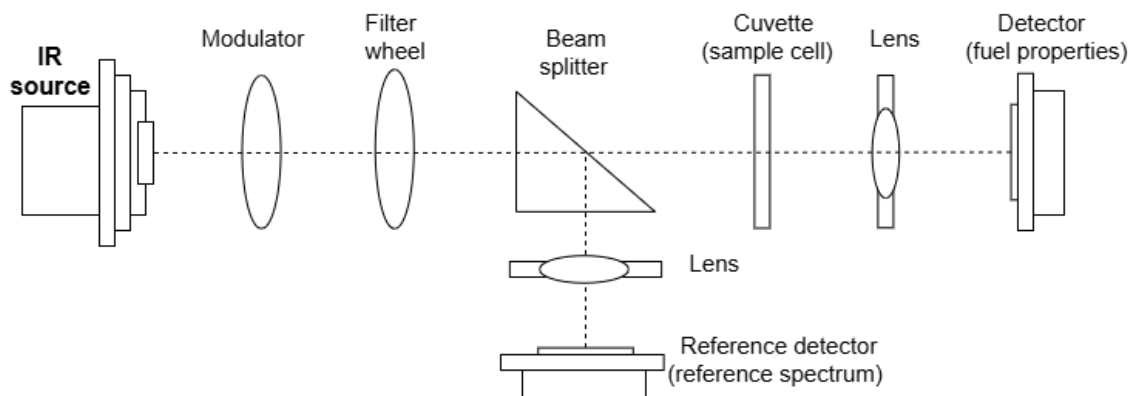


Fig. 1. Structural diagram of the optical infrared analyzer

The proposed schematic of the infrared fuel analyzer is based on the principle of generating and subsequently processing IR radiation in the mid-infrared spectral range. The radiation source serves as a generator of electromagnetic waves within the range of 4000–400 cm⁻¹ – precisely in this region, the most intense absorption bands characteristic of most hydrocarbon and sulfur-containing compounds are observed [15].

At the first stage, the radiation passes through a rotating chopper wheel that interrupts the beam and converts it into a pulse sequence. This solution improves the signal-to-noise ratio.

Next, the light flux passes through a wheel equipped with a set of optical filters. Each filter isolates a narrow spectral region corresponding to certain vibrational modes of chemical bonds (for example, C–H, O–H, S=O). This makes it possible to perform selective analysis and to form an individual spectral “fingerprint” of the examined fuel sample. The beam, focused by a lens, then reaches a beam splitter, which divides it into two components: one passes through the sample cuvette, while the other goes directly to the reference detector. This allows simultaneous recording of both reference and measured signals.

In the cuvette, the IR beam interacts with the fuel molecules. Part of the energy is absorbed by the functional groups of organic and sulfur-containing compounds, forming characteristic spectral bands listed in Table 2.

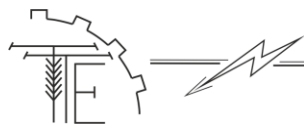
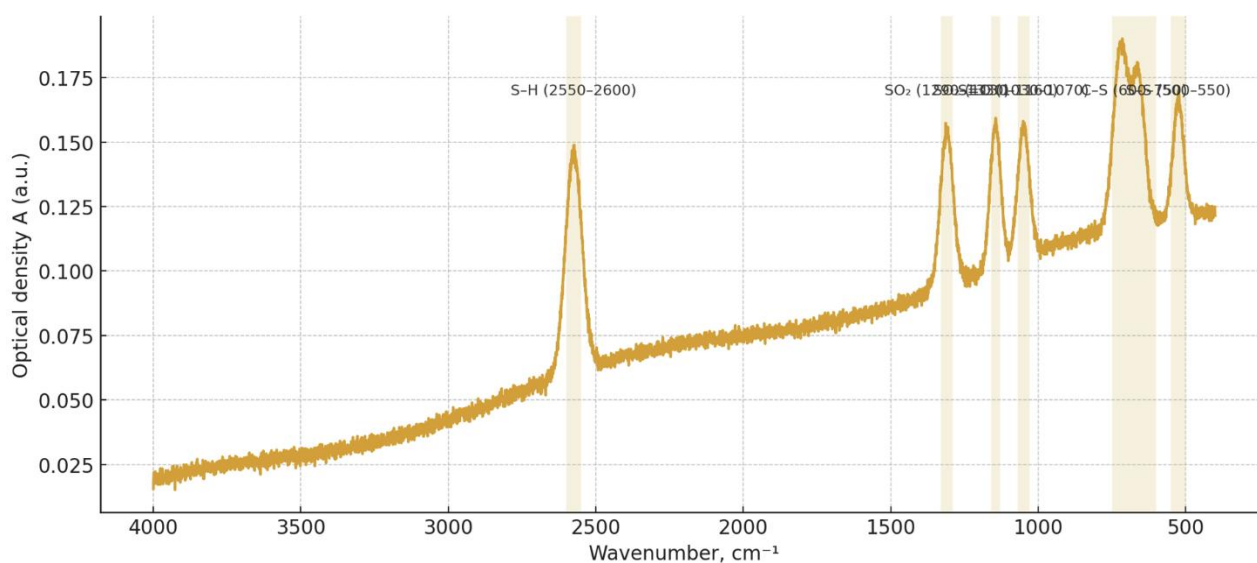


Table. 2

Characteristic IR absorption bands of sulfur-containing compounds [16]

Type of bond / ompound	Wavenumber, cm ⁻¹	Example of compounds
S–H	2550–2600	mercaptans (R–SH)
C–S (alkyl sulfides)	600-750	R–S–R'
S–S (disulfides)	500-550	R–S–S–R'
Aromatic thiophenes	700-900	benzo- and dibenzothiophenes
Sulfoxides (R–S(=O)–R')	1030-1070	oxidized compounds
Sulfones (R–SO ₂ –R')	1290-1330; 1130-1160.	oxidation products

The detector located after the cuvette records the modified signal containing information about the sample composition, while the reference channel captures the baseline spectrum for correction. At the output, we obtain the spectrum shown in Fig. 2.

**Fig. 2. IR spectrum with characteristic bands of sulfur-containing compounds**

Further data processing is performed by the analyzer's software, which compares the signals from both detectors. As a result, a complete infrared spectrum of the analyzed sample is formed. The subsequent application of chemometric methods, particularly multiple linear regression, makes it possible to construct mathematical models that predict the physicochemical properties of the fuel, its sulfur content, and other important characteristics, which will not be discussed in detail here.

However, it is necessary to begin with the relationship between radiation intensity and the concentration of sulfur-containing compounds, which forms the basis of the method [17]:

$$A = \varepsilon \cdot c \cdot l, \quad (1)$$

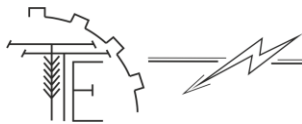
where $A = \log\left(\frac{I_0}{I}\right)$ optical density.

- molar absorption coefficient;
- concentration of the substance, mol/L;
- optical path length (cuvette), cm.

According to the analyzed sources, the following coefficient values can be considered [9, 10].

$\varepsilon = 1500 \text{ l} / \text{cm} \cdot \text{mol}^{-1}$, cm^{-1} The molar absorption coefficient (ε) determines how strongly a particular functional group of a molecule absorbs infrared radiation at a specific frequency. For sulfur-containing compounds in the mid-IR range (4000–400 cm^{-1}), this parameter characterizes the intensity of absorption bands associated with S–H, C–S, S=O, and related vibrations.

Let $l = 1 \text{ cm}$ – this choice of cuvette thickness ($l = 1.0 \text{ cm}$) is due to the fact that it is the standard value in most spectroscopic studies within the mid-IR range. Such a thickness provides an optimal balance between signal intensity and transmission.



To achieve a concentration corresponding to the regulatory level of 5–10 ppm, we will calculate the optical density that should be observed.

First, let us determine the molar concentration corresponding to 5 ppm (mass fraction):

$$c = \frac{\text{ppm} \cdot \rho}{M \cdot 10^6} = \frac{5 \cdot 800}{32.065 \cdot 10^6} \approx 1.25 \cdot 10^{-4} \text{ mol/L}, \quad (2)$$

where $\rho = 32.065 \text{ g/mol}$ – molar mass of sulfur (S); $\approx 800 \text{ g/L}$ – mass of 1 L of fuel (density $\approx 0.8 \text{ g/mL}$).

The expected optical density will be:

$$A = 1500 \cdot 1.25 \cdot 10^{-4} \cdot 1 \approx 0.1875. \quad (3)$$

The corresponding transmittance is within the range of:

$$T = 10^{-A} = 10^{-0.1875} \approx 0.65. \quad (4)$$

A value of $T = 0.65$ means that only 65% of the IR radiation passes through a 1 cm layer of fuel, while the rest is absorbed by S–H bonds.

Based on these calculations, we will plot the dependence of optical density on sulfur concentration for different cuvette thicknesses (Fig. 3), as well as the dependence of infrared transmittance on sulfur concentration (Fig. 4).

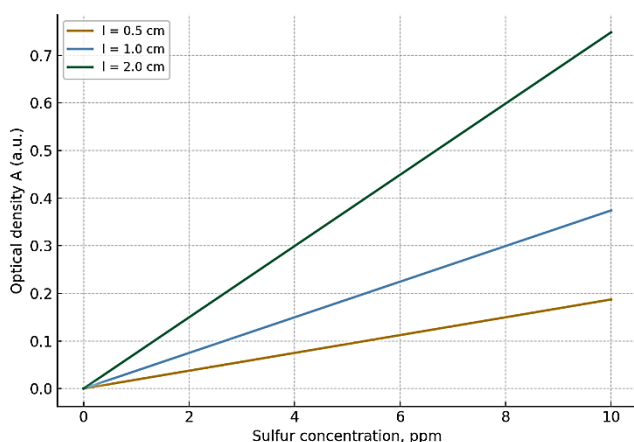


Fig. 3. Optical density as a function of sulfur concentration for different cuvette thicknesses.

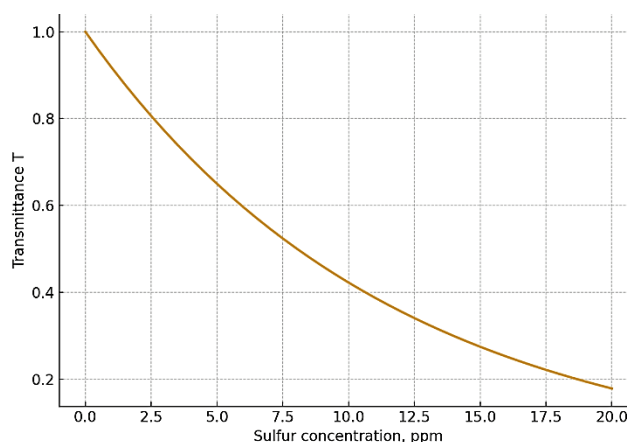


Fig. 4. Infrared transmittance as a function of sulfur concentration.

According to these dependencies, the following conclusions can be made:

- increasing the cuvette thickness leads to a proportional increase in optical density A , which confirms the linear nature of the relationship according to the Beer–Lambert–Bouguer law;
- the infrared transmittance T decreases with increasing sulfur concentration in the fuel, which is consistent with the theoretical model;
- the obtained dependencies can be used to develop calibration models and to select the optimal cuvette thickness when designing express methods for determining sulfur content in fuels.

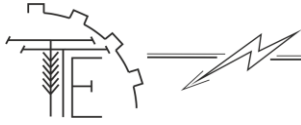
Calibration models for such analysis are built using the mathematical apparatus of multiple linear regression [14]. Their general form is described by the equation:

$$P_x = M_0 + M_1 F_{11} + M_2 F_{11} + \dots + M_z F_{1z}; \quad (5)$$

where P_x is the concentration of the component or the value of the property x ; F_z is the absorption value obtained through filter z ; M_z is the estimated parameter for filter z , calculated using the multiple linear regression method; M_0 is the intercept (free term) of the equation.

The coefficients M_z and M_0 form the basis of the calibration model, which is used to predict the value of parameter P_x based on the measured absorbance F_z . To construct such a model, a system of equations is created for each sample in the calibration dataset. In these equations, known reference values of the property P_x (dependent variable) and the corresponding absorbance values F_z (independent variables) are substituted.

The multiple linear regression method is applied to determine the optimal coefficients M_z and M_0 , which most accurately describe the relationship between spectral characteristics and the measured fuel



parameters. The optimal solution is found by minimizing the difference between the predicted values P_x and those obtained using standard (reference) methods.

As a result, for each sample in the calibration dataset, a system of equations of the following form is obtained:

$$\begin{aligned} P_{x1} &= M_0 + M_1 F_{11} + M_2 F_{11} + \dots + M_z F_{1z} \\ P_{x2} &= M_0 + M_1 F_{21} + M_2 F_{22} + \dots + M_z F_{2z}, \\ &\vdots \\ P_{xn} &= M_0 + M_1 F_{n1} + M_2 F_{n2} + \dots + M_z F_{nz} \end{aligned} \quad (6)$$

where n – is the number of samples in the calibration dataset.

In matrix form, this can be written as:

$$P = FM + \varepsilon, \quad (7)$$

where:

- is the vector of dependent variables (known property values obtained by reference methods);
- is the matrix of independent variables (absorbance values for each filter);
- is the vector of regression coefficients to be determined;
- is the vector of model errors.

The problem is solved using the least squares method (LSM), which minimizes the sum of squared deviations between the experimental and predicted values:

$$\min \sum_{i=1}^n (P_{xi}^{\text{exp}} - P_{xi}^{\text{exp}})^2. \quad (8)$$

The analytical solution for determining the regression coefficients is as follows:

$$M = (F^T F)^{-1} F^T P. \quad (9)$$

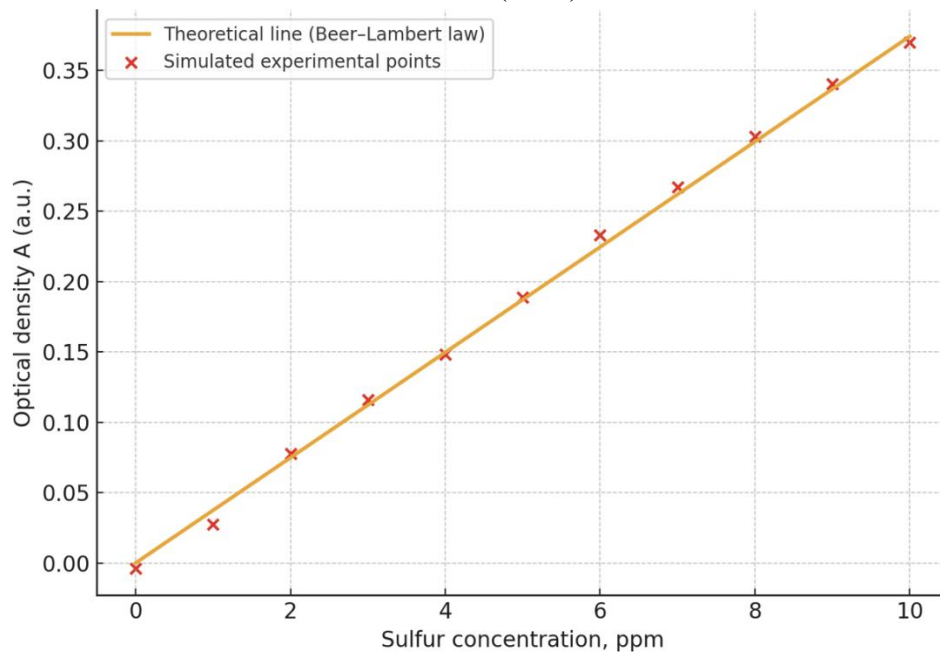
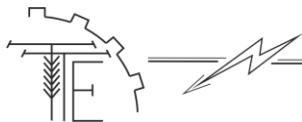


Fig. 5. Calibration curve of the dependence of optical density on sulfur concentration

The obtained coefficients M_z and M_o form the basis of the calibration model. Subsequently, this model is used to predict the properties of new fuel samples based on spectral data. The reliability and accuracy of the constructed model are verified using several indicators: the coefficient of determination (R^2), which reflects the degree of correspondence between experimental and predicted results; the root mean square error (RMSE), which characterizes the deviation of predictions from reference values; and the residual variance, which indicates the level of unaccounted errors. The calibration curve showing the dependence of optical density on sulfur concentration is presented in Fig. 5.

5. Conclusion

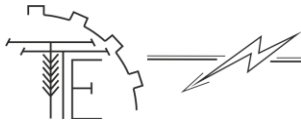


The conducted study confirmed the high effectiveness of infrared spectroscopy as a tool for enhancing the reliability of intelligent analysis of sulfur-containing compounds in petroleum fuels. The obtained results made it possible to formulate the following summarized conclusions:

- it was established that an increased sulfur content in fuel leads to the formation of sulfur oxides during combustion, which cause corrosion of engine components, reduce their service life, and create significant environmental impact;
- it was proven that the mid-infrared range ($4000\text{--}400\text{ cm}^{-1}$) is the most informative for identifying characteristic absorption bands of functional groups S–H, C–S, S=O, SO₂, and S–S, typical of sulfur-containing compounds;
- the developed schematic optical analyzer confirmed the validity of the Beer–Lambert–Bouguer law for low sulfur concentrations (5–10 ppm) and demonstrated the possibility of quantitative determination of sulfur content based on the relationship between optical density and transmittance;
- the feasibility of combining IR spectroscopy with chemometric methods, particularly multilinear regression, was substantiated. This combination improves the accuracy of predicting the physicochemical parameters of fuels, reduces interference effects, and enables the creation of efficient calibration models;
- practical results showed that the application of IR spectroscopy significantly reduces analysis time and sample volume and enables the development of portable express instruments for on-site quality control of gasoline and diesel fuels in industrial conditions.

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**ІНТЕЛЕКТУАЛЬНІ СИСТЕМИ ПІДВИЩЕННЯ НАДІЙНОСТІ ВИМІРЮВАННЯ ВМІСТУ СІРКИ В ПАЛИВАХ**

У статті розглядається інфрачервона спектроскопія як ефективний інструмент для підвищення надійності інтелектуального аналізу сірковмісних сполук у нафтовому паливі. Обґрунтовано доцільність використання цього методу як сучасного підходу до визначення масової частки сірки в нафтопродуктах, який поєднує високу точність вимірювання з можливістю швидкого експрес-аналізу без складних процедур підготовки зразків. Особлива увага приділяється дослідженню середнього інфрачервоного діапазону ($4000\text{--}400\text{ см}^{-1}$), де спостерігаються характерні смуги поглинання, що відповідають коливанням зв'язків S–H, C–S, S=O, SO₂ та S–S. Ці смуги пов'язані з функціональними групами сірковмісних сполук. Показано, що застосування вузькосмугових оптичних фільтрів дозволяє виділити інформативні спектральні області та зменшує вплив шумових складових, тим самим підвищуючи надійність спектральних вимірювань.

Запропоновано концептуальну оптичну схему інфрачервоного аналізатора, яка включає джерело випромінювання, систему оптичних фільтрів, кювету для зразка, фокусуючі лінзи та пару детекторів – робочий та опорний. Ця архітектура забезпечує одночасну реєстрацію опорних та вимірювальних сигналів, що дозволяє автоматично коригувати результати та компенсувати флуктуації випромінювання. На основі отриманих експериментальних даних побудовано залежності між товщиною шару палива, оптичною густиною та коефіцієнтом пропускання. Результати підтверджують лінійну кореляцію, описану законом Бера-Ламберта-Бугера, що формує основу для кількісного визначення концентрації сірки у зразках палива з низьким вмістом сірки (5–10 ppm).

Було продемонстровано, що поєднання інфрачервоної спектроскопії з математичним апаратом хемометрії та множинної лінійної регресії значно підвищує точність прогнозування фізико-хімічних властивостей палив, дозволяє створювати калібрувальні моделі та мінімізує похибки вимірювань. Результати дослідження формують наукову основу для розробки інноваційних інтелектуальних експрес-систем моніторингу якості нафтопродуктів. Такі системи придатні як для лабораторних, так і для польових застосувань, а також для інтеграції в інфраструктуру технічного обслуговування паливно-енергетичних комплексів.

Ключові слова: інфрачервона спектроскопія, сірковмісні сполуки, нафтопродукти, експрес-вимірювання, оптична густина, пропускання, закон Бугера–Ламберта–Бера, калібрувальна модель, інтелектуальний аналіз, моніторинг якості палива.

Ф. 9. Рис. 5. Табл. 2. Літ. 14.

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