

Studying optical characteristics of aviation fuels samples stored under various conditions

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Abstract. In this work the SPR method has been investigated. And it has been shown that this SPR method is the simple and reliable approach to study the quality of aviation kerosenes. The device "Plasmon-71" developed at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, with account of measured values of refraction index, has enabled to reveal changes in the kerosene composition after storing and applying it under conditions of aviation enterprise. The results of SPR measurements have been confirmed using infrared spectrometry, which allows revealing the presence of iron-, molybdenum- and chromium-containing organic compounds.

Keywords: surface plasmons, refraction index, SPR-sensor, infrared spectrometry, IR spectroscopy.

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1. Introduction

It is well known that safety of aircraft flights depends to a great extent on reliability and regularity of aircraft engine operation. As it follows from literature data of exploitation of turbojet engines, 40–55% of faultinesses and failures fall on the fraction of fuel system [1, 2]. To provide quality of aviation fuel foresees thorough control for the correspondent quality of aviation fuels and lubricants during all the stages from their production up to fuelling the aircraft. Therefore, it is topical to solve the problem of keeping the cleanness of fuel in transportation means as well as when preserving it in internal voids of technological equipment at airfield warehouses, including obtaining and storing at the warehouses of aircraft factories, where the aircrafts are created, repaired and tested. To technical supporting the fuel cleanness, it is necessary to regularly check it up.

Up to date, produced in Ukraine are two grades of aviation fuel for jet engines operating with kerosene, namely: PT and TC-1 (in Ukrainian specification) [3]. The main producers are Odesa, Kremenchuk and Lysychans'k petroleum refineries. Requirements concerning quality of these fuels are regulated by branch standards OCTY 320.00149943.007-97 "Fuel of the grade PT for

jet engines. Technical conditions" and OCTY 320.00149943.011-99 "Fuel TC-1 for jet engines. Technical conditions". Quality of domestic fuels is regulated using 19 factors that define physical-and-chemical as well as operational performances of kerosenes of corresponding grades, in particular: their density, kinematic viscosity, fractional composition, specific electrical conductivity, *etc.* In addition, they determine the dirtyness with mechanical additives and admixtures of water, since availability of water lowers the fluidity of fuels under low temperatures, while the mechanical additives can clog filters in the aircraft fuel system, which results in stopping the fuel feed to the jet engine and crashing the aircraft [4].

The main and most widely spread methods for diagnostics of the kerosene quality are as follows: absorption photometry [5], liquid chromatography [6], X-ray fluorescent analysis [7], infrared (IR) spectroscopy, atomic absorption spectrometry, impedance measurement and weighting, as well as methods of chemical diagnostics, for example titration.

Common deficiencies of photometric absorption and impedance methods are their low accuracy and impossibility to ascertain the reasons for changing the optical density and dielectric permittivity of kerosene,

which prevents to separate the contribution from the very substance oxidation and availability of foreign particles from store holders, lubricants, water, *etc.* X-ray fluorescent analysis requires expensive equipment, and chemical methods are based on costly reagents. The method of weighting has low accuracy and requires a long period for accumulation of sufficient mass of impurities, in particular inside filtration systems.

Thus, the currently existing methods have a number of deficiencies, which not only increase the cost of aviation fuel diagnostics but require a long period of its realization. An alternative method to diagnose the cleanness of oil products is that based on the surface plasmon resonance phenomenon (SPR), which implies determination of changes in resonance conditions for excitation of surface optical plasmon-polariton waves as a consequence of changes in the dielectric function of the studied substance after embedding foreign impurities. This method is the express one and enables to carry out the investigations in the real-time mode. Using the SPR method, the authors earlier performed studying the availability of wear and oxidation products in motor oils for various terms of their operation [8] and developed the complex way to determine the kind of motor oils [9]. The known methods based on SPR phenomenon for studying the fuel quality use in experiments pure samples of gasoline and diesel fuel intentionally doped with kerosene as a harmful impurity [10, 11]. When analyzing known literature sources, we did not find respective publications concerning the diagnostics of kerosene quality in various operation conditions.

Therefore, the aim of this work was to ascertain regularities in changes of optical characteristics inherent to kerosene samples as a consequence of their degradation under various conditions of keeping them at airlines by using the methods of optical refractometry and SPR. In addition, we used the method of IR spectroscopy and performed the correlation analysis of results obtained with these methods.

2. Materials and methods

We studied four samples of TC-1 kerosene that were kept under various conditions of aviation plant, namely: in supplier's container (TC-1, pure, reference), in production shop of logistics, delivery and storage, in the storehouse and in the fueller tank (residues of fuel).

To ascertain degradation of the samples, we studied changes of the following optical characteristics:

- refraction indexes (RI) for the sodium yellow line $\lambda = 589.3$ nm (n_D) and for the cesium infrared line $\lambda = 852.1$ nm (n_r) as well as changes in their dispersion ($n_D - n_r$);
- angular positions of minima inherent to their refractometric characteristics of reflection, when SPR is excited with laser irradiation by the wavelength $\lambda = 852.1$ nm;
- characteristic absorption bands in the infrared range of wavelength with the aim to determine changes in the chemical composition of kerosene when storing it under various conditions.

Metrological investigations of refraction index changes for the sodium yellow line n_D were made by direct measurements when using the refractometer RL-3, while for the cesium infrared line n_r – by indirect measurements with the two-channel device “Plasmon-71” with account of measured positions of minima inherent to refractometric characteristics of the studied kerosene samples, when SPR was excited by radiation of the wavelength $\lambda = 852.1$ nm. The absolute inaccuracy in measurements of refraction index changes for the studied substances was no higher than $\Delta n = \pm 0.00002$. When using the device RL-3, the absolute error in measurements of refraction index was $\Delta n = \pm 0.0002$. Both kinds of measurements were performed using the devices under normal conditions ($P = 10^5$ Pa, $T = 293$ K). At the initial stage, we measured RI n_D for the studied samples by using the device RL-3, then – the SPR one.

With this aim, the containers with the kerosene samples and the device “Plasmon-71” were placed into the thermo stating box, where the temperature was kept within the limits ± 0.2 K. Then, via the first channel of the device measuring flow cell having the volume $70 \mu\text{L}$ (placed above the sensitive element), we pumped through it the kerosene samples with the velocity $5 \mu\text{L}/\text{min}$ as well as the water solution of ethanol (96 vol.%) that served as a reference substance.

Then, we measured the temporal changes of angular positions of SPR resonance characteristic minima with simultaneous registration of these characteristics. To compensate possible temperature variations, the second channel was used for pumping through it the only ethanol solution. The measured values of angular positions minima were used to calculate RI n_r of the kerosene samples and to determine the RI dispersion.

Investigation of changes in characteristic absorption bands in the infrared range was made using the IR Fourier spectrometer Infracum FT-801 within the range 500 up to 5000 cm^{-1} with the resolution 2 cm^{-1} .

3. Results and discussion

3.1. Refractometric methods

The measured and calculated characteristics of studied and reference samples have been summarized in Table, namely: refraction index for the sodium yellow line n_D , values of angular positions for minima of SPR refractometric characteristics θ_{sp} as well as their relative shift when substituting the ethanol solution with the corresponding kerosene sample $\Delta\theta_{sp}$, refraction index for the infrared cesium line n_r and the dispersion value ($n_D - n_r$). The dependence of SPR-sensor response to substitution $\Delta\theta_{sp}$ on the refraction index n_D of kerosene samples is shown in Fig. 1. The plot of this dependence can be well approximated with the linear function $y(x) = 83.0172 \cdot x - 113.126$ with the matching factor $R^2 = 0.98$, while the correlation coefficient is equal to $\rho = 0.990$, which is indicative of a direct relation between these values.

Table. Measured and calculated characteristics of the studied samples.

No	Title of the sample	n_D (589.3 nm)	θ_{sp} , deg	$\Delta\theta_{sp}$, deg	n_r (852 nm)	$n_D - n_r$
	Deionized water	1.3330	58.536		1.32780	0.00520
	Ethanol	1.3640	60.759	0	1.35670	0.00730
1	Kerosene TC-1	1.4422	67.350	6.6013	1.42946	0.01274
2	Shop for logistics, delivery and storing	1.4418	67.393	6.5753	1.42990	0.01190
3	Storehouse	1.4415	67.351	6.5385	1.42947	0.01203
4	Residue from the fueller container	1.4425	67.418	6.6244	1.43014	0.01236

The correlation coefficients between n_D and SPR minima θ_{sp} and calculated n_r values are practically the same and considerably lower $\rho = 0.566$ and $\rho = 0.559$, respectively. It means that, to determine RI changes, it is purposeful to apply the SPR method, since it is more accurate (relative error of measurement results is no higher than 3...9%) as compared with the results obtained using optical refractometry when RI values were close to the errors of the device RL-3 (where the relative error of measurements reaches 28...67%).

Since the kerosene samples from the same initial substance under different storing conditions show different RI dispersions that have only a weak correlation with RI n_D ($\rho = 0.672$), then it is reasonable to conclude that these deviation values of the dispersion relatively to the initial one of the original substance (0.01274) occur as a consequence of varying content and composition of impurities of different nature in these kerosene samples. To ascertain the nature of these impurities, we applied the method of infrared spectrometry.

3.2. The method of infrared spectrometry

Considering the transmission spectra of the studied kerosene samples, one can separate two sub-ranges concerning their information capability with account of availability of characteristic absorption bands, namely: the short-wave sub-range from 4 up to 6 μm (1700...2500 cm^{-1}) and the long-wave one between 15 and 19 μm (526...670 cm^{-1}). In the former, we revealed 5 characteristic bands, while in the latter – 4 bands. Fig. 2 shows the fragment of transmission spectrum with the characteristic bands of long-wave sub-range where one can observe the largest difference between the transmission values.

In this case, the decrease in transmission intensity of characteristic bands inherent to the kerosene sample relatively to the reference one (TC-1) was indicative of available impurities or products of degradation processes, while the increase in the transmission intensity confirmed destruction of chemical bonds inherent to definite components (caused by stratification by fractions). Shown in Fig. 3 is the fragment of transmission spectrum with characteristic bands of the short-wave sub-range, where one can observe the largest difference in transmission values.

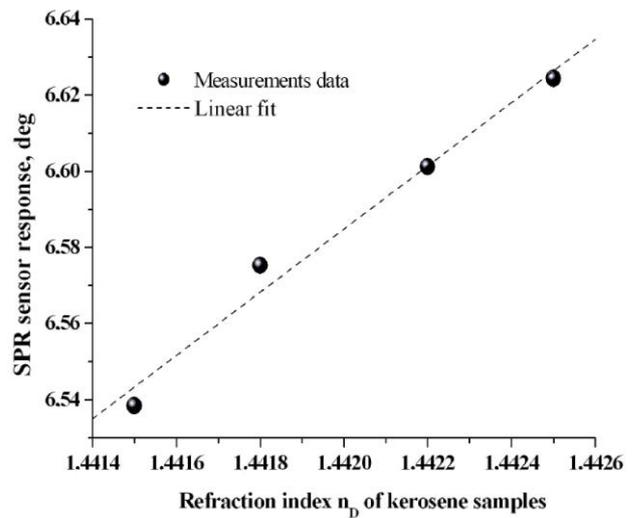


Fig. 1. Measured dependence of the changes in angular position for the minimum of refractometric characteristics (SPR sensor response) for the kerosene samples on their refractive index.

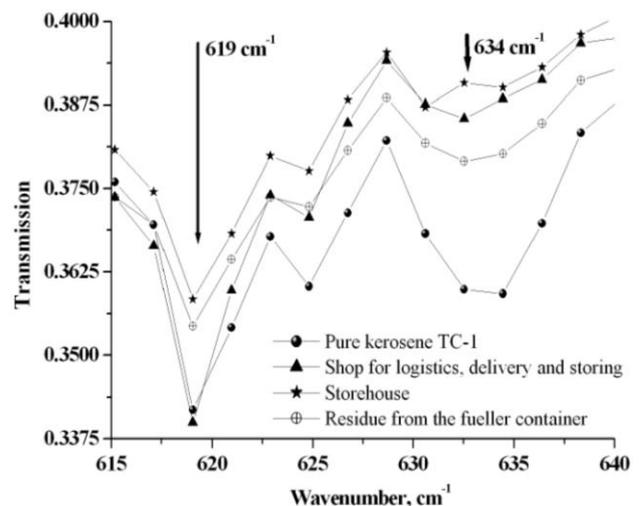


Fig. 2. Measured transmission spectra in the long-wave sub-range for the kerosene samples stored under various conditions.

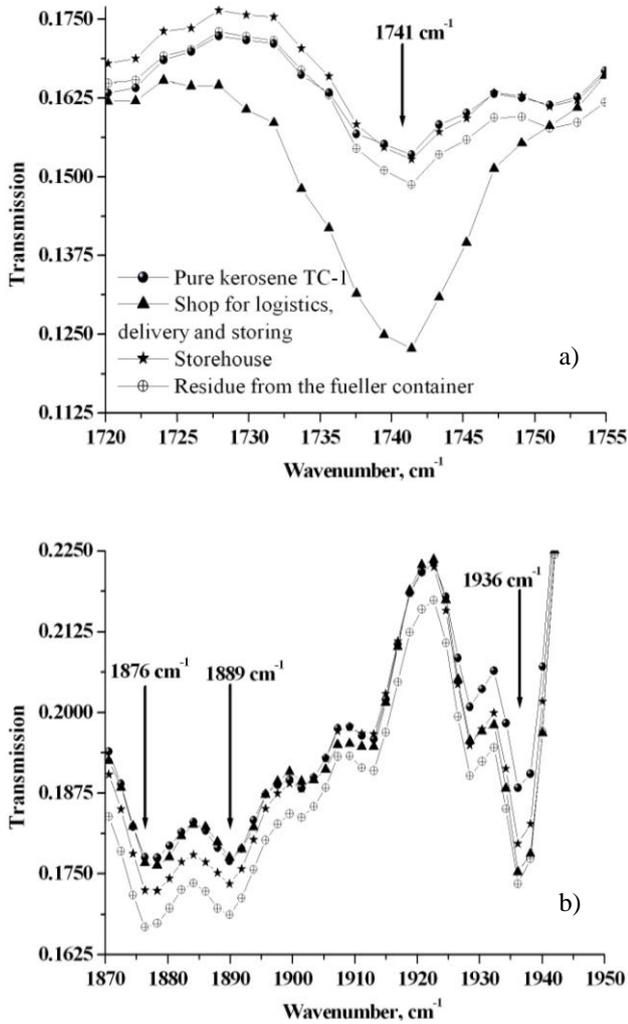


Fig. 3. Measured transmission spectra in the short-wave sub-range for the kerosene samples stored under various conditions.

Our analysis of the measured transmission spectra have shown that in the long-wave sub-range the transmission intensity for the most kerosene samples is increased, which is indicative of decomposition processes in kerosene components during their storing, the intensity being changed in the different manner, which can be the consequence of both different climatic conditions for their storing and various duration. In the short-wave sub-range, the transmission intensity decrease was dominant for the most of kerosene samples, which indicates the growth of impurity concentration or that of reaction products between kerosene components and organic or inorganic substances present in the premises for storing the respective samples (through stratification by fractions).

In the obtained spectra within the short-wave sub-range, the most attractive one lies in the region between 1700 and 1770 cm^{-1} . Here, in the case of kerosene sample from the shop for logistics, delivery and storing we observed the considerable decrease in the transmission intensity of the characteristic band 1741.41 cm^{-1} .

To perform a more scrupulous analysis of changes in the chemical composition of the studied kerosene samples, we explored changes $\Delta T = T - T_{ref.}$ in the characteristic transmission bands as compared with those of the reference sample TC-1 (Figs 4 and 5).

The bands 1951 and 1936 cm^{-1} indicate the presence of iron-containing compounds ferric cyclo-penta-dienyl-dicarbonyl-iodide ($\text{C}_7\text{H}_5\text{FeIO}_2$) and ferric cyclo-octa-tetraene-tricarbonyl ($\text{C}_{11}\text{H}_8\text{FeO}_3$), and the bands 1889 and 1876 cm^{-1} are related to the presence of molybdenum- and chromium-containing compounds: molybdenum cyclo-penta-dienyl-tricarbonyl ($\text{C}_{16}\text{H}_{10}\text{Mo}_2\text{O}_6$) and chromium toluene-tricarbonyl ($\text{C}_{10}\text{H}_8\text{CrO}_3$), respectively. Identification of compounds responsible for decreasing the intensity of the band 1741 cm^{-1} needs an additional analysis of information sources, which is caused by too large variation set of organic and inorganic substances that define transmission at this band.

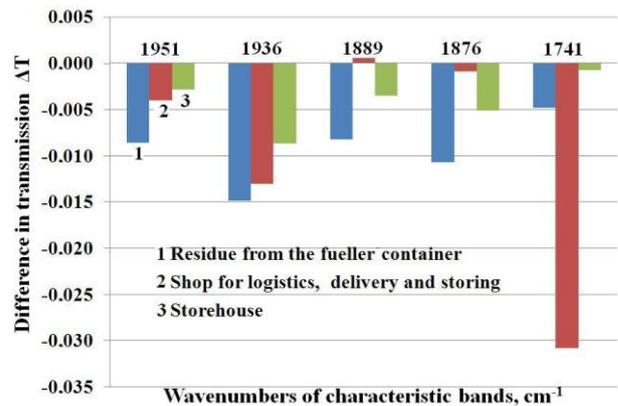


Fig. 4. Calculated difference in transmission ΔT for characteristic bands within the short-wave sub-range for the kerosene samples stored under various conditions.

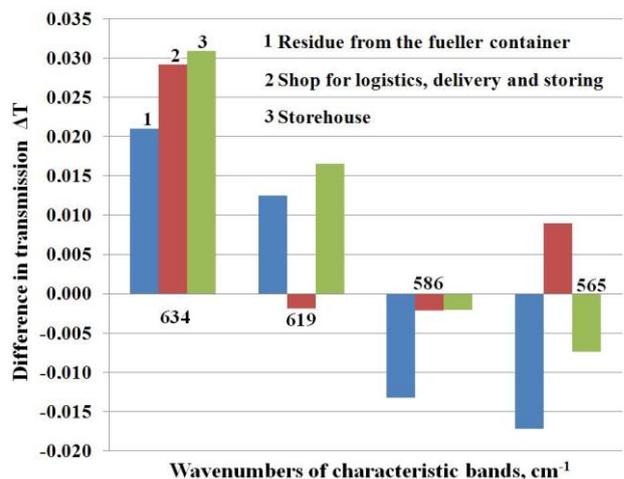


Fig. 5. Calculated difference in transmission ΔT for characteristic bands of the long-wave sub-range for the kerosene samples stored under various conditions.

3.3. Correlation and regression analyses of the results of complex investigations

We performed the correlation analysis of relative changes inherent to minima of SPR refractometric characteristics, changes in dispersion and relative changes in transmission for the characteristic bands in the infrared range. The obtained results of correlation analysis enabled to ascertain that the strongest correlation takes place between the band 1936 cm^{-1} ($\text{C}_{11}\text{H}_8\text{FeO}_3$) and the shift θ_{sp} ($r = -0.996$); between the bands 1889 cm^{-1} , 1876 cm^{-1} ($\text{C}_{16}\text{H}_{10}\text{Mo}_2\text{O}_6$ and $\text{C}_{10}\text{H}_8\text{CrO}_3$) and the changes in respective dispersions ($n_D - n_r$) ($r = -0.980$ and $r = -0.987$). The plot of dependence describing changes in transmission for the band 1936 cm^{-1} on the shift θ_{sp} can be ideally approximated by the parabolic function $y = 0.482x^2 - 0.126x - 0.009$ with the matching factor $R^2 = 1$ (Fig. 6).

For all of these bands, the dependences are reversed, *i.e.*, the increase in the shift of the minimum SPR caused by a decrease in transmission, which indicates an increase in the absorption and increase the refractive index of the studied kerosene samples. The above dependences can be applied to qualitatively evaluate changes in the composition of the TC-1 brand kerosene during storage.

4. Conclusions

These investigations have shown that the SPR method is the simple and reliable approach to study the quality of aviation kerosenes. The device "Plasmon-71" developed at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, with account of measured values of refraction index, has enabled to reveal changes in the kerosene composition after storing and applying it under conditions of aviation enterprise. The results of SPR measurements have been confirmed using infrared spectrometry, which allows revealing the presence of iron-, molybdenum- and chromium-containing organic compounds.

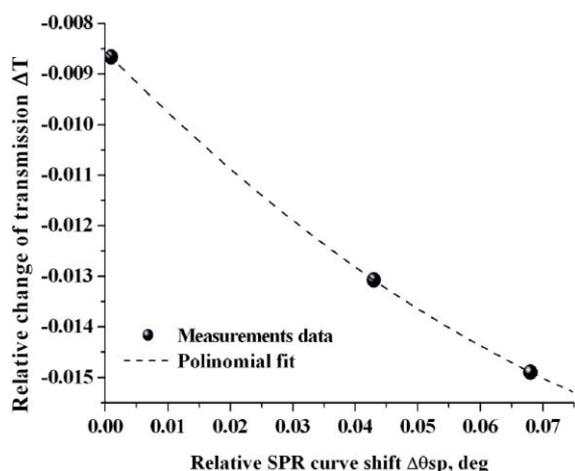


Fig. 6. Dependence of the relative change in transmission ΔT on the magnitude of the relative shift of the minimum SPR for the band 1936 cm^{-1} of the transmission spectrum.

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