# Scientific Journal of Silesian University of Technology. Series Transport

Zeszyty Naukowe Politechniki Śląskiej. Seria Transport



Volume 127

2025

p-ISSN: 0209-3324

e-ISSN: 2450-1549

DOI: https://doi.org/10.20858/sjsutst.2025.127.15



Silesian University of Technology

Journal homepage: http://sjsutst.polsl.pl

# Article citation information:

Szczucka-Lasota, B., Węgrzyn, T., Chen, F., Turoń, K. Monitoring the quality of liquid fuels using spectroscopy methods - selection of a light source. *Scientific Journal of Silesian University of Technology. Series Transport.* 2025, **127**, 257-265. ISSN: 0209-3324. DOI: https://doi.org/10.20858/sjsutst.2025.127.15

# Bożena SZCZUCKA-LASOTA<sup>1</sup>, Tomasz WĘGRZYN<sup>2</sup>, Feng CHEN<sup>3</sup>, Katarzyna TUROŃ<sup>4</sup>

# MONITORING THE QUALITY OF LIQUID FUELS USING SPECTROSCOPY METHODS – SELECTION OF A LIGHT SOURCE

**Summary.** The aim of the article is to develop a new measurement station for assessing the quality of liquid fuels using light spectroscopy methods. Tests were carried out using various light sources, transmittance and absorbance were determined, and sources for liquid fuel tests were selected. Fuel samples were prepared. At the developed stand, it was checked whether the developed measurement method is suitable for determining the quality of liquid fuel. The novelty of the article is to show that spectroscopy methods using appropriate light sources are a prospective solution for determining the quality of liquid fuels during continuous monitoring. The research was performed in laboratory conditions. The technology requires development and adaptation to real conditions; the research conducted is qualitative and not quantitative.

Keywords: liquid fuels, fuels quality; automotive

<sup>&</sup>lt;sup>1</sup> Faculty of Transport and Aviation Engineering, The Silesian University of Technology, Krasińskiego 8 Street, 40-019 Katowice, Poland. Email: bozena.szczucka-lasota@polsl.pl. ORCID: https://orcid.org/0000-0003-3312-1864

 <sup>&</sup>lt;sup>2</sup> Faculty of Transport and Aviation Engineering, The Silesian University of Technology, Krasińskiego 8 Street, 40-019 Katowice, Poland. Email: tomasz.wegrzyn@polsl.pl. ORCID: https://orcid.org/0000-0003-2296-1032
<sup>3</sup> Sino-US Global Logistics Institute, Antai College of Economy & Management, Shanghai Jiao Tong University, College of Economy & Management

Shanghai 200240, China. Email: fchen@sjtu.edu.cn. ORCID: https://orcid.org/0000-0001-8656-7910 <sup>4</sup> Faculty of Transport and Aviation Engineering, The Silesian University of Technology, Krasińskiego 8 Street,

<sup>40-019</sup> Katowice, Poland. Email: katarzyna.turon@polsl.pl. ORCID: https://orcid.org/0000-0001-6744-8887

#### **1. INTRODUCTION**

By adopting the Act of the August 26, 2006 on the monitoring and control of the quality of liquid fuels, together with supplementary provisions, the Parliament of the Republic of Poland implemented a fuel quality control system consistent with the system operating in the European Union, which came into force in 2007. The quality control system in force in the country is managed by the President. The Office of Competition and Consumer Protection (UOKiK), inspections are carried out by the Trade Inspection (IH), and the tested parameters and their scopes are determined by regulations of the Minister of Economy [1]. In general terms, the national system for quality control of liquid fuels consists in controlling the quality parameters of fuels throughout the entire supply chain, i.e., at every stage of their operation, i.e., ready-made fuels are tested at producers, intermediaries, wholesalers, and gas stations. However, laboratory research methods are long-lasting. Therefore, new methods are being sought to assess the quality of liquid fuels, enabling quick feedback. A problem that has not yet been solved is the constant monitoring of liquid fuels. Newly developed liquid fuel quality methods presented around the world have a number of limitations. According to the data literature [2-11]:

- the majority of methods still require downloading samples of laboratory fuels and specialist apparatus;
- for safety reasons, including the possibility of ignition, some methods cannot be approved for the continuous monitoring of long-term stordf fuels, e.g., the method using a fiber optic optrode system;
- measurement sensors used in some methods interact with the fuel, reducing the operational properties of the fuel, which significantly limits the possibility of using them during long-term monitoring;
- modern equipment used in some solutions is extensive and requires laboratory working conditions, therefore its use to assess the quality of fuels at storage stations is impossible or significantly difficult.

In the article, it was decided to develop a model of a simplified station for monitoring the quality of liquid fuels. The research is preliminary research conducted as part of a research project.

#### 1.1. Development of a model station and principle of operation

First, a station for spectrometric measurements in the range of UV-VIS-NIR radiation was developed. The site presented in Fig. 1 consisted of:

from a white light source (1), an optical fiber supplying light to a quartz glass cuvette (3), in which samples of the tested fuel (4) are placed. The optical fiber is coupled with an optical system that converts the divergent beam coming from the optical fiber into a quasi-parallel (collimated) one. The diameter of the outgoing beam is 5 mm.

After passing through the fuel cuvette, the light enters the output fiber (5), an output fiber arranged concentrically in relation to the axis of the input system. The optical fiber introduces them to (6) a UV-VIS-NIR spectrometer, with a measurement range of 200-1000 nm (Thorlabs, model CCS 200/M).



Fig. 1. Station for preliminary measurements

Therefore, the task of the output system is to focus a beam of parallel rays into the optical fiber. Using a USB cable, the spectrometer is connected to a computer (7) where the measurement results are saved in the form of spectral spectra.

Due to the fact that the system should operate in specific conditions, an important step was to select the appropriate type of light source. Measurements of the spectral spectra of selected light sources and their analysis are presented in the next chapter.

### 2. MEASUREMENTS OF SPECTRAL SPECTRA OF SELECTED LIGHT SOURCES

#### 2.1. Selection of light sources

For the first tests, a halogen lamp, a krypton lamp, a laboratory illuminator with an optical fiber cutting off infrared radiation, a white RGB LED, and a white LED with one chip were used. The choice of light sources was dictated by practical considerations:

- halogen and krypton sources have a continuous spectrum in the VIS range, so if unusual changes occur in this spectral range, they will be noticed. The disadvantage, from the point of view of the target design, is the relatively low efficiency of converting electric current into light,
- therefore, sources with low-power, high-efficiency, and many times higher durability, i.e., light-emitting diodes LEDs, were also selected for testing.

#### 2.2. Selection of light sources

At the presented research stand (Figure 1), spectral spectra of selected light sources were measured. The results of the measurements carried out on the preliminary test stand are presented in Figure 2.



Fig. 2. Spectrum Analysis Chart for various light sources

At this stage of design work, attention should be paid to:

- the large differences between the spectrum of a halogen lamp (blue graph) and the FLQ-150 halogen laboratory illuminator (green graph), shown in Figure 2. A clear registered difference in the spectrum (for a halogen laboratory illuminator) appears in the range above 600 nm and is caused by the use of optical fiber attenuating infrared radiation. These types of optical fibers are used, for example, in microscopy to examine biological preparations in order to cut off infrared radiation, which could cause an unfavorable increase in the sample temperature, which may also be important in the long-term process of monitoring fuel quality.
- on the width of the obtained spectrum for a given lighting source. According to the attached graphs, the halogen lamp (blue graph in Figure 2) and krypton lamp (red graph in Figure 2) had the widest spectrum range.
- characteristic curve for the spectrum obtained using the LED-white\_lW520A lamp, with a clear maximum for a wavelength of approximately 460 nm.

Due to the possibility of an unfavorable increase in the sample temperature by a halogen lamp, a krypton lamp, characterized by the widest spectrum, and a LED-white\_lW520A lamp were used to carry out measurements on the initial test samples of diesel fuel, for which a characteristic course of the recorded curve was obtained in the wavelength range of 400-500 nm.

# 2.3. Material for research

The first measurements were carried out on diesel oil samples (Table 1).

Tab. 1

Symbol	Characteristic
HE	ON- from the refinery (delivered as "reference material"), FAME content
	below 0.5% v/v,
HE/H	diesel oil containing more than 200 mg/kg of water
ON/6/2	diesel oil containing less than 0.5% v/v FAME from the storage tank from the
	middle layer,

Test samples

ON/H/6/2	diesel oil containing approx. 7% v/v FAME from the storage tank in the middle layer,
ON/H/B	diesel oil containing approx. 7% FAME, aged in a bomb from the induction period.

Fifteen samples of each material were prepared for testing. The results obtained were similar for each material; therefore, only selected, representative test results are presented in the next section.

#### **3. FINDINGS**

The results of the transmission spectra obtained and recorded on the developed test stand using a krypton lamp are presented in Fig. 3. Preliminary analysis indicates that changes occur in the initial VIS range, at the level of 400-500 nm and around 720 nm.



Fig. 3. Normalized transmission spectra of diesel fuel samples in the light of a krypton lamp, sample markings in accordance with the text

Absorbance was also calculated in accordance with those known from the literature. Figure 4 shows the results of the appropriate conversions.

Based on the obtained measurement results, it can be concluded that below 400 nm the signal coming from the source is very weak and, therefore, it is characterized by high noise in the measured signal (Figure 4). In the range from 400 to 500 nm, large changes in absorbance occur. Therefore, this is the most characteristic range for the light source used - a krypton lamp. The changes observed in the wavelength range above 500 nm are many times smaller. Therefore, it was concluded that the analysis of the remaining scope does not provide useful information. Analogous measurements were carried out using a light source in the form of a white LED – LW-520A.



Fig. 4. Absorbance of diesel fuel samples in relation to a krypton lamp, sample markings in accordance with the text



Fig. 5. Standardized transmission spectra of diesel fuel samples in LED light, sample markings in accordance with the text

The normalized transmission spectra of diesel fuel samples in the light of the white LED – LW-520A are shown in Figure 5. A clear recorded difference in the spectrum appears in the range of 450 nm and in the range of approximately 580 nm. However, significant changes in intensity were obtained for individual fuel samples only in the 450 nm peak area; in this area the recorded curves do not overlap, indicating differences between the tested materials. Therefore, when assessing the quality of liquid fuels using a light source in the form of a white LED - LW-520A, the wavelength range between 400-500 nm should be taken into account for the analysis of the quality of diesel fuels. The absorbance graph - Figure 6 - shows clear differences recorded for individual samples of aged fuels.



Fig. 6. Absorbance of diesel fuel samples in LED light, sample markings according to the text

The differences are so significant that they can be considered sufficient to analyze changes occurring in the fuel. Comparison of the results for selected light sources allows us to conclude that both light sources used in the tests provide information that can be used to determine fuel quality, but more characteristic changes for the tested fuel samples are recorded using a light source in the form of an LED diode. Moreover, when using the white LED light - LW-520A, the electrical power requirement was 96 mW, and in the case of the krypton bulb used in the previous tests, the electrical power requirement was 6.75 W. Therefore, the benefits of using it as LED light source. Additionally, LED diodes, according to the manufacturer's data, are characterized by significant durability, many times higher than the durability of other light sources.

# 4. SUMMARY AND CONCLUSIONS

The analysis of the obtained measurement results indicates that each diesel oil sample behaved differently than the others. Analyzing the absorbance graphs presented in Figures 4 and 6, it can be seen that individual samples reach a specific absorbance level for different wavelengths. Therefore, a method can be used to determine the wavelength at which the absorbance reaches a specific value. In this manner, the condition of the fuel that has been stored is easily comprehensible.

Based on the measurement results obtained, it can be concluded that:

- 1. The tested LED sources have a more favorable spectral distribution, with the maximum located in the range of 400-500 nm, where the greatest changes were observed for the individual tested liquid materials,
- 2. Krypton and halogen lamp light sources in the range of up to. 400 nm, due to the very weak signal coming from the source and high noise in the measured signal, are not sufficient to determine qualitative changes in the tested materials. The sensitivity of the method using the analyzed light sources in the range of up to 400 nm is insufficient.
- 3. Analysis of the measurement range from 400 nm for a halogen lamp is not sufficient to determine qualitative changes in fuel such as diesel oil because in the above-mentioned range there are initially large changes in absorbance and then many smaller changes,
- 4. When LED light is used, sufficient information is obtained to analyze changes occurring in diesel fuels due to much greater intensity changes in the 450 nm peak area. The light emitted by the LED source can therefore be used to test the quality of fuels, such as diesel oil.
- 5. The tests were carried out independently on 50 samples, revealing and confirming the observed relationship between the type of light source used and the type of sample.

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Received 19.10.2024; accepted in revised form 23.01.2025



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