

Laboratory work:

Determination of engine oil quality by infrared spectroscopy

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Motor oils are produced by blending the various oil fractions resulting from the vacuum distillation of crude oil. They are mainly used to reduce friction between the moving parts of petrol and diesel engines. To increase their performance, oils are additivated, e.g. against abrasion or premature oxidation. In addition, they are also used to remove dirt and deposits produced during engine operation, to cool the engine by direct dissipation of heat generated by combustion and friction, to seal the spaces between pistons and cylinders, to preserve the metal surface during engine shutdown, etc. [1].

They are classified, for example, according to API (American Petroleum Institute) specifications. According to this standard, a distinction is made between oils for petrol (gasoline) engines, designated by the letter 'S' (Service), and oils for diesel (diesel) engines, designated by the letter 'C' (Commercial). Most oils are applicable to both types of engines and are then marked with a combination of both letters. [2]

Theoretical introduction

The use of engine oils is also related to the phenomenon of oil contamination by fuel penetration from the combustion chamber in the areas between the piston rings and the cylinder wall (Figure 1). This fuel penetration into the oil cannot be completely prevented because certain minimum clearances between the piston rings and the cylinder wall are necessary for smooth engine operation.

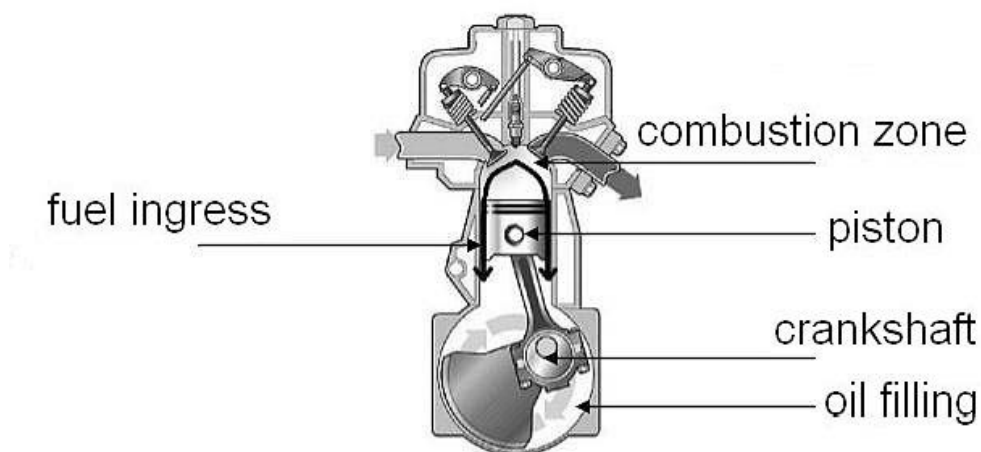


Figure 1. Fuel ingress into the oil

On the cylinder walls and in the space below the piston, the fuel meets the engine oil in which it dissolves. The presence of a small amount of fuel in the engine oil (about 1 to 2 % w/w) is, for the reasons mentioned above, a relatively common phenomenon encountered in both petrol and diesel engines. However, if the fuel content in the oil is higher, it is probably the result of some technical fault in the engine, such as damage to piston rings, fuel injection fault, etc. A limit of 4 % w/w is considered to be the maximum acceptable concentration of fuel in engine oil [3].

Tribotechnical engine oil diagnostics (TTD) is an instrumental analytical method for assessing the degree of contamination and the progress and degree of wear of engine oils. In tribology, FTIR-spectrometry is used as a suitable method for identification and structural characterization of mainly organic compounds. The introduction of TTD is a significant contribution to energy savings, contributing to the conservation of petroleum feedstock, fuel, lubricants, construction materials and human labor. These savings are made possible through the prevention of equipment breakdowns, reduction of lubricant consumption and the resulting reduction of environmental burdens. TTD is based on an individual assessment of the degree of oil degradation in each engine based on an analysis of the oil used. It uses lubricant as a source of information about processes and changes in both the technical systems in which the lubricants are applied and the lubricant itself. Proper interpretation of the analysis results not only allows early warning of signs of impending machine failure, but in many cases also allows the location of the mechanical fault to be determined. [4]

Method of determination

The most common way to evaluate the fuel content is to determine the oil flash point, which is one of the so-called indirect methods of determination. In addition, gas chromatography or non-destructive infrared spectroscopy can also be used.

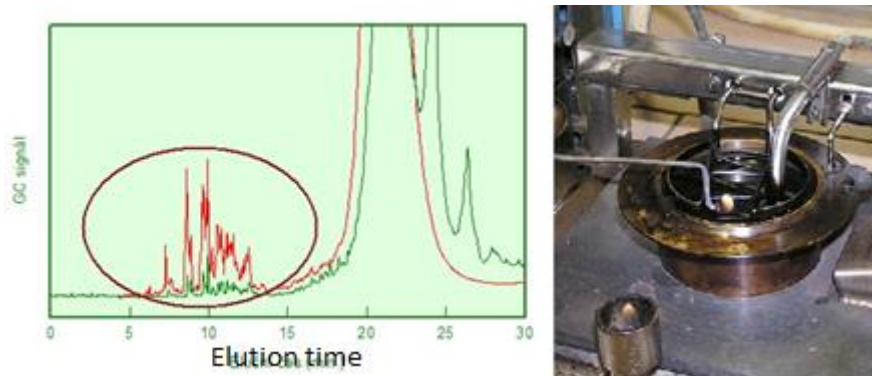


Figure 2: Gas chromatogram recording on the left, flash point determination in an open crucible on the right.

Infrared spectrometry is an analytical method based on the principle of measuring the absorption of infrared radiation. The output of infrared spectroscopy is an infrared spectrum in which different types of chemical bonds can be identified based on characteristic wavelengths (or wavenumbers). With this modern instrumental method, it is possible to identify the type of lubricant and at the same time to observe the chemistry of the changes taking place during oil degradation in the engine, which is practically impossible with conventional methods.

The analysis of spectra is based on knowledge of the wavelengths (or wavenumbers) corresponding to specific compounds or characteristic structural groups. An overview of typical groups and compounds characteristic of engine oils is given in Table 1.

Tab. 1: Wavenumber values of characteristic compounds [4]

Peak position [cm^{-1}]	Compound	Note
3640 - 3540	Water	In ester oils
3600 - 3150 (max 3400)	Water	In petroleum oils
3540	Degradation of esters	
2000	Carbon black	
1800 - 1670	Oxidation products	
1748	Esters	Synthetic oils
1650 - 1600	Nitro compounds	
1180 - 1120	Sulphur compounds	Sulfur additives, fuel sulfur

1070, 1040	Ethylene glycol	Coolant
1025 - 960	Antifouling additives	Zinc dialkyl dithio phosphate
1000	High temperature antioxidant	Zinc dialkyl dithio phosphate
990 - 960	Anti-abrasion additives	Tricresyl phosphate (TCP)
815 - 805	Diesel	
755 - 748	Kerosene	Lighter components

The characteristic IR spectrum of engine oil is shown in Figure 3. The characteristic bands for oils and lubricants are those with bands in the interval $3000\text{--}2800\text{ cm}^{-1}$ and in the interval $1500\text{--}1300\text{ cm}^{-1}$, representing the $-\text{CH}_3$ - and $-\text{CH}_2$ - groups. The bands in the $1500\text{--}400\text{ cm}^{-1}$ region are called the 'fingerprint region' and it is in this region that the additives and impurities present in the oil are monitored. [4]

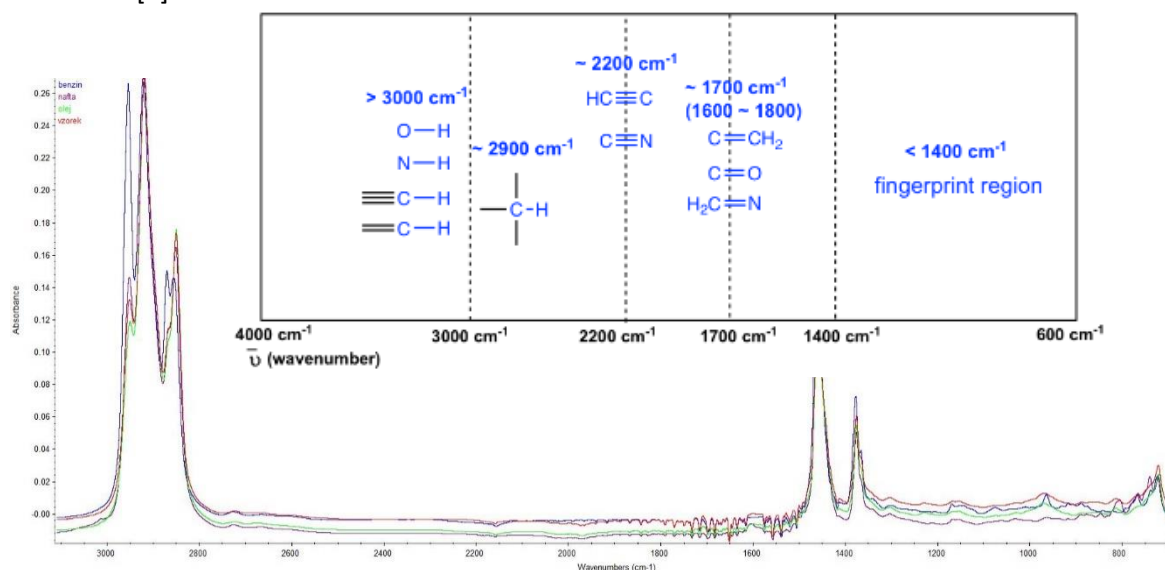


Figure 3: IR spectrum of gasoline, diesel, clean and used oil samples.

The presence of fuel in engine oil is monitored in the wavenumber region around 750 cm^{-1} (gasoline) and in the region $815\text{--}805\text{ cm}^{-1}$ (diesel). However, the absorption of infrared radiation in these regions can also be affected by aromatics present in pure engine oil [4]. For a more reliable determination of the fuel, it is therefore necessary to have clean oil whose spectrum is subtracted from that of the sample to be analyzed.

The aim of the work

The aim of this work is to determine the content of fuel component in engine oil by FTIR-spectrometry method, which is used in tribomechanical diagnostics of engine oils. Based on this analysis, to determine which component is involved (petrol, diesel), what is its content and whether this content does not exceed the permissible limit for the content of motor fuels in lubricating oils. From this information it can then be deduced whether the engine has failed during operation.

Experimental procedure and apparatus

The measurements should be carried out according to the instructions on the Nicolet FTIR spectrometer equipped with ATR adapter and designed for the mid-infrared region 7800-350 cm^{-1} . Measurements are set at the spectral resolution of 0.4 cm^{-1} , and at scan rate 1 scan per second. The spectrometer is controlled by Omnic software and data evaluated by TQ Analyst software.

First, a calibration series of fresh engine oil with an additive content of 0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, ~~22.5~~, 25% vol should be prepared, see Annex for the details. Later, two samples of used engine oil A, B will be measured and compared to this calibration.

Omnic spectrometer with ATR adapter attached should be prepared prior to the measurement. On connected the PC, start the OMNIC program and check this presetting of the "Expt set" tab in the top bar:

- In the "Collect" tab the "No. Of scans" is set to "64" and the "Resol." to "4".
- In the "Bench" tab, the measurement range is set from 4000 - 600 cm^{-1} using the "Max and Min range limit" parameters.
- In the "Diagnostic" tab and wait until the "Max", "Min" and "Loc" values are stable at around "6.4"; "6.4" and "2050". Once steady, write the values in the service booklet.

Return to the main screen and use the "Col Bkg" and subsequent "Start collection" tab to measure the background spectrum. This spectrum is automatically saved.

To measure samples and standards, press "Col Smp", enter the name of the sample you are currently measuring (e.g.: calibr0, calibr5, SmpA, SmpB) and before applying the sample to the crystal, make sure the crystal is free of any impurities, indicating the displayed spectrum in the 4000 - 350 cm^{-1} region as a clean line, otherwise the crystal should be cleaned. Next, apply a drop of sample to the crystal with a glass rod, making sure that it is free of air bubbles and impurities. Press "Start Collection" and save the spectrum in the folder you created in the "Spectra/labs/your_name" directory after each measurement. Clean the crystal thoroughly, first with ethanol (or acetone), until the currently measured spectrum appears as a straight line again. After measuring the spectra of the calibration solutions and samples, leave the Omnic software.

Proceed to the **TQ ANALYST EZ Edition program**. In the "Description" tab, fill in the "method title" field with any name of the analysis (e.g. "lab-your-name") in the "analysis type" section, tick the "simple Beer's law" box. In the "Pathlength" tab check "constant" and in the "Components" tab enter the data for the component to be determined in the following order - name: oil/additive, abbrev.: vol/vol, unit: %, Ic: 2, AL: 0, AH: 20, thus defining the unit by which the amount of the substance is determined and the calibration range. Finally, in the "Standards" tab, retrieve all measured standards using the "Open standard" button from the folder you created. For each standard, fill in the corresponding additive content (0-20%). In the "Regions" tab, use the "Suggest" button to instruct the instrument to select the wavelength region in which to analyze. In the best case, the program will then determine the wavelength region around 750 cm^{-1} (or 810 cm^{-1}), which is characteristic of petrol (or diesel). Finally, press "Calibrate" to create a calibration line. If any point significantly disturbs the linear relationship or you are aware of an error, the point can be omitted from the calibration after discussion with the supervisor. To evaluate both samples, then press "Quantify" and load the spectra of the measured samples one by one. The measured value of the component in the oil in %vol. will then be displayed automatically. Write down the values and process them in a report.

Processing of results

Process the measured results clearly in a table to be included in the report, together with the attached measured spectra of the unknown sample and the pure oil with the characteristic peaks marked. The report must contain a brief description of the work, results, and a conclusion.

In the Results/Conclusion section, try to answer the following questions:

1. What was the accuracy of your measurement? State the R2 parameter of the calibration curve.
2. What is the effect of the oil matrix if real (used) versus new oil is used?

Literature

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- [2] Specifikace motorových olejů, Petroleum.cz. Dostupné z URL: <http://www.petroleum.cz/vyrobky/oleje-motorove-specifikace.aspx>
- [3] ČERNÝ, Jaroslav. Díl osmý – Palivo v oleji. *AutoExpert: časopis profesionálů v autoopravárenství: technika - autodílna - obchod*. 2006, č. 10, s. 40-42. ISSN 1211-2380. Dostupné z URL: <http://www.oleje.cz/clanek/Vlastnosti-motorovych-oleju---Palivo-v-oleji>
- [4] SEJKOROVÁ, Marie. Aplikace FTIR spektrometrie v tribotechnické diagnostice motorových olejů. Dislokované pracoviště dopravní fakulty Jana Pernera [online]. 2005 [cit. 2012-05-17]. Dostupné z URL: ct.upce.cz/ph/sejkorova.doc

The Annex

Procedure for setting up a calibration series in volume percent.

Volume fraction, %vol	Fresh Oil # of drops	Additive # of drops
0	1	0
2.5	38	1
5	19	1
7.5	37	3
10	9	1
12.5	7	1
15	17	3
17.5	33	7
20	4	1
22.5	45	2
25	3	1